

Department of Chemical Engineering

Natural Gas Hydrate Production

Sam Battah

**This thesis is presented for the Degree of
Master of Science
of
Curtin University of Technology**

August 2002

Declaration

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgement has been made.

Signature _____

Date: _____

7/8/02

ACKNOWLEDGEMENT

I wish to take this opportunity to express my thanks to a number of my colleagues at the petroleum Engineering Department for their contribution to the research of the Natural Gas Hydrate, in particular, I wish to acknowledge the support and advice of my supervisor Dr Robert Amin and my associates Nimalan Gnanendran, Ileana Manescu and Jing Wang during the various stages of testing and data acquisition and recording.

I also wish to thank Woodside Energy (Metasource) hydrates project manager Mr. Alan Jackson for his support and contribution during the many technical meetings, which took place during this research period.

ABSTRACT

The concept which led to the establishment of the research in natural gas hydrate production, was born by Dr. Robert Amin (currently Professor of Petroleum Engineering at Curtin University and Chair of the Woodside Research Foundation) and Alan Jackson of Woodside Energy.

The intended research in this field is to establish the viability of utilizing a synthesised natural gas hydrate as a means to allow a cheaper form of transportation of natural gas from the wellhead to the customer in direct competition with liquefied natural gas (LNG).

Natural gas exists in ice-like formations called hydrates found on or under sea-beds and under permafrost. Hydrates trap methane molecules inside a cage of frozen water, where the amount of hydrates trapped is dependent on surrounding formation pressure.

The amount of natural gas trapped in hydrates is largely unknown, but it is very large. A number of scientists believe that hydrates contain more than twice as much energy as all the world's coal, oil, and natural gas combined, hence making it a viable option of fuel in the 21st century, in a world constantly seeking cleaner sources of energy.

The feasibility of production of natural gas hydrates on offshore installations and onshore facilities makes this development a viable option. As such this technology requires detailed research and development in a laboratory environment coupled with a pilot plant construction for commercial operation.

Current estimates for onshore based facilities for the production of hydrates show a cost reduction of approximately 25% compared with LNG plants of the same energy capacity.

There are two major issues which require detailed research and development in order to progress this technology. First is the enhancement of the hydrates production by the use of other additives, and second, the continuous production at near atmospheric pressures.

Other research related to transport methodology and re-gasification will be essential for the overall success of this technology; however, this work is outside the scope of this research.

CONTENTS

<u>CHAPTER</u>	<u>PAGE</u>
ABSTRACT	1
1 - OBJECTIVE	9
2 - INTRODUCTION	11
3 - BACKGROUND	13
3.1 - Natural Gas Hydrate Structure.....	14
3.2 - Prior Research.....	18
3.3 - Potential Carriers.....	19
3.4 - Regasification.....	19
3.5 - The NGH Project.....	21
3.5.1 Preliminary Project Work.....	21
3.5.2 Preliminary Laboratory Results.....	22
4 - CHEMICAL ADDITIVES	23
5 - LABORATORY EXPERIMENTATION	24
5.1 - Safety.....	24
5.2 - Disposal and Environmental Considerations.....	25
5.3 - Uncertainty.....	25
5.4 - Method of Preparation.....	26
5.4.1 Preparation of Cylinders.....	26
5.4.3 Venting Excess Gas.....	29
5.4.4 Measuring Evolved Hydrate Gas Volume.....	29
5.4.5 Cleaning Experimental Cylinders.....	30
5.5 - Laboratory Test Results and Discussion.....	31
5.5.1 Introduction.....	31
5.5.2 Gas Chromatography Analysis.....	31
5.5.3 Physical Observation.....	36
5.5.4 Problems.....	36
5.5.5 Recommendation.....	37
5.5.6 Summary Results.....	37
5.5.6.1 Toluene Sulfonic Acid (TS).....	37
5.5.6.2 Sodium Lauryl Sulphate (SLS).....	40
5.5.6.3 Carboxyl Methyl Cellulose Sodium Salt (CC).....	40
5.5.6.4 Nitromethan (NTM), Nitropropane (NTP), Dioxane (DX) & Propylene Oxide (PPO).....	41
5.5.6.5 Other, Oleyl Alcohol (OA), Di_isopropyl Ether (DIPE) and Sodium Tripolyphosphate (TP).....	41
5.5.7 Conclusion.....	42
5.5.8 HYSYS simulation and results.....	44
5.5.9 Continuous Joule-Thomson.....	53
5.5.10 CSTR.....	53
5.5.11 Batch Closed Cylinder.....	53
5.6 - Nitrogen Separation.....	54
6 - THE PROJECT PLAN	59
6.1 - Pilot Project Scope.....	59

6.2 - Project Deliverables	59
6.3 - Pilot Plant Conceptual Design	61
6.4 - Electrical Power	61
6.4.1 Reference Codes and Standards	61
6.4.2 Service Conditions	62
6.4.3 General Description	62
6.4.5 Switchboard Doors.....	64
6.4.6 Equipment Within Cubicles	64
6.4.7 Labels and Name Plates	65
6.4.8 Fasteners.....	65
6.4.9 Earthing.....	66
6.4.10 Termination and Wiring.....	66
6.4.11 Electrical Certificates and Reports.....	66
6.5 - Pilot Plant Piping and Instruments.....	67
6.6 - Fluid flow calculations	68
6.6.1 Calculation of flow rates of gas and liquid required to form hydrates at 870 psi (Sample Calculation).....	68
6.6.1.1 Design Basis.....	68
6.6.1.2 Assumptions.....	68
6.6.1.3 Calculations.....	68
6.6.1.4 Cooling Rate Calculation	70
6.6.2 Calculation of Amount of Gas In Hydrate	72
6.6.2.1 Case 1	72
6.6.2.2 Case 2	73
6.6.2.3 Case 3	73
6.6.2.4 Case 4.....	74
6.6.3 Pressure vessel design and specifications	75
6.6.3.1 Vessel Data:	75
6.6.3.2 Materials and design tensile strengths	76
6.6.3.3 Design of allowable tensile strength for material	77
6.6.3.4 Calculation of hazard level for vessel in accordance with AS3920.1...	78
6.6.3.5 Design of shell subject to internal pressure.....	78
6.6.3.6 Design of seamless shell subject to internal pressure	79
6.6.4 Pressure safety values (PSV)	79
6.6.4.1 Determining the mass flow per hour.....	81
6.6.4.2 Determining the pressure drop in the line	82
6.6.4.3 Determining the mass flow per hour.....	83
6.6.4.4 Determining the pressure drop in the line.....	84
6.6.4.5 Determining the mass flow per hour.....	85
6.6.4.6 Determining the pressure drop in the line.....	85
6.6.5 Determination of Bursting Disc Size	86
6.7 - Project Schedule	89
6.8 - Construction and Commissioning.....	91
6.9 - Hazard and Operability (HAZOP)	102
6.9.1 Instrumentation	103
6.9.2 LP Gas Supply – Page 1 of 2	104
6.9.3 Electrical instrumentation	106

6.9.4 Refrigeration system	106
6.9.5 Hot Water System	107
6.9.6 Production vessel – Page 1 of 2	108
6.9.6 Production vessel – Page 2 of 2	109
6.9.7 HP gas supply – Page 1 of 5.....	110
6.9.8 HP Liquor Supply – Page 1 of 2	115
6.9.9 Venting.....	117
7 - HYDRATE PRODUCTION (PILOT PLANT).....	118
7.1 - Hydrate Gas /Liquor Concentrations	118
7.2 - Gas Formation /Liquor Ratios and Hydrate Volume formation factors	118
7.3 - Bulk Densities and Energy Densities	119
7.4 - Hydrate Formation/Phase Envelope Curves	120
7.5 - Nozzle Basis of Design.....	121
7.6 - Test Report Procedure	122
7.7 - Liquor/Gas Phase Envelope Diagram (Computer Model).....	122
7.7.1 Liquor Phase Envelope Diagram	122
7.7.2 Phase Envelop Model Description.....	123
7.7.3 PV Sym Model Description	123
7.7.4 Hydrate Calculation	124
7.7.5 Hydrate Formation Curves (Computer Model).....	128
7.7.6 Hydrate Stability Curves.....	129
7.7.7 Heat Transfer.....	129
7.7.8 Thermal Conductivity	129
7.7.9 Hydrate heat of formation	130
7.8 - Pressure Drop.....	131
7.9 - Flow Regimes and Flow Rates	131
7.10 - Data that requires further evaluation	132
7.10.1 Ambient Temperature.	132
7.10.2 Flash Chamber Vessel Temperature Control	133
7.10.3 Pressure Control.....	134
7.10.4 Conversion efficiency	134
7.10.5 Compressor Flow rate	135
7.10.6 Pump Flow rate	135
7.10.7 Residence Time.....	136
7.10.8 Nozzle Temperature	137
7.11 - Gas Composition	138
7.12 - Water and Additive.....	138
7.13 - Hydrate Appearance	139
7.14 - System Instrumentation	139
7.15 - Material Corrosion Tests	140
7.16 - Foaming and Defoaming Agents	141
7.17 - Summary	142
7.18 - Alternative Method.....	144
7.19 - Proposed Working Plan.	145
8 - PILOT PLANT SAFETY AND OPERATING PROCEDURE.....	152
8.1 - Introduction	152

8.2 - Plant Identification And Labelling	152
8.3 - Safety	153
8.3.1 Personal Safety	153
8.3.2 Visitors	153
8.3.3 Fire Fighting Equipment	154
8.3.4 Fire Alarm System	154
8.4 - Hazardous Area Classification.....	154
8.5 - Plant description	155
8.6 - Handling of hydrate/liquor	160
8.6.1 General Liquor Handling	160
8.6.2 Removal of Hydrate From Pilot Plant.....	161
8.6.3 Storage	161
8.6.4 Hydrate Ignition	162
8.6.5 Disposal.....	162
8.7 - Operating Procedures.....	162
8.7.1 General	162
8.8 - Training.....	163
8.9 - Security	163
9 - PILOT PLANT INSPECTION PROCEDURE.....	164
9.1 - Introduction	164
9.2 - Statutory Requirements.....	164
9.3 - Plant Isolation Procedure	165
9.4 - Inspection Schedule	165
9.4.1 Routine Plant Inspection	165
9.4.2 Monthly Inspection Schedule.....	166
9.4.3 Annual Inspection/Maintenance Program.....	166
9.5 - Detail description of inspection tasks	168
9.5.1 Measuring /Transmitting Instruments	168
9.5.2 Production Vessels / Nozzles.....	168
9.5.3 Gas Storage Cylinders.....	168
9.5.4 Liquor Storage Tank and Pump	169
9.5.5 Knock-out vessel.....	169
9.5.6 Filters	169
9.5.7 HP/LP Regulators and Valves.....	169
9.5.8 Piping and Connection	169
9.5.9 PSVs and Rupture Discs	169
9.5.10 Compressor Unit	170
9.5.11 Refrigeration Unit	170
9.5.12 Nozzle Heating Unit.....	170
9.5.13 Mixer.....	170
10 - REFERENCES	171
11 - NOMENCLATURE	177
12 - APPENDICES.....	178
APPENDIX A - Pilot Plant Operation Summary.....	179
APPENDIX B - Calibration Curves for Compressor and Liquor Pump.....	182
APPENDIX C - Measuring Hydrate Formation Volume Factor.....	184

APPENDIX D - Hydrate Bulk Density Measuring Procedure.....	188
APPENDIX E – NGH Pilot Plant Test Record Sheet.....	190
APPENDIX F – NGH Pilot Plant Monthly Plant Inspection Log	192
APPENDIX G - Instrumentation Schedule.....	193
APPENDIX H - Prestart Plant Alignment and Purge	198
APPENDIX I - High Pressure Production, Shutdown& Hydrate Removal.....	199
APPENDIX J - Plant Make Safe (Page 1 of 2).....	202
APPENDIX K - Natural Gas Hydrate Project	204

TABLE OF FIGURES

Fig. 1 Natural Gas Flame from Hydrate.....	14
Fig. 2 The Ice Lattice Structure Entraps Within the Methane Molecules.....	15
Fig. 3 Hydrate Structure I.....	15
Fig. 4 Hydrate Structure II.....	16
Fig. 5 Hydrate Structure H.....	16
Fig. 6 Equilibrium Curve for Methane and Natural Gas Hydrate.....	17
Fig. 7 Hydrate Production Flow Diagram.....	18
Fig. 8 Regasification Block Diagram.....	19
Fig. 9 Alternative Continuous Production	20
Fig. 10 Laboratory Test Cylinder.....	26
Fig. 11 Comparison of Methane Content for Different Additives.....	34
Fig. 12 Comparison of Nitrogen Contents for Different Additives	34
Fig. 13 Mole percent of components in excess and hydrate gas.....	35
Fig. 14 Hydrate Gas Volumes for 1.0g TS.....	39
Fig. 15 Hydrate Gas Volume for 1.5g TS using the Mixing machine	39
Fig. 16 Hydrate Gas Volumes versus Concentration of TS.....	40
Fig. 17 Hydrate Gas Volume Ratios for NTM, NTP, DX & PPO.....	41
Fig. 18 Alinta Gas Phase Envelope.....	122
Fig. 19 Hydrate formation curve for Alinta gas.....	128
Fig. 20 Calculated Press. Temp. Curve for TSA-Water-Gas System at 1.2 g/l.....	128
Fig. 21 HFVF (V/V) vs Avg. Nozzle Pressure	146
Fig. 22 HFVF vs Gas-Liquor Injection Time.....	146
Fig. 23 HFVF (V/V) vs Vessel Pressure.....	147
Fig. 24 HFVF (v/v) vs Ambient Temperature	147
Fig. 25 HFVIFig. 20 HFVF (L) vs UnCompacted Bulk Density.....	148
Fig. 26 HFVF (L) vs Compacted Bulk Density	148
Fig. 27 HFVF(L) vs Liquor Injection Rate	149
Fig. 28 HFVF vs Gas Injection Rate.....	149
Fig. 29 HFVF as a Function of TSA Concentration	150
Fig. 30 Bulk Density (Compacted) vs Vessel Top Temperature	150
Fig. 31 Calculated Thermal Conductivity as a Function of Pressure.....	151

TABLES

Table 1 (Feasibility of Natural Gas Production).....	14
Table 2 GC Analysis, Methane-Nitrogen Gas	31
Table 3 GC Analysis, Natural Gas.....	32
Table 4 GC Analysis, Natural Gas.....	33
Table 5 Average Hydrate Gas Volumes for TS	38
Table 6 Hydrate Gas Volume Ratios for Combinations of Chemicals	42
Table 7 Inlet stream (Water added pure in streams)	44
Table 8 Cooler Outlet Stream	44
Table 9 Nitrogen Separation Trials from GC Analysis.....	54
Table 10 Nitrogen Separation at 1500kPa	55
Table 11 Nitrogen Separation at 10,000kPa	55
Table 12 Nitrogen Hydrate Formation.....	56
Table 13 Methane Hydrate Formation	56
Table 14 Higher Hydrocarbon Formation.....	56
Table 15 CO ₂ Hydrate formation	56
Table 16 Heavier Hydrocarbons	57
Table 17 Nitrogen Free Formation.....	57
Table 18 Heavier Hydrocarbons	57
Table 19 Nitrogen Formation Lab.	58
Table 20, Natural Gas Composition.....	71
Table 21 Condition Specification for PSV Operation @ 34.46 kPa.....	80
Table 22 Condition Specification for PSV Operation @ 16000 kPa.....	82
Table 23 Condition Spec. for PSV Op. @ 344.64 Disc Rupture Pressure in kPa.	84
Table 24 Hysis Input Data.....	46
Table 25 Hysis Material Stream Specs sheet.....	47
Table 26 Hysis Component Data Sheet.....	48
Table 27 Hysis Material Stream Specs sheet Coolout.....	49
Table 28 Hysis Component Data Overall.....	50
Table 29 Hysis Coolout Data.....	51
Table 30 Hysis Material Stream Specs sheet (Utility).....	52
Table 31 Vessel Data	75
Table 32 Materials and Design Tensile Strengths.....	76
Table 33 Design of Allowable Tensile Strength for Material.....	77

Table 34 Calculation of Hazard Level for Vessel.....	78
Table 35 Design of Shell Subject to Internal Pressure.....	78
Table 36 Fluid Properties at 1500.00 psi and 20.00C.....	114
Table 37 Hydrate Cavities Structure.....	115
Table 38 Calculated Hydrate Composition at 11Mpa and -20C using PVTSim	116
Table 39 Calculated Hydrate Composition at 2.75Mpa and -20C using PVTSim	116
Table 40 Calculated Hydrate Composition at 2.75Mpa and -15C using PVTSim	117
Table 41 Calculated Hydrate Composition at 6.7Mpa and -20C using PVTSim	117
Table 42 Calculated Hydrate Composition at 6.7Mpa and -10C using PVTSim	118
Table 43 AlintaGas Composition Measured on 2 February 2001.....	129
Table 44 Gas Compressor Throughput at 22C Ambient.....	173
Table 45 Gas Compressor Throughput at 15C Ambient.....	174
Table 46 Water Pump Throughput.....	174

TABLE OF DRAWINGS

Page 93	Hydrate Module Support Frame
Page 94	Hydrate Module Spray Pressure Vessel
Page 95	Hydrate Module Electrical Wiring Diagram
Page 96	Hydrate Module Control Panel Layout
Page 97	Hydrate Module Control Panel Material List
Page 98	Hydrate Module Spray Nozzle Details
Page 99	Hydrate Module Piping and Instrument Diagram
Page 100	Hydrate Module Spray Pressure Vessel Door Closure
Page 101	Hydrate Module Spray Pressure Vessel Door Lock and Seal

1 - OBJECTIVE

The objective of the overall phase one of the hydrate project was to design a small pilot plant that would produce natural gas hydrates (NGH) at pressures of 3445 kPa up to a maximum of 14950 kPa. The intent of this research was to devise a method by which natural gas could be formulated in a manner that could be commercially viable. More specifically, the objective was to utilise and improve this technology in an effort to make the process efficient and viable for the commercialization phase.

This project was proposed by Dr. Robert Amin and Mr. Alan Jackson and funded by Woodside Petroleum. The success of this research will add another dimension to the methodology of transporting natural gas as an alternative fuel to LNG and CNG.

The concept of transforming natural gas into hydrate is envisaged to revolutionize the industry making the transportation of gas much safer than current practices of transporting natural gas as LNG. The pilot plant was considered to be the first step in producing NGH on an experimental basis. In the first phase of the project high quality NGH was produced in the laboratory. The method of producing NGH was refined over time to obtain consistent results and excellent quality hydrates. The quality of hydrates can be determined primarily by measuring the unit volume of gas stored per unit volume of water. Hydrate density and stability are also very important factors in the overall consideration of total hydrate suitability for production, transportation and re-gasification. The production of high quality hydrate was achieved at high pressures, with consistent repeatable results; however, the capital cost for production and storage of hydrates at high pressure will have serious ramifications on the overall capital cost of the project. For this reason, production of hydrates at lower pressures was considered a more economically viable option. The manufacturing of pressure vessels capable of withstanding in excess of 14950 kPa is very costly; therefore, the effort was now focused on hydrate production at low pressures.

Synthetic production of natural gas hydrates requires the inducement of an additive to promote a rapid production of hydrates. Various additives have different characteristics,

which can affect the end results of hydrates in terms of quality, quantity, toxicity and foaming effect during production and re-gasification. A significant number of chemical additives were employed in the production of NGH. However only two additives have given very encouraging results. Details related to these additives will be discussed later in this thesis.

Production of low pressure NGH (LPNGH) at or near atmospheric conditions added a new dimension to the complexity of the process. The technical issues arising from this application were overcome over a period of time and with additional expenditure.

Energy consumed during the production of hydrates was also investigated to determine the economic feasibility of this research. Details related to this exercise are discussed later in this thesis.

During hydrate formation, different gases have greater affinity to form hydrates than others within the same mixture. In the research associated with hydrate production utilizing natural gas, it was found that gases such as nitrogen (N_2) were not readily absorbed into the water molecule leaving most of the N_2 outside the clathrate structure.

2 - INTRODUCTION

Australia's North West Shelf Gas Project draws natural gas from fields in 120 metres of water 135km off the north west coast of Western Australia. The project is divided into two separate parts, domestic gas and liquefied gas. Since 1984, the \$2.5b domestic phase (the Domgas project) has supplied Western Australian users via onshore processing facilities at Mermaid Sound.

Building gas pipelines is an expensive task especially over long distances. Costs can run into billions of dollars, and often the cost of building pipelines to supply consumers in remote areas is so expensive that companies choose to disregard users in those areas. The cost becomes so high that there is no incentive for the company to add a new user to the pool of users it already has unless the rate of return is favourable. Such a case would be to build a pipeline to supply a power station 100 km away from the nearest gate station.

It should be realised that gas can also be transported as Liquefied Natural Gas (LNG), which is a more expensive option due to the high cost of refrigeration and re-liquefaction of boil-off liquids and a high risk of over-pressurization (Gudmundsson, 7, 1996).

Frozen hydrate can be used to transport large volumes of natural gas over long distances, and if refrigeration costs are inexpensive then this can prove to be a viable option. The frozen hydrate concept is based on the discovery that natural gas hydrate remains stable at atmospheric pressure when stored under near adiabatic conditions. Past work has been done by the Norwegian University of Science and Technology and Aker Engineering (in September 1995), which investigated the production of NGH. The information gained from such work was considered prior to the design and construction of the hydrates pilot plant (module).

The formation of hydrates can also be useful in separating out other gases from natural gas. Some gases do not form hydrate as easily as the light hydrocarbons and are left in the purge stream. During re-gasification the other gases will evolve first. A controlled method of heating the hydrate can separate the gases. Previous work by Hnatow and Happel has been used as a background to the separation of other gases from the NGH.

The formation of NGH in the laboratory was successful using pure methane and/or wellhead gas. The separation of nitrogen from the gas stream was also successful. Further investigation was necessary for achieving a more pure stream of nitrogen from the natural gas.

3 - BACKGROUND

In the past, hydrates were looked upon in the oil and gas industry as undesirables; hydrates often blocked pipelines and equipment causing a malfunction of instruments and exposing employees to dangerous situations. When hydrates are formed in pipelines, they block the flow of gas in the system increasing the pressure in the line. This potentially can cause a blowout in the line as a result of a back-pressure buildup. Gas hydrates can form in pipelines and equipment carrying natural gas, associated gas and mixtures of associated gas and oil, provided liquid water is present at a moderate pressure.

The use of hydrates as a transportation fuel was the idea of the Norwegian University of Science and Technology (Department of Petroleum Engineering and Geophysics), Trondheim. The intent was to find out how competitive this method is in relation to LNG. The study took place to determine if large scale transportation of NGH is feasible over long distances.

The work under consideration consisted of three phases: a production plant, hydrate carriers (transportation), and a regasification plant. Past work showed that NGH did not decompose when stored at temperatures in the range of -15 to -5°C at atmospheric pressure. In order to establish the economic viability of this process, a feasibility study was conducted for the transport of 400MMscf of natural gas over 3500 nautical miles under European conditions. From this feasibility study it was found that the NGH transportation chain was found to be 24% lower in capital cost than the LNG chain.

The cost of transportation of NGH was similar to that of LNG even though the volume of NGH to be transported was about 6 times that of LNG. The regasification was found to be 21% lower than the LNG process.

This can be seen in Table 1 below.

Table 1 (Feasibility of Natural Gas Production)

Chain	LNG	NGH	Difference
Production	1220	792	428 (35%)
Carriers	750	704	46 (6%)
Regasification	400	317	83 (21%)
Total	2370	1813	557 (24%)

3.1 - Natural Gas Hydrate Structure

NGH can be produced anywhere and when its produced in the laboratory, high quality hydrates look like snow, being white and fluffy. When held in the hand, tend to fizz and give off large quantities of gas. Poor quality hydrates are also white but the fluffy texture that is exhibited by good hydrates is no longer apparent, instead the poor quality hydrates are like ice, slightly gray in colour. The hydrate can form at temperatures above the freezing point due to the application of high pressure, and it is for this reason that hydrates are often formed at the bottom of the sea in deep waters but at a temperature of 5°C.

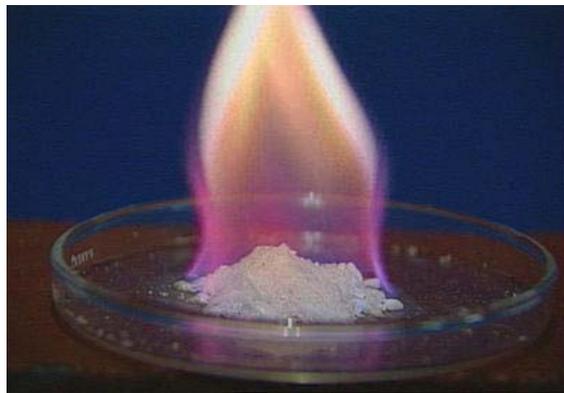


Figure 1 Natural Gas Flame from Hydrate

NGH has a similar structure to that of frozen water, except with frozen water, air molecules are trapped in the structure. With NGH gas is trapped in the water molecules.

The water and methane molecules contain hydrogen molecules; the methane molecule has four hydrogen molecules bonded to its lattice structure (CH_4) and the water molecule contains one oxygen molecule surrounded by two-hydrogen molecules (H_2O).

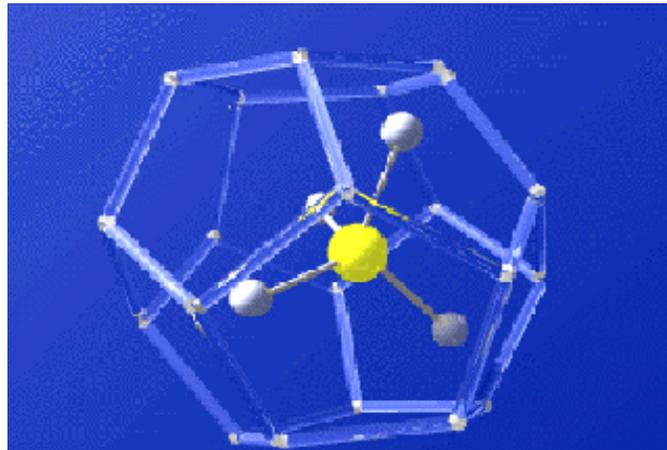


Fig. 2 The ice lattice structure entraps within the methane molecules, (Source USGS)

There are three hydrate structures: I, II, and H. Each of these structures has a different number of water and gas molecules. The ratio of water molecules to gas molecules is called the "hydrate number." The amount of gas actually contained within hydrate structures is called the "degree of filling."

If completely filled:

- Structure I hydrate contains 46 water molecules per 8 gas molecules. The hydrate number is 5.75. In this hydrate structure the water molecules are capable of forming two small dodecahedral voids and six large tetradehedral voids. These voids can hold only small gas molecules (methane, ethane) with molecular diameters not exceeding 5.2 angstroms.



Figure 3 Hydrate structure I (Source: Sassen et al., 2000)

- Structure II hydrates were first produced in 1983 after being observed in their natural environment at a depth of 530 metres. Structure II hydrates contains 136 water molecules per 24 gas molecules. The hydrate number is 5.67. The water molecules in hydrate II structures form 16 small dodecahedral voids and 8 large hexakaidecahedral voids. Gases with molecular dimensions from 5.9 to 6.9 , such as propane, a three-carbon hydrocarbon, and isobutane are often contained within.



Figure 4 Hydrate structure II (Source: Sassen)

- Structure H was first found in nature in 1993 in a large oil and gas producing area in the Gulf of Mexico, at a water depth of 530 metres near the Jolliet Field. This structure H hydrates contains 34 water molecules per 6 gas molecules. The hydrate number is 5.67. This structure is capable of holding molecules like isopentane, a branched-chain hydrocarbon molecule with five carbon atoms.



Figure 5 Hydrate structure H (Source: Sassen)

It appears possible that other hydrate structures remain to be discovered. The average radius is about 4.0 angstroms. (Source: A.K. Soper et al., "In Situ Study of Gas Hydrate Formation in Aqueous Solution, ISIS Annual Report), An angstrom is one ten-billionth of a metre.)

About 15 percent of the weight of naturally occurring hydrocarbon hydrate is gas, and 85 percent is water. The density is about 950 kg/cubic metre. These measurements vary with the gas composition and the pressure and temperature at the time the hydrate is formed. (Source: J.S. Gudmundsson et al., 1997.)

Hydrates are formed in the presence of liquid water and the associated equilibrium line determines whether it will be formed or not. The equilibrium line represents the thermodynamic equilibrium between a gas mixture and a hydrate. The equilibrium depends on many factors, including gas composition, pressure, and temperature. For the project presently undertaken pure methane and well head gas was used to form hydrate, and the associated equilibrium line is also shown in Fig. 6. In industrial processes, however, the water and gas volumes are finite, and the gas composition and hydrate compositions change with time and location. Compositional changes are expected to be greater in batch processes compared to continuous processes.

Gas hydrates have properties that make them useful in many applications. The volumetric property of interest is that gas hydrate contains 180 Sm³ of gas per m³ of solid hydrate.

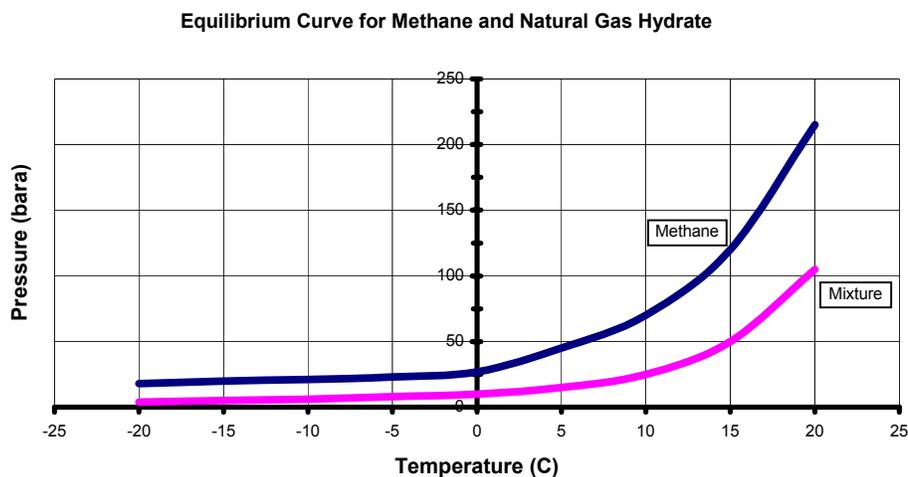


Figure 6 Equilibrium Curve for Methane and Natural Gas Hydrate

3.2 - Prior Research

At the Norwegian University of Science and Technology hydrate was produced in a high-pressure reactor operated at 50-70 bars and 2-10°C. The 600cm³ reactor was filled with 100cm³ of liquid water and the remaining natural gas mixture containing, 92 mol% methane, 5 mol% ethane and 3 mol% propane. Hydrate formation was started by agitation with a magnetic stirrer at 500rpm. The pressure drop was monitored and stirring stopped after an hour. The reactor was then tipped upside down to separate the liquid water and solid hydrate. The remaining hydrate contained some free water (Hydrate formation in stirred tank reactor) M.Mork and J.S. Gudmundsson.

The hydrate was stored in a freezer at -18°C. From the experiment the heat of formation was taken as 410kJ/kg and the specific heat was 2kJ/kgK. The density was 948kg/m³ and the free water estimated at 10wt% and 25vol% porosity due to the packing density of frozen hydrate as particles in bulk. In the actual process developed by Gudmundsson et al, it is assumed that a stirred tank reactor was used with fresh water at 2°C is pumped into the system, and will operate at 10°C. The proposed system is shown in Fig.7.

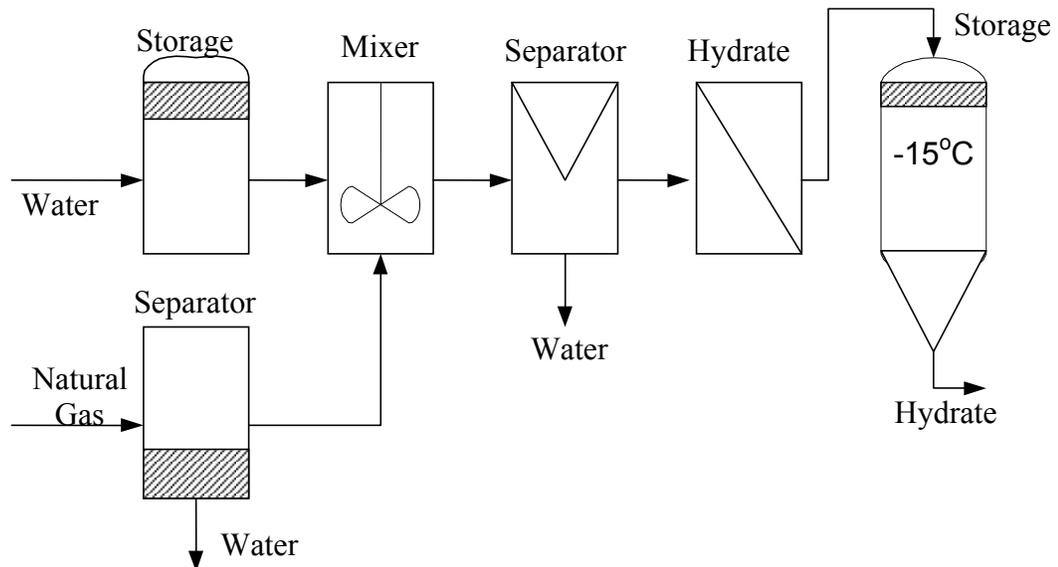


Figure 7 Hydrate Production Flow Diagram (J.S.Gudmondsson)

3.3 - Potential Carriers

The specification found by the Norwegians was done by Shipping Research Services in Oslo in 1990. The carrier (barge) designed was 357m long, 60m wide, and with 20m draught. The maximum cargo volume was 460,000 m³. Transportation of the NGH involves much larger volumes than LNG. One cubic metre is equivalent to about 600Sm³ of methane. The NGH volume is about 4 times that of LNG if the gas content of the NGH is 150Sm³/m³. What was assumed in this research was that the NGH volume would be six times that of LNG.

3.4 - Regasification

After the NGH is transported, the gas has to be obtained from the crystal. Water at 20°C is pumped into the carrier, the hydrate melts in the tanks and the natural gas pumped off to compressors on land. The gas is compressed from atmospheric pressure to around 80bar of which the total compression duty is 100MW. The process flow diagram is shown in Fig. 8.

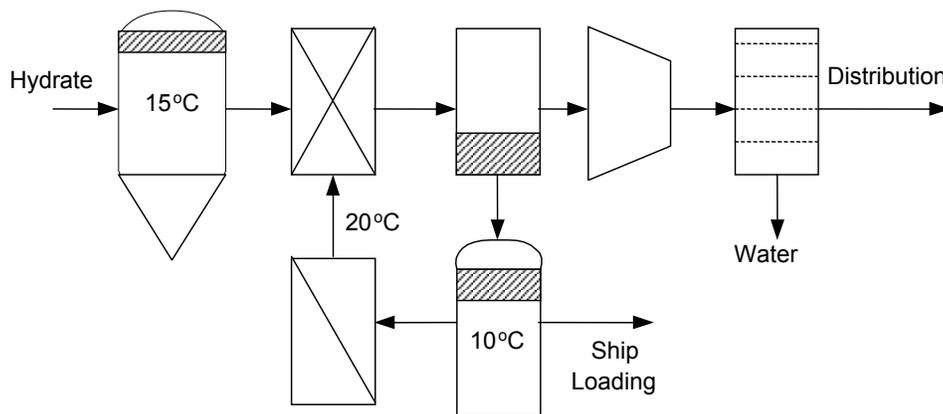


Figure 8 Regasification Block Diagram (J.S.Gudmondsson)

After the initial experiments the Norwegians tried to perfect the formation of hydrate. The maximum content was found to be 161Sm³ gas per m³ of hydrate. The results also showed that gas-content differed for differing sub-cooling temperatures, the stirrer rate had no effect; the formation time was a function of gas-content where the relationship

was shorter with greater gas-content. Other information gained was that hydrates should be produced at around 10°C and 35bar, and stored at -32°C. The process diagram for the further modified system is shown in Figure 9. J.S.Gudmondsson (NTNU).

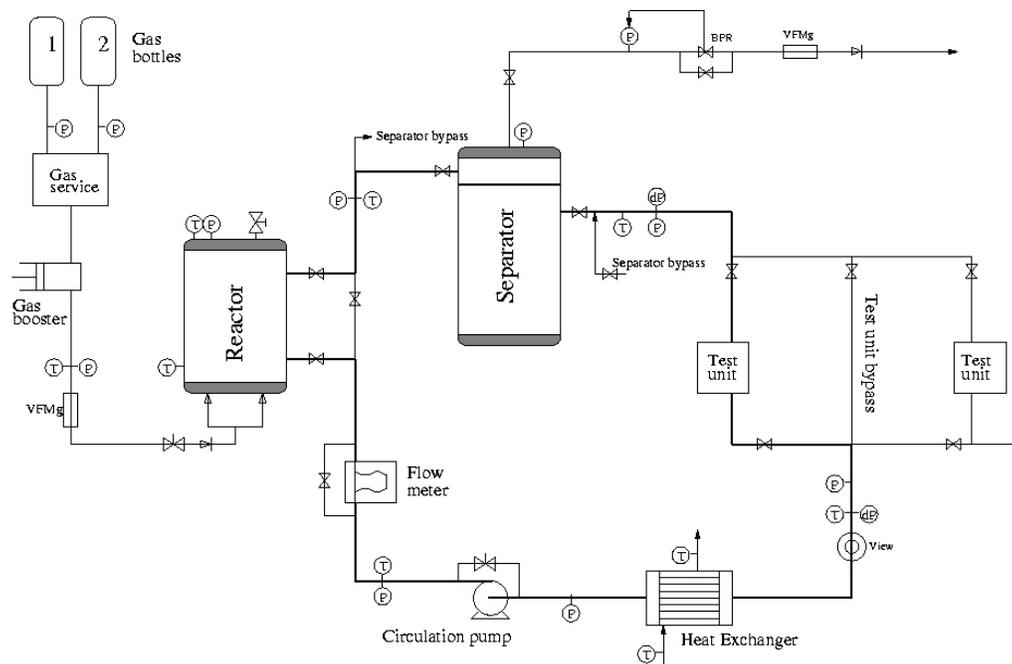


Figure 9 Alternative Continuous Production (Gudmondsson et al. 1997)

3.5 - The NGH Project

For this research the situation and conditions such as temperature and long transportation distances in Australia differ from those found in Norway. The background information can only be used as a guideline for the project as the method of production, storage, and transportation would be different for the conditions that exist in the State of Western Australia.

The Norwegian study was concerned about natural gas hydrate production, transportation and regasification utilizing well established chemical process methodology of synthetic hydrate production. This thesis however, discuss as the production of natural gas hydrate utilizing a variety of new additives that significantly increased natural gas yield from the same volume of water compared to the Norwegian study.

3.5.1 Preliminary Project Work

The preliminary work for the project was a literature search. The literature search found past information that provided a background to the project. The literature is listed in the reference section of the thesis. Other information involving the transportation of NGH was also found. Information relating to the formation and transport of NGH similar to 'dry ice' was found and discarded as inapplicable to the project. A range of trials in the laboratory produced NGH using methane and wellhead gas. The various trials and the equipment used are listed in (Section 5.4.1). The separation of nitrogen from the natural gas stream was also investigated in the laboratory on a preliminary basis and also during the research period. Some work in this area shed further light on the feasibility of nitrogen separation from natural gas. The tests related to nitrogen separation are found in (Section 5.6).

The process simulation (Hysys) investigates the use of different systems to produce hydrate. The simulation of hydrate formation and separation of nitrogen from the natural gas stream using the Equi-phase Hydrate program can be found in (Section 5.5.9). The work was also done on the economic viability and transport of NGH by tankers. The system proposed is economical at this stage so the project is applicable and further work is expected to continue in this area.

3.5.2 Preliminary Laboratory Results

The main results obtained from the laboratory experiments are presented in (Section 5.5). The main results that were obtained are that methane gas hydrate was formed and was more stable than the wellhead gas hydrate that was also formed. The wellhead gas hydrate burned better and for a longer period of time. The surfactant in the wellhead gas hydrate decreased the surface tension allowing more gas to cross the gas-liquid barrier causing more gas to enter the crystal structure.

The separation of nitrogen from the natural gas stream was trialed in the laboratory and produced favourable results. The amount of nitrogen was less in the hydrate than the gas purge, as the nitrogen formed hydrate at different pressure and temperature. For trial one the nitrogen content was near 50mol% in the gas purge while only 30% in the hydrate.

The methane content went from 44-61% between gas purge and hydrate. The second trial showed 50mol% nitrogen in the gas purge while only 20mol% in the hydrate.

The separation was better with less nitrogen. When only 31 kPa pressure was added the difference was 30%, but when 5160 kPa pressure was added the difference was only 20%. The last trial was done only at 800psi and the difference in concentration was large and representative of what was predicted by the simulation. A decrease from 2.48% to 0.53% was shown in the gas chromatograph (GC) analysis.

4 - CHEMICAL ADDITIVES

Hydrates were formed in the laboratory with varying concentrations of different additives, namely Toluene Sulfonic Acid, Sodium Lauryl Sulphate, Oleyl Alcohol and Di-isopropyl Ether. The action of these additives is to decrease the surface tension at the gas-liquid phase boundary, permitting more gas to penetrate the hydrate crystals.

For each sample, one or more of the following tests were performed: (i) Volumetric measurement of excess purge gas, (ii) GC Analysis of free gas and hydrate gas, and (iii) physical observation of the hydrates, in particular, stability and burning period.

The GC analysis described the composition of the excess gas and the gas in the hydrates, providing an indication of the separation properties of the hydrates. The results indicated that Toluene Sulfonic Acid produced the greatest degree of separation, followed by Sodium Lauryl Sulphate and Oleyl Alcohol. A greater concentration of the chemical will give a greater separation, however the difference is minimal.

The volumetric measurements gave consistent results indicating larger amounts of hydrate gas for Toluene Sulfonic Acid than either individual or the mixture of Di-isopropyl Ether and Sodium Lauryl Sulphate. Toluene Sulfonic Acid therefore produces the best hydrates, However it should be handled with care due to its medium toxicity level. Hydrates with Sodium Lauryl Sulphate were also of high quality, but large amounts of foam were produced which may cause blockages in pipelines and damage equipment on large scale production.

Conditions can be estimated using a number of methods based on equilibrium calculations analogous to standard vapour-liquid dew point calculations.

The addition of certain chemicals can inhibit or promote formation. Many of the previous studies into gas hydrates have focused on prevention of hydrate formation. This is because hydrates form in oil and gas pipelines under certain conditions causing

blockages and subsequent pressure damage. Thus a great degree of research has been conducted into chemical inhibitors that reduce the size of crystal hydrate structure to eliminate blockages. Inhibitors suppress hydrate formation by changing the ‘freezing point’ of water (e.g. methanol), attack of the water structure by a hydrogen dipole (e.g. ammonia) or decreasing the activity of the water through a solute (e.g. sodium chloride). Conversely, hydrate formation can be promoted through surfactants, which decrease the surface tension at the gas-liquid phase boundary, permitting more gas to dissolve in the water molecule. The focus of this project was the latter type of chemical, allowing more gas to be transported by ship.

5 - LABORATORY EXPERIMENTATION

5.1 - Safety

Due to the employment of various chemicals as process enhancers for the production of hydrates, specific safety measures were required during these experimental trials.

The minimum safety requirements when working in the laboratory were:

- Long sleeve cotton shirt and long trouser or cotton lab coat
- Clear safety glasses
- Latex gloves
- Safety shoes

All chemicals brought into the laboratory were labeled with the product name, concentration and precautionary statements recommended by the material safety data sheets (MSDS).

Checks were made of the MSD for all chemicals before use. All recommended personal protection items and exposure controls were used while handling the chemicals in its pure form and in mixtures.

When working with Test Cylinders at freezing temperatures, leather gloves were worn.

Whenever venting gases from a Test Cylinder, the Test Cylinders were connected to an external exhaust system.

blockages and subsequent pressure damage. Thus a great degree of research has been conducted into chemical inhibitors that reduce the size of crystal hydrate structure to eliminate blockages. Inhibitors suppress hydrate formation by changing the ‘freezing point’ of water (e.g. methanol), attack of the water structure by a hydrogen dipole (e.g. ammonia) or decreasing the activity of the water through a solute (e.g. sodium chloride). Conversely, hydrate formation can be promoted through surfactants, which decrease the surface tension at the gas-liquid phase boundary, permitting more gas to dissolve in the water molecule. The focus of this project was the latter type of chemical, allowing more gas to be transported by ship.

5 - LABORATORY EXPERIMENTATION

5.1 - Safety

Due to the employment of various chemicals as process enhancers for the production of hydrates, specific safety measures were required during these experimental trials.

The minimum safety requirements when working in the laboratory were:

- Long sleeve cotton shirt and long trouser or cotton lab coat
- Clear safety glasses
- Latex gloves
- Safety shoes

All chemicals brought into the laboratory were labeled with the product name, concentration and precautionary statements recommended by the material safety data sheets (MSDS).

Checks were made of the MSD for all chemicals before use. All recommended personal protection items and exposure controls were used while handling the chemicals in its pure form and in mixtures.

When working with Test Cylinders at freezing temperatures, leather gloves were worn.

Whenever venting gases from a Test Cylinder, the Test Cylinders were connected to an external exhaust system.

5.2 - Disposal and Environmental Considerations

MSDS contain information regarding the disposal of pure chemicals. These procedures were followed for the disposal of all pure chemicals.

When acquiring chemicals it was necessary to confirm with the supplier the dilution required before chemicals could safely be poured down the drain. If there was no acceptable level of dilution this was recorded on the MSDS and the spent chemical was collected in an approved storage container, and disposed of via the disposal procedure described for pure chemicals.

The MSDS lists the toxic fumes emitted by combustion and decomposition. Before using any chemical it was ensured that the exhaust system in place was approved for venting these toxic fumes. If the exhaust system used was not approved for venting these gases, use of the chemical was not permitted. Accidental release procedures were outlined in the MSDS to describe the method required for handling the chemicals when approved ventilation is unviable. These procedures were followed to contain and remove spilled chemicals.

5.3 - Uncertainty

There were a number of minor errors encountered in the experimental procedure.

- The volume of water filled in the graduated cylinders was to a tolerance of +/- 2ml that compounds to +/-4ml when decanted into the Test Cylinder.
- The pressure gauge on the gas cylinder was not a certified gauge which calibrated and therefore had an accuracy of +/- 172 kPa.
- No degree of accuracy could be assumed for the bleed of excess gas. There may be free gas trapped in the hydrate.
- The temperature of the freezer had an accuracy of +/-2 degrees Celsius.
- There will always be some liquid volume lost to the surfaces of the graduated cylinders when decanting from the batch cylinder to the smaller graduated cylinders and then to the Test Cylinder.

5.4 - Method of Preparation

5.4.1 Preparation of Cylinders

1. A clean Test Cylinder is placed firmly in the vice on a 30-45 degree angle with the high side plug end removed.
2. The O-ring seal is coated with grease.
3. A large measuring cylinder is filled with exactly 200ml of tap water for each Test Cylinder to be prepared.
4. Test chemical is selected, then quantity needed is measured as described.
5. The measured quantity is placed in to the large measuring cylinder. Stirring is done with a mixing stainless steel rod until the chemical is totally dissolved.
6. A 200ml portion of the prepared solution is accurately decanted from the large measuring cylinder into smaller measuring cylinders and then transferred into the open clamped Test Cylinder. The plug-end is replaced with the valve in the open position. Once the plug-end is tightly closed, the valve is closed.
7. The identification number on the Test Cylinder, the volume of water used and the additive name and concentration are recorded on the test data sheet.
8. For subsequent Test Cylinders, repeat preparation steps 1 through 7.

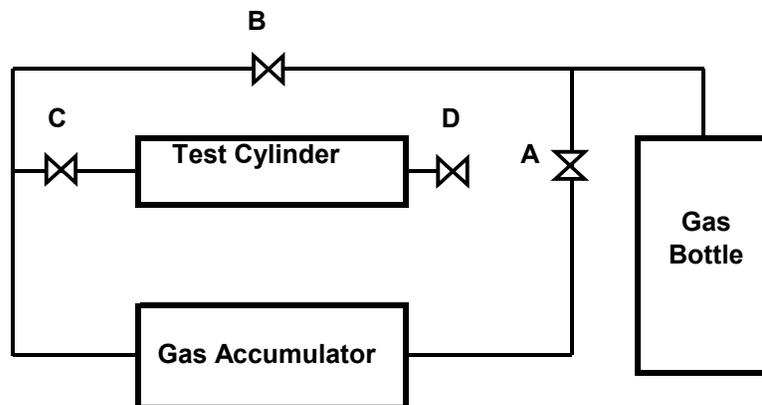


Figure 10 Laboratory Test Cylinder

5.4.2 Cylinder Pressurization

9. The Test Cylinder is connected to the gas bottle and gas accumulator as shown in Figure 5.
10. Check that valve B is closed, valve A to the gas accumulator is closed and both Test Cylinder valves (C and D) are closed.
11. Connect the Test Cylinder to the high-pressure tubing coming from the regulator of the gas bottle and rest the Test Cylinder on the secured block to keep the test solution away from the elevated valve D.
12. Open the gas bottle by rotating the key through a maximum arc of 120 degrees.
13. Check the maximum pressure allowable through the low-pressure regulator. If greater than 690 kPa, close the regulator.
14. Open valve B below the regulator. Read the low pressure gauge on the gas bottle regulator. Adjust the regulator to allow gas flow from the gas bottle at 690 kPa.
15. Open valve D on the Test Cylinder. Close valve D after five seconds of gas flow.
16. Close valve B.
17. Invert the Test Cylinder and vent the gas through valve C. Close valve C when a clear gas stream is observed.
18. Replace the Test Cylinder on the secured block.
19. Open valve B then valve D into the Test Cylinder and pressurise to either 9990 kPa or the working pressure in the gas bottle. Close valve D and valve B.
20. If it is necessary to pressurize the Test Cylinder from the working pressure of the gas bottle to 9990 kPa the gas accumulator is used. Open valve A to the gas accumulator. Turn the gas accumulator air supply on with valve E. When pressure gauge X reads a pressure greater than the working pressure of the gas bottle (i.e. the pressure inside the Test Cylinder) open valve D.
21. Close valve D when pressure gauge X reads 9990 kPa. Turn the gas accumulator air supply off at valve E. Close valve A.
22. Disconnect the high-pressure tubing attached to valve D and place the Test Cylinder on a mixing table for a minimum period of one hour.
23. Repeat steps 9 through 22 for all remaining Test Cylinders.

24. When all Test Cylinders have been pressured to 9990 kPa, close the gas bottle key.
25. Following the one-hour mixing period, the Test Cylinders are re-pressured to the final test pressure.
26. Reconnect the Test Cylinder as shown in Figure 5. Check that valve A and valve B are closed and both Test Cylinder valves C and D are closed.
27. Rest the Test Cylinder on the secured block to keep the fluid away from valve D.
28. Open the gas bottle by rotating the key through a maximum arc of 120 degrees.
29. Check the maximum pressure allowable through the low-pressure regulator. If this is greater than 690 kPa, close the regulator and set to approximately 690 kPa when the gas accumulator is turned on.
30. Open valve A to the gas accumulator. Turn the gas accumulator air supply on at valve E. When pressure gauge X reads a pressure greater than 9990 kPa (or the pressure inside the Test Cylinder) open valve D on the Test Cylinder.
31. Close valve D when the pressure gauge X reads 10335 kPa. Close valve E and then valve A.
32. Disconnect the high-pressure tubing attached to valve D and carry the Test Cylinder to the freezer with the elevated end vertical.
33. Place the Test Cylinder in the freezer with the same end elevated to prevent hydrate from obstructing valve D.
34. Repeat steps 24 through 33 for all remaining Test Cylinders.
35. When all Test Cylinders are pressured to 10335 Kpa, close the gas bottle key and bleed the gas remaining in the line running to the gas accumulator and in the line to valve B.
36. The Test Cylinders should be left in a freezer at -15 to -25 degrees Celsius overnight.

5.4.3 Venting Excess Gas

37. Protective leather gloves **MUST** be worn when handling Test Cylinders at freezing temperatures.
38. Remove the Test Cylinder from the freezer and cover the elevated valve D with a hose leading to an external exhaust or place the Test Cylinder in a fume cupboard. Slowly open valve D.
39. Allow all excess gas to bleed from the Test Cylinder. Record any relevant observations regarding the characteristics of the excess gas bleed-down – e.g., speed, volume, crackling (in Test Cylinder), etc.
40. Close Valve D and place the Test Cylinder in a water bath to defrost. This will take between one to two hours depending on the water temperature.
41. Repeat steps 37 through 40 for all Test Cylinders.

5.4.4 Measuring Evolved Hydrate Gas Volume

42. Check the Wet Test Gas Meter is level, there is no water in the ballast and the water level inside the Wet Test Gas Meter is at the appropriate height.
43. Remove Test Cylinders from the water bath and towel dry.
44. Connect the Test Cylinder to the Wet Test Gas Meter with high-pressure tubing via a Liquid Knock-out bottle.
45. Rest the Test Cylinder on a secured block to keep the fluid away from the valve connected to the Wet Test Gas Meter.
46. Record the number on the counter on the face of the Wet Test Gas Meter.
47. Very slowly open the elevated valve on the Test Cylinder. Gas cannot be vented into the Wet Test Gas Meter any faster than 2 liters/second.
48. As the gas flow into the Wet Test Gas Meter slows valve D can be opened further.
49. When no flow is recorded into the Wet Test Gas Meter, close the valve on the Test Cylinder and carefully invert 3-4 times. Open the Test Cylinder valve to the Wet Test Gas Meter. If there is additional gas flow from the Test Cylinder, repeat this process until no further gas evolves.

50. Close the Test Cylinder valve and record the number on the face of the Wet Test Gas Meter.
51. Disconnect the high-pressure tubing from the Test Cylinder valve and remove the Test Cylinder for cleaning.
52. Repeat steps 42 through 51 for all remaining Test Cylinders.

5.4.5 Cleaning Experimental Cylinders

53. Place the Test Cylinder in a bench mounted vice on an angle of 30-45 degrees. Open the high side valve and remove the plug end from the Test Cylinder.
54. Using paper hand towels wipe excess grease from the thread and O-ring seal of the plug end and the Test Cylinder.
55. Unclamp the Test Cylinder and empty liquor into a basin.
56. Fill Test Cylinder with water and 10ml of Quantum clean (laboratory glass cleaner).
57. Using a long handled brush with a bristle diameter at least 1cm greater than the internal diameter of the Test Cylinder clean the inside of the Test Cylinder, paying special attention to the seal and thread of the open end.
58. To conserve cleaning fluid, pour the contents of the Test Cylinder into the next Test Cylinder waiting to be cleaned.
59. Rinse the cleaned Test Cylinder thoroughly with tap water.
60. When satisfied that no cleaning fluid remains in the Test Cylinder leave inverted on a piece of paper hand towel to allow the excess water to drain.
61. Clean the removed plug end and valve with a small amount of the cleaning solution and rinse thoroughly with tap water. Flow water through the open valve.
62. Place the cleaned plug end beside the cleaned Test Cylinder to dry.
63. Repeat steps 53 through to 62 for all remaining Test Cylinders.

5.5 - Laboratory Test Results and Discussion

5.5.1 Introduction

Subsequent to the extensive testing and trialling of various concentrations of chemical additives, pressure variable and temperature of hydrate formation, an HFVF of 202 was achieved and tests were repeated to ensure accuracy of the results. In this section, the method for hydrate production and the results achieved will be discussed. With all chemicals tested to-date, one specific chemical additive achieved the best results in terms of chemical stability, its impact on the process and repeatability of tests.

5.5.2 Gas Chromatography Analysis

The Gas Chromatography analysis results are shown in Tables 2 and 3 below. Two different gases were used in the laboratory - initially a mixture of methane and nitrogen, then switching to a natural gas mixture, which was used on the hydrate module. The exact composition of the natural gas mixture is shown in Table 4.

Additive	Oleyl Alcohol		Toluene Sulfonic Acid		Sodium Lauryl Sulfate		Sodium Lauryl Sulfate	
Mass (g)	1.0		1.0		1.0		0.5	
Vol. Water (cc)	120		120		120		120	
<u>Mole Percent</u>								
Excess Gas	#1	#2	#1	#2	#1	#2	#1	#2
Methane	95.39	95.59	95.08	95.17	94.87	94.87	94.87	94.85
Nitrogen	4.61	4.41	4.92	4.83	5.13	5.13	5.13	5.15
Hydrate Gas	#1	#2	#1	#2	#1	#2	#1	#2
Methane	97.16	-	97.75	97.75	97.41	97.39	97.32	97.36
Nitrogen	2.84	-	2.25	2.25	2.59	2.61	2.68	2.64

Table 2 GC Analysis, Methane-Nitrogen Gas

Additive	Oleyl Alcohol	Oleyl Alcohol	TolueneSulfonicAcid
Mass (g)	0.5	5.0	1.0
Vol. Water (cc)	120	120	120
Mole Percent	-	-	-
Excess Gas	-	-	-
CO2	2.17	2.26	2.12
N2	2.75	2.85	2.72
C1	85.05	86.10	85.05
C2	6.26	5.88	6.24
C3	2.70	1.96	2.80
i-C4	0.39	0.28	0.39
n-C4	0.60	0.58	0.60
i-C5	0.05	0.05	0.05
n-C5	0.02	0.03	0.02
C6	0.01	0.01	0.01
C7	0.00	0.00	0.00
Hydrate Gas			
CO2	2.56	2.15	2.54
N2	3.98	2.65	1.34
C1	89.75	85.00	67.11
C2	3.02	6.61	12.22
C3	0.26	2.60	10.76
i-C4	0.05	0.34	1.86
n-C4	0.28	0.58	3.54
i-C5	0.05	0.04	0.35
n-C5	0.04	0.02	0.22
C6	0.01	0.01	0.05
C7	0.00	0.00	0.01

Table 3 GC Analysis, Natural Gas

Component	Mol %
CO2	2.2
N2	2.59
C1	84.25
C2	6.78
C3	3.11
i-C4	0.41
n-C4	0.59
i-C5	0.04
n-C5	0.02
C6	0.01
C7	0

Table 4 GC Analysis, Natural Gas

The GC analysis provides an indication of the separation properties of the hydrates formed by the various additives. Examination of Table 1 can be interpreted to give the following results:

The amount of nitrogen in the hydrate gas is approximately half that in the free gas, confirming previous findings that nitrogen will not form hydrates easily.

The different chemical additives give different hydrate gas compositions and thus different degrees of separation. In terms of removing nitrogen from the hydrate gas, Toluene Sulfonic Acid is the most successful, followed by Sodium Lauryl Sulphate and Oleyl Alcohol. Graphs comparing the degree of separation for the different additives are shown in, Figures 11 and 12.

- The concentration of the additive has an effect on the hydrate gas composition. The 1.0g mixture of Sodium Lauryl Sulphate produces less nitrogen in the hydrate than the 0.5g mixture. However, the effect is very small.
- The variation between runs was minimal, indicating a good degree of accuracy in the analysis.

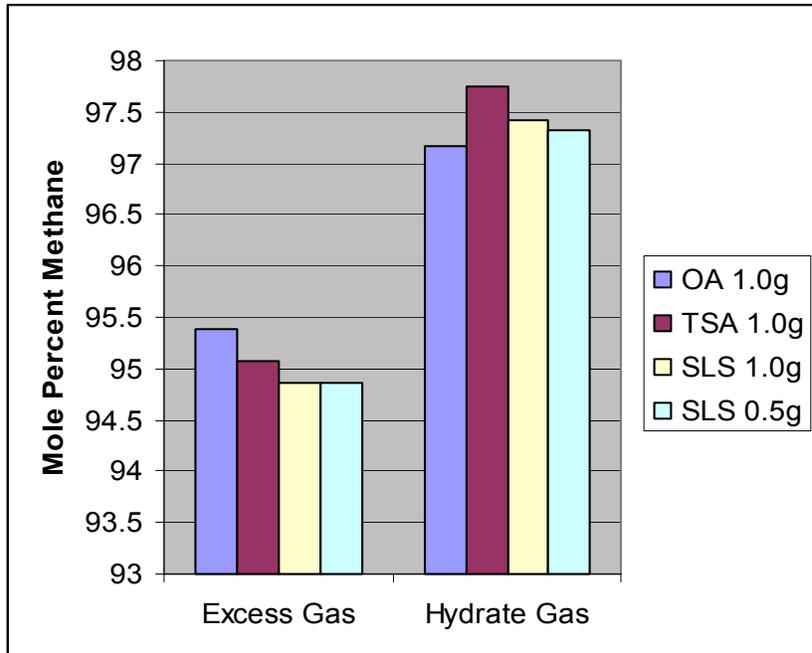


Figure 11 Comparison of Methane Content for Different Additives

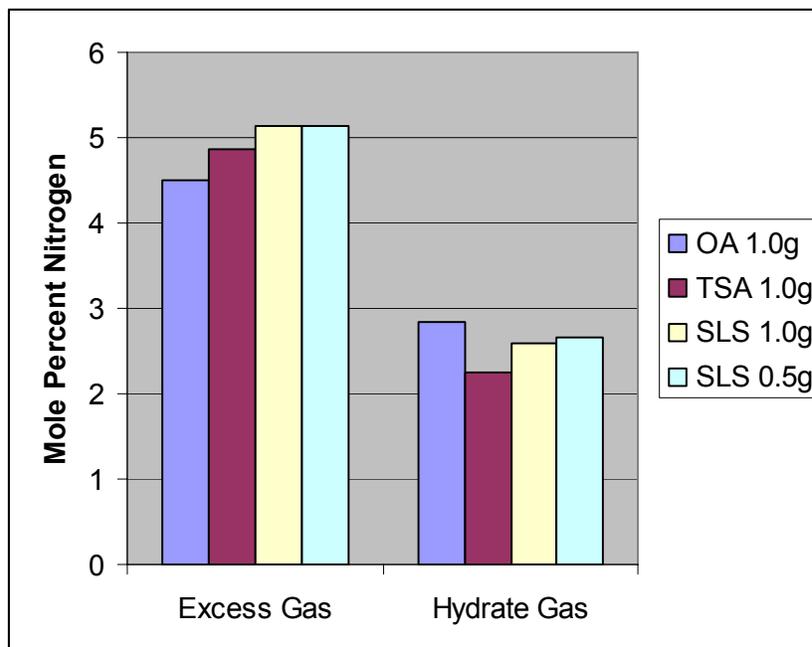


Figure 12 Comparison of Nitrogen Contents for Different Additives

The GC analysis using the natural gas has more relevance to the objective of the project in giving a better indication of composition of the transported gas. The following plot represents the separation of the various components.

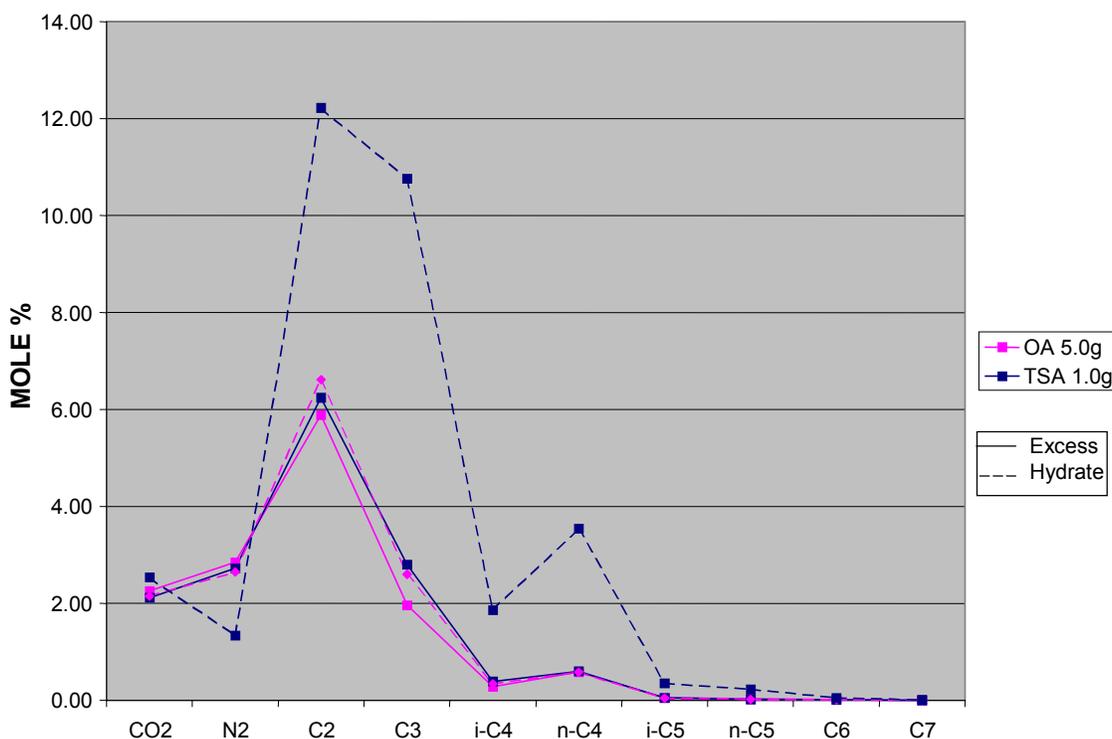


Figure 13 Mole percent of components in excess and hydrate gas

The data for 1.0g of Oleyl Alcohol has been omitted in this graph since it appears as erroneous. There is more nitrogen in the hydrate gas than the excess gas, and as the separation of nitrogen in hydrates has been extensively proven, the primary explanation would be erroneous data.

Consequently, the effect of the different concentrations of Oleyl Alcohol cannot reasonably be compared. Physical inspection of the hydrates formed, however, indicated that any difference was minimal, and similar to results found with the nitrogen-methane gas and Toluene Sulfonic Acid.

A result which can be concluded from Figure 8, is that Toluene Sulfonic Acid provides a greater degree of separation than Oleyl Alcohol, further supporting the results found previously.

In terms of the separation of certain components, it can be seen that lighter hydrocarbons such as ethane and propane form hydrates preferentially over larger components. The amount of n-butane in hydrates is higher than that of i-butane, indicating straight chain hydrocarbons will enter the cage-like water structure easier than branched hydrocarbons.

5.5.3 Physical Observation

For each specified concentration, usually the cylinders were first opened for physical inspection before mixing more cylinders for GC analysis and volumetric measurements.

The Toluene Sulfonic Acid produced hydrates that were stable and burned for a long period. Increasing the concentration had little effect on the hydrates formed, producing good hydrates with concentrations as small as 0.5g and 1g per 200cc.

The Sodium Lauryl Sulphate also produced high quality hydrates. However, it had a tendency to generate large amounts of foam. Such foam could possibly cause blockages in pipes and damage equipment. A mixture of Sodium Lauryl Sulphate and Di-isopropyl Ether was tested but similar foaming problems occurring. In fact, this foam penetrated the volumetric meter during testing. The meter required servicing, and during subsequent testing, a buffer flask was attached to trap the foam.

5.5.4 Problems

Leaks in the cylinders were encountered shortly after commencement of testing. Immediately after pressurization, all cylinders were checked as part of the procedure. In every instance, no leaks were present. However, after the cylinders were removed from the freezer, leaks occurred at various stages of the cylinder warming. Given the condition and age of the seals which impacted on the seals' elasticity, deterioration

was further caused by the low temperatures in the freezer. After cylinders were removed from the freezer, they were placed in a water bath to check for leaks. During freezing and re-warming the seals deformed and thus some of the sealing capability was lost. Subsequently, it was decided to replace all cylinders seals to ensure accuracy of the test results.

5.5.5 Recommendation

The main immediate requirement was to eliminate the leaks occurring from the cylinders by inspection of the end cap seals and regular replacement of the cap seals. Any further discrepancies can be concluded as being due to other factors, which would subsequently be investigated.

None of the chemicals tested were completely satisfactory. Therefore, the testing procedures have and will be continued as outlined in this report with new chemicals and at a greater rate. For each new chemical tested, physical observation, volumetric measurement and GC analysis had and will continue to be performed. Considering the time required for GC analysis, the former two procedures were executed first such that those chemicals that do not produce enough gas in the hydrates were immediately discarded. Chemicals deemed favourable in the laboratory would be tested further on the hydrate pilot plant (module) to evaluate success on a larger scale.

5.5.6 Summary Results

5.5.6.1 Toluene Sulfonic Acid (TS)

TS gives the best results of all chemicals tested so far. TS has been tested at concentrations of 0.2, 0.25, 0.35, 0.5, 0.75, 1, 1.25, 1.5 and 2 grams per 180cc of water, and 1 and 1.25g per 120cc of water. Later tests were conducted on 200cc of water of varying concentrations, giving promising results as seen in Table 5.

Average hydrate gas volume ratios were in the order of 99 to 202. A summary of results is also given in Table 5. (note that all the results shown in table 5, excluding

the last five results, have some inaccuracies, as these results were obtained prior to any knowledge of the hygroscopic property of TS. This meant that the mass measured were not exact).

Compound	HFVF
TS (0.2g/180cc)	99
TS (0.25g/180cc)	165
TS (0.35g/180cc)	147
TS (0.5g/180cc)	175
TS (0.75g/180cc)	180
TS (1g/180cc)	176
TS (1.25g/180cc)	182
TS (1.5g/180cc)	179
TS (2g/180cc)	176
TS (0.2g/180cc)	130
TS (1g/190cc)	187
TS (1g/200cc)	195
TS (1.5g/230cc)	187
TS (1.5g/250cc)	121
TS (1.25g/200cc)	196
TS (1.5g/200cc)	202

Table 5 Average Hydrate Gas Volumes for TS

TS is a hygroscopic, has an affinity for absorbing moisture in the atmosphere. In our experiment a 2.7g sample was left overnight exposed to the atmosphere and recorded a 25% increase in weight. In an attempt to standardize results, TS is dried to 90 Degrees Celsius prior to mixing in the pressure cylinders.

Experimentation with TS showed that if a sample is left in the oven over night at 90 Degrees Celsius, it would melt. In a separate experiment TS has been allowed to melt before allowing the sample to re-crystallize in a sealed container. The TS proved to be of very fine powder but had no impact on the quality of hydrates produced. In the past average hydrate gas volumes vary somewhat due to environmental conditions that existed during testing (mainly ambient temperatures), recently an error of $\pm 6\%$ existed between results. This can be seen with the

following data from 1.0g TS using the old method (Figure 14) and TS 1.5g using the mixing machine (Figure 15).

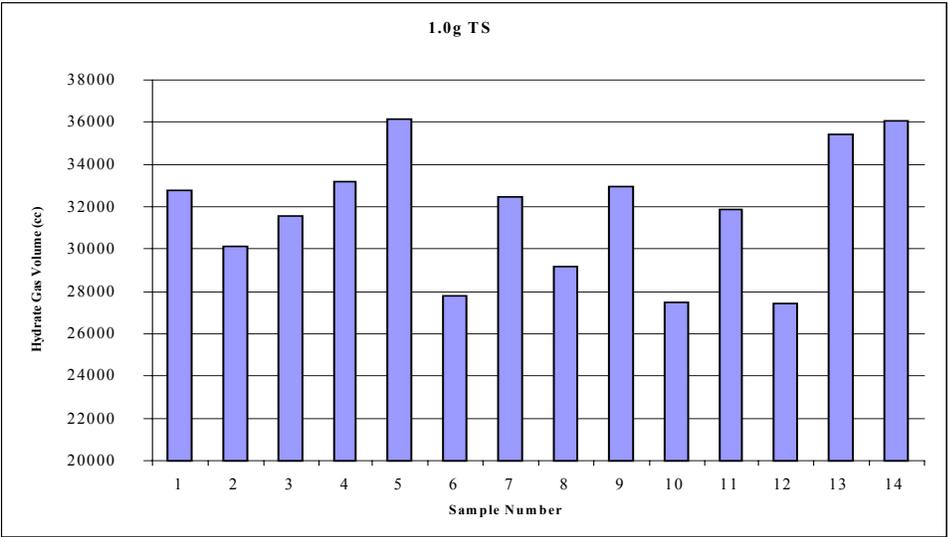


Figure 14 Hydrate Gas Volumes for 1.0g TS

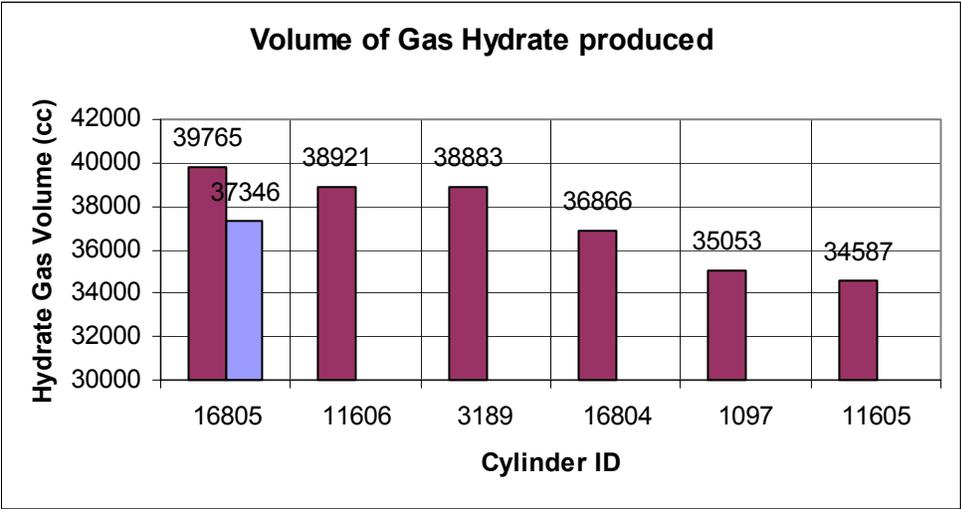


Figure 15 Hydrate Gas Volume for 1.5g TS using the Mixing machine

An approximation of gas volumes versus TS concentration is shown in Fig. 16. The volumes appear to increase reaching a limiting value of HFVF of 202 at a TS concentration of 1.5g.

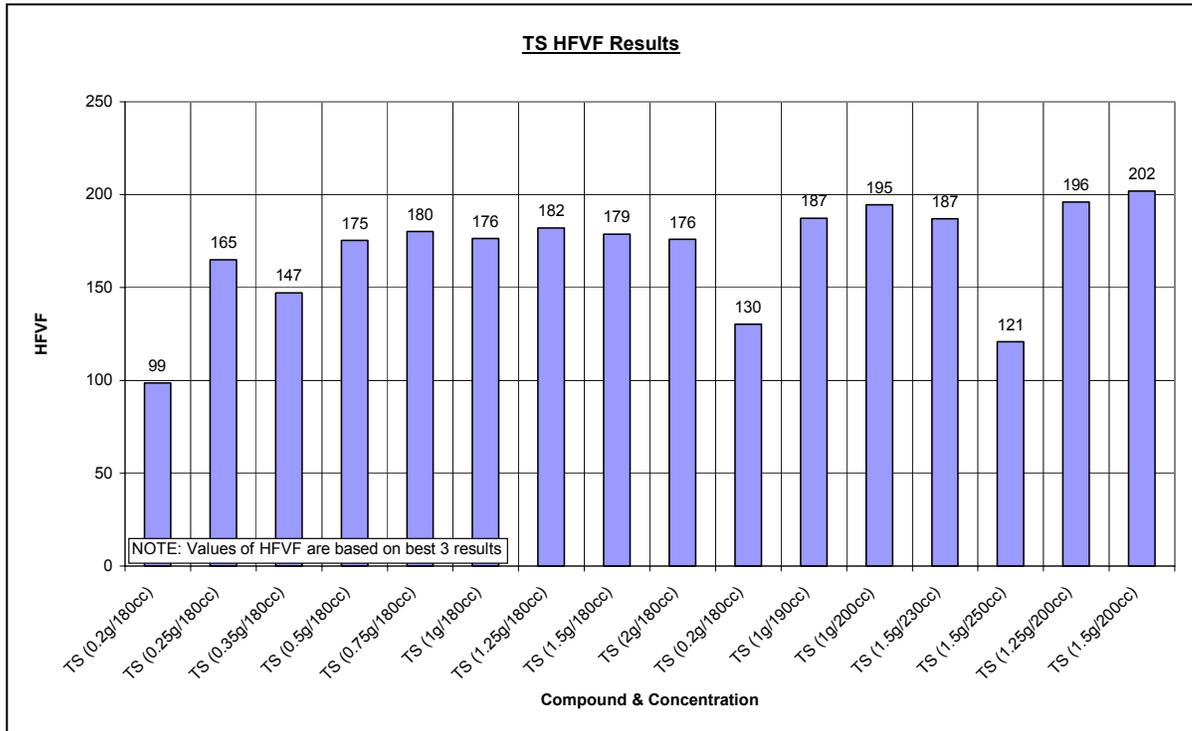


Figure 16 Hydrate Gas Volumes versus Concentration of TS

5.5.6.2 Sodium Lauryl Sulphate (SLS)

This was tested solely and in combination with other chemicals giving good chromatograph and volumetric results. It forms significant amounts of foam, blocking pipes and may possibly cause damage to equipment. Foaming does not subside when combined with other chemicals. SLS appears to hinder the performance of TS.

5.5.6.3 Carboxyl Methyl Cellulose Sodium Salt (CC)

Very low hydrate gas volume ratios of approximately 10. do not appear to improve with greater concentrations.

5.5.6.4 Nitromethan (NTM), Nitropropane (NTP), Dioxane (DX) & Propylene Oxide (PPO)

All gave approximately similar results, with hydrate gas volume ratios in the order of 5 to 10, as summarized in Figure 17. they did not appear to improve with greater concentrations. The chemicals are toxic and highly flammable, with DX and PPO to a greater extent.

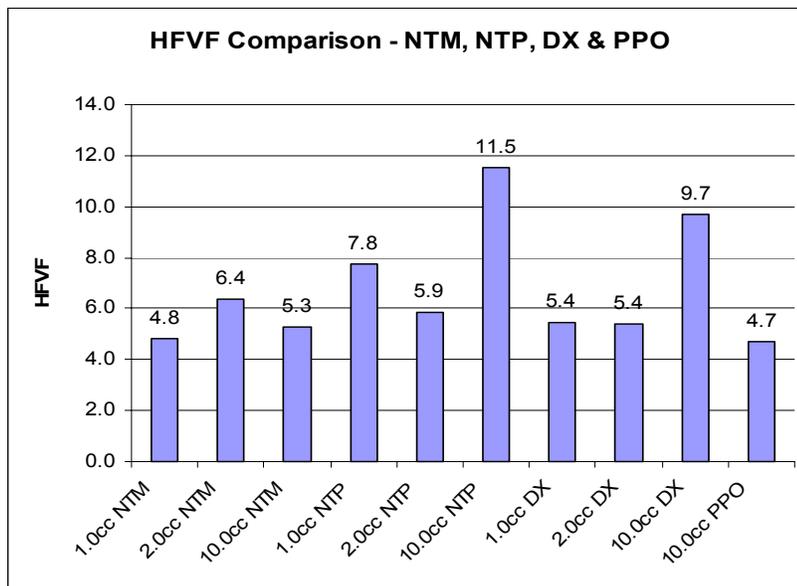


Figure 17 Hydrate Gas Volume Ratios for NTM, NTP, DX & PPO

5.5.6.5 Other, Oleyl Alcohol (OA), Di_isopropyl Ether (DIPE) and Sodium Tripolyphosphate (TP)

Improvement of unsuccessful individual chemicals was attempted by combination with another chemicals. Combination results are generally not much better than those of the more successful chemical. This is demonstrated in Table 6.

For example, CC individually does not produce good hydrates, while TS does. Combining the two significantly improves the hydrate gas volume above that of CC, but not that of TS. This also occurs when CC is combined with SLS, and with other combinations of DIPE, TP and OA.

Concentration	Average	HFVF
1.25g TS	32782	182.1
1.25g CC; 1.25g TS	31033.3	172.4
0.5g TS	31584	175.5
0.5cc DIPE; 0.5g TS	24576.3	136.5
1.25gCC; 1.25g SLS	27625.7	153.5
5.0g OA; 1.0g TP	2455.0	20.5
5.0g OA; 5.0g TP	1320.0	11.0
0.5cc DIPE; 0.5g SLS	26237.3	145.8

Table 6 Hydrate Gas Volume Ratios for Combinations of Chemicals

5.5.7 Conclusion

The main conclusion which may be drawn from the GC analysis and volumetric results was that Toluene Sulfonic Acid additive produces the best hydrates of those additives tested, in terms of separation characteristics and hydrate gas volumes. When tested on the hydrate Pilot Plant (module), excellent hydrates were produced under lower concentrations and pressures. However, Toluene Sulfonic Acid is considered a toxic substance. The North American Emergency Response Guidebook, Guide 153 (Substances Toxic and/or Corrosive) describes the following for solid Toluene Sulfonic Acid with no more than 5% free Sulfuric Acid. Inhalation, ingestion or skin contact with material may cause injury. Contact with molten substance may cause severe burns to skin and eyes. As such, it would be preferable to take caution with this additive in industrial production of hydrates if possible.

Sodium Lauryl Sulphate also produced good quality hydrates and has a good degree of separation. The main problem with using this chemical is the large amount of foam produced. The hydrates have a different physical appearance and the foam does not collapse readily. This could create major problems with blockages in pipes and equipment damage. For this reason, testing Sodium Lauryl Sulphate on the hydrate pilot plant (module) would be avoided. A mixture of Di-isopropyl Ether and Sodium Lauryl Sulphate was tested in the hope of maintaining the good hydrate-forming properties of Sodium Lauryl Sulphate while eliminating the foaming problems. The hydrates thus formed were indeed of good quality, however large amounts of foam were still produced. As before, this foam does not collapse readily, and actually penetrated and damaged the volumetric meter.

Oleyl Alcohol was dismissed as a possible additive. In most tests, the results produced a large amount of ice instead of hydrate, and the GC Analysis indicates low separation properties. Furthermore, Oleyl Alcohol is not miscible with water and a high degree of dispersion in the mixture is difficult to maintain. The laboratory testing was more of a screening process to eliminate chemicals deemed immediately unworthy. The testing procedures were somewhat inconsistent to attain exact relationships of the effect of different chemical concentrations on the hydrates formed. The GC Analysis was accurate, however it takes a long time to complete and cannot be executed concurrently with volumetric measurements. The volumetric data of excess gas is unstable and does not agree with theoretical trends. This is due in part to the unreliability of the volumetric meter as the meter does not correct for pressure or temperature.

The following points can be concluded as a result of these tests:

- From all experimentation work performed utilizing small lab cylinders, TS time and gain have proven to produce the best results of hydrates.
- Current testing method is yielding consistent results.

- Further testing is planned for TS, with efforts being concentrated on changing the concentrations, the volume used, mixing time, and pressures. These parameters will be altered in a bid to obtain optimal conditions for the best hydrates.

5.5.8 HYSYS simulation and results

The HYSYS system that produced hydrate was a system with two streams a gas and water stream entering a separator. The vapour outlet was then compressed and put through a cooler where hydrate formed in the outlet stream. The composition on the inlet stream and the outlet stream are shown in Table 7 and Table 8.

COMPOUND	MOLE FRACTION
Nitrogen	0.0120
Carbon Dioxide	0.0270
Methane	0.0875
Ethane	0.0560
Propane	0.0220
n-Butane	0.0080
Water	0.0000

Table 7 Inlet Stream (Water added pure in streams)

COMPOUND	MOLE FRACTION
Nitrogen	0.01187
Carbon Dioxide	0.02671
Methane	0.08656
Ethane	0.00540
Propane	0.02176
n-Butane	0.007914
Water	0.01074

Table 8 Cooler Outlet Stream

The results from the program show the difference between the nitrogen content of the purge gas and the hydrate gas, also the formation temperature for two pressures. The difference in nitrogen concentration was from 2.5 % to 0.3 % for the optimum pressure and 2.5 % to 0.6 % for the laboratory pressure used. Note that the simulation works off a free water calculation and is more applicable to a continuous process where the hydrate formed is only with water vapour in the gas stream determined by its vapour pressure. The results also show the different formations: carbon dioxide easily forms hydrate; pure nitrogen forms hydrate only at extremely low temperatures; pure methane hydrate is harder to form than a mixture; and ease of formation of the hydrate increases with addition of carbon dioxide and the heavier hydrocarbons. The charts obtained from the simulation show that the optimum separation of nitrogen occurs when there is the least amount of nitrogen in the hydrate, which occurs at 220psi. It also shows that the decrease of methane in the hydrate is negligible. The simulation program is also accurate in producing a NGH curve for different pressures.

Domgas		Compressor Outlet	
Temperature	20.00 °C	Temperature	467.7 °C
Pressure	101.2 Kpa	Pressure	1.0E+4.0 kPa
Molar Flow	1.780E+04 kg mole/h	Molar Flow	1.799E+04kg mole/h

Water		Cooler Outlet	
Temperature	20.00 °C	Temperature	15.00 °C
Pressure	101.2 kPa	Pressure	8000 kPa
Molar Flow	1108 kg mole/h	Molar Flow	1.799E+04 kg mole/h

Liquid		Vapour	
Temperature	8.543 °C	Temperature	8.543 °C
Pressure	101.2 kPa	Pressure	101.2 kPa
Molar Flow	914.8 kg mole/h	Molar Flow	1.799E+04 kg mole/h

Compressor		Energy 1	
Feed Pressure	101.2 kpa	Heat Flow	4.15E+08 kJ/h
Product Pressure	1.0E+ 4 kpa		
Molar Flow	1.799E+04 kg mole/h		
Energy	4.15E+08 kJ/h		

Cooler		Energy 2	
Duty	4.533E+08 kJ/h	Heat Flow	4.533E+08 kJ/h
Feed Temperature	467.7 °C		
Product Temperature	15.0 °C		

Separator	
Separator Type	Separator
Vessel Temperature	8.543 °C
Vessel Pressure	101.2 kPa
Liquid Molar Flow	914.8 kg mole/h
Duty	0.0 kJ/h

Table 24 HYSIS Simulation Input Data

DOMGAS

FEED TO	PRODUCT FROM	LOGICAL CONNECTION
Separator: Sep		

General Properties	Overall	Vapour Phase
Vapour/Phase Fraction	1.000	1.000
Temperature (°C)	20.00 *	20.00
Pressure kPa	101.2 kpa*	101.2 kPa
Molar Flow (kg mole/h)	1.78E+04	1.78E+04
Mass Flow (m ³ /h)	3.325E+05	3.325E+05
Liquid Volume Flow (m ³ /h)	1000 *	1000
Molar Enthalpy (kJ/kg mole)	-8.442E+04	-8.442E+04
Mass Enthalpy (kJ/kg)	-4519	-4519
Molar Entropy (kJ/kg mole-C)	186.5	186.5
Mass Entropy (kJ/kg-C)	9.986	9.986
Heat Flow (kJ/m ³)	-1.502E+09	-1.502E+09
Molar Density (kg mole/ m ³)	0.04168	0.04168
Mass Density (kg/ m ³)	0.7787	0.7787
Std. Liquid Mass Density (kg/m ³)	-	-
Molar Heat Capacity (kJ/kg mole-C)	38.13	38.13
Mass Heat Capacity (kJ/kg-C)	2.041	2.041
Thermal Conductivity (W/m-K)	0.03082	0.03082
Viscosity (cP)	0.01114	0.01114
Surface Tension (dyne/cm)	-	-
Specific Heat (kJ/kg mole-C)	38.13	38.13
Act. Vol. Flow (m ³ /h)	4.269E+05	4.269E+05
Molecular Weight	18.68	18.68
Z Factor	0.9971	0.9971

Table 25 HYSYS Material Stream Specification Sheet

COMPONENT DATA

OVERALL PHASE (Vapour Fraction 1.000)						
Components	Molar Flow (kg mole/h)	Mole Fraction	Mass Flow (kg/h)	Mass Fraction	Liquid Volume Flow (m ³ /h)	Liquid Volume Fraction
Methane	1.557E+04 *	0.8750 *	2.498E+05 *	0.7514 *	834.4 *	0.8344 *
Ethane	996.6 *	0.0560 *	2.997E+04 *	0.09014 *	84.26 *	0.08426 *
Propane	391.5 *	0.0220 *	1.727E+04 *	0.05193 *	34.08 *	0.03408 *
n-Butane	142.4 *	0.0080 *	8275 *	0.02489 *	14.19 *	0.01419 *
H ₂ O	0.0 *	0.0000 *	0.0 *	0.0 *	0.0 *	0.0 *
CO ₂	480.5 *	0.0270 *	2.115E+04 *	0.06361 *	25.62 *	0.02562 *
Nitrogen	213.6 *	0.0120 *	5983 *	0.01799 *	7.419 *	0.007419 *
Total	1.78E+04	1.0000	3.325E+05	1.0	1000 *	1.0

Vapour Phase (Phase Fraction 1.000)						
Components	Molar Flow (kg mole/h)	Mole Fraction	Mass Flow (kg/h)	Mass Fraction	Liquid Volume Flow (m ³ /h)	Liquid Volume Fraction
Methane	1.557E+04 *	0.8750 *	2.498E+05 *	0.7514 *	834.4 *	0.8344 *
Ethane	996.6 *	0.0560 *	2.997E+04 *	0.09014 *	84.26 *	0.08426 *
Propane	391.5 *	0.0220 *	1.727E+04 *	0.05193 *	34.08 *	0.03408 *
n-Butane	142.4 *	0.0080 *	8275 *	0.02489 *	14.19 *	0.01419 *
H ₂ O	0.0 *	0.0000 *	0.0 *	0.0 *	0.0 *	0.0 *
CO ₂	480.5 *	0.0270 *	2.115E+04 *	0.06361 *	25.62 *	0.02562 *
Nitrogen	213.6 *	0.0120 *	5983 *	0.01799 *	7.419 *	0.007419 *
Total	1.78E+04	1.0000	3.325E+05	1.0	1000 *	1.0

Table 26 HYSIS Component data sheet

* = Values as specified by User

FEED TO	PRODUCT FROM	LOGICAL CONNECTION
	Cooler	

GENERAL PROPERTIES			
General Properties	Overall	Vapour Phase	Aqueous Phase
Vapour/Phase Fraction	0.9896	0.9896	0.01043
Temperature (°C)	15.00 *	15.00	15.00
Pressure kPa	1161*	1161	1161
Molar Flow (kg mole/h)	1.799E+04	1.780E+04	187.7
Mass Flow (m ³ /h)	3.359E+05	3.326E+05	3385
Liquid Volume Flow (m ³ /h)	1003	1000	3.393
Molar Enthalpy (kJ/kg mole)	-8.867E+04	-8.659E+04	-2.861E+05
Mass Enthalpy (kJ/kg)	-4748	-4635	-1.586E+04
Molar Entropy (kJ/kg mole-C)	143.8	144.8	51.04
Mass Entropy (kJ/kg-C)	7.703	7.752	2.830
Heat Flow (kJ/m ³)	-1.595E+09	-1.541E+09	-5.37E+07
Molar Density (kg mole/ m ³)	4.302	4.260	56.41
Mass Density (kg/ m ³)	80.33	79.59	1017
Std. Liquid Mass Density (kg/m ³)	-	-	1015
Molar Heat Capacity (kJ/kg mole-C)	53.60	53.35	77.61
Mass Heat Capacity (kJ/kg-C)	2.871	2.856	4.303
Thermal Conductivity (W/m-K)	-	0.03951	0.5953
Viscosity (cP)	-	0.01382	1.136
Surface Tension (dyne/cm)	-	-	73.76
Specific Heat (kJ/kg mole-C)	53.60	53.35	77.61
Act. Vol. Flow (m ³ /h)	4182	4179	3.327
Molecular Weight	18.68	18.68	18.04
Z Factor	-	0.7838	0.0592

Table 27 HYSYS Material Stream Specification Sheet Coolout

COMPONENT DATA						
Overall Phase (Vapour Fraction 0.9896)						
Component s	Molar Flow (kg mole/h)	Mole Fraction	Mass Flow (kg/h)	Mass Fraction	Liquid Volume Flow (m ³ /h)	Liquid Volume Fraction
Methane	1.557E+04	0.8656	2.498E+05	0.7437	834.4	0.8315
Ethane	996.6	0.0554	2.997E+04	0.08921	84.26	0.08396
Propane	391.5	0.02176	1.727E+04	0.05139	34.08	0.03396
n-Butane	142.4	0.007914	8275	0.02463	14.19	0.01414
H ₂ O	193.1	0.01074	3479	0.01036	3.486	0.03474
CO ₂	480.5	0.02671	2.115E+04	0.06295	25.62	0.02563
Nitrogen	213.6	0.01187	5983	0.01781	7.419	0.007393
Total	1.799E+04	1.0000	3.359E+05	1.0	1003	1.0

Vapour Phase (Phase Fraction 0.9896)						
Component s	Molar Flow (kg mole/h)	Mole Fraction	Mass Flow (kg/h)	Mass Fraction	Liquid Volume Flow (m ³ /h)	Liquid Volume Fraction
Methane	1.557E+04	0.8747	2.498E+05	0.7512	834.4	0.8344
Ethane	996.6	0.05598	2.997E+04	0.09012	84.26	0.08425
Propane	391.5	0.02199	1.727E+04	0.05192	34.08	0.03407
n-Butane	142.4	0.007998	8275	0.02488	14.19	0.01419
H ₂ O	5.627	0.0003161	101.4	0.0003048	0.1016	0.0001016
CO ₂	480.3	0.02698	2.114E+04	0.06357	25.62	0.02561
Nitrogen	213.6	0.0120	5982	0.01799	7.419	0.007418
Total	1.780E+04	1.0000	3.326E+05	1.0	1000	1.0

Table 28 HYSIS Component data (Overall)

COOLER OUTLET						
Aqueous Phase					(Phase Fraction: 0.01043)	
Components	Molar Flow (kg mole/h)	Mole Fraction	Mass Flow (kg/h)	Mass Fraction	Liquid Volume Flow (m³/h)	Liquid Volume Fraction
Methane	2.839E-05	1.513E-07	0.0004554	1.346E-07	1.521E-06	4.483E-07
Ethane	1.737E-08	9.258E-11	5.224E+07	1.543E-10	1.469E-09	4.329E-10
Propane	2.216E-11	1.181E-13	9.77E-10	2.886E-13	1.928E-12	5.683E-13
n-Butane	1.377E-14	7.338E-17	8.00E-13	2.365E-16	1.327E-15	4.045E-16
H ₂ O	187.5	0.9992	3378	0.998	3.385	0.9975
CO ₂	0.1546	0.000824	6.805	0.002011	0.008246	0.002430
Nitrogen	0.002618	1.395E-05	0.07333	2.167E-05	9.094E-05	2.680E-05
Total	187.7	1.0000	3385	1.0	3.393	1.0

Table 29 HYSIS Coolout data

Utility - 8	
Stream Name: Cooler Outlet	Property Pkg: Peng Robinson

Hydrate Formations

Conditions	Hydrate Type Formed	Calculation Mode
Hydrate formation at stream conditions will form:	Type II	Free Water Found
Formation at Temperature at Stream Pressure: 15.64C	Type I & II	Free Water Found
Formation Pressure at Stream temperature: 16.69 psi	Type I & II	Free Water Found

Properties: Cooler Outlet	Overall	Vapour Phase	Aqueous Phase
Vapour/Phase Fraction	0.9896	0.9896	0.01043
Temperature (°C)	15.00 *	15.00	15.00
Pressure kPa	8000 *	8000	8000
Molar Flow (kg mole/h)	1.799E+04	1.780E+04	187.7
Mass Flow (m ³ /h)	3.359E+05	3.326E+05	3385
Liquid Volume Flow (m ³ /h)	1003	1000	3.393
Molar Enthalpy (kJ/kg mole)	-8.867E+04	-8.659E+04	-2.861E+05
Mass Enthalpy (kJ/kg)	-4748	-4635	-1.586E+04
Molar Entropy (kJ/kg mole-C)	143.8	144.8	51.04
Mass Entropy (kJ/kg-C)	7.703	7.752	2.830
Heat Flow (kJ/m ³)	-1.595E+09	-1.541E+09	-5.37E+07
Molar Density (kg mole/ m ³)	4.302	4.260	56.41
Mass Density (kg/ m ³)	80.33	79.59	1017
Std. Liquid Mass Density (kg/m ³)	-	-	1015
Molar Heat Capacity (kJ/kg mole-C)	53.60	53.35	77.61
Mass Heat Capacity (kJ/kg-C)	2.871	2.856	4.303
Thermal Conductivity (W/m-K)	-	0.03951	0.5953
Viscosity (cP)	-	0.01382	1.136
Surface Tension (dyne/cm)	-	-	73.76
Molecular Weight	18.67	18.68	18.04
Z Factor	-	0.7838	0.0592

Table 30 HYSYS Material Stream Specification Sheet (Utility)

*) Specified by user

5.5.9 Continuous Joule-Thomson

This process involves the mixing of the natural gas and water and then compression to a high pressure. The mixture was then flashed through a nozzle or valve to atmospheric pressure. The associated temperature drop forms the hydrate and the crystals can be collected in a vessel continuously with the natural gas not used recycled. Excess water can also be recycled. This process is the one that will be mostly focused upon to produce hydrate continuously.

5.5.10 CSTR

This process (Continuous Stirred Tank Reactor) is similar to the one undertaken by the Norwegians where a mixture of gas and water is placed into a pressurized CSTR and stirred until hydrate is formed. More gas can be added to keep the pressure up until enough hydrate is formed. The formed hydrate and the unused water are separated and the resulting hydrate filtered and dried. Other literature shows that hydrate can be formed in a stirred tank, except the time of formation depends on the pressure and temperature used. Further work in this area may yield new information that can be beneficial to the project.

5.5.11 Batch Closed Cylinder

This process is exactly what was replicated in the laboratory for the project. Equimolar amounts of natural gas and water are added to a closed cylinder at a certain pressure. The mixture is then rapidly cooled and stirred until hydrate is formed. The cylinder is opened, the hydrate removed and stored in a freezer. This is a reasonable process and could run numerous cylinders so becomes practically continuous. Problems with this are the agitation of the mixture and the cooling required.

5.6 - Nitrogen Separation

Table 9 below summarizes the findings from the Gas Chromatograph (GC) analysis. All sample tests were conducted at 6890 kPa and 22°C. The volume of nitrogen was less in the hydrate than the gas purge, as the nitrogen does not form hydrate as readily as methane. For trial number one, the nitrogen content was near 50mol% in the gas purge while only 30% in the hydrate. The methane content increased from 44% to 61% between gas purge and hydrate. The second trial showed 50mol% nitrogen in the gas purge while only 20mol% in the hydrate. The less nitrogen present the better the separation. When pressure was increased by 3030 kPa, the difference was 30%, but when the increase in pressure attained 5064 kPa, the difference was only 20%. For the first two trials the amount of nitrogen in the hydrate was high due to the low temperatures. It was proven in the simulation that nitrogen hydrate forms at high pressure and low temperature. The last trial was carried out at 5512 kPa and the difference in concentration was large and representative of what was predicted by the simulation. Decrease from 2.48% to 0.53% shown in the GC analysis and 2.5% down to 0.3% from the simulation. A continuous stream cycling through a hydrate-forming vessel would increase the nitrogen purity until at the purity set point.

Sample	Trial 1		Trial 2		Trial 3	
	Gas Purge	Hydrate	Gas Purge	Hydrate	Gas Purge	Hydrate
Component	Mol%					
Carbon Dioxide	2.78	3.15	2.16	16.42	4.78	11.3
Nitrogen	48.69	30.19	52.40	21.74	2.48	0.53
Methane	44.23	61.03	41.81	51.58	87.57	79.6
Ethane	2.51	3.42	2.31	3.05	4.91	4.82
Propane	1.03	1.33	0.76	1.45	0.16	1.9
iso-Butane	0.22	0.28	0.16	0.44	0.03	0.36
n-Butane	0.27	0.36	0.21	0.70	0.04	0.49
iso-Pentane	0.10	0.13	0.08	0.78	0.01	0.20
n-Pentane	0.07	0.09	0.05	0.79	0.01	0.15
Hexanes	0.06	0.07	0.04	1.46	0.01	0.20
Heptanes	0.03	0.04	0.02	1.07	-	0.23
Octanes	0.01	0.01	-	0.45	-	0.17
Nonanes	-	-	-	0.06	-	0.04
Decanes	-	-	-	0.01	-	0.01
Totals	100.00	100.00	100.00	100.00	100.00	100.00
Critical Pressure (psia)	592.60	626.20	683.90	584.00	683.20	705.3
Critical Temp (R)	304.60	330.70	393.50	296.80	361.3	387.9
Calculated Gas Gravity	0.82	0.76	0.96	0.82	0.637	0.750
Average Molecular Wt	23.67	21.86	27.77	23.73	18.46	21.73

Table 9 Nitrogen Separation Trials from GC Analysis

The results shown below were taken from the Equi-phase Hydrate Program.

Tables 10 and 11 show the difference between the nitrogen content of the purge gas and the hydrate and the formation temperature for two pressures. The two pressures are the optimal pressure for the least nitrogen in the hydrate and the pressure the laboratory analysis pressure. Note that the simulation works off a free water calculation and is more applicable to a continuous process where the hydrate formed is only that formed with the water vapour in the gas stream determined by its vapour pressure. The last set of the tables shows the different formations. Table 12 shows that the formation of nitrogen hydrate by itself only occurs at very low temperatures.

Table 13 shows that methane hydrate is just as difficult to form (this form of hydrate is more stable). The other tables (14,15,16,17,18 & 19) show that the ease of formation of the hydrate increases with the addition of carbon dioxide and the heavier hydrocarbons. The charts below the tables show that the optimum separation of nitrogen occurs when there is the least amount of nitrogen in the hydrate, which occurs at 14950 kPa. The decrease of methane in the hydrate is negligible.

Pressure	1500kPa	
Temp	0.022C	
Component	Gas	Hydrate
C1	0.8848	0.65144
C2	0.065	0.30587
C3	0.0012	0
i-C4	0.0001	0
n-C4	0.0001	0
CO2	0.0233	0.03889
N2	0.0255	0.00383

Table 10 Nitrogen Separation @ 1500kPa

Pressure	10000kPa	
Temp	17.478C	
Component	Gas	Hydrate
C1	0.8848	0.76456
C2	0.065	0.19474
C3	0.0012	0
i-C4	0.0001	0
n-C4	0.0001	0
CO2	0.0233	0.0344
N2	0.0255	0.0063

Table 11 Nitrogen Separation @ 10,000kPa

Temperature	-69.55	(C)
Component	Gas	Hydrate
N2	1.00	1.00

Table 12 Nitrogen Hydrate Formation

Nitrogen by itself does not form hydrate unless at extremely low temperatures.

Temperature	-16.428	(C)
Component	Gas	Hydrate
C1	1.00	1.00

Table 13 Methane Hydrate Formation

Methane by itself forms hydrate only at -16C and below.

Temperature	0.006	(C)
Component	Gas	Hydrate
C1	0.90	0.59799
C2	0.1	0.40201

Table 14 Higher Hydrocarbon Formation

When you add higher hydrocarbons ease of formation increases.

Temperature	1.717	(C)
Component	Gas	Hydrate
CO2	1.00	1.00

Table 15 CO2 Hydrate Formation

Carbon Dioxide forms hydrate easily by itself.

Temperature	0.944	(C)
Component	Gas	Hydrate
C1	0.91000	0.62714
C2	0.08810	0.37286
C3	0.00150	0.00000
i-C4	0.00020	0.00000
n-C4	0.00020	0.00000

Table 16 Heavier Hydrocarbons

With heavier hydrocarbons the temperature of formation increases.

Temperature	0.656	(C)
Component	Gas	Hydrate
C1	0.89480	0.62767
C2	0.07500	0.32770
C3	0.00130	0.00000
i-C4	0.00020	0.00000
n-C4	0.00020	0.00000
CO2	0.02850	0.04463

Table 17 Nitrogen Free Formation

Without Nitrogen, the temperature formation is higher as Nitrogen is an inhibitor.

Temperature	0.444	(C)
Component	Gas	Hydrate
C1	0.89480	0.63698
C2	0.06850	0.30706
C3	0.00130	0.00000
i-C4	0.00020	0.00000
n-C4	0.00020	0.00000
CO2	0.03500	0.05596

Table 18 Heavier Hydrocarbons

Increase the CO2 content and the temperature does not increase. Only forms hydrate well by itself.

Pressure of 9990 kPa		
Temperature	-14.472	[C]
Component	Gas	Hydrate
N2	1.00	1.00

Table 19 Nitrogen Formation Lab.

At high pressure nitrogen hydrate does form at reasonable production temperature.

6 - THE PROJECT PLAN

6.1 - Pilot Project Scope

This stage of the project involves the design, procurement, and construction of a mobile test module generally in accordance with the preliminary piping and instrument diagram (P&ID) included in section 6.5. The module consists of filtering, compression, cooling, injection, mixing and reaction equipment as detailed in the P&ID. The process allows for natural gas to be mixed with water and other proprietary chemicals to produce a batched sample of stabilized hydrate. The module is currently being used to produce natural gas hydrates on a batch basis. The module has the capability to produce NGH at various differential pressures, temperatures and liquor injection rates. Testing of the various types and concentrations of proprietary chemicals on the quality and stability of the produced hydrates has also been done and continues to be carried out.

The module was built to be mobile so that it can be moved and hooked up to various gas sources both in metropolitan Perth and out in producing gas fields. As a “gas processing unit”, the module has been operating under statutory approval of the local authorities and was designed and manufactured to meet such codes.

Should this stage of the project be deemed acceptable then the project will progress to Stage Two, (this involves the design and construction of a larger scale pilot plant).

6.2 - Project Deliverables

The following activities are required for Stage One of the project:

- Detailed design of the test module. This included undertaking a hazard and operability (HAZOP) and finalization of the P&ID, process design checks, selection of equipment, preparation of equipment data sheets and specifications, general arrangement and piping detail drawings, structural details and instrument/electrical drawings.
- Procurement of all items of equipment. This included the preparation and award of equipment purchase orders and inspection of all delivered equipment.

- Fabrication and delivery of the test module was carried out internally at Curtin University. Statutory approval from the department of industry and resources (DME) and road registration of the trailer was granted.
- Process design and project management.
- Supply of (proprietary) chemicals, water, and natural gas for the test module.
- Test module operation and optimization.
- Preparation of any Safety Cases required by the DME or any other statutory authority.
- Preparation of operating and test procedures.
- Preparation of a Hazard and Operability (HAZOP) process.
- Preparation of patent applications and grant submissions as necessary.
- Project management including cost and schedule controls.

As a result of those activities, the following documents were prepared by the Petroleum Engineering Department.

Deliverable	Quantity
HAZOP report	1
As-built P&ID and detailed drawings	1
As-built equipment specifications and data sheets	1
Manufacturers Data Records (MDR)	1
Consolidated Vendor Operating and Maintenance manuals	1

It was expected that a Woodside representative be involved in the finalization and approval of the (Approved for Construction) P&ID and general arrangement drawings. All other documentation were prepared and issued by the Department of Petroleum Engineering to the relevant departments within Curtin University for information only.

6.3 - Pilot Plant Conceptual Design

The pilot plant (module), is the first such experimental laboratory equipment in the world proposed for the production of natural gas hydrates on a batch basis. The small plant design parameters were conceived during the initial period of experimental work with methane gas hydrates. Several obvious issues related to capacity, power consumption, physical sizing, geometrical configuration and overall costs were considered. Other matters related to heat transfer, process flow, instrumentation, structural and mechanical maintenance and safety requirements were also engineered to suit the system's intended production rate. Atomization of the liquor particles utilizing a spray nozzle was a somewhat difficult matter to correctly envisage and implement without further research and experimentation, this matter did prove to be one of the most difficult issues to overcome after the module was completed and testing commenced.

6.4 - Electrical Power

This section of the Specification defines the minimum requirements for the design, material, fabrication and supply of switchboards, panels and cubicles for use in Curtin University natural gas hydrate facility.

6.4.1 Reference Codes and Standards

The applicable sections of the latest edition of the American and Australian standards were followed for the design and construction of the relevant equipment.

The Equipment and materials supplied in accordance with this section of the Specification complied with the latest relevant Australian standards together with the requirements of the competent Authorities having jurisdiction over all or part of their design, manufacture, installation, and operation.

Australian Standards

AS 100 The International System of Units (SI) and its application

AS 1939 Degrees of protection provided by enclosures for electrical equipment

AS 2381.1 General requirements

As 3000 SAA Wiring Rules

6.4.2 Service Conditions

All system shall be suitable for operation under the following service conditions:

Max ambient air shade temperature	50 °C
Direct sunlight temperature	80 °C
Min ambient temperature	0 °C - Not Freezing
Daily temperature range	30 °C
Maximum Relative humidity (condensing)	100%
Location	Indoors and Outdoors
Maximum Solar Radiation	1.0 kW/m ²
Air Quality	High dust content
Earthquake Vibration	0-200 Hz

6.4.3 General Description

All cubicles, panel switchboards and junction boxes shall conform to the following requirements:

- Rated AC voltage shall be 415 V three phase and 240 V phase to neutral.
- Rated diversity factor to as 3439 shall be 1.0.
- All equipment and cubicles of the same type shall be uniform.
- Live circuits above extra low voltage, which are exposed when door of an enclosure is opened, shall be fully shrouded and labeled.
- Unless noted elsewhere segregation to, AS 3439 shall be form 1.0.
- Cubicles shall be of single front or back construction as specified.
- Cubicles shall be supplied complete with silica-gel bags (s) within the cubicle.
- Cubicles shall have bottom cable entry unless otherwise specified.
- Cubicles shall be arranged to permit easy removal of all components without interference to the structure, other component service entry or outgoing connections.

6.4.4 Construction

All cubicles including control panels, marshalling boxes, switchboards, junction boxes and the like complies with the following:

- All materials shall be new and unblemished, of the manufacture, type and quantity as listed herein and as shown on the drawings.
- Any materials and equipment not used in the construction of the cubicle shells shall not be exposed to any process used for surface preparation or painting.
- Except for proprietary type cubicles, all cubicles were fully folded, constructed and manufactured from no less than 2.5 mm grade brushed aluminum or 2 mm minimum mild steel bright sheet free from mill scale and rust.
- All folds were machine folded. Welds were continuous unless noted otherwise and were free from burrs and scale. Exterior welds were filled with "non-Shrink" filler before smoothing. Bracing to maintain rigidity shall be provided where required.
- Where dissimilar metals are installed adjacent to one another, bi-metallic corrosion was prevented by the use of a non-metallic insulator or other approved method. All equipment and materials were in metric dimensions and SI units shall be used throughout.
- Unless noted otherwise, overall tolerances shall be ± 2 mm.
- Tolerances do apply to the dimensions noted on the Superintendent or vendor's drawings unless noted otherwise thereon.
- Before proceeding with a change, the vendor had to obtain a certified dimension drawing of the component to be altered from the component supplier, or the actual component which can be measured.
- Cut outs with dimensions greater than 20 mm shall have tolerances of ± 1 mm.
- Where specified, equipment-mounting calls shall allow for vertical adjustment of racks in 10 mm increments without additional drilling of holes.

- Cubicles have a minimum degree of protection to comply with AS 1939 as follows:

Indoor - general	- IP 51
Indoor (fire water spray areas)	- IP 53
Outdoor	- IP 56

6.4.5 Switchboard Doors

Doors shall comply with the following:

- Have chromium plated lever type door handles, and 3 point locking system. Outdoor cubicles to be equipped with locking facilities.
- Doors provided with folded metal stiffeners and bracing to achieve rigidity and prevent warping or sagging.
- Side hinged on chromium plated lift-off pintle type hinges.
- Provided with chromium plated lifting handles on doors larger than 1 metre high or 1 metre long and fitted with heavy duty closed cell neoprene dust seals within a metal channel.
- Be arranged such that access to internal wiring and equipment by opening of escutcheons (where specified) is possible with no need to remove the door. Have earthing connections of live equipment door mounted.

6.4.6 Equipment Within Cubicles

All equipment inside cubicles were;

- Arranged in a logical, neat and convenient manner.
- Note: Terminal strips were installed vertically only.
- Installed on 3 sides of the cubicle where desirable and practical.
- Mounted no lower than 300 mm or higher than 1800 mm above floor level (unless otherwise specified).
- Have adequate access space for operation and maintenance of equipment and wiring without interfering with or removing any other equipment.
- Have all wiring installed in vertical and horizontal PVC wiring ducts complete with suitable clip and covers.

- Plug in equipment where likely to vibrate loose with suitable clip type restraints.

6.4.7 Labels and Name Plates

All cubicles and equipment were identified in accordance with the panel drawings. The Project Manager prior to manufacture submitted fully detailed engraving schedules for approval.

6.4.8 Fasteners

All bolts, studs nuts, washers and associated items were in accordance with the "Fasteners" details listed in Clause 5.0 of "General Electrical" Technical Documents No: cs00/202/3020 in Section g and the following:

- All screw fixings were provided with captive nuts. Trapping of panels is permitted only when the material to be trapped is equal to or greater than the thickness of a standard nut of the same thread size.
- All fasteners and nuts that are visible from the exterior of the cubicle are of the "Acorn" or "Knurled Knob" type. For internal doors fasteners were chrome plated and external doors were stainless steel.
- Threaded steel fastenings for electrical components shall be zinc-plated.
- Miscellaneous fittings such as saddles, clamps and fastenings including metal threads, screw and bolts used, were either stainless steel, chromium, or zinc-plated.

6.4.9 Earthing

All cubicles, doors, panels and equipment pans were earthed in accordance with the relevant Australian Standards.

6.4.10 Termination and Wiring

All equipment wiring and terminations were carried out in accordance with recognized Best Practice, this Specification, Drawings and Current Australian Standards. No more than 2 wires per terminal.

6.4.11 Electrical Certificates and Reports

The following reports were included:

- Insulation and high voltage test report
- High voltage test report
- Electrical performance test report
- Electrical functional test report
- Other - Electrical test report

6.5 - Pilot Plant Piping and Instruments

The plant was designed to produce synthetic natural gas hydrate at a range of pressures by mixing natural gas and liquor at high pressure and forcing the mixture through a nozzle into a reaction chamber. The plant piping, except in the pressure vessel, was constructed of stainless steel tubing suitable for the plant design pressure and temperature. The reactor vessels were constructed of carbon steel with 3% allowance for corrosion.

All valves including shut-off, non-return, pressure relief, rupture discs, metering and control are stainless steel rated at pressures of a minimum of 17225 kPa. All instruments are designed to operate in a hydrocarbon environment and are protected by pressure relief and rupture discs. Instruments, digital indicators and data recorders are located outside the hazardous area of the module frame. The control of the module and its equipment can be manipulated from two separate areas, first via the main flow controllers from the operator platform and the second from the static and dynamic saturation vessels.

A schematic layout of the plant and its associated services is shown in Appendix E.

There are several sections within the plant which can be categorized into the following subsystems.

- High Pressure Gas Supply System
- High Pressure Liquor Supply System
- Static and Dynamic Saturation Systems
- Hydrate Production Vessel and Refrigeration System
- Power Supply System
- Instrumentation System
- Venting System

These are described in more detail in section 7 below.

6.6 - Fluid flow calculations

6.6.1 Calculation of flow rates of gas and liquid required to form hydrates at 870 psi (Sample Calculation)

The aim is to form hydrates at 5994 kPa in a pressure vessel. From literature, it is found that hydrates form at 5994 kPa and 16.5°C. However, the reactor temperature is maintained at -10°C. This helps in recovering hydrates at lower pressures. Table 20 indicates the composition of natural gas utilized for the sample calculations as shown below.

6.6.1.1 Design Basis

The pressure vessel was assumed to have been pressurized with dry gas to 5994 kPa and cooled to 10°C prior to the introduction of gas and water simultaneously.

The Molecular weight of natural gas = 19.21 (calculated – see Reference 1)

The gas to water volume ratio = 185:1

The density of hydrate = 850kg/m³

The compressibility factor (2) at 6000 kPa = 0.74 (from GPSA – see Reference 2)

Ambient temperature = 30°C (assumption)

The inlet temperature of gas and water to the reactor = 30°C (assumption – conservatively)

The hydrate formation temperature at 6000 kPa = 16.5°C (from literature)

Vessel volume = 24 lt

6.6.1.2 Assumptions

The temperature of the vessel is maintained at -10°C by the refrigeration system throughout the reaction time i.e. the refrigeration system has adequate capacity.

6.6.1.3 Calculations

Gas to water volume ratio = 185

Gas volumetric flow in 5 m³/m to water volumetric flow in m³/m is 185:1

The weight of 185 sm³ of natural gas = 185x19.21/23.65 = 150.27 kg

$$\begin{aligned} \text{The weight of } 1 \text{ m}^3 \text{ of water} &= 1000 \text{ kg} \\ \text{The number of moles of water in } 1 \text{ m}^3 &= 1000/18 = 55.56 \text{ kg moles} \\ \text{The number of moles of gas} &= 185/23.65 = 7.82 \text{ kg moles} \\ \text{Moles of water to moles of gas} &= 55.56/7.82 = 7.10 \end{aligned}$$

When the reactor vessel is pressurized to 6000 kPa and cooled to -10°C , the amount of dry gas in the pressure vessel is:

$$\underline{6000 \text{ kPa} \times 19.21 \text{ MW} \times 24 \text{ lt}} = 1710 \text{ g} = 1.71 \text{ kg}$$

$$0.74 \times (273-10)^\circ\text{K} + 8.314 \text{ kPa l/gmol}^\circ\text{K}$$

$$\text{Or: } 1.71 \times 23.65/19.21 = 2.11 \text{ sm}^3 = 74.3 \text{ scf}$$

$$\text{The density of gas} = 1.71 \text{ kg}/24 \text{ lt} = 0.071 \text{ kg/lt}$$

When the vessel is pressurized and cooled, then the gas and water are introduced simultaneously to form hydrates. Let the water flow rate be $x \text{ lt/min}$ ($= X \times 60/18 \text{ kg moles/hr}$) $= X \text{ kg/min}$

The corresponding gas flow rate required to form hydrates is $X \times 60/18/7.1 = (0.47X) \text{ kg moles/hr}$

$$\begin{aligned} &= 0.47X \times 19.21 \text{ kg/hr} \\ &= 9.02X \text{ kg/hr} \\ &= 0.47X \times 23.65 \times 35.3/60 \text{ scf/min} \\ &= 6.54X \text{ scf/min} \end{aligned}$$

$$\begin{aligned} \text{Mass flow rate of hydrates formed} &= X \text{ kg/min} + 9.02X/60 \text{ kg/min} \\ &= 60X + 9.02X/60 \text{ kg/hr} \\ &= 69.02X \text{ kg/hr} \end{aligned}$$

$$\begin{aligned} \text{Volume flow rate of hydrates formed} &= 69.02X \text{ kg/hr}/850 \text{ kg/m}^3 \\ &= 0.08X \text{ m}^3/\text{hr} \end{aligned}$$

$$\begin{aligned} \text{Rate of gas inlet limited by compressor} &= 5.5 \text{ scf/min} \\ &= 5.5 \times 1000 \times 60/35.3 \text{ slt/hr} \\ &= 9348.4 \text{ slt/hr} \\ &= 9.3484 \text{ sm}^3/\text{hr} \\ &= 9.3484 \times 19.21/23.65 \text{ kg/hr} \\ &= 7.59 \text{ kg/hr} \end{aligned}$$

Rate of dry gas (initially present at 6000 kPa and -10°C) participating in the reaction $= (9.02X - 7.59) \text{ kg/hr}$

$$\begin{aligned}
&= (6.54X \text{ scf/min} - 5.5) \text{ scf/min} \\
&= (9.02X - 7.59) \text{ kg/hr} / 0.071 \text{ kg/lt} \\
&= 14.1 (9.02X - 7.59) \text{ lt/hr}
\end{aligned}$$

Rate of pressure loss or gain in the pressure vessel =

$$\begin{aligned}
&= \text{Volume flow rate of hydrates formed} - \text{Volume flow rate of initial dry gas disappearance} \\
&= 0.08X \text{ m}^3/\text{hr} - 14.1(9.02X - 7.59)/1000 \text{ m}^3/\text{hr} \\
&= X (0.08 - 0.0141 \times 9.02) + 0.107 \text{ m}^3/\text{hr}
\end{aligned}$$

For no change in pressure in the reactor, the above value should be zero:

$$X (-0.047) + 0.107 = 0$$

$$X = 0.107 / 0.047 = 2.28 \text{ lt/min}$$

$$\begin{aligned}
\text{Mass flow rate of hydrates formed} &= 69.02X \\
&= 69.02 \times 2.35 = 162.2 \text{ kg/hr}
\end{aligned}$$

$$\text{Mass flow rate of gas sent with water} = 7.59 \text{ kg/hr}$$

6.6.1.4 Cooling Rate Calculation

$$\begin{aligned}
\text{Heat capacity of water} &= 4.30 \text{ kJ/kg K} \\
\text{Heat capacity of dry gas} &= 2.72 \text{ kJ/kg K} \\
\text{Heat capacity of hydrate} &= 2 \text{ kJ/kg K (Gudmundsson's report)} \\
\text{Heat of formation of hydrate} &= 410 \text{ kJ/kg K (Gudmundsson's report)}
\end{aligned}$$

$$\text{Temperature of gas and water at the entry to the vessel} = 30^\circ\text{C}$$

$$\text{Hydrate formation temperature} = 16.5^\circ\text{C (from Hysys)}$$

$$\text{Surface area of the reactor} = 0.77 \text{ m}^2 \text{ (from Pressure Vessel -see pressure vessel specs.)}$$

$$\text{Uheat transfer value from vessel to atmosphere} = 10 \text{ W/m}^2 \text{ K (assumption)}$$

$$\text{Ambient temperature} = 35^\circ\text{C}$$

$$\begin{aligned}
\text{Cooling rate} &= \text{rate of cooling required to bring the temperature of gas and water from } 30^\circ\text{C to } 16.5^\circ\text{C} \\
&+ \text{rate of cooling required to form hydrates} \\
&+ \text{rate of cooling required to bring the temperature of hydrates from } 16.5^\circ\text{C to } -10^\circ\text{C} \\
&+ \text{rate of cooling required to compensate the heat loss of the vessel and its contents to the atmosphere} \\
&= [2.35 \text{ lt/min} \times 1 \text{ kg/lt} \times 4.3 \text{ kJ/kg K}
\end{aligned}$$

$$x (30 - 16.5) \times 60 + 7.59 \text{ kg/hr} \times 2.72 \text{ kJ/kg K} \times (30 - 16.5)] + 69.02 \times 2.35 \text{ kg/hr} \times 410 \text{ kJ/kg K} + 69.02 \times 2.35 \text{ kg/hr} \times 2 \text{ kJ/kg K} \times (16.5 + 10) + 10 \text{ W/m}^2 \text{ K} \times 0.77 \text{ m}^2 \times (35 + 10) \times 3.6$$

$$= 8185 + 278.7 + 66500.8 + 8596.4 + 1247.4 = 84808 \text{ kJ/hr}$$

COMPONENT	COMPOSITION	MW	Weight of each component
CO2	2.2	44	96.8
N2	2.59	28	72.52
C1	84.25	16	1348
C2	6.78	30	203.4
C3	3.11	44	136.84
I-C4	0.41	58	23.78
n-C4	0.59	58	34.22
I-C5	0.04	72	2.88
n-C5	0.02	72	1.44
C6	0.01	86	0.86
C7	0	100	0
Grand Total			1920.74

Table 20 Natural Gas Compositions

MW (average) = 1920.74/100 = 19.21

6.6.2 Calculation of Amount of Gas In Hydrate

Mixture:

$$M = 0.65 \text{ kg}$$

$$\text{Vol} = 0.792 \text{ L}$$

$$\text{Density} = M/\text{Vol} = 0.65/0.792 = 0.821 \text{ kg/L}$$

Assume the gas is predominantly methane (~ 9 %), with a mw = 17

Assume the hydrate structure is Type I with 46 water molecules per 8 gas molecules. Assume test/measuring conditions at 0 °C, 101.135 kPa.

6.6.2.1 Case 1

Assume 40 mass % of mix is gas:

$$\begin{aligned} \text{Gas present} &= 0.4 * 0.65 \text{ kg} = 0.26 \text{ kg gas} \\ &= 0.26 \text{ kg} / (17 \text{ kg/kg mol}) \\ &= 0.015 \text{ kg mol gas} \end{aligned}$$

$$\begin{aligned} \text{Vol gas present} &= 0.015 \text{ kg mol} * 22.4 \text{ m}^3/\text{kg mol} (0 \text{ }^\circ\text{C}, 101 \text{ kPa}) \\ &= 0.34 \text{ m}^3 \text{ (assume gas under standard conditions)} \end{aligned}$$

$$\begin{aligned} \text{Density of hydrate} &= 0.26 \text{ kg}/0.34 \text{ m}^3 \\ &= 0.76 \text{ kg/ m}^3 \end{aligned}$$

For 45 mass % of mix is gas:

$$\begin{aligned} \text{Gas present} &= 0.45 * 0.65 \text{ kg} = 0.29 \text{ kg gas} \\ &= 0.29 \text{ kg} / (17 \text{ kg/kg mol}) \\ &= 0.017 \text{ kg mol gas} \end{aligned}$$

$$\begin{aligned} \text{Vol gas present} &= 0.017 \text{ kg mol} * 22.4 \text{ m}^3/\text{kg mol} \\ &= 0.39 \text{ m}^3 \text{ (assume gas under standard conditions)} \end{aligned}$$

$$\begin{aligned} \text{Density of hydrate} &= 0.29 \text{ kg}/0.39 \text{ m}^3 \\ &= 0.75 \text{ kg/ m}^3 \end{aligned}$$

For 50 mass % of mix is gas:

$$\begin{aligned}\text{Gas present} &= 0.5 \cdot 0.65 \text{ kg} = 0.325 \text{ kg gas} \\ &= 0.29 \text{ kg} / (17 \text{ kg/kg mol}) \\ &= 0.019 \text{ kg mol gas} \\ \text{Vol gas present} &= 0.019 \text{ kg mol} \cdot 22.4 \text{ m}^3/\text{kg mol} \\ &= 0.43 \text{ m}^3 \text{ (assume gas under standard conditions)} \\ \text{Density of hydrate} &= 0.325 \text{ kg}/0.43 \text{ m}^3 \\ &= 0.76 \text{ kg/ m}^3\end{aligned}$$

6.6.2.2 Case 2

Assume density of mixture is 0.85 kg/L so mass of mixture would be 0.85kg/L
*0.792 L = 0.67 kg mixture

For 40 % gas by mass: = 0.27 kg gas (0.36m³, assume gas under standard conditions)

For 45 % gas by mass: = 0.30 kg gas (0.40m³, assume gas under standard conditions)

For 50 % gas by mass: = 0.34 kg gas (0.44m³, assume gas under standard conditions)

6.6.2.3 Case 3

Assume density of mixture is 0.9 kg/L so mass of mixture would be 0.9kg/L
*0.792 L = 0.71 kg mixture

For 40 % gas by mass: = 0.28 kg gas (0.37m³, assume gas under standard conditions)

For 45 % gas by mass: = 0.32 kg gas (0.42m³, assume gas under standard conditions)

For 50 % gas by mass: = 0.36 kg gas (0.47m³, assume gas under standard conditions)

6.6.2.4 Case 4

Assume a hydrate number of 5.75 (unlikely to be exact due to the chemicals present in the hydrate promoting additive, a mixture of structure types sI and sII and sH, pressure and temperature conditions, void and porosity of the packing in a bucket).

$$46 \text{ kg mol water} * 18 \text{ kg/kg mol} = 826 \text{ kg water}$$

$$8 \text{ kg mol gas} * 17 \text{ kg/kg mol} = 136 \text{ kg gas.}$$

So the mass ratio is around 6:1 or water is 86 mass % of the bulk by weight and gas 14 mass %.

Assuming an ice density of around 0.916 kg/L,

$$\begin{aligned} \text{The volume of ice} &= 0.86 \text{ mass \%} * (0.65 \text{ kg})/0.916 \text{ L} \\ &= 0.61 \text{ L (or 0.031 kg mol) ice} \end{aligned}$$

$$\begin{aligned} \text{Gas (as a solid)} &= 0.792 \text{ L} - 0.61 \text{ L} \\ &= 0.18 \text{ L (or 0.0031 kg mol) gas} \end{aligned}$$

$$\begin{aligned} \text{Or gas (as a gas)} &= 0.14 \text{ mass \%} * 0.65 \text{ kg}/(17 \text{ kg/kg} \\ &\text{mol}) * 22.4 \text{ m}^3 \text{ (standard conditions)} \\ &* 1000 \text{ L/m}^3 = 120 \text{ L} \end{aligned}$$

Hence this gas hydrate is carrying around 120 L/0.792 L mixture, or 150 vol gas per vol hydrate mixture (which is exactly as per literature - only so because of the assumptions).

If the hydrate was considered to be in a gaseous form then: total density should be density of ice * vol ice + density of gas (as gas) * vol gas $0.821 \text{ kg/L} = 0.916 \text{ kg/L} * 0.61 \text{ L}/120.792 \text{ L} + \text{density of gas (as gas)} * 120 \text{ L}/120.792 \text{ L}$ methane density = 0.82 kg/L (as a gas) which makes nonsense of the test mixture density.

If the hydrate was considered to be in a liquid form, then: total density should be density of ice * vol ice + density of gas (as liquid) * vol gas $0.821 \text{ kg/L} = 0.916 \text{ kg/L} * 0.61 \text{ L}/0.792 \text{ L} + \text{density of gas (as liquid)} * 0.18\text{L}/0.792\text{L}$ methane density = 0.5 kg/L. Using molal volumes give the same result.

6.6.3 Pressure vessel design and specifications

The pressure vessel design has taken into consideration several operational and maintenance considerations in an effort to meet the relevant codes and the maintenance and operational requirements. It is with that in mind that the pressure vessel was selected from a suitable carbon steel alloy to meet the high temperature differentials and for compatibility with the quick closure door supplied by GD Closures of the UK. The vessel complies with A333 Gr. 6 and provided with an 200 NB flange rated at 1500Psig. The vessel has been certified by the local authority in Western Australia and tested in accordance with AS 1210.

6.6.3.1 Vessel Data:

REFERENCE DRAWING (Description)	DETAIL	UNITS
Class of vessel:	2B	AS1210
Internal design pressure:	14950	kPa
External design pressure	0	kPa
Design temperature (max):	100	DEG. C
Design temperature (min):	-25	DEG. C
Corrosion allowance:	0.50	mm
Static head acting on vessel:	1115	mm
Sg of contents:	1	(ratio to water)
Inside diameter of shell:	182.58	mm
Outside diameter of shell:	219.10	mm
Shell thickness:	18.26	mm
Tolerance on shell thickness: TOL	12.5%	-
Tan to tan length:	1115	mm
Does vessel include cone?	NO	(yes or no)

Table 31 Vessel Data

6.6.3.2 Materials and design tensile strengths

LOCATION	MATERIAL	Design tensile strength f	Design tensile strength f_h
Shell	ASTM A333 Gr6	119	119
Flanges	ASTM A 350 LF2	121	121

JOINT EFFICIENCIES	
Shell longitudinal joint	1.00
Shell circumferential joint	0.65
Dished ends	1.00
Nozzles longitudinal joints	1.00
Nozzles circumferential joints	1.00

DESIGN OF HYDROSTATIC TEST PRESSURE		
Internal Design Pressure	15000 kPa	2170 psi
Design Tensile Strength	119 MPa	17270 psi
Design Tensile Strength at AMB	119 MPa	17270 psi

CALCULATIONS		
Design Pressure: P	14950 kPa	-
Design Tensile Strength: f	118990 kPa	-
Design Tensile Strength: f_h	118990 kPa	-
Hydrostatic Test Pressure: Ph	-	-
$1.5 * P * f_h / f$	22495 kPa	Clause 5.10.2
Hydrostatic Test Pressure	22495 kPa	

DESIGN OF CALCULATION PRESSURE AT BOTTOM OF VESSEL	
Internal Design Pressure	14950 kPa
Static Head	11.23 kPa
Calculation Pressure	15000 kPa

Table 32 Materials and Design Tensile Strengths

6.6.3.3 Design of Allowable Tensile Strength for Material

DATA	
AS 1548-7-460 at design temperature	100 DEG. C
Minimum specified tensile strength: R_m	460 Mpa
Specified yield strength: R_s	305 Mpa
Calculations	
Design tensile strength: f	-
Least of ($R_m/3.5, R_s/1.5$)	130 Mpa

DATA	
ASTM A516 GR'D 70 at design temperature	100 DEG. C
Minimum specified tensile strength: R_m	483 Mpa
Specified yield strength: R_s	305 Mpa
Calculations	
Design tensile strength: f	-
Least of ($R_m/3.5, R_s/1.5$)	138 Mpa

DATA	
ASTM A106 GR'D B at design temperature	100 DEG. C
Minimum specified tensile strength: R_m	412 Mpa
Specified yield strength: R_s	280 Mpa
Calculations	
Design tensile strength: f	-
Least of ($R_m/3.5, R_s/1.5$)	118 Mpa

DATA	
ASSAB 750 (EN14A) at design temperature	100 DEG. C
Minimum specified tensile strength: R_m	510 Mpa
Specified yield strength: R_s	353 Mpa
Calculations	
Design tensile strength: f	-
Least of ($R_m/3.5, R_s/1.5$)	146 Mpa

Table 33 Design of Allowable Tensile Strengths for Material

6.6.3.4 Calculation of hazard level for vessel in accordance with AS3920.1

DATA	
Internal design pressure:	14950 kPa
Volume of vessel: V	24 Liters
Contents:	Harmful liquid (water)
Calculations	
Design pressure: p	14950 kPa
Value of pV	3.6E+02 MPa.L
Resulting hazard level:	C AS3920.1 Table B1

Table 34 Calculation of Hazard Level for Vessel

6.6.3.5 Design of shell subject to internal pressure

DATA	Measures
Internal calculation pressure:	15000 kPa
Weld joint eff. (longi. Joint):	1.00
Weld joint eff. (circ.Joint):	0.65
Design tensile strength:	119 Mpa
Corrosion Allowance	0.5mm
Outside diameter of shell:	219mm
Shell thickness	18.26mm
Tolerance on wall thickness	12.%

Calculations	Results
Calculation pressure: P	15000 kpa
Under tolerance inside diameter: ID	187.1 mm
Corroded inside diameter: d	188.1 mm
Design strength at temp: f	17270 psi
Based on circumferential stress (longitudinal joints) – t =P*D/(2*f*n-P)	12.71 OK
Based on longitudinal stress (circumferential joints) – t =P*d/(4*f*n-P)	9.63
Minimum calculated thickness: t	12.71mm
Corrosion allowance: c	0.50mm
Minimum thickness	13.21mm
Actual thickness	18.26mm

Table 35 Design of Shell Subject to Internal Pressure

6.6.3.6 Design of seamless shell subject to internal pressure

Calculations for Nozzle Reinforcement

$$\text{Based on circumferential stress: } t = P \cdot d / (2 \cdot f \cdot n - P) = 12.71 \text{ mm}$$

$$\text{Minimum Thickness: } T = 12.71 \text{ mm}$$

MOT- 25 °C

CL 2.6.3.1

MDMT

CL 2.6.3.2 membrane stress at design

$$\sigma_h = PD / (2t)$$

$$t = 18.26 - 0.5 = 17.76 \text{ mm}$$

$$P = 2170 \text{ psi}$$

$$D = 219.1 - 17.76 \times 2 = 183.58 \text{ mm}$$

$$\sigma_h = 11248 \text{ psi}$$

$$2/3 f \text{ for longitudinal joint } f = 17126 \text{ psi} = 2/3 \times 118 \times 10 = 11407 \text{ psi (78.6}$$

Mpa)

$$\text{ii MDMT} = -15 \text{ °C}$$

MATERIAL REF. THICKNESS

CL 2.6.4 T_m

For slip on flange

$$t_2 = 23.01$$

$$0.25 \times t_1 = 0.25 \times (92.0 + 7.0) = 24.75$$

$$T_m = 24.75 \text{ mm}$$

6.6.4 Pressure Safety Valves (PSV)

Pressure safety valves are devices that can protect systems and vessels from over-pressurization. The correct selection for a specific plant or system is critical for the safe operation of the facility or plant. A hazard and operability procedure HAZOP must be completed for a plant or facility to determine the location and number of the pressure safety valves (PSV's) required. Their location within a plant is also very

important. Prior to the installation, the PSV's must be set for the specific pressure determined by a qualified authority and locked into position with a tag as specified by the manufacturer. Below are examples of calculations for sizing of the PSV's for the pilot plant.

PSV Operation Pressure	34.46 kPa	5.001451 Psig	0.33677 atm
Bursting Disc Pressure	68.93 kPa	10.00435 Psig	0.673638 atm
Line volume	7952.156 cm ³	7.952156 L	-
Vessel Design Temperature	25 °C	298 K	-
Molecular mass of gas	16	-	-
Z at 1235 Psig	-	-	-
Constant (R) cm ³ atm/[K(gmol)]	82.06	-	-
Pc	45.8 atm	-	-
Tc	190.7 K	-	-
Vc	99 cm ³ /gmol	-	-
Zc	0.29	-	-
Sp Gr	0.554 (A)	-	-
Delta H, fusion	0.941 kJ/gmol	-	-
Melting temp	90.68 K	-	-
Normal BP	111.67 K	-	-
Pr = P/Pc	0.014708	-	-
Tr = T/Tc	1.562664	-	-
Z	1	-	-
n = m/M	-	-	-
Density = m/V PV = ZnRT	0.000441 g/cm ³	0.440757 Kg/m ³	-

Table 21 Condition Specification for PSV Operation @ 34.46 kPa

Pipe dimensions

$$\text{ID} = 0.402 \text{ in} = 10.2108 \text{ mm}$$

$$\text{OD} = 0.451 \text{ in} = 11.4554 \text{ mm}$$

$$\text{WT} = 0.049 \text{ in} = 1.2446 \text{ mm}$$

Hence, we need to relieve 11% of the volume in the vessel in 15 seconds.

This is 0.874737 L/15sec

Convert to hr: 209.9369 L/hr = 0.209937 m³/hr

6.6.4.1 Determining the Mass Flow Per Hour (a)

$$\begin{aligned} W = \rho V &= 0.09025311 \text{ kg/hr} \\ &= 0.2035683 \text{ lb/hr} \end{aligned}$$

$$C \text{ for methane} = 346$$

$$K \text{ for 10.4 mm orifice} = 7.5$$

$$P_1 = 10.004354 \text{ psia (68.9 kPa)}$$

$$F = \text{Flow}$$

Hence

$$M \text{ in lb/ft}^3 = 0.0274584 \text{ lb/ft}^3$$

$$\text{Velocity in the pipe } V = 183.4 \times W_h / (3600 \times d^2 \times \rho) = 2.3371171 \text{ ft/sec}$$

Viscosity of gas at 25 °C and 10 psia (68.9 kPa)

Hence from figure 16-27 viscosity of $\mu/\mu_A = 1$

Viscosity is 0.01cP

Using the Moody Diagram Tables, then $e/D = 0.0028$

The Reynolds number can be determined by $Re = 6.32W_h/dz = 320.0378$

From the Moody Table, this is laminar flow type and f can be approximated by

$$f = 64/Re = 0.1999764 \text{ lb/hr}$$

6.6.4.2 Determining the Pressure Drop in the Line (a)

$$P_d = 3.36 (10^{-6})fLW^2 / (d^2\rho) = 0.0003088 \text{ psia} (0.0021276 \text{ kPa})$$

Back Pressure Determination

$$\% \text{ absolute back pressure} = \text{back pressure (psia)} \times 100 / [\text{set pressure} + \text{over pressure (psia)}]$$

Hence $K_b = 1$

$$\text{Orifice size } A = W \times \text{Sqrt}(T) \times \text{Sqrt}(Z) / [C \times K \times P_1 \times K_b \times \text{Sqrt}(M)]$$

$$A = 4.543\text{E-}05 \text{ in}^2 = 0.0002931\text{cm}^2$$

$$d = \sqrt{4A/\pi} = 0.0193172 \text{ cm}$$

Minimum Diameter of bursting disc is 0.193172 mm.

Variables	Units		
	PSV Operation Pressure	15000 kPa	2177.068 Psig
Bursting Disc Pressure	16000 kPa	2322.206 Psig	156.3645 atm
Vessel volume	24 L	-	-
Vessel Design Temperature	-25 °C	248 K	-
Molecular mass of gas	16	-	-
Z at 1235 Psig	-	-	-
Constant (R) cm ³ atm/[K(gmol)]	82.06	-	-
Pc	45.8 atm	-	-
Tc	190.7 K	-	-
Vc	99 cm ³ /gmol	-	-
Zc	0.29	-	-
Sp Gr	0.554 (A)	-	-
Delta H, fusion	0.941 kJ/gmol	-	-
Melting temp	90.68 K	-	-
Normal BP	111.67 K	-	-
Pr = P/Pc	3.414073	-	-
Tr = T/Tc	1.300472	-	-
Z	0.68	-	-
n = m/M	-	-	-
Density = m/V PV = ZnRT	0.180787 g/cm ³	180.7865 Kg/m ³	-

Table 22 Condition Specification for PSV Operation @ 16000 kPa

Pipe dimensions

$$\text{ID} = 0.402 \text{ in} = 10.2108 \text{ mm}$$

$$\text{OD} = 0.451 \text{ in} = 11.4554 \text{ mm}$$

$$\text{WT} = 0.049 \text{ in} = 1.2446 \text{ mm}$$

Hence, we need to relieve 11% of the volume in the vessel in 15 seconds

This is 417.0493 L/15sec

Convert to hr: 100091.8 L/hr = 100.0918 m³/hr

6.6.4.3 Determining the Mass Flow Per Hour (b)

$$W = \rho V = 18095.255 \text{ kg/hr}$$

$$= 39809.56 \text{ lb/hr}$$

$$C \text{ for methane} = 346$$

$$K \text{ for 10.4 mm orifice} = 7.5$$

$$P_1 = 2322.2061 \text{ psia}$$

Hence

$$M \text{ in lb/ft}^3 = 11.262683 \text{ lb/ft}^3$$

$$\text{Velocity in the pipe } V = 183.4 \times W_h / (3600 \times d^2 \times \rho) = 1114.2695 \text{ ft/sec}$$

Viscosity of gas at 25 °C and 50 psia

$$\text{Hence viscosity } \mu/\mu_A = 2.5$$

Viscosity is 0.025 cP

Using the Moody Diagram Tables, then $e/D = 0.0028$

The Reynolds number can be determined by $Re = 6.32W_h/dz = 25034470$

From the Moody Table, this is laminar flow type and f can be approximated by

$$f = 64/Re = 0.024$$

6.6.4.4 Determining the Pressure Drop in the Line (b)

$$Pd = 3.36 (10^{-6})fLW^2 / (d^2\rho) = 3455.4737 \text{ psia}$$

Back Pressure Determination

$$\% \text{ absolute back pressure} = \text{back pressure (psia)} \times 100 / [\text{set pressure} + \text{over pressure (psia)}]$$

$$\text{Hence } K_b = 0.81$$

$$\text{Orifice size } A = W \times \text{Sgrt}(T) \times \text{Sqrt}(Z) / [C \times K \times P_1 \times K_b \times \text{Sqrt}(M)]$$

$$A = 0.0355478 \text{ in}^2 = 0.229341 \text{ cm}^2$$

$$d = \sqrt{(4A/\pi)} = 0.5403747 \text{ cm}$$

Minimum Diameter of bursting disc is 5.403747 mm.

Variables	Units		
PSV Operation Pressure	34.46 kPa	5.001451 Psig	0.33677 atm
Bursting Disc Pressure	344.64 kPa	50.02032 Psig	3.368092 atm
Line volume	7952.156 cm ³	7.952156 L	-
Vessel Design Temperature	25 °C	298 K	537 R
Molecular mass of gas	16	-	-
Z at 1235 Psig	-	-	-
Constant (R) cm ³ atm/[K(gmol)]	82.06	-	-
Pc	45.8 atm	-	-
Tc	190.7 K	-	-
Vc	99 cm ³ /gmol	-	-
Zc	0.29	-	-
Sp Gr	0.554 (A)	-	-
Delta H, fusion	0.941 kJ/gmol	-	-
Melting temp	90.68 K	-	-
Normal BP	111.67 K	-	-
Pr = P/Pc	0.073539	-	-
Tr = T/Tc	1.562664	-	-
Z	1	-	-
N = m/M	-	-	-
Density = m/V PV = ZnRT	0.002204 g/cm ³	2.203719 Kg/m ³	-

Table 23 Condition Spec. for PSV Op. @ 344.64 Disc Rupture Pressure in kPa.

Pipe dimensions

$$\text{ID} = 0.402 \text{ in} = 10.2108 \text{ mm}$$

$$\text{OD} = 0.451 \text{ in} = 11.4554 \text{ mm}$$

$$\text{WT} = 0.049 \text{ in} = 1.2446 \text{ mm}$$

Hence, we need to relieve 11% of the volume in the vessel in 15 seconds

This is 0.874737 L/15sec. Convert to hr: 209.9369 L/hr = 0.209937 m³/hr

6.6.4.5 Determining the Mass Flow Per Hour (c)

$$W = \rho V = 0.4626419 \text{ kg/hr}$$

$$= 1.0178122 \text{ lb/hr}$$

$$C \text{ for methane} = 346$$

$$K \text{ for 10.4 mm orifice} = 7.5$$

$$P_1 = 50.020319 \text{ psia}$$

Hence

$$M \text{ in lb/ft}^3 = 0.1372878 \text{ lb/ft}^3$$

$$\text{Velocity in the pipe } V = 183.4 \times W_h / (3600 \times d^2 \times \rho) = 2.3371171 \text{ ft/sec}$$

Viscosity of gas at 25 °C and 50 psia

Hence from figure 16-27 viscosity of $\mu/\mu_A = 1$

Viscosity is 0.0105cP

Using the Moody Diagram Tables, then $e/D = 0.0028$

The Reynolds number can be determined by $Re = 6.32W_h/dz = 1523.9453$

From the Moody Table, this is laminar flow type and f can be approximated by

$$f = 64/Re = 0.0419963$$

6.6.4.6 Determining the pressure drop in the line (c)

$$Pd = 3.36 (10^{-6})fLW^2 / (d^2\rho) = 0.0003242\text{psia}$$

Back Pressure Determination

$$\% \text{ absolute back pressure} = \text{back pressure (psia)} \times 100 / [\text{set pressure} + \text{over pressure (psia)}]$$

$$\text{Hence } K_b = 0.01$$

$$\text{Orifice size } A = W \times \text{Sgrt}(T) \times \text{Sqrt}(Z) / [C \times K \times P_1 \times K_b \times \text{Sqrt}(M)]$$

$$A = 0.0045427 \text{ in}^2 = 0.0293075\text{cm}^2$$

$$d = \text{SQRT}(4A/\pi) = 0.193172 \text{ cm}$$

Minimum Diameter of bursting disc is 1.9317204 mm.

6.6.5 Determination of Bursting Disc Size

Bursting discs are devices that add critical safety factors to equipment and facilities operating under pressure, or facilities that may experience a sudden increase in pressure. The bursting discs have a feature additional to pressure safety valves in that they open fully and allow full flow from a vessel out to a secondary chamber at lower pressure or to the environment. However, their placement within a facility must be determined through a HAZOP study to ensure the correct positioning of these devices within the facility. Sizing of the bursting discs is also important to ensure an accurate and safe depressurization of equipment within the facility.

The following are calculations to determine the size of bursting discs for the pilot plant given the operating pressure, temperature, and capacity of the various systems.

Ideal Gas equation:-

$$PV = ZnRT$$

$$\text{Since } n = m/M$$

$$\rho = m/V$$

$$\text{Then } n = \rho V/M$$

$$\text{Hence } PV = Z\rho VRT/M$$

$$\rho = PM/(ZRT)$$

$$\rho = 177.376(\text{atm}) \times 16 (\text{K/g mol})/[0.68 \times 82.06 (\text{cm}^3/\text{atm}) \times 248 (\text{K mol})]$$

$$\rho = 0.205 \text{ g/cm}^3$$

Converting to kg/m^3

$$\rho = 205 \text{ kg/m}^3$$

It was derived that are needs to relieve 11% of the Gas volume in the pressure vessel in the first 15 seconds.

$$\text{Hence } P_1V_1 = P_2V_2$$

$$V_2 = 413.06 \text{ lt in 15 seconds.}$$

Hence, volume relieved per second is: $413.06/15 = 27.54 \text{ lt/sec}$

So volume relieved in 1 hr = $27.54 \times 60 \times 60 = 99134.7 \text{ lt/hr}$

Using equation (3.1) for sizing the orifice

$$\text{Hence } A = W \sqrt{T} \sqrt{Z} / (CKP_1K_b \sqrt{M}) (\text{in}^2)$$

Where:-

W = Flow through valve lb/hr

C = Ratio of specific head of the gas at standard conditions

K = Coefficient of Discharge (Manufacturer)

A = Discharge Area (in²)

P₁ = Upstream pressure = set pressure + overpressure + Atmosphere

M = Molecular weight of gas

K_b = Capacity correction factor due to bulk pressure from Figure 3.3

T = °F (Absolute temperature of water vapor)

Z = Compressibility factor

G = Specific gravity of gas referred to air = 1 at 60°F and 14.7 psia

Now determining the mass flow per hour (lb/hr)

$$W = \rho V \quad (\text{kg/m}^3) \times (\text{m}^3/\text{hr}) = (\text{kg/hr})$$

$$W = 205 \times 99140/1000 = 20324 \text{ kg/hr}$$

$$\text{In lb/hr} \Rightarrow 20324 \times 2.2 = 44712.2 \text{ lb/hr}$$

C = from Figure 3.2 for Methane = 346

K = 7.5 for a value of 10.4 mm diameter

$$P_1 = 2300 \text{ psia}$$

Now for the 15 m of 1/2" tubing available for the Discharge pipe from the vessel

The IP = 10.21 mm

$$\text{OP} = 1/2" = 12.7 \text{ mm}$$

$$\text{WT} = 0.0409 \text{ in}$$

Hence, since

$$M = 205 \text{ kg/m}^3$$

$$M = 205 \times 2.2 = 451 \text{ lb/m}^3 \times \text{m}^3 / (\text{ft}^3 \times 35.314)$$

$$M = 12.77 \text{ lb/ft}^3$$

$$V = 183.4 \times Wn / (3600 \times d^2 \times \rho)$$

$$V = 183.4 \times 44712 / [3600 \times (0.402)^2 \times 12.77]$$

$$V = 1103.76 \text{ ft}^3/\text{s}$$

Hence

$$\text{Re} = 6.32W/dz = 6.32 \times 44712 / (0.402 \times z)$$

Find the viscosity of the gas at 2300psia

Hence $-25^{\circ}\text{C} = -13^{\circ}\text{F} = 447^{\circ}\text{R}$

From Figure 16.27

$Pr = 3.87$

$Tr = 1.3$

Hence viscosity = $\mu/\mu_A = 2.5$

μ_A = viscosity at 14.7 psia, or 1 atm and operating temperature (cP)

$\mu_A = 0.01\text{cP}$

Hence $\mu = 2.5 \times 0.01 = 0.025 \text{ cP} = Z$

From table assume $e/D = 0.0022$ Thus from Moody Diagram $e/D = 0.0022$

Hence $f = 0.024$

$Re = 6.32 \times 44712 / (0.402 \times 0.025) = 28 \times 10^6$

$Pd = 336(10^{-6}) \times 0.024 \times (15/0.3048) \times 44712^2 / [(0.402)^2 \times 12.77]$

$Pd = 3844.4 \text{ lb/in}^2 = 264989 \text{ kPa}$

Thus the back pressure determination: % absolute back pressure= back pressure

(psia) $\times 100 / [\text{set pressure} + \text{over pressure (psia)}$

$= 2300 \times 100 / (2300 + 3844.4) = 37.43 \%$

$K_b = 1.0$

Hence Area of the Bursting Disc is:

$A = W\sqrt{T}\sqrt{Z} / (CKP_1K_b\sqrt{M})$

$A = 44712 \times \sqrt{447} \times \sqrt{6168} / (346 \times 7.5 \times 2300 \times 1.0 \times \sqrt{16})$

$A = 0.03265 \text{ in}^2$

$A = 0.0327 \times (2.54\text{cm}/1 \text{ in})^2$

$A = 0.2107 \text{ cm}^2$

Hence $\pi/4 D^2 = 0.2107 \text{ cm}^2$

$D = \sqrt{(0.2107 \times 4/\pi)}$

$D = 0.518 \text{ cm} = 5.2 \text{ mm}$

Minimum Bursting Disc required is 0.3 mm Diameter.

6.7 - Project Schedule

The proposed scope of supply was completed in accordance with the master schedule included. It was considered that there was sufficient time to achieve this schedule by timely consultation and review of documentation with the relevant personnel.

6.8 - Construction and Commissioning

The initial steps required for the construction of the module were to identify and prioritize issues which could affect the timing of the overall project schedule. Due to the duration of time required for delivery of particular components the following items were placed on order without delay; the refrigeration system, the gas compressor and the water injection pump.

The module mainframe and other associated equipment such as the injection nozzle, storage tanks and electrical instrumentation were either designed internally within the University, or subcontracted off campus due to the specialized equipment or expertise required not accessible within Curtin.

The pressure vessels were designed and constructed in accordance with the specific Australian standard and certified by the appropriate authorities (as per 6.6.3).

All of the components including piping, tubing and fittings for the total equipment were completed in-house at the University. The commissioning of the module included the operation of the various equipment and components either individually or in association with other equipment within the module. Pressure testing of all the systems was conducted and placed under a 24-hour leak test. The refrigeration system was tested for compliance and did achieve its specific temperature rating. All electrical and instrumentation equipment was tested and met with the engineering specification.

Production of hydrates commenced after a five day testing and experimentation period on the various components within the module.

6.8.1 Pilot Plant Drawings

6.9 - Hazard and Operability (HAZOP) A Procedure Prepared by Woodside and Curtin University Personnel (Nov. 2000)

6.9.1 Instrumentation

PROJECT	NGH (HAZOP) – PILOT PLANT			DATE APPROVED
PROJECT No				NOV.2000
MEETING DATE	7th March, 2001	MEETING NO	2	
DRAWING No	NGH-E-001-01-A			
SUBSYSTEM	1.0 INSTRUMENTATION			SIGNED

GUIDE PHRASE	POSSIBLE CAUSES	CONSEQUENCES	SAFEGUARDS	ACTION	ACTION BY	ACTION No	CLOSE OUT REQUIREMENTS
Over Pressure	Blockage – leading to overpressure of low range gauges	Gauge damage and possible release	Isolation and vent on these gauges	Add to procedures way to check pressure is in range of instruments	RMG	2.1	Details added in rev C of operating procedure. See appendix B
				Confirm Gauges are rated to 2200 psi	RMG	2.2	See appendix E
Under Pressure	None						
Low Temperature	Freezing of gauges in vessels (free water)	Pressure gauges cease to operate	<ul style="list-style-type: none"> • 3 checks to ensure gauge is correct, using gauges in pipe-work external to vessel • also vent before opening door 	Confirm in operating procedures	RMG	2.3	Confirmed in rev C of operating procedures Checks as follows: Pressure gauge Check. Vessel Vent valve check. Break up of ice with steel bar through vessel opening See Appendix B
Locations			All gauges are seen to be working	None			

6.9.2 LP Gas Supply – Page 1 of 2

PROJECT	NGH (HAZOP) – PILOT PLANT			DATE: NOV. 2000			
PROJECT No				SIGNED			
MEETING DATE	7 th March, 2001	MEETING NO	2				
DRAWING No	NGH-E-001-01-A						
SUBSYSTEM	2.0 LP GAS SUPPLY (pag.1)						

GUIDE PHRASE	POSSIBLE CAUSES	CONSEQUENCES	SAFEGUARDS	ACTION	ACTION BY	ACTION No	CLOSE OUT REQUIREMENTS
Over Pressure	<ul style="list-style-type: none"> Venting from HP system stops LP PSVs from relieving due to overpressure 	PSVs on LP don't lift		Segregate LP vent lines PSVs from HP PSVs	SAA/SB	1.1	Complete See P&ID in Appendix A
	<ul style="list-style-type: none"> Back-flow from HP system 	Regulator and NRV will limit flow	Regulator, NRV	None			
	<ul style="list-style-type: none"> University supply (unlikely) 						
Low Pressure	Close OTSRV40-1	Compressor may be damaged	<ul style="list-style-type: none"> Gauges can go negative Operating procedures 	None			
High Temp	None						
Low Temp	During recycle, but pipe-work heats up gas to close to ambient	LPR-1 blocks and HPR-1 passes causing overpressure of F-001 and LPR-1		<ul style="list-style-type: none"> Check temperature ratings on F-001 and F-004 	NG	1.2	F-004 is rated at –15 °C F-001 is rated at –10 °C See Appendix E
				<ul style="list-style-type: none"> Install PSV in line upstream of F-005 at approx 50psi setpoint 	SAA/SB	1.3	See Appendix E
Liquids	Foam forming in V-001	Foam/Liquid can move all the way to the Compressor	Check all chemicals in the lab for foaming characteristics	None			

6.9.2 Gas Supply – Page 2 of 2

PROJECT		NGH (HAZOP) – PILOT PLANT				DATE		
PROJECT No						NOV. 2000		
MEETING DATE		7 th March, 2001	MEETING NO		2			
DRAWING No		NGH-E-001-01-A				SIGNED		
SUBSYSTEM		2.0 LP GAS SUPPLY (pag. 2)						
GUIDE PHRASE	POSSIBLE CAUSES	CONSEQUENCES	SAFEGUARDS	ACTION	ACTION BY	ACTION No	CLOSE OUT REQUIREMENTS	
Testing / Equipment				Catalogue all filter and regulator pressure rating certificates	NG	1.4	See inspection procedures in Appendix C	
Contamination Materials		Acidic liquid carryover causing failure of filters etc		Filter checks in maintenance procedures (Aluminum, brass etc)	RMG	1.5	See Inspection Procedures in Appendix C	
Effluent		Minor						
Fire/Explosion		Covered in HP Gas system						
Safety		Covered in HP Gas system						

6.9.3 Electrical instrumentation

PROJECT	NGH (HAZOP) PILOT PLANT			DATE	NOV. 2000	
PROJECT No				SIGNED		
MEETING DATE	7 th March, 2001	MEETING NO	2			
DRAWING No	NGH-E-001-01-A					
SUBSYSTEM	3.0 ELECTRICAL INSTRUMENTATION					

GUIDE PHRASE	POSSIBLE CAUSES	CONSEQUENCES	SAFEGUARDS	ACTION	ACTION BY	ACTION No	CLOSE OUT REQUIREMENTS
ALL				Electrical Engineer required to review single line diagram	RMG	3.1	Electrical engineer reviewed system 13/3/00. Report issued and actioned See appendix F

6.9.4 Refrigeration system

PROJECT	NGH (HAZOP) PILOT PLANT			DATE	NOV. 2000	
PROJECT No				SIGNED		
MEETING DATE	7 th March, 2001	MEETING NO	2			
DRAWING No	NGH-E-001-01-A					
SUBSYSTEM	4.0 REFRIGERATION SYSTEM					

GUIDE PHRASE	POSSIBLE CAUSES	CONSEQUENCES	SAFEGUARDS	ACTION	ACTION BY	ACTION No	CLOSE OUT REQUIREMENTS
CONSIDERED SYSTEM AS A SINGLE VENDOR SUPPLIED SYSTEM LOCATED IN NON-HAZARDOUS AREA WITH OUR CONTROL SYSTEM IT WAS AGREED TO LEAVE OUT OF HAZOP. NO CONTACT WITH PROCESS i.e. NO CONTAMINATION							
Maintenance				Subject to maintenance procedure and vendor requirements	RMG	4.1	Covered in Inspection procedure See Appendix C

6.9.5 Hot Water System

PROJECT	NGH (HAZOP) PILOT PLANT			DATE NOV. 2000
PROJECT No				
MEETING DATE	7th March, 2001	MEETING NO	2	SIGNED
DRAWING No	NGH-E-001-01-A			
SUBSYSTEM	5.0 HOT WATER SYSTEM			

GUIDE PHRASE	POSSIBLE CAUSES	CONSEQUENCES	SAFEGUARDS	ACTION	ACTION BY	ACTION No	CLOSE OUT REQUIREMENTS
High flow	Motor going to high speed	Top part of vessel gets too hot – effects the refrigeration efficiency	NR	None			
Low flow		Nozzle freezes and pressure increases	PSVs and Rupture disks	Install rupture discs	SAA/SB	5.1	Covered in P&ID See appendix A
Reverse flow		N/A					
High Pressure	Closed valve	No overpressure consequences	none	None			
High temp		N/A					
Low temp	Heater off	Nozzle freezes and pressure increases	PSVs and Rupture disks	Install rupture discs	SAA/SB	5.2	Covered in P&ID See appendix A
Impurities	Ethylene glycol	Freeze hot water system	Replace every 6 months due to degradation	Add to maintenance procedure to check and replace EG when required	RMG	5.3	Covered in plant inspection procedures Appendix C
Testing Equipment			Data sheets from manufactures	None			
Testing instruments			Temperature alarms	None			
Toxicity			Material handling data sheet available as per operating procedures	None			

6.9.6 Production vessel – Page 1 of 2

PROJECT	NGH (HAZOP) PILOT PLANT			DATE NOV. 2000
PROJECT No				
MEETING DATE	7 th March, 2001	MEETING NO	2	SIGNED
DRAWING No	NGH-E-001-01-A			
SUBSYSTEM	6.0 PRODUCTION VESSELS (pag. 1)			

GUIDE PHRASE	POSSIBLE CAUSES	CONSEQUENCES	SAFEGUARDS	ACTION	ACTION BY	ACTION No	CLOSE OUT REQUIREMENTS
Material			Stainless steel or plastic material selection	None			
Startup / Shutdown		Damage to equipment	Operating procedures for safe shutdown	None			
Effluent	Change out / maintenance	little	Store glycol in bottles Closed system	None			
High level		Block PSV, block nozzle, overpressure via back-flow through vent line and IVSH-2	4R3A-1 will lift				
Low level			None				
Empty	Removing hydrates	Air ingress	Purged NG before startup	See operating procedures	RMG	6.1	Confirmed in rev C of operating procedures See Appendix B
Reverse flow			Non-return valves	None			
High Pressure		Overpressure in vessel	PSVs lift, rupture discs lift	None			
Low pressure	Recycling Closed system		Vessel designed for vacuum	None			
Low temp	De-pressure from cold	Go as cold as -45 deg C during de-pressurising only	Design temp of vessel -25 C , valves -30 C	Review ways to ensure vessel and valves do not exceed min negative temp limits	SAA/SB	6.2	See Appendix E
				Add alarm at -25 deg C on 4P4T - 10	SAA/SB	6.3	See Appendix E

6.9.6 Production vessel – Page 2 of 2

PROJECT	NGH (HAZOP) PILOT PLANT			DATE	NOV. 2000		
PROJECT No				SIGNED			
MEETING DATE	7th March, 2001	MEETING NO	2				
DRAWING No	NGH-E-001-01-A						
SUBSYSTEM	6.0 PRODUCTION VESSELS (pag. 2)						

GUIDE PHRASE	POSSIBLE CAUSES	CONSEQUENCES	SAFEGUARDS	ACTION	ACTION BY	ACTION No	CLOSE OUT REQUIREMENTS
Changes in composition / Impurities	Mal-operation (failure to add chemicals)	Make an ice hard monolith. Mechanically stress vessel as ice expands	Limit hydrate production to 5 litres	In the operating procedures	RMG	6.4	Added to Rev C of operating procedures See Appendix B
				UV (visual) NDT of vessels to ensure no stressing	JM	6.5	See Appendix D
				Procedures to have routine UV detection	RMG	6.6	See inspection procedures Appendix B
				Examine “crumple zone” shape inside vessel to take stress	RMG/SB	6.7	See Appendix E
Testing / Equipment			Pressure test certificates	None			
Toxicity / Effluent		Hydrate chemical remnants	Covered in Hydrate removal procedure	None			
Corrosion	Chemicals	Pitting of material	Check pitting regularly	NDT as periodic routine procedure	RMG	6.8	See inspection procedures Appendix B

6.9.7 HP gas supply – Page 1 of 5

PROJECT	NGH (HAZOP) PILOT PLANT			DATE
PROJECT No				NOV. 2000
MEETING DATE	6th March, 2001	MEETING NO	1	
DRAWING No	NGH-E-001-01-A			
SUBSYSTEM	7.0 HP GAS SUPPLY			SIGNED

GUIDE PHRASE	POSSIBLE CAUSES	CONSEQUENCES	SAFEGUARDS	ACTION	ACTION BY	ACTION No	CLOSE OUT REQUIREMENTS
High Flow/ High Pressure	<ul style="list-style-type: none"> Failure of manual control over Pressure 	PSVs V1 lift PSVC-1 lift Inter-stage discharge compressor	PSV on compressor set at 3000 psi PSV-V1 2170 psi PSV-V2 2170 psi	None			
	<ul style="list-style-type: none"> Failure of wellhead regulator on new gas supply 			HAZOP when modification occurs	NOTE	7.1	Included in design change request form See Appendix C
	<ul style="list-style-type: none"> Blocked nozzle on hydrate vessel 	PSVC-1 lift					
	<ul style="list-style-type: none"> Compressor changed out for recycle flow 			HAZOP when modification occurs	NOTE	7.2	Included in design change request form See Appendix C
	<ul style="list-style-type: none"> Hydrate forms in PSVC-1 	Over pressure to above 3000 psi	None	Consider use of bursting discs instead of PSVs to reduce chance of over pressure	SAA/SB	7.3	See Appendix E
Low Pressure / Vacuum	Not seem as likely	Suck air into the suction of compressor	Not required in HP system	None			

6.9.7 HP gas supply – Page 2 of 5

PROJECT	NGH (HAZOP) PILOT PLANT			DATE	NOV. 2000	
PROJECT No						
MEETING DATE	6th March, 2001	MEETING NO	1			
DRAWING No	NGH-E-001-01-A					
SUBSYSTEM	7.0 HP GAS SUPPLY			SIGNED		

GUIDE PHRASE	POSSIBLE CAUSES	CONSEQUENCES	SAFEGUARDS	ACTION	ACTION BY	ACTION No	CLOSE OUT REQUIREMENTS
Reverse flow	<ul style="list-style-type: none"> Leak in fitting in between compressor and vessel 	Vapor release	Non return valves CHS8-2, CHS8-1 CHS6-1, inlet of C-001 and bypass NRV-003	None			
	<ul style="list-style-type: none"> Failure of NRN seats 	Back flow through compressor and PSV lifts Over pressurise LP gas supply	VITON seats to prevent NRV failure	Install rupture discs in parallel to the LP PSVs	SAA/SB	7.4	See P&ID Appendix A
High Temp	Compressor inefficiency	Process inefficiency Extra cooling from compressor intercooler	None required	Install rupture discs in parallel to the LP PSVs	SAA/SB	7.5	See P&ID Appendix A
Low Temp	Very cold day	Blockage of MX-001	Non required	Check operating procedures for removing water from 'lines' before shutdown	SAA/SB	7.6	Included in Rev C of operating procedures See Appendix B
Impurities : Sand	Dust from natural gas supply	Damage compressor	Filter in LP section F-004	None			
Composition	Change in fields supplying excessive LPG/ Cs+	Liquid knock-out vessel in F-003	Sufficient via F-003	None			

6.9.7 HP gas supply – Page 3 of 5

PROJECT	NGH (HAZOP) PILOT PLANT			DATE NOV. 2000
PROJECT No				
MEETING DATE	6th March, 2001	MEETING NO	1	SIGNED
DRAWING No	NGH-E-001-01-A			
SUBSYSTEM	7.0 HP GAS SUPPLY (pag. 3)			

GUIDE PHRASE	POSSIBLE CAUSES	CONSEQUENCES	SAFEGUARDS	ACTION	ACTION BY	ACTION No	CLOSE OUT REQUIREMENTS
Increased CO2	Gas field variations	Premature blockage	See high pressure	None			
		• Corrosion	Stainless steel	None			
Electrical				Covered under separate subsystem	NOTE	7.7	Reviewed by electrical engineer on 13/3/00. See Appendix F
Instruments	Lack of gauges	As manual control can cause PSVs to lift	Pressure indicators on all HP lines and visible from operator location PI-07, PI-06, PI-09, PI-01, PI-15	V-001 PI does not have a number HPR-1 PI does not have a number	NG	7.8	See P&ID Appendix A
Toxicity	Covered in liquid systems (acids)						
Testing / Equipment		Equipment failure		Visual inspection before start	RMG	7.9	Included in Rev C of operating procedures See Appendix B
				Keep log of all vender test certificates	RMG	7.10	Included in inspection procedures See Appendix C
				PSVs to be bench tested calibrated once a year	RMG	7.11	Included in inspection procedures See Appendix C
				Similar visual inspection on bursting discs	RMG	7.12	Included in inspection procedures See Appendix C

6.9.7 HP gas supply – Page 4 of 5

PROJECT	NGH (HAZOP) PILOT PLANT			DATE NOV. 2000
PROJECT No				
MEETING DATE	6th March, 2001	MEETING NO	1	
DRAWING No	NGH-E-001-01-A			
SUBSYSTEM	7.0 HP GAS SUPPLY			SIGNED

GUIDE PHRASE	POSSIBLE CAUSES	CONSEQUENCES	SAFEGUARDS	ACTION	ACTION BY	ACTION No	CLOSE OUT REQUIREMENTS
Testing / Equipment				Modification procedure to be prepared and adhered to. Sam Battah has the template.	SB	7.13	See action 7.1
Security	Unauthorized student interference	System unsafe	Lock shed and instrument cabinet. Pre-start check list	Ensure plant is always attended in operating procedures.	RMG	7.14	Included in Rev C of operating procedures
Material	<ul style="list-style-type: none"> Acid attack on carbon steel vessels 	Equipment failure	Periodic inspection of compressor and vessels	Check corrosion allowance of vessel as part of maintenance procedures	RMG	7.15	Confirmed as 5 mm. See drawing 7868/1
	<ul style="list-style-type: none"> Piping stainless steel compressor various 		Tubing stainless steel	Compressor checked during overhaul as part of maintenance procedures	RMG	7.16	Included in inspection procedures See Appendix C
Commissioning / Startup		Mal operation	Covered in procedures (startup, modification and shut down)	None			

6.9.7 HP gas supply – Page 5 of 5

PROJECT	NGH (HAZOP) PILOT PLANT			DATE NOV. 2000
PROJECT No				
MEETING DATE	6th March, 2001	MEETING NO	1	
DRAWING No	NGH-E-001-01-A			
SUBSYSTEM	7.0 HP GAS SUPPLY			SIGNED

GUIDE PHRASE	POSSIBLE CAUSES	CONSEQUENCES	SAFEGUARDS	ACTION	ACTION BY	ACTION No	CLOSE OUT REQUIREMENTS
Gas effluent		Potential gas release	<ul style="list-style-type: none"> • Vent is in safe location • Timing at low university traffic • Shed naturally vented in above AS • Gas detector above compressor gas seal 	Buy new gas detector	RMG	7.17	Quote received. See Appendix E
Noise	Compressor 80db Refrigerator 80db	Ear damage	Check noise levels	Check noise levels	JM	7.18	To be undertaken once plant is commissioned
Fire/ Explosion	Release and ignition		<ul style="list-style-type: none"> • Evacuation procedure • Fire extinguishers • Area is non-hazardous (by AS standards) • Emergency procedures to contact of security • 2 means of escape 				

6.9.8 HP Liquor Supply – Page 1 of 2

PROJECT		NGH (HAZOP) PILOT PLANT			DATE		
PROJECT No					NOV. 2000		
MEETING DATE		6 th March, 2001	MEETING NO	1			
DRAWING No		NGH-E-001-01-A			SIGNED		
SUBSYSTEM		8.0 HP LIQUOR SUPPLY					
GUIDE PHRASE	POSSIBLE CAUSES	CONSEQUENCES	SAFEGUARDS	ACTION	ACTION BY	ACTION No	CLOSE OUT REQUIREMENTS
Over pressure	Closure of valve 44S6-7 or 44S6-6	Reach design pressure of system PSV R3AE	PSV R3AE	None			
Corrosion	Chemicals	PSV corrodes rust, pumps damaged, liquid discharge	None	None			
Low flow	No level in tank	Damage pump	Low level trip	None			
Zero flow	No level in tank	Damage pump	Low level trip	None			
	PSV passing	No liquor into experiment	Visual check of level in T-002	None			
High Temp	High ambient	None	None	None			
Low Temp	Low ambient	None	None	None			
Impurities	Sediments	Blockage	Filter and drain line	None			
Two Phase	Not foreseen always considered as single phase						
Testing			<ul style="list-style-type: none"> Pump to have pressure certificate PSV tested on bench 	Install small lab tank next to permanent tank and install LI-01 in this lab tank	SAA/SB	8.1	Visual inspection of plant
Instruments	Low level trip fails to operate	Damage pump	LI-01 trip	Test LI-01 trip function	SB/SAA	8.2	Test trip during commissioning of plant

6.9.8 HP Liquor Supply – Page 2 of 2

PROJECT		NGH (HAZOP) PILOT PLANT			DATE NOV. 2000		
PROJECT No							
MEETING DATE		6 th March, 2001	MEETING NO	1			
DRAWING No		NGH-E-001-01-A					
SUBSYSTEM		8.0 HP LIQUOR SUPPLY			SIGNED		
GUIDE PHRASE	POSSIBLE CAUSES	CONSEQUENCES	SAFEGUARDS	ACTION	ACTION BY	ACTION No	CLOSE OUT REQUIREMENTS
Toxicity	Splashes etc	Operator injury	PPE	Plant safety procedures to reflect the handling of the most hazardous chemicals whether they are used regularly or not	RMG	8.3	Covered in rev C of operating procedures See Appendix B
Material		All stainless (HP) or plastic and SS (LP)	Materials OK	None			
Startup/ Shutdown	General						
Effluent	Draining tank	Disposal of liquor	Covered in procedures	Check procedures	RMG	8.4	Covered in rev C of operating procedures See Appendix B
Safety	General			Refer procedure	RMG	8.5	Covered in rev C of operating procedures See Appendix B

6.9.9 Venting

PROJECT		NGH (HAZOP) PILOT PLANT				DATE NOV> 2000		
PROJECT No								
MEETING DATE		7 th March, 2001		MEETING NO		2		
DRAWING No		NGH-E-001-01-A				SIGNED		
SUBSYSTEM		9.0 VENT						
GUIDE PHRASE	POSSIBLE CAUSES	CONSEQUENCES	SAFEGUARDS	ACTION	ACTION BY	ACTION No	CLOSE OUT REQUIREMENTS	
Over pressure	Blockage	Over- pressurize F-005	PSV and Rupture Discs PSV vents separate to venting lines. No valves in PSV vent line	Install MT-03 upstream of F-005 rather than down stream of F-005	SB/SAA	9.1	See Appendix E	
Vacuum	No possibility							
Storage system		Isolate vent system		Review Gas storage philosophy. Remove storage from dedicated safety vent line	SB	9.2	Storage philosophy reviewed. See P&ID Appendix A	
Low Temp	Vent very low rate so cannot get cold							
Impurities	Foam	Foam discharge to atmosphere	Test additives in laboratory for foaming	Refer relevant procedures	RMG	9.3	Covered in rev C of operating procedures See appendix B	
Material	All stainless steel							
Effluent	Gas discharge	Smell of odourant	none	Consider methods of gas storage on vent during HP hydrate operations	SB	9.4	Storage philosophy reviewed. See P&ID Appendix A	

7 - HYDRATE PRODUCTION (PILOT PLANT)

7.1 - Hydrate Gas /Liquor Concentrations

Laboratory testing using concentrations of chemical additives were carried out in 700 cc titanium cylinders. Water and different chemical additives were mixed at pressures above 10335 kPa. TSA yielded high hydrate formation volume factor (HFVF) results that were consistent and repeatable at high pressures of (10335 kPa). Due to the effects on the physical properties of a solution, critical micelles concentration of the TSA surfactant around 1.25gm/l is found to greatly enhance hydrate formation.

The results from the cylinder were transferred to the pilot plant with a gas/liquor injection ratio of 0.01% (by volume) liquor and 999.99% gas at tubing pressure of 12,500 kPa (1810 psia) and ambient temperature. The effect of ambient temperature on the hydrate quality is shown in Figure 7.0. This liquor gas ratio was determined experimentally to provide, on average, an HFVF factor of 200 at pressure of 11024 kPa (1600 psig). Hydrate quality as a function of liquor concentration is shown in Figure 24.

7.2 - Gas Formation /Liquor Ratios and Hydrate Volume Formation Factors

Low pressure hydrate production testing started at 2756 kPa (400 psia). Initial hydrate formation volume factors near 100 volume of gas per volume of hydrate with a residence time of 30 minutes was achieved. Subsequently, it was decided to operate at the lowest possible pressure which was 689 kPa(100 psia).

Hydrate quality with gas content per volume of hydrate in the order of 40 to 160, has been produced at measurable quantities. Although hydrate FVF higher than 250 was achieved on several occasions, it was decided not to report the results because of the quantity of the produced volume. One run did produce an HFVF of 250 with sufficient gas-water volumes. A minimum of 2 litres of gas and 20 cc of liquor was set to be considered acceptable for reporting. This was set to reduce the error margin associated with the measurements.

It is quite obvious from Figure 16. that the upstream nozzle pressure played a significant role in HFVF, as higher pressure will produce a higher JT (Joule Thompson) effect (lower temperature) and possibly better atomization and turbulence. These parameters are known to have a direct effect on hydrate nucleation and formation rate. It is also clear from Figures 22 and 23 that lower injection time produced higher HFVF due to the following factors:

Hydrate formation generates heat (heat of formation) which if prolonged and not compensated with additional refrigeration, will reduce the HFVF of the hydrate during testing.

The above observations are consistent with hydrate nucleation theory, where the rate of homogeneous nucleation increases exponentially with increasing subcooling. In addition hydrate crystal growth rate is increasing linearly with increasing subcooling. Furthermore secondary nucleation and heterogeneous nucleation also increases with subcooling.

7.3 - Bulk Densities and Energy Densities

The free bulk density and the compacted bulk density for the low pressure hydrate have been determined experimentally on a series of runs with the flash chamber operating at 700kPa (100psig) and an average temperature of -10 to -18°C . The density units are g/cc.

The density-temperature graph is shown in Figure 30.

The data to date indicates that the free bulk densities for the produced hydrate are nominally around 200 kg/m^3 and the compacted bulk density is nominally around 350 kg/m^3 .

Preliminary examination of the bulk density results suggests that the bulk density is related to the hydrate volume formation factor. Generally higher HFVF produced bulk density between $2\text{-}3 \text{ g/cc}$, and lower qualities were normally higher by 0.5g/cc due to

high water (ice) content. The effect of the nozzle is also very important as the main objective is to produce a spray of high surface-to-mass ratio droplets (ideally of equal size), which are exposed to low temperature gas (-6 to -15) which the moisture rapidly absorbs.

Thus it appears very likely that the hydrates fall into the same isomechanical class as water-ice because the bonding is very similar, although the crystal structure is different. The density of hydrate even as high as at 0.58×10^{-3} kg/cm is low compared to that of water-ice so it is to be expected that the elastic properties will be similarly reduced, simply on a basis of the number of H-bonds per unit volume. Therefore it seems sensible to estimate the fundamental elastic moduli of hydrate to be 58% of that of ice.

However, it should be emphasised that additional parameters such as nozzle geometry, fluid flow properties and effective nozzle diameter need to be considered to better understand the process.

7.4 - Hydrate Formation/Phase Envelope Curves

See Items 7.7 and 7.7.5

7.5 - Nozzle Basis of Design

The factors affecting the spray nozzle performance such as viscosity and temperature were considered in the design. However, spray angle and coverage, impact and nozzle wear were not taken into account due to the extensive prior testing which would be required to design and construct the best suitable nozzle for this application. Some of the key considerations for the design of the heated nozzle were as follows:

- The overall length of the nozzle to ensure the spray jet located at the bottom of the nozzle is below the bottom surface of the blind flange and fully exposed to the cavity of the vessel.
- Overall diameter of the nozzle not to exceed 1.00 inch in diameter, as the 8-inch (10335 kPa class) blind flange could not be drilled any larger without impacting on the integrity of the vessel design (Vessel design pressure at 14950 kPa).
- The nozzle to be equipped with an inlet and outlet connection for heating using ethylene glycol solution.
- The nozzle to be equipped with a gas inlet tube to carry gas/liquor mix from the injection system to the spray nozzle through a heated chamber.
- The spray jet to be located as close as possible to the heated glycol to allow for the best possible heat transfer.
- Accessibility to the jet for removal and replacement be simple and expedient to reduce exposure of the vessel interior to ambient conditions.
- Size of the spray jet to be compatible with the liquor flow rate to maintain a continuous pressure differential across the spray nozzle.

The newly introduced Nozzle with opening of 0.25mm ID is operational. With this nozzle we are able to maintain the upstream tubing pressure within 344 kPa. Three sets of data obtained to date show promise in terms of consistency with hydrate FVF (between 90-150).

7.6 - Test Report Procedure

See Appendix A

7.7 - Liquor/Gas Phase Envelope Diagram (Computer Model)

7.7.1 Liquor Phase Envelope Diagram

Liquor-gas phase envelope diagrams have been generated using pressure-volume-temperature (PVT) sim and are shown below:

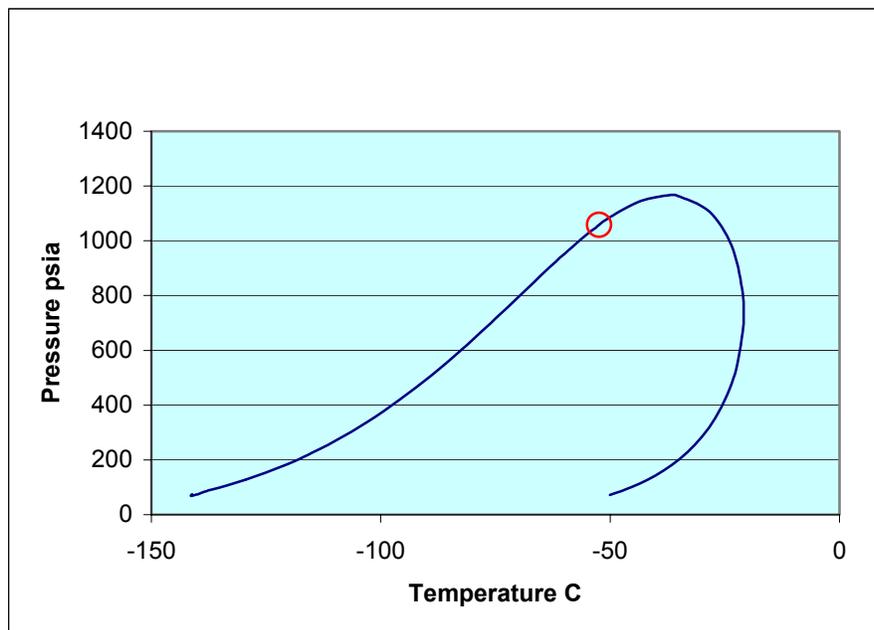


Figure. 13 AlintaGas Phase Envelope

The diagram above is based on gas without the TSA additive concentrations outlined in 1.1.

7.7.2 Phase Envelop Model Description

The phase envelope model consisted of corresponding values of T and P for which the vapor fraction β of a given mixture equals a specified value. The vapour fraction can either be a mole fraction or a volume fraction. The phase envelope option in PVTsim (based on Michelsen, 1980) was used to construct dew and bubble point lines, i.e. corresponding values of T and P for which β equals 1 or 0, respectively. Inner lines ($0 < \beta < 1$) may also be constructed. The construction of the outer phase envelope ($\beta = 1$ and $\beta = 0$) and inner molar lines follows the procedure outlined below. The first (T, P) value of a phase envelope is calculated by choosing a fairly low value for the pressure (P) (default in PVTsim is 5 Bar).

7.7.3 PVT Sym Model Description

The PVTsim input data comprises the fluid composition and operating conditions (P&T) depending on the type of simulation.

Table Fluid Properties at 1500.00 psi and 20.00C			
Property	Total	Vapour	Aqueous
Mole%	100.00	99.37	0.63
Weight%	100.00	99.26	0.74
Volume	182.61	183.66	18.77cm ³ /mol
Volume%	100.00	99.93	0.07
Density	0.105	0.1048	1.1955 g/cm ³
Z Factor	0.7748	0.779	0.0796
Molecular Weight	19.28	19.26	22.44
Enthalpy	-1977	-1694.0	-46363.9 J/mol
Entropy	-37.03	-36.47	-124.93 J/mol C
Heat Capacity (Cp)	60.0	59.88	86.86 J/mol C
Heat Capacity (Cv)	32.23	32.03	64.29 J/mol C
Kappa (Cp/Cv)	1.863	1.870	1.351
J-T Coefficient	-	0.3796	-0.0155 C/Bar
Velocity of Sound	-	397.9	2713.9 m/s
Viscosity	-	0.0153	0.9975cP
Thermal Conductivity	-	44.791	612.157 mW/mC
Surface Tension	-	70.917	70.917 mN/m

Table 36 Fluid Properties at 10.3 Mpa and 20.00C

Note: Volume, Enthalpy, Cp and Cv are per mole phase

7.7.4 Hydrate Calculation

In the calculation model (using PVT-Sim) we considered three different types of hydrate lattices, structures I, II and H. Each type of lattice contains a number of small and a number of large cavities. In a stable hydrate, gaseous compounds called guest molecules occupy some of the cavities.

Structure I and II hydrates can only accommodate gases of rather modest size and appropriate geometry. The table below indicates which compounds enter into the small and large cavities of each of the hydrate structures. The cavities may contain one kind of a gaseous compound or they may contain gas molecules of different chemical species. Not all cavities need to be filled in a stable hydrate.

Compound	Structure I		Structure II	
	Small cavities	Large cavities	Small cavities	Large cavities
C1	+	+	+	+
C2	-	+	-	+
C3	-	-	-	+
iC4	-	-	nil	+
nC4	-	-	-	+
CO ₂	+	nil	+	+
N ₂	+	+	+	+

Table 37 Hydrate Cavities Structure

Structure H consists of three different cavity sizes. These were PVTsim modeled as just two cavity sizes, a small/medium cavity and a large cavity. The large cavity accommodates molecules containing 5 to 8 carbon atoms. The small/medium sized molecules will usually be associated with N₂ or C1. The below table gives an overview of structure H formers considered in the calculation.

Compound	Total	Hyd-II	Hyd-H
H2O	95.000	86.127	86.075
N2	0.130	0.361	0.502
CO2	0.109	0.304	0.000
C1	4.211	11.691	10.893
C2	0.339	0.944	0.000
C3	0.156	0.434	0.000
iC4	0.020	0.057	0.000
nC4	0.029	0.082	0.000
iC5	0.002	0.000	2.530
nC5	0.001	0.000	0.000
C6	0.000	0.000	0.000

Table 38 Calculated Hydrate composition at 11 Mpa and -20C Using PVT-Sim

Compound	Total	Hyd-II	Hyd-H
H2O	95.000	86.213	86.155
N2	0.130	0.358	0.499
CO2	0.109	0.303	0.000
C1	4.211	11.619	10.813
C2	0.339	0.938	0.000
C3	0.156	0.431	0.000
iC4	0.020	0.057	0.000
nC4	0.029	0.081	0.000
iC5	0.002	0.000	2.533
nC5	0.001	0.000	0.000
C6	0.000	0.000	0.000

Table 39 Calculated Hydrate composition at 2.75 Mpa and -20C Using PVT-Sim

Compound	Total	Hyd-II	Hyd-H
H2O	95.000	86.280	86.245
N2	0.130	0.357	0.469
CO2	0.109	0.301	0.000
C1	4.211	11.563	10.750
C2	0.339	0.933	0.000
C3	0.156	0.429	0.000
iC4	0.020	0.056	0.000
nC4	0.029	0.081	0.000
iC5	0.002	0.000	2.536
nC5	0.001	0.000	0.000
C6	0.000	0.000	0.000

Table 40 Calculated Hydrate composition at 2.75 Mpa and –15C Using PVT-Sim

Compound	Total	Vapour	Hyd-II
H2O	95.000	0.009	86.666
N2	0.130	3.451	0.059
CO2	0.109	2.252	0.271
C1	4.211	91.514	8.769
C2	0.339	2.457	2.368
C3	0.156	0.093	1.438
iC4	0.020	0.010	0.190
nC4	0.029	0.116	0.239
iC5	0.002	0.056	0.000
nC5	0.001	0.028	0.000
C6	0.000	0.014	0.000

Table 41 Calculated Hydrate composition at 6.89 Mpa and –20C Using PVT-Sim

Compound	Total	Vapour	Hyd-II
H2O	95.000	0.025	87.544
N2	0.130	2.927	0.048
CO2	0.109	2.300	0.180
C1	4.211	87.868	7.413
C2	0.339	5.700	1.761
C3	0.156	0.638	2.476
iC4	0.020	0.063	0.343
nC4	0.029	0.398	0.235
iC5	0.002	0.046	0.000
nC5	0.001	0.023	0.000
C6	0.000	0.011	0.000

Table 42 Calculated Hydrate composition at 6.89 Mpa and –10C Using PVT-Sim

7.7.5 Hydrate Formation Curves (Computer Model)

Natural gas sample composition, mol % (84.35CH₄, 7.1C₅H₁₂, 3.2C₃H₈, 2.4C₂H₆, 2.0C₄H₁₀, 0.87N₂).

Hydrate formation Curves have been generated using PVTsim and are shown below:

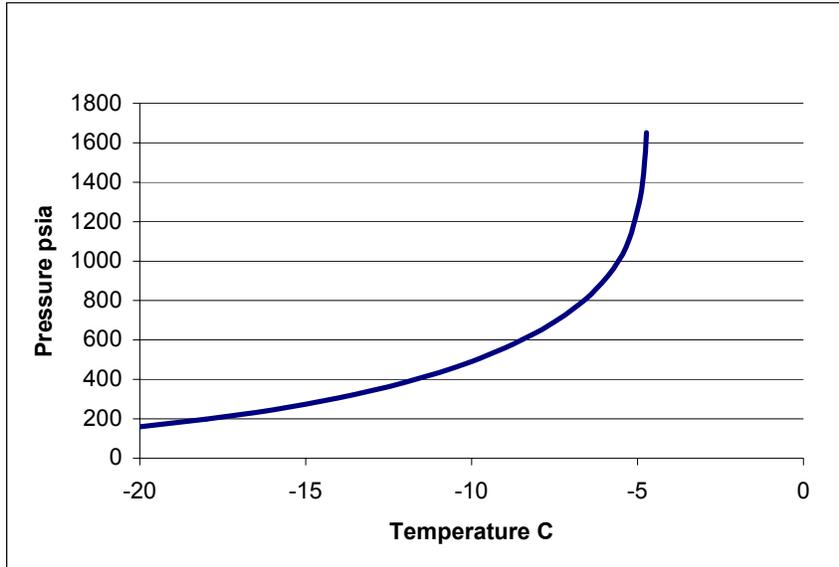


Figure 14 Hydrate formation curve for Alinta gas

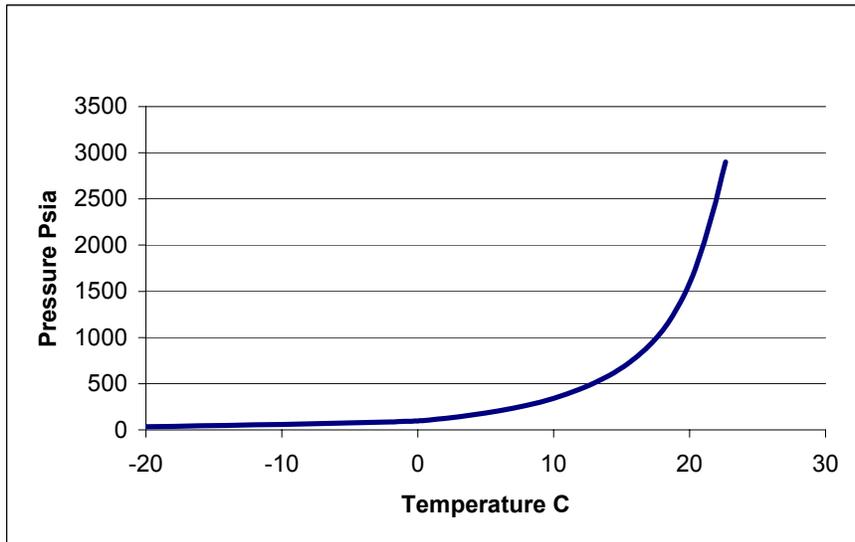


Figure 15 Calculated Press. Temp. Curve for TSA-Water-Gas System at 1.2 g/l

7.7.6 Hydrate Stability Curves

In order to establish some interim data, further testing on high pressure hydrate samples using the batch hydrate production method will be necessary and should be carried out in the future.

7.7.7 Heat Transfer

Several tests were conducted to determine heat transfer of the water TSA mix.(liquor) to determine whether TSA had any impact on heat transfer characteristics of the liquid. It was discovered that TSA did not modify heat transfer properties of the gas and water. The laboratory capability is not currently sufficient to perform detailed physical testing to verify these assumptions.

7.7.8 Thermal Conductivity

The modified PVT-SIM with (TSA enrichment) simulation program was used to determine the thermal conductivity of the produced hydrate, the calculation results are shown in the Figure 31.

Thermal conductivity of the produced gas hydrate ranges between 0.59 and 0.35 W/(m·K) for temperatures between -30° and 10°C. The conductivity values decrease with temperature from -30° to 0°C, then abruptly increase by 0.2 W/(m·K) at 0°C.

This abrupt increase was probably caused by the release of liquid water, the higher thermal conductivity of the water increased the thermal conductivity of the system. These results are consistent with thermal conductivity data on hydrates published by Sloan (1999).

7.7.9 Hydrate Heat of Formation

Formation of methane hydrate is not exothermic. Formation of the crystal does not give off heat. Heat is extracted by the environment to form the crystal. Heat extraction is not an exothermic bond forming or molecular or chemical reaction.

The stability of NGH is closely related to the heat of formation. It follows that considerable heat must be removed before natural gas hydrate forms. The heat of hydrate formation reported in the literature in 1990 is estimated to be about 410 kJ/kg (Selim and Sloan 1990) compared to 333.5 kJ/kg for ice. The reported number is for pure hydrate with no additives and I do not recommend using the above number, It is believed that the numbers experienced herein are lower than that because of the additives.

The higher heat of formation of hydrate is due to the inclusion of gas molecules in the ice-like hydrate structure.

The water heat transfer coefficient with an additive concentration of 1250ppm TSA is expected to have the same physical heat transfer coefficient as normal water listed in chemical physical data books. (Note TSA is a surfactant. A surfactants prime function is to modify the water's surface tension aiding enhanced gas /liquor equilibrium kinetics).

It is possible that surfactants will improve the heat transfer of crystals as they melt against a solid because of the improved wettability of the solid surface. This changes the heat path from solid point contact to a static film thus giving a greater heat transfer area.

The gas heat transfer coefficient is dependent on composition properties and any effect of the surfactant will be well within the accuracies of normal empirical correlations for saturated gas systems, predicted by the various software packages.

System heat transfer is specific to the pilot plant configuration. The trial observed that external heat transfer to the system's piping and fluids saturates any microscopic losses from the piping and fluids. This means control of the system temperature with varying ambient temperatures is key to a successful plant scale up.

7.8 - Pressure Drop

The pilot plant flash chamber injection nozzle controls the system pressure. The tubing and flow rates were selected to allow experimental production of high-pressure hydrates.

When operated for production of low-pressure hydrates the pilot plant can initiate hydrate formation in elbows and valves. These small hydrates can agglomerate and result in complete system blockage. This unstable operation results in interrupted experimental trials.

The design of the system needs to ensure that pipework avoids sudden contractions, system restrictions and reduced ported valves, which will result in high pressure losses. The design must ensure that the pressure loss is limited to the injection nozzle.

7.9 - Flow Regimes and Flow Rates

The premise is for the pilot plant to inject gas and water at constant rates into the reaction chamber. This pilot plant was originally constructed for the experimental testing of high-pressure hydrates.

The pilot plant equipment has defined limitations that have set the envelope that can be tested. Flow rates are shown on the test data presented.

It has been demonstrated that gas saturation (alone) has very little effect on the hydrate formation and hydrate quality.

7.10 - Data Requiring Further Evaluation

- Control variable ranges
- Temperature changes

The following items outline issues with the hydrate pilot plant operation.

The plant has been operated under standard atmospheric conditions. Experimentation at these changing ambient conditions highlighted technical concerns that could not be solved with the current pilot plant. However provisions were made for the actual control parameters and the results of each set listed in the appendix. The following is a dialogue on each item.

7.10.1 Ambient Temperature

Trials of the pilot plant identified that temperature has a significant influence on the ability to operate and control the plant. The production trials experienced ambient temperature variations from 4 degrees centigrade through to 40 degrees centigrade.

The pilot plant recognized that the high summer temperatures would influence the plant's operation so a cooling tank was incorporated into the design (refer to the P&ID). Winter ambient conditions required this tank to be converted to a heating tank with the aim of mitigating hydrate formation in the tubular reactor and process filters.

The pilot plant did not recognize that the ambient temperature would have such a large influence on the plant's operation so no provision was made to provide constant temperature control for the following:

- Liquor temperature
- Mixing chamber
- Tubular reactor

As the ambient temperature varied the project observed variations in the hydrate quality produced. The project could not however repeat these conditions as the

change in ambient temperature affected most of the process variables and it was not possible to isolate which of these was the controlling variable.

During the coldest ambient temperatures, even with very low inlet pressures of 1200 psig (inside the phase envelope two phase curve), hydrates formed in the reaction chamber and pilot plant piping. With low ambient temperatures hydrate blockages could be experienced throughout the completed pilot plant.

7.10.2 Flash Chamber Vessel Temperature Control

The pilot plant refrigeration plant could not maintain the flash chamber temperature constant for the durations required for the trial period 60 minutes at continuous operating conditions where heat is continuously added to the vessel and cool is continuously removed by gas circulation. The flash chamber temperature followed a consistent pattern for all runs. The temperature of the vessel was circa minus 10 degrees at commencement of the run.

Temperature in the vessel decreased to nominally minus 20 degrees as the Joule Thompson cooling occurred with the introduction of high-pressure gas. The temperature warmed up in the vessel as the pressure drop across the nozzle decreased and the gas became water saturated.

Additionally other sources of heat that effected flash chamber temperature were heat associated with hydrate formation, free water carryover and nozzle heater radiation. Figure 20.

7.10.3 Pressure Control

The flash chamber injection nozzle controls the gas flow-rate and hence the system inlet pressure of the pilot plant. The nozzle size for the various experimental runs was fixed at 0.35mm (the smallest nozzle size possible to drill at Curtin University). This nozzle orifice could not maintain a constant inlet pressure in the system. Experimental run trial lengths were set at nominally 30 minutes to ensure sufficient sample for measurement purposes was collected in the flash chamber collection vessel. Figure 21.

An external engineering company was commissioned to drill smaller nozzle (nozzle sizes of 0.25mm and 0.30mm) orifices to improve the length of the periods at which the compressor discharge pressure remained constant. The 0.25mm ID Nozzle was operational and it was possible to maintain the upstream tubing pressure within 345 kPa. Three sets of data obtained to date showed very promising results in terms of consistency with hydrate formation volume factor (HFVF) (between 90-150).

7.10.4 Conversion efficiency

Experimentation found that the conversion efficiency on the pilot plant is in the order of 5 to 10% for hydrates produced at 700 kPa (100 psig). This is crucial in determining the long-term economics of the hydrate plant.

During experimentation all excess gas from the flash chamber was vented as the pilot plant recycling system was designed for use with the high-pressure hydrate test chamber. Additionally the current configuration of the test rig did not facilitate recycling this gas to the gas compressor. A new compressor was used for this purpose for this purpose.

Conversion efficiency is a key design issue for the demonstration plant to address.

7.10.5 Compressor Flow Rate

The pilot plant reciprocating gas compressor had 3 stages. The compressor compressed gas from nominally 50 pa to 15000 kPa. The compressor had an air-cooled fin system to remove heat of compression.

Flow curves were produced by experimental measurement for the compressor and are included in the attachments. A pressure reservoir was included in the system to allow improved pressure regulation. This extend the period of operation at which the pilot plant could operate at a constant pressure.

Alternative means of increasing the gas flow were not practical as it would have required a larger compressor, or required an additional compressor to recycle gas. Both options were not implemented, as it would require significant modifications to the existing pilot plant.

Secondary technical limitations that eliminated the use of a larger compressor were: Limited gas quantity through the 2” supply line. Limited ability to vent gas due to gas dispersion and the proximity of vents to the International School HVAC intakes.

7.10.6 Pump Flow rate

The pilot plant water injection pump is a reciprocating chemical injection pump. The pump flow rate is controlled on stroke length. Experimental trials have water injection rates in the order of 5 to 15 ml/minute in the pilot plant configuration.

Trial runs adjusted the liquor flow rates to provide fixed gas/liquor volumes at the various operating pressures.

Experimentation showed that the water injection pump is operating at the edge of its operational envelope. Flow rates were adjusted by varying the pump stroke length.

Trials identified the pump could not be adjusted below the 3.0% setting for stroke length.

7.10.7 Residence Time

Residence of the gas in contact with the water and additive is not critical to the quality of hydrates formed. However the hydrate residence time during and after formation has proven to be critical, which is also known as hydrate equilibrium time. Trials were performed on the pilot plant using different gas liquid contact systems. The trials considered:

Injection of a fixed volume (50ml) of liquid into the system and saturate for nominally 12 hours. Injection of a fixed volume (400ml) of liquid into the system and injection of gas continuously (limited residence time).

Injection of gas and liquid at fixed rates based on hydrate volume formation factors.

The method adopted for the majority of the tests involved injecting liquor and gas at fixed flowrates for the duration of the trial. Liquid volumes injected were limited to less than the total system volume of 800ml to avoid free liquid injection into the vessel.

Laboratory trials were conducted to determine the minimum gas-liquid contact time required. The trial recorded the time for the gas and liquid in the sample bomb to come to a new equilibrium pressure after starting with a fixed gas pressure and a fixed volume of TSA additive in a gas sample bomb. The trials agitated the gas and TSA solution recording the pressure at 5 minute intervals until no change in pressure was recorded for at least a 15 minute duration.

The trials were not exhaustive but provided an indication of the time required for the gas and liquid to come to equilibrium. These trials did not indicate whether the gas saturation with water or the water saturation with gas was the variable changing the pressure drop.

Further trials were needed to allow measurements to determine the kinetics and if full saturation was required to form high energy-density hydrates. The trials did indicate that the pressure dropped increased for increasing volume and the time to reach constant pressure remained constant at nominally 10 minutes of contact time.

7.10.8 Nozzle Temperature

Joule Thompson expansion cools the gas as it passes through the nozzle. Without nozzle heating the orifice blocks with ice and hydrate. To alleviate nozzle blockage a water jacket heating system maintains the nozzle at a constant temperature. Heated ethylene glycol solution was circulated through a water jacket located adjacent to the nozzle.

Experimental trials using heating temperatures between 40 and 55 degrees centigrade have been used. Trials found the lowest temperature at which the nozzle could be operated was 40 degrees centigrade.

Generally higher temperatures were avoided as these imposed a large heat load on the vessel refrigeration and impacted the Joule Thompson cooling which adversely affected the quality of hydrate produced.

7.11 - Gas Composition

Gas used in the production trials was city supply gas from the AlintaGas system. One test was carried out in August 2000 and the second performed in February 2001, in which the composition changed quite significantly during that period – the variability of gas composition is expected to have an effect on hydrate production. Below is the gas composition measure in February 2001.

AlintaGas composition measured on the 02-02-01.

Component	Gas mol %
CO2	2.1899
N2	2.5998
C1	84.2245
C2	6.7896
C3	3.1198
i-C4	0.41
n-C4	0.59
i-C5	0.04
n-C5	0.02
C6	0.01
H2O	0.0064

Table 43 AlintaGas Composition measured on 2 February 2001

7.12 - Water and Additive

The TSA additive was diluted using the WA Water Corporation University supply tap water, and the mixture (1120ppm) produced a PH level of 2.4. No regular monitoring of the tap water was performed to assess the effect of water quality on the hydrate production.

A spot test of pH test revealed the tap water at Curtin University has a pH of 6.7. This number indicates that carbon dioxide is dissolved in the tap water.

7.13 - Hydrate Appearance

Hydrates produced by the methods described above can have one of the following appearances:

- Fluffy like powder fine snow/ icing sugar crystals (most common for high quality hydrate >70).
- Sticky (most common for hydrate quality < 50) and very unstable.
- Hard glazed/ crystalline usually for very poor quality hydrate.

Characterization of hydrate quality could be correlated to appearance. Two observations can be made.

- The hard crystalline hydrate was predominantly iced and was not good quality. The samples did not burn.
- The soft fluffy hydrate almost always burned when ignited. This was usually a sign of good hydrate quality. The fluffy hydrates typically have gas formation factors in the order of (50 –250). An explanation for this is fluffy hydrates have a large surface area from which to release trapped gas.

7.14 - System Instrumentation

The hydrate pilot plant process is essentially a mechanical process to provide contacting of gas and liquor to produce the building blocks to make Type I hydrates. As such, the pilot plant has been provided with instrumentation to measure the basic parameters of pressure, temperature and flow.

Gas liquid kinetics is the key to hydrates' production. It was observed that ambient temperature impacts upon hydrate quality. The variations in ambient temperature can lead to variations in all process variables. However the current pilot plant has no means of isolating the effect of these variables on gas liquid kinetics. Consideration should be given to what is the most appropriate means of determining plant kinetics during the run, and what effect this has on plant operation rather than observing a poor result at the end

of the run. One obvious parameter that could be measured is the gas dewpoint into and out of the flash chamber.

7.15 - Material Corrosion Tests

The data requested on the corrosive effects of the liquor is not available.

The initial inspection by a corrosion chemist revealed that the corrosion inside the high-pressure vessel is mostly due to the oxygen content in the water phase. However the following test will be required in the future.

- Measuring the effect of TSA on corrosion at Ambient, 0 and –15C
- Measuring the effect of TSA concentration on corrosion

It may be stated that there has been no corrosion observed on the stainless tubing or pump components during modifications and routine maintenance. Additionally there has been no obvious effect on the plastics and polymers used in the system. The bulk TSA liquor is stored in a PVC plastic storage container. The pilot plant liquor is stored in a Perspex storage container, the food grade plastic tubing has no signs of deterioration and the PTFE tape and valve seals have not shown any signs of degradation.

Some corrosion on the flash chamber walls was observed however this is most likely attributable to the vessel materials of construction and the batch mode of operation. The flash chamber operation results in atmospheric water freezing on the walls of the vessel. This water then melts when the flash chamber warms up on a unit shutdown during the weekend and periodic vessel cleaning times.

Some of the TSA salts have been observed as a hard white precipitate in the storage tank, pump and nozzles at various times. These precipitates have resulted in pump malfunction and injection nozzle blockages.

The pH of the diluted TSA solution was tested. The pH was recorded as 2.17 for fresh and aged liquor indicating that there is a high hydrogen ion concentration.

In order to verify materials, compatibility testing should to be performed.

7.16 - Foaming and Defoaming Agents

One of the main constraints in hydrate production experienced while using the agent SLS was the formation of foam in the process piping and in the production vessel.

Foam formation during hydrate production caused two main problems:

- High-pressure drop within the module tubing.
- Serious problems with the gas compressor operation during recycling of the gas and attack and damage of the compressor rings and liners.

As a result of these difficulties and given agent TS testing produced better results in hydrate production without the problems associated with foaming, the use of agent SLS was discontinued.

Therefore, an investigation into defoaming agents and testing associated with defoaming was not carried out.

The recommended TSA surfactant required to achieve good quality hydrate does not include SLS. Therefore it is not anticipated that foaming will be a design problem at the next stage of plant design.

7.17 - Conclusion

It was discovered during this work that by using hydrate promoters, we could reduce the amount of water occlusion in hydrate and thus produce high quality hydrate for gas storage. The first type of promoter was used in a very low dosage of kinetic inhibitor and dissolved in water, such as Iso-popyl Alcohol, Methanol and Salt, but this was enough to alter the morphology of hydrate growth. The other was a chemical that reduced the interface tension between the guest (gas) and host-species (water) which included surfactants.

The research to date has identified a number of additives that can be used towards enhancing the formation of gas hydrates such as TSA and SLS. Each additive establishes a variation in the “quality” of the NGH, initially the primary focus has been on increasing the energy density of the resultant hydrate. The target has been to produce a hydrate with a comparable energy density to that of Compressed Natural Gas (CNG) or gas content >200 v/v.

The work so far has indicated that this goal is achievable. However, it has become apparent that other factors will influence the feasibility of hydrate production for our specific commercialization applications. As a result of our overall evaluation of the current production method, the following outcomes have been identified:

One of the most important outcomes of the low-pressure (689 kPa) hydrate production carried out in the past three months has been the production efficiency. The gas conversion efficiency to hydrate has been in order of 7-10 %, regardless of the hydrate quality or vessel temperature. This raises a serious question on the feasibility of hydrate production at atmospheric pressure using the saturated gas injection method employed to date.

The formation rate of natural gas hydrate is governed by multiple factors including the pressure, temperature and gas composition, also called PVT-effects. The rate of hydrate formation is also determined by the combined effects of heat, mass and momentum transport. Cooling is required to remove the hydrate heat of formation. Mass transport is required to dissolve the natural gas in liquid water or vice versa, and to bring the dissolved gas molecules in contact with a growing hydrate crystal which requires some residence time.

It is also well known that crystallization is more or less a random phenomenon and, in particular, the nucleation step is merely a stochastic one. So aiming at increasing hydrate formation rate at such unfavourable thermodynamically changing conditions is not an easy task. It is apparent from the results and discussion above that multiple parameters acted on the produced hydrate quality. However the most important parameters have been hydrate nucleation and induction time and hydrate formation rate. In conclusion, the proposed atmospheric method for hydrate production can not provide the sufficient induction-time for hydrate nucleation process, growth and agglomeration of hydrate particles; or what is known as hydrate equilibrium-time, defined as stable time required for the gas molecules to inter the molecular cage structure arrangement.

7.18 - Alternative Method

Work was conducted recently on an alternative method which included the injection of the liquor into vessels which will be operating at low temperature and high pressure (11024 kPa) and -15C. The process in simple form can be described as follows:

To start, the pressure vessel is filled with gas at low temperature (-15C), water would first be mixed with the additives and additional gas may have to be used to saturate the gas to minimize the density of the liquor and optimise the flow and nucleation rate.

The nucleated water would be injected into the mainstream of cold gas. Gas hydrates and LPG would form in the vessel. Liquid LPG, now separated from the gas and mixed with hydrates, would continuously be removed from the system. Make-up gas will provide the loss of pressure and as hydrate forms the equilibrium gas will be circulated and pass through a chiller system to maintain low temperature. The hydrate slurry would then be pumped to another vessel where the hydrate stability curve can be maintained under low temperature or/and high pressure.

The preliminary results are very promising and can be summarized as follows:

- a) Hydrate formation volume factor is very consistent and higher than 160 HFVF during the initial runs.
- b) The process is much easier to run and manage.
- c) LPG is produced as a by-product.

This last point is likely to play a very important role in providing a medium for hydrate slurry short-term transportation (loading and un-loading) using an LPG pump.

7.19 - Proposed Working Plan.

A research program should be carried out to verify the initial results in terms of gas content for each additive at different pressure and temperature. These data needs to be scientifically validated and confirmed. New issues such as patents, both new and existing, are under investigation.

Bulk energy density (post hydrate-LPG separation). This work will be carried out on a daily basis at different injection flow rates as well as variable vessel temperature. The stability of the produced hydrate at high temperature and under different production/storage/transportation conditions should be investigated and documented. This work should also include finding the optimum additive for each condition and purpose. Modification of the pilot plant is required to pump the produced LPG-Hydrate slurry at high pressure. This work will only be carried after confirming the feasibility of the above steps.

Slurry stability temperature. The study of the slurry stability temperature should include developing and testing the LPG slurry concept for the hydrate transportation without affecting the produced gas or the economy of the process.

The hydrate molecular structure is a very important part of the patenting process as it may carry the vital scientific evidence of the quality of the hydrate. A new arrangement with other specialists (scientists) is currently being considered to assist in this area.

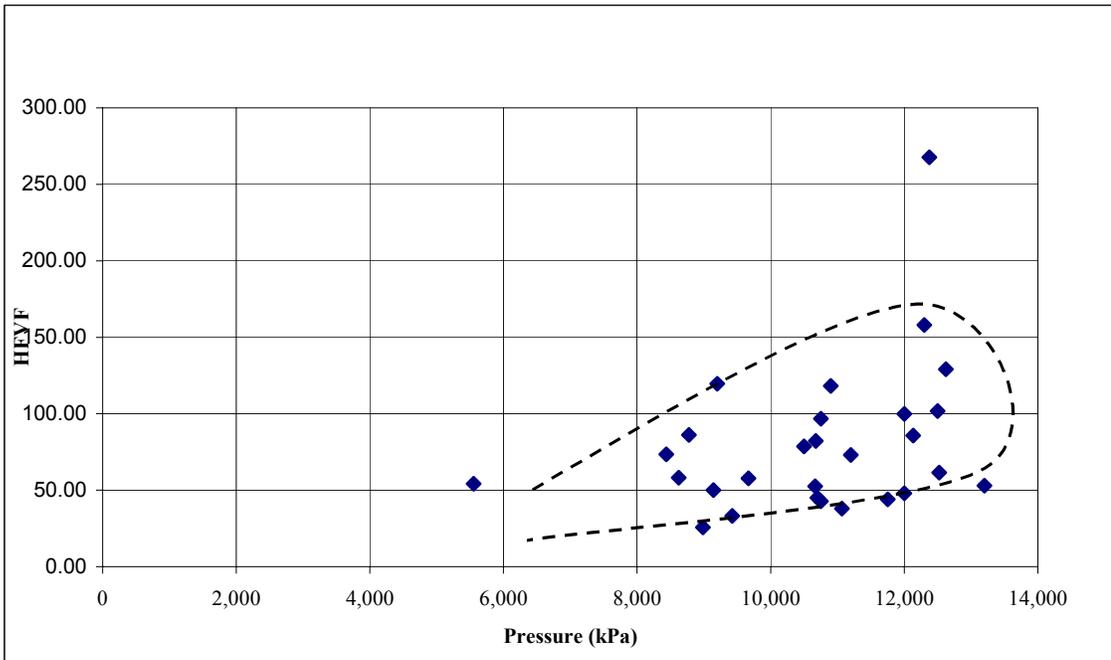


Figure 21 HFVF (V/V) vs Avg. Nozzle Pressure

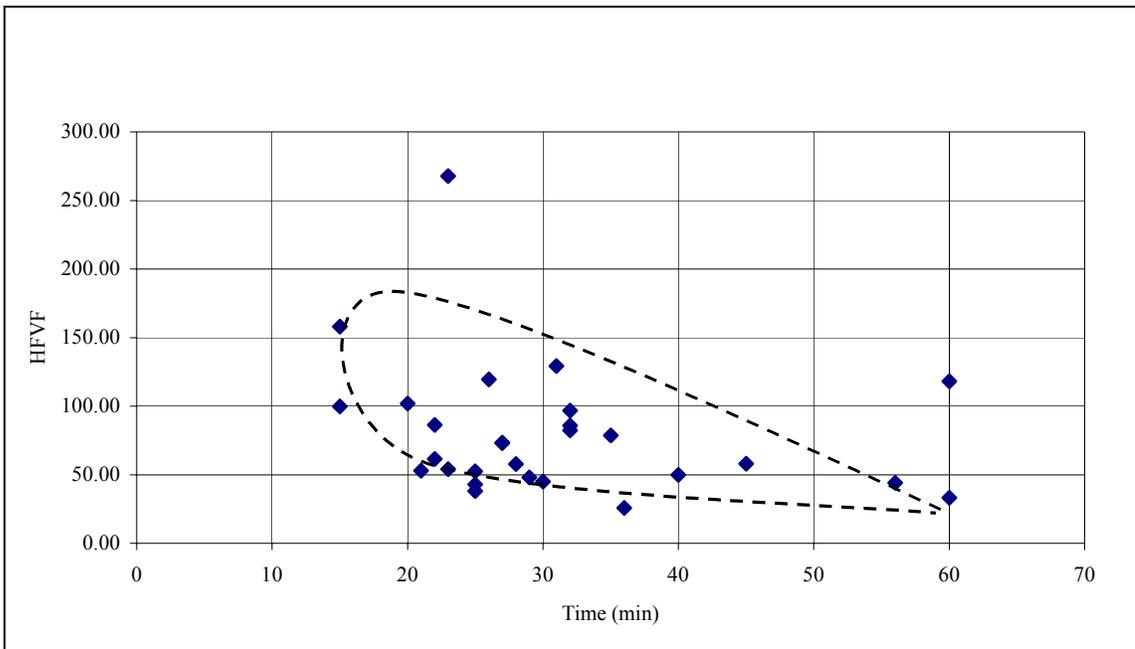


Figure 22 HFVF vs Gas-Liquor Injection Time

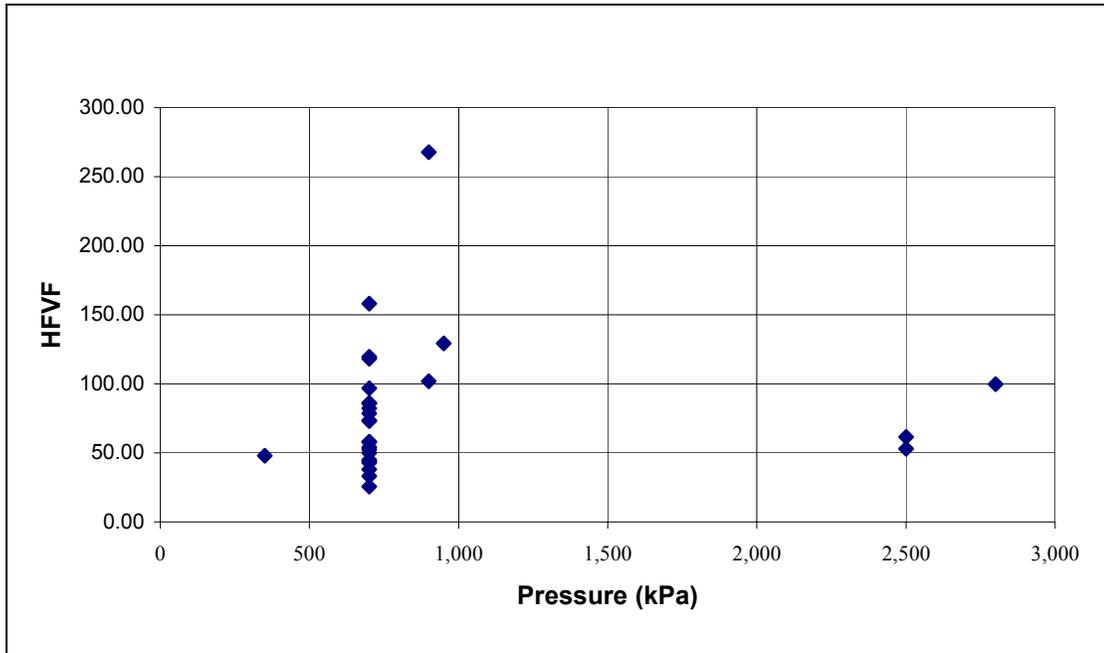


Figure 23 HFVF (V/V) vs Vessel Pressure

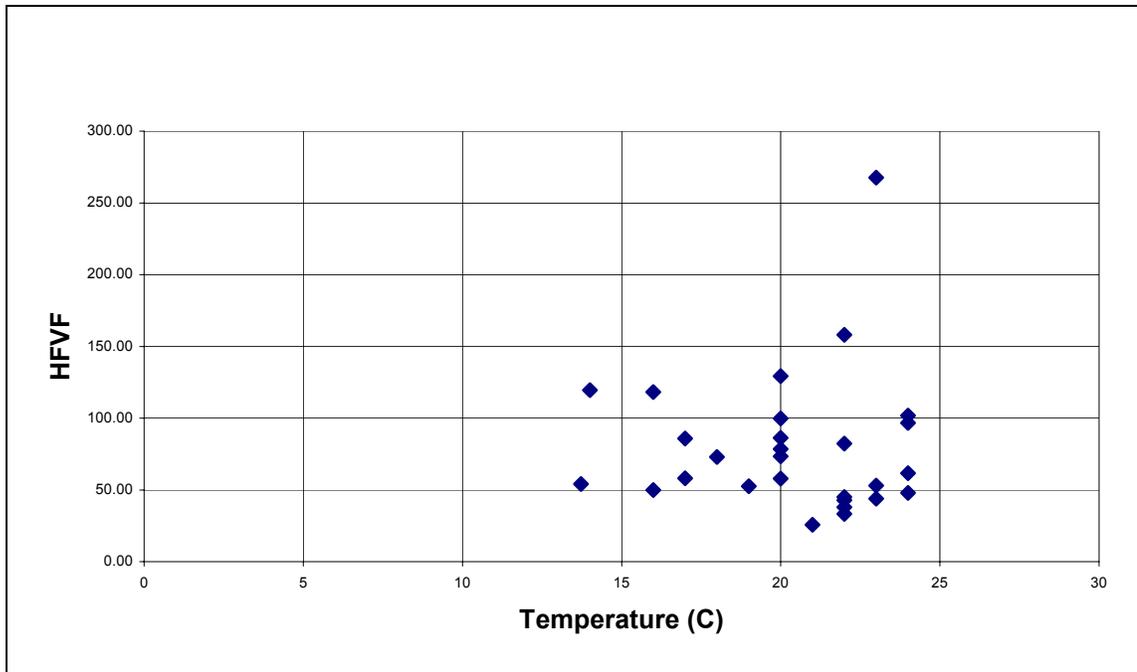


Figure 24 HFVF (v/v) vs Ambient Temperature

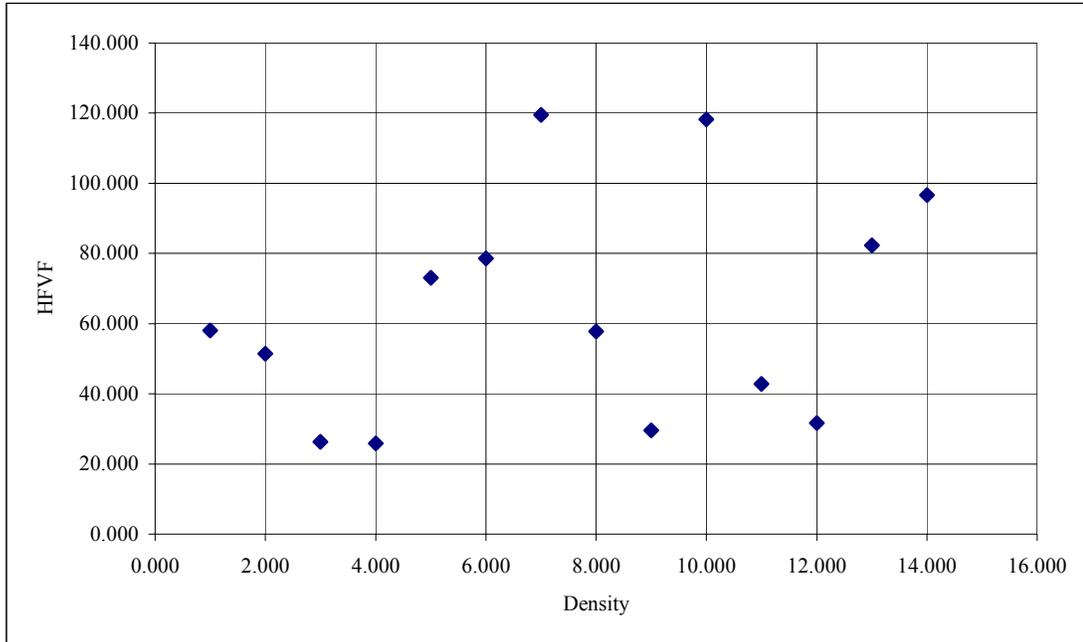


Figure 25 HFVF (L) vs UnCompacted Bulk Density

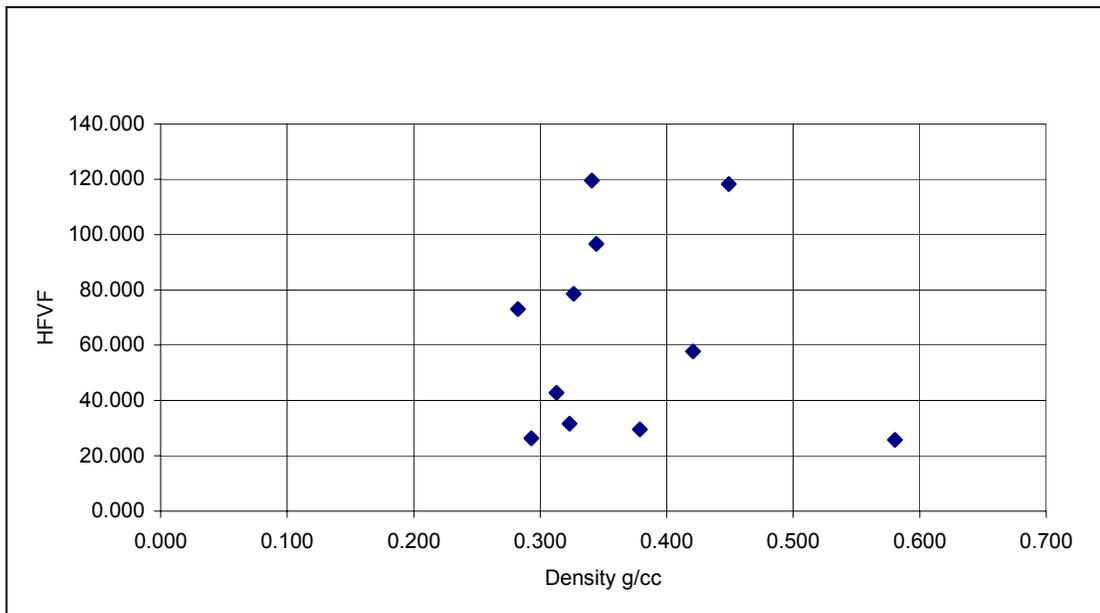


Figure 26 HFVF (L) vs Compacted Bulk Density

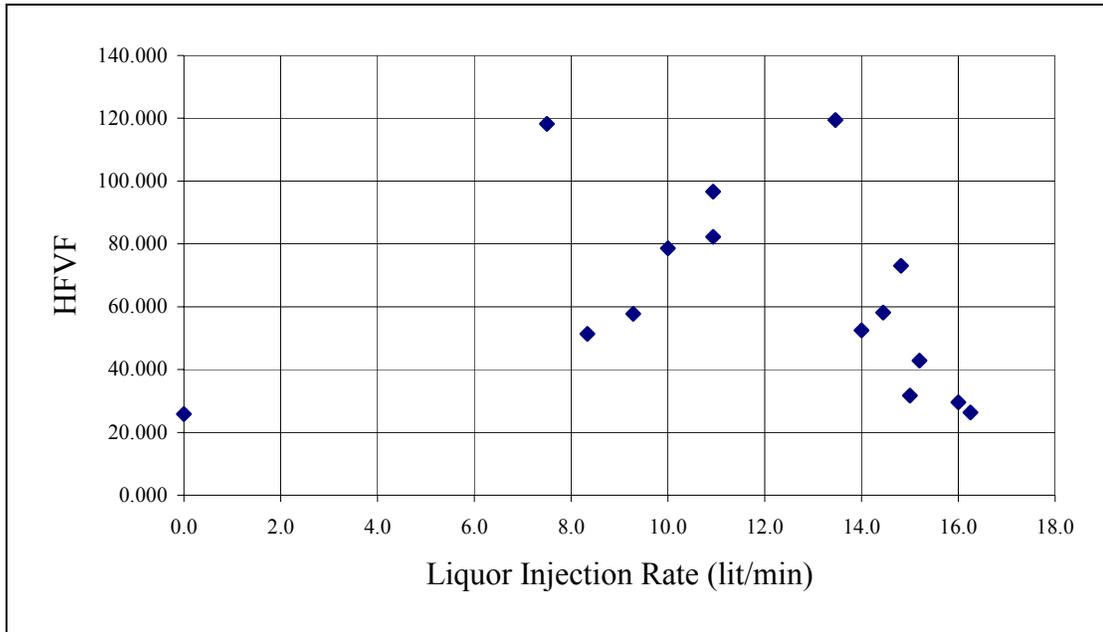


Figure 27 HFVF(L) vs Liquor Injection Rate

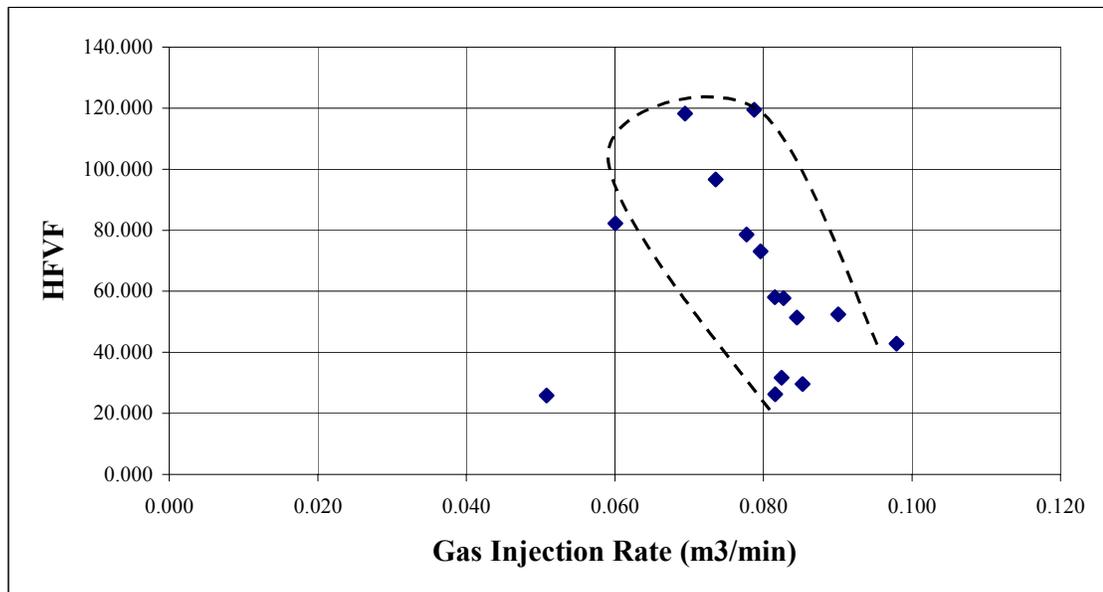


Figure 28 HFVF vs Gas Injection Rate

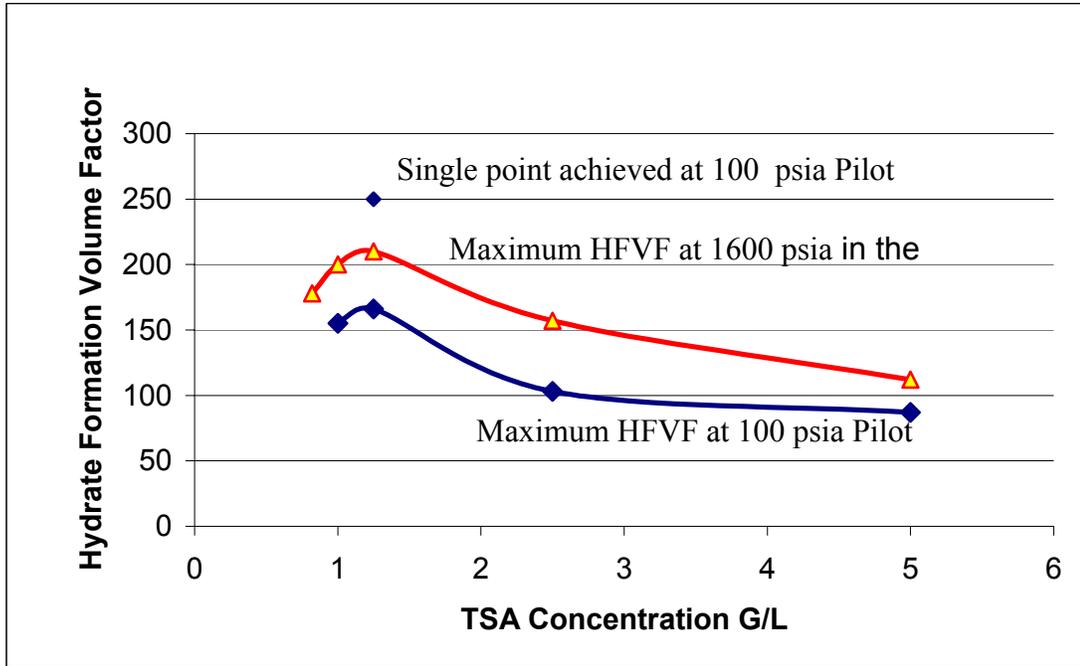


Figure 29 HFVF as a Function of TSA Concentration

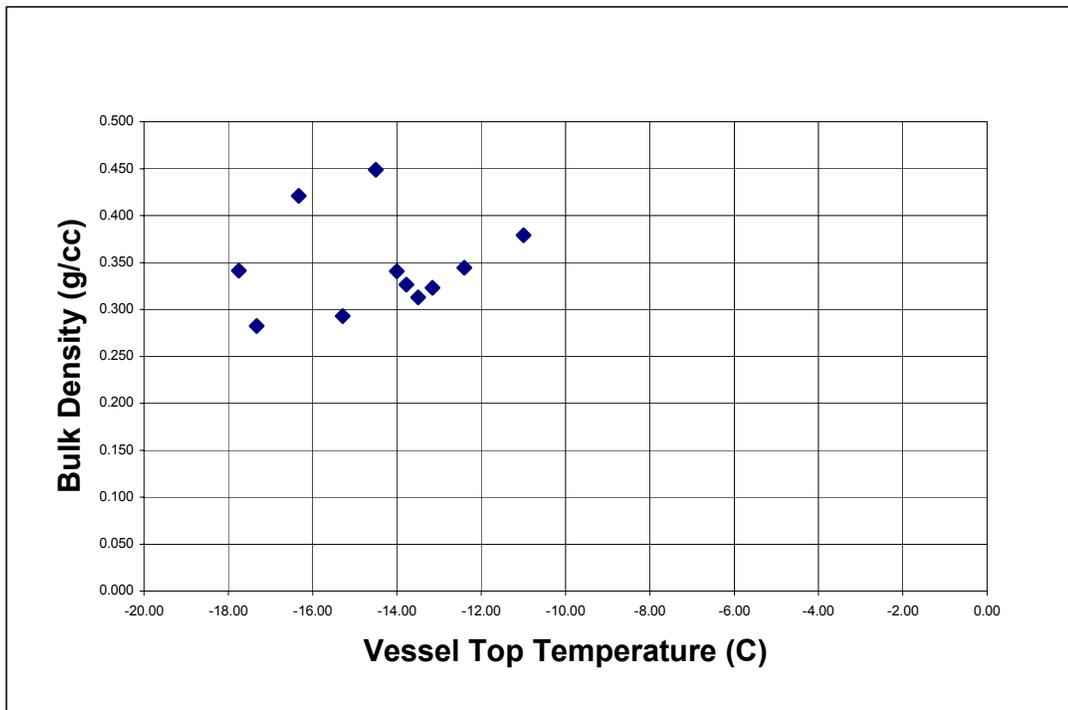


Figure 30 Bulk Density (Compacted) vs Vessel Top Temperature

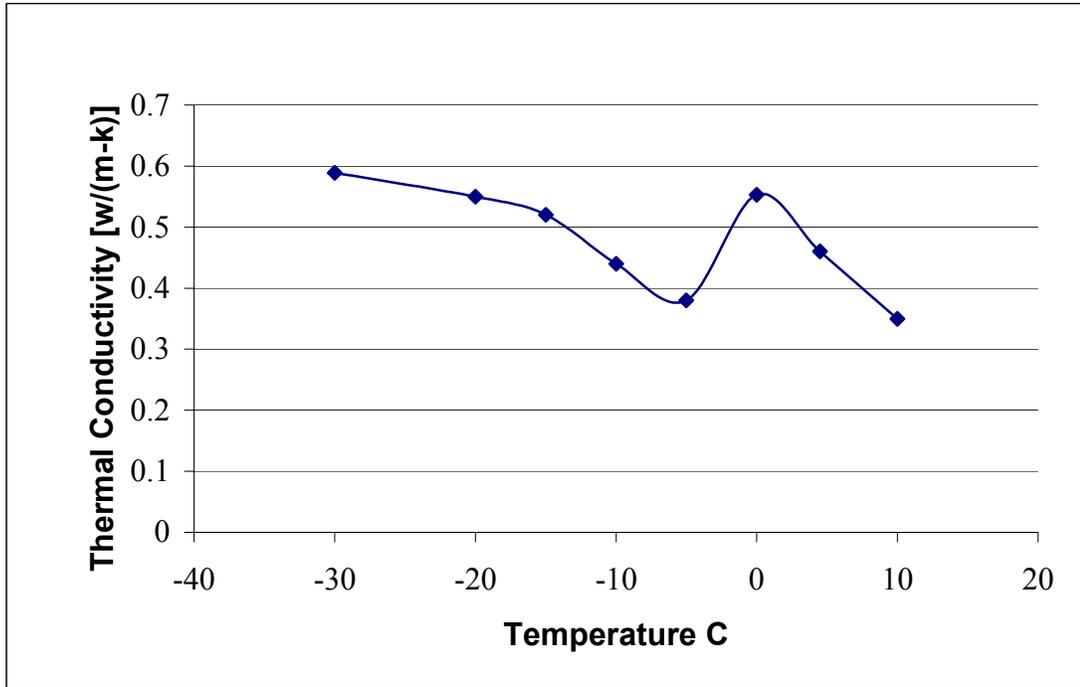


Figure 31 Calculated Hydrate Thermal Conductivity as a Function of Pressure

8 - PILOT PLANT SAFETY AND OPERATING PROCEDURE

8.1 - Introduction

Curtin University (Petroleum Engineering Department) and Woodside Energy are currently researching the commercial viability of using hydrate matrices as a means of energy storage and transportation. This research involves the synthetic production of hydrate using a pilot plant which has been designed and fabricated by the Curtin research team. The plant was originally designed to produce hydrate under high pressure but has been modified to allow production at lower pressures. Additional instrumentation has also been provided to better assess the energy transfers that occur during hydrate production.

This document outlines those procedures required to safely operate the plant and also cover general safety issues associated with all aspects of hydrate production.

It should be noted that whilst safe working practices are the major objectives of the research team, the plant described in this document is essentially research apparatus and should be considered in this context.

8.2 - Plant Identification And Labelling

The pilot plant has been fully labeled. All equipment (eg Meters, filters pumps valves etc) were given a unique identifiable label which is referenced in the P&ID. A plant identification schedule is shown in Appendix A that describes the equipment in further detail. The P&ID is shown in Appendix B.

The pipe-work is also labeled and follows the colour codes shown in AS 1345- 1995. In accordance with this standard the water pipe-work is identified as green, and gas pipework is identified as yellow. The gas/water direction of travel is also shown on pipes

in the form of coloured arrows. The procedures described below will incorporate use of the identification system above.

8.3 - Safety

8.3.1 Personal Safety

Personal safety is considered the highest priority when operating or maintaining the pilot plant. Whilst not a construction site, the following Personal Protective Equipment is mandatory when maintaining or operating the plant.

- Eye wash facilities are located at the laboratory and inside the shed
- Personal protective Equipment PPE
- Eye Protection
- Safety boots
- Cotton based clothing
- Protective gloves (where appropriate)
- Facemask and full visor (where appropriate)
- Chemical suit (where appropriate)

The following practices are prohibited within shed under all operating conditions.

- i) Smoking
- ii) Drinking alcohol
- iii) Naked flames within building and 1 metre from building
- iv) Hot work (eg welding) unless accompanied by a permit/procedure
- v) Activation and use of mobile phones (except in a designated area)

Any deviations from the procedures in this document require completion and authorisation of a change procedure prior to implementation in order to ensure that unsafe operating procedures are not in-advertently implemented.

8.3.2 Visitors

Visitors are allowed by invitation only. The request can only be approved by Alan Jackson or Robert Amin. Visitors shall be required to comply with the PPE and

safety requirements above. Photographs of the plant and lab experiments are only permissible following approval from Robert Amin. Where the visitors are invited to witness the operation of the hydrate plant, at least 48 hours notice is required by the research team to prepare the equipment. Before witnessing the operation of the plant visitor shall be provided with a verbal brief covering the following:

- Description of the plant
- Hazards associated with the plant
- PPE requirements
- Emergency alarm warnings
- Emergency evacuation procedure

8.3.3 Fire Fighting Equipment

The following fire fighting equipment shall be provided for the equipment shed and the engineering labs

- Portable CO2 fire extinguisher
- Portable Dry powder fire extinguisher

8.3.4 Fire Alarm System

The shed is not equipped with its own fire alarm system. An automatic detection system is not considered necessary, as plant operation will only occur when trained personnel are in the shed. Furthermore, gas detectors are provided above the pilot plant which raise an audible alarm after sensing methane gas.

The engineering labs are provided with smoke detectors connected to the building complex fire panel.

8.4 - Hazardous Area Classification

In accordance with AS 2430.1 and AS 2430 .3 the classification of the shed is considered non hazardous. This is mainly due to the small inventory of gas used in the process. It is therefore unnecessary to provide hazardous rated instrumentation or the relocation of electrical equipment outside hazardous zones. Notwithstanding this

existing compliance the pilot plant has been designed with natural draft roof ventilation and power supplies located in a separate cabinet adjacent to the plant. Pressure and temperature transmitters, where cost and lead-time have permitted, is rated for operation in hazard zones. All other instrumentation is panel mounted in the shed but outside the hazardous zones envelopes associated with the plant. A more detailed assessment of the hazards associated with the plant and compliance with the Australian Standards is outlined in Appendix C.

8.5 - Plant description

The plant is designed to produce synthetic natural gas hydrate at a range of pressures by mixing natural gas and liquor at high pressure and forcing the mixture through a nozzle into a reaction chamber. The liquor consists of small amount of chemical additive and water. The ratios of which may be changed. The process of discharging this mixture through the nozzle at the top of the reaction vessel causes a high pressure-drop in the mixture that assists in cooling the mixture. Hydrate is formed as a result of this temperature drop. The hydrate generally has the consistency of compacted snow/ice and forms a matrix that traps the natural gas in the hydrate. Significant quantities of gas can be trapped in the hydrate which remains stable at atmospheric pressure and temperatures of between - 5 °C and – 20 °C. A schematic layout of the pilot plant and it's associated services is shown in Appendix E.

The purpose of the plant was to research the following parameters

- a) Produce hydrates with high hydrate formation volume factors (HFVF) ie hydrate with high volume of natural gas trapped within their matrix.
- b) Experiment with a range of chemical additives and concentrations to maximise the HFVF.
- c) Produce hydrates with high HFVF at a range of vessel pressures from 15,000 kPa to atmospheric pressure.
- d) Investigate a range of engineering issues associated with hydrate production and handling (eg nozzle ice formation due to high pressure drop etc).

The pilot plant can be categorised into the following subsystems.

- High Pressure gas supply system
- High Pressure Liquor supply system
- Hydrate production Vessel and refrigeration system
- Power supply system
- Instrumentation system
- Venting system

These are described in more detail below:

i) High Pressure Gas Supply System

While the pilot plant was originally designed to produce hydrates at high vessel pressures (2170 psi). It has been modified to produce them also at low pressures. Consequently vessel (V-003) has been modified to produce LP hydrate and Vessel (V-002) produced hydrates in the high-pressure range.

The gas supplied to the pilot plant is quality pipeline gas. This is a low-pressure gas supply of around 0.25 psig. It is filtered and metered by MT-01 before being fed into the gas compressor (C1). The compressor is a three stage reciprocating compressor and is cooled by an ambient heat exchanger system. The compressor has an inter stage and final stage pressure relief valve built into the unit and is driven by a three phase 415 volt motor. A pressure indicator (PI-02) is provided on the discharge side of the compressor together with a pressure relief valve (PSVC-1). The discharge from the compressor is fed into a four-way branch.

The first branch is fed to a high-pressure cylinder (V-004). This is designed as a buffer vessel to eliminate the pressure pulsing behavior of the compressor and provide a buffer store.

Two branch connections lead to two hydrate reaction vessels (V-003 and V-002). A proportion of the gas may be re-circulated from each reaction vessel through a non-return valve, one per vessel, (CHS4-1) and (CHS4-2) and returned to pressure

vessel (V-001). Two discharges exist on this vessel. The first is directed to the inlet of the gas compressor via HP and LP regulation valves (HPR-1) and (LPR-2), a filter (F-001) and a meter (MT-02). The second is directed to the vent via valve 4P4T. This valve is designed to drain any liquid formed in the vessel. During low-pressure hydrate production, vessel (V-003) pressure is controlled using valve (APDGF4-1). For high-pressure hydrate production the vessel (V-002) pressure is controlled using valve (APDGF4-2). This is the conventional operating regime for both HP and LP hydrate production. Under some circumstances it may be necessary to vent the gas to the atmosphere via gas meter MT-03 and through pressure gas regulators (LPR-3) or (LPR - 4). Each valve has a different pressure regulation range. One ranges from 0 - 50 psi (345 kPa) the other from 0-500 psi (3450 kPa). This allows accurate pressure regulation and metering of the vent gas across the whole low-pressure range. The metered gas then passes into the venting system for discharge. Once set, the above automatic regulating valves, together with the manually set regulating valves APDGF4-1 and APDGF4-2, control the vessel pressure during hydrate formation. The final branch connection is fed to the nozzles located at the top of the vessel via a mixing chamber where pressurised liquor is fed in to the gas line.

ii) High pressure Liquor Supply System

In order to produce hydrates at any pressure liquor needs to be added to the gas. The liquor consists of a mixture of water and a chemical additive to assist in the formation of hydrate. The liquor is premixed and then placed into the tank T-002. The liquor is passed through a mixing chamber via the filter (F-002) and a water meter (MT-04). The liquor is pressurized using a multistage water pump (P-002). A re-circulation line and pressure relief valve is provided to allow for water circulation when the pump is operating on a closed discharge to protect the pump bearings.

Additional re-circulation is provided via a needle valve (IVS6-02) to assist with pump flow optimisation. The non-return valve (CHS6 -1) is installed in the line to prevent liquor/gas back flow in to the gas line.

It should be emphasized that the liquor is liquid until fed into the mixing chamber.

Mixing of liquor with gas at pressures from 9887 kPa to 14950 kPa at ambient temperature causes the mixture to form a two-phase fluid. The mix of liquor and gas is forced through a pressure regulation valve (HPR-2) and then through a nozzle into each vessel. The feed lines to each nozzle may be isolated by isolation valves (18RF8-1) and (18 RF8-2).

iii) Hydrate Production Vessel and Refrigeration System

There are two hydrate production vessels (V-002 and V-003) each consisting of a fabricated steel vessel with instrumentation, process feed, vent and drain connections. Each vessel has a quick release bottom closure which allows access to the hydrate formed within the vessel. Connected to the top of the vessel is a nozzle with an orifice sized to suit the specific application. The nozzle is heated by a hot water system to prevent the nozzle freezing and blocking during hydrate production. Each vessel is cooled using refrigeration coils attached to and surrounding the vessel. The coils around both vessels are insulated with a jacket. The vessels are designed for a maximum pressure of 14950 kPa.

iv) Power supply system

The power supply to the plant consists of a 240 volt three phase supply board which has both three phase 415 V and single-phase 240 V outlets. The following outlets are provided from the main switchboard. A schematic drawing of the power supply system is shown in Appendix D.

Refrigeration package	Single phase, 240 V
Gas compressor motor (M-001)	Three phase, 415 V
Liquor Pump (P-002)	Single phase, 240 V
Water heater and pump	Single phase, 240 V
Emergency shut down system	Single Phase, 240 V
Instrumentation supply	Single Phase, 240 V
Lighting/ miscellaneous power supplies	Single phase, 240 V

Before maintaining or servicing any electrical equipment the power supply to the equipment should be isolated at the switch-board.

v) Instrumentation System

The instrumentation on the pilot plant is shown in P&ID NGH-G-001-01. The only control loop in the plant is the level indicator in tank T-002 that controls the liquor pump initiation. This is to ensure that the pump never runs dry.

All other instrumentation is for indication only and consists mainly of pressure and temperature indicators mounted around the plant. Four flow meters have also been installed on the plant. A Rosemount magnetic flow meter is installed in the vertical leg of the liquor supply line and measures flow induced by a change in the magnetic field produced by the instrument.

Gas meters are provided in the gas vent line to the compressor and gas circulation line from vessel (V-001). The gas meters are provided with sensors which compensate for fluctuations in the temperature and pressure of the gas. Each meter has a flow computer located on the instrument panel adjacent to the pilot plant.

Additional temperature sensors have been provided for vessel (V-003) only. This consists of four bare wire thermo-couples attached to the following:

- Gas vent line
- Liquor/gas supply line
- Nozzle heating water inlet line

Nozzle heating water outlet line

Two magnetic temperature thermo couples are also provided which can be moved manually to check the vessel surface temperature along its length. A thermal probe is connected at the bottom of the vessel to measure the temperature of the hydrate formed.

The above instrumentation is connected to a rotary switch and digital temperature indicator both mounted on the instrument panel. The temperature of each thermocouple can be obtained by turning the rotary switch to the appropriate channel. A key on the panel identifies each thermo-couple and its related channel.

vi) Venting System

Three venting systems are provided. The first is a high pressure safety venting system which connects vents from the HP pressure relief valves and bursting discs to an atmospheric vent. There is also a low pressure safety vent system connecting the low pressure safety relief valves and bursting disc to an atmospheric vent. The vent line is a metered HP/LP vent line which is also vented to the atmosphere.

Venting of the gases should be minimised and two HP gas cylinders, V-005 and V-006 are provided to minimise the venting of natural gas.

Bursting discs have been provided on all the LP and HP gas vent lines on the plant where there is a risk of the pressure relief valves icing up during normal operation.

8.6 - Handling of Hydrate/Liquor

8.6.1 General Liquor Handling

Liquor consists of a mixture of Water (95%) and various chemical compounds (5%), although this ratio can vary. Some chemical additives may be toxic. When handling the chemical additives reference should always be made to the material safety data sheet (MSDS). This provides guidance on the level of PPE required when handling the chemical. Compliance with the MSDS is mandatory. When testing a series of liquors with different chemical additives, the level of PPE protection shall be determined by the MSDS requirements of the most toxic chemical used. Before any liquor is used in the pilot plant, the mixture shall be tested in the laboratory. This is required to assess the liquor foaming properties and ensure that plant safety is not compromised.

8.6.2 Removal of Hydrate from Pilot Plant

The hydrate produced by the plant normally consolidates at the bottom of the vessel in the form and consistency of compacted snow, although other forms are possible. The vessel bottom closure cap is made of steel and caution required as it is heavy. The closure cap should only be removed once the vessel has been completely vented and checked that there is no residual pressure inside. It is essential to refer to the venting procedures in check-lists 2 and 3 before opening the closure cap. Additional hazards during removal of the hydrate include falling ice, the presence of liquor that may be acidic and escaping gas. Full personnel protective equipment should be used when removing the hydrate. This includes safety boots, cotton overalls, safety glasses and gloves.

Hydrate removal is achieved by the following:

- i) The insulation case is first removed by releasing clips located each side of the vessel.
- ii) The mobile jack located under the vessel is jacked up to support the closure. The mobile jack is clamped to the closure cap for safety.
- iii) The central nut is then loosened and the flange separated from the vessel.
- iv) The flange is then lowered away from the vessel using the jack.
- v) The jack is withdrawn for the plant to gain access to the hydrate.
- vi) A plastic bucket is located under the vessel to catch the hydrate.

8.6.3 Storage

Samples of hydrate must be uniquely identified, placed within a plastic bag and stored at ambient pressure at - 20 °C in the freezer provided. Samples should not be left exposed at room temperature in the lab.

8.6.4 Hydrate Ignition

When exposed to room temperature hydrate will give off flammable natural gas as it decomposes and melts. No less than a face mask and gloves should be worn when igniting the hydrate. The hydrate should be ignited in a well-ventilated area such as a dish and disposed in the incinerator using the ignition tool provided.

8.6.5 Disposal

Some hydrates contain acidic compounds that are hazardous to personnel. Hydrates and any decomposed products should not be disposed in the sink. Disposal advice for chemicals is provided in the MSDS data sheet which should be followed.

8.7 - Operating Procedures

8.7.1 General

The plant procedures shown in this section provide a step-by-step approach to using the pilot plant under a range of operating conditions. The operating scenarios are summarized below:

- 1.0 Pre Start Plant Alignment and Purge
- 2.0 Plant Start up LP Hydrate Production, shut down and Hydrate removal
- 3.0 Plant Start up HP hydrate Production, shut down and Hydrate removal
- 4.0 Plant Make Safe
- 5.0 Emergency plant shut down

For each scenario a checklist has been provided for the operator to ‘tick off’ tasks when they have been completed. Each task relates to a specific operation and uses the plant identification and labeling system as a reference.

Experimental data also needs to be recorded during the hydrate production process. An example of a data recording sheet (EXSH-1) is shown in Appendix F. Reference to the completion of this sheet is outlined in the procedures.

8.8 - Training

The training of personnel on this plant should only be undertaken by personnel competent in this task. This is currently Sam Battah. No research personnel should attempt to operate this plant unless supervised by Sam Battah and until written authorisation is provided upon the successful completion of training.

Personnel planning to use this equipment unsupervised shall first undergo a formal training programme.

8.9 - Security

The pilot plant is located within the campus grounds between the Sir Charles Court Promenade and the Mechanical Engineering Building. The plant's location therefore subjects it to heavy student traffic. To ensure students do not inadvertently enter the shed, it should be locked when not in use.

9 - PILOT PLANT INSPECTION PROCEDURE

9.1 - Introduction

Curtin University (Petroleum Engineering Department) and Woodside are currently researching the commercial viability of using hydrate matrices as a means of energy storage and transportation. This research involves the synthetic production of hydrate using a pilot plant, which has been designed and fabricated by the Curtin research team. The plant was originally designed to produce hydrate under high pressure but has been modified to allow production at lower pressures. Additional instrumentation has also been provided to better assess the energy transfers that occur during hydrate production. The Plant Inspection Procedure has been prepared to ensure that the plant is operated in a safe manner. Good operating practices are encouraged in this plant to achieve this goal. Therefore, it is essential that all personnel involved in this research to be aware of these Inspection routines.

The Inspection Procedure has two main sections: Plant Isolation Procedure and Plant Inspection Schedule. During monthly and annual inspection plant isolation procedure should be followed. The Engineering Change Request Form out lines the process to document all replacements and modifications done in the plant, this record sheet should be approved prior to any change in the plant. **See Appendix E.**

9.2 - Statutory Requirements

The production vessel is classified as C according to AS 3920. A commissioning inspection was carried out according to AS/NZS 3788:1996. A first yearly internal and external inspection shall be carried out on the vessel and based on this the subsequent inspection frequency shall be determined. Further, this standard stipulates an external inspection period of 2 years and a nominal internal inspection period of 4 years. This period could be extended to 8 years with justifications based on the above standard. According to AS 3873-2001 documentation for safety management should be maintained. An inspection program has to be arranged according to AS/NZS 3788 taking into account the manufacturer's recommendations and any other requirement found

necessary for the safe and secure operation of the equipment. Incidents, damages, faults must be recorded and rectified.

9.3 - Plant Isolation Procedure

The Plant has to be isolated before any maintenance/inspection activity is carried out. It is unsafe both to the personnel and to the plant when maintenance activities are carried out without a proper isolation of the power and gas supply. Where it is necessary for inspection, maintenance or other purposes, provision shall be provided to isolate the pressure equipment from all pressure sources according to AS 3873-2001.

The aim of this procedure is to ensure that all supply lines of power and raw material are shut-off and any material left in the process is removed prior to the commencement of maintenance activities. The plant isolation procedure is very much the same as the 'Plant Make Safe' procedure, which is described in **Appendix C** of the Plant Operating Procedure Manual. Therefore the Plant Make Safe Procedure has been adapted for the Plant Isolation Procedure as well. The checklist is given in Appendix C in this Manual.

9.4 - Inspection Schedule

The inspection schedule lists all the maintenance/inspection activities to be carried out in the pilot plant and the respective time intervals to carryout these activities. The comment column should be used as a guide when performing these activities, giving additional information.

9.4.1 Routine Plant Inspection

A routine plant inspection is carried out prior to the start of every hydrate production operation. The plant should be inspected for gas or liquid leaks. The portable gas detector should be taken around the plant to ensure no higher gas levels are detected in the plant site. Further, all measuring gauges and meters should be checked for proper functioning. The Instrumentation panel should be checked to ensure all the indicators are properly functioning.

Further more, as part of the routine inspection procedure the plant should be kept clean and all unattended previous work should be done prior to the commencement

of operation. The '*Sheet EXSH-1*' (see Appendix D) should be completed and any faults identified should be noted. In case of serious faults the Plant Manager should be consulted prior to operation. The list given in Table 1 indicates the tasks to be carried out as part of the Routine Inspection Schedule.

9.4.2 Monthly Inspection Schedule

The monthly inspection should be carried out on the last day of the month fulfilling the tasks listed in the schedule given below. The attended work should be recorded in the Monthly Inspection Log (see Appendix D). Replacement of parts and alterations to the equipment must be recorded in a separate log sheet used for recording plant modifications, an example is provided in Appendix E.

9.4.3 Annual Inspection/Maintenance Program

An annual inspection program and mandatory testing of equipment is carried out for a period of three weeks where the plant is isolated and subjected to a thorough inspection operation. An inspection/maintenance routine is incorporated to ensure all measuring gauges and vessels are leak tested and subjected to NDT tests and the PSVs are bench tested. The process is outlined below in the Plant Inspection Schedule. The annual maintenance is scheduled for the month of March in every calendar year.

PILOT PLANT INSPECTION SCHEDULE

ITEM	FREQUENCY			COMMENTS
	ROUTINE	MONTH	ANN	
Temp Gauges	✓	✓	✓	This includes analog and Thermocouple transmitters.
Pressure Gauges	✓	✓	✓	This includes analog gauges and transmitters
Flow Meters	✓	✓	✓	Remotely read gas meters and liquor flow meter
Instrument Panel		✓	✓	Flow, Temperature and pressure digital indicators
Level Controller	✓	✓	✓	Check Trip-off function of the control loop
Liquor Storage Vessel	✓	✓	✓	Corrosion
Production Vessels	✓	✓	✓	Corrosion tests, NDT tests for cracks and general inspection
Nozzles	✓	✓	✓	NDT tests for cracks general tests for wear
Gas Storage Cylinders		✓	✓	Regulators, indicators and general tests
Knock-Out Vessel	✓	✓	✓	Corrosion tests functional tests
Filters		✓	✓	Filter media checks, corrosion, liquid stains
Pressure Regulators			✓	Valve seats, corrosion, functional test
PSVs		✓	✓	Functional tests and calibration
Rupture Discs		✓	✓	Corrosion tests
Compressor Unit	✓	✓	✓	Compressor overhaul, corrosion and noise levels
Liquor Pump		✓	✓	Corrosion
Refrigeration Unit		✓	✓	Regulating function
EG Heating Unit	✓	✓	✓	Regulating function
Mixer			✓	Corrosion
General Valves			✓	Seats, corrosion
Non-Return Valves			✓	Functional tests
Connections and Lines		✓	✓	Corrosion
Quick Closure Doors	✓	✓	✓	-

9.5 - Detailed Description of Inspection Tasks

A detailed description of the tasks to be performed is provided below. These should be checked against the items listed in the above checklist.

9.5.1 Measuring /Transmitting Instruments

The temperature and pressure gauges, flow meters, the level controller and the instrument panel are addressed here. These items should be routinely checked prior to operation to ensure their correct functioning, as they are critical for the day-to-day operation of the plant. Further, the gauges and transmitters should be calibrated annually to ensure their integrity and reliability. The ‘trip off’ function should be checked in the level gauge as part of the annual inspection procedure. The oil level in the gas flow meters must be checked after every two months.

9.5.2 Production Vessels / Nozzles

The two production vessels should be cleaned leaving no ice inside, irrespective of their operating nature, and should be inspected for corroding parts, leaks, insulation, among other items, on a monthly basis. The vessel should be subjected to NDT testing annually to ascertain the effects caused by the internal stresses. Further, the annual inspection required by the Australian Law on Pressure Vessels must be performed. The nozzles play a critical part in the formation of hydrates in the vessel and should be inspected once a month to ensure no wear or blockage had occurred.

9.5.3 Gas Storage Cylinders

The three cylinders used for storage and purging the system should be tested and the gauges on the cylinders should be calibrated on an annual basis. The cylinder gauges and the amount of gas in the cylinders should be checked on a weekly basis and recorded in the Inspection Log.

9.5.4 Liquor Storage Tank and Pump

The raw material used for Hydrate production may be highly corrosive; therefore the liquor tank and the pump should be cleaned and checked on a monthly basis to ensure no corroding elements are present. The pump should be subjected to an annual inspection - refer vender maintenance certificates.

9.5.5 Knock-out Vessel

The Knock-out vessel should be checked every day and drained routinely to ensure that no liquid has collected in it. The vessel should be subjected to an annual overhaul to ensure the strainer and the parts are functioning properly.

9.5.6 Filters

The filters should be dismantled and checked annually. The filter media should be replaced according to the specifications given in the vender maintenance certificates. Further, the filters should be drained off monthly.

9.5.7 HP/LP Regulators and Valves

The HP/LP regulators and valves should be checked and cleaned to the required level for safe operation on an annual basis.

9.5.8 Piping and Connection

As the liquor carried in the lines is very corrosive, the tubing and connections are to be checked during the annual maintenance period. Leak testing on all fittings should be carried out annually.

9.5.9 PSVs and Rupture Discs

These are critical safety components installed to protect the plant. Rupture discs should be inspected regularly for corrosion and replaced when required. The PSVs should be bench tested annually according to vender test certificates.

9.5.10 Compressor Unit

The compressor unit is checked regularly for smooth operation and lubricated once a month. The compressor unit is subjected to an annual inspection and possible overhaul if required.

9.5.11 Refrigeration Unit

The refrigeration unit is routinely checked to ensure its efficient functioning. The refrigerant is replaced according to the manufacturer recommendation.

9.5.12 Nozzle Heating Unit

The nozzle-heating unit is to be checked during the routine inspection to ensure proper functioning. The heating liquid - Ethylene Glycol must be replaced after every 6 months.

9.5.13 Mixer

The mixer should be checked and cleaned during the annual maintenance program.

10 - REFERENCES

1. Aker Engineering A/S, Natural Gas Hydrates for Large Scale, Long Distance Gas Transportation - A Feasibility Study, Internal Report in the NGH Project Group, First Proposal, Oslo, September 1995, 80 pp.
2. Avlonitis, D., Danesh, A., Todd, A.C., Baxter, T., "The Formation Of Hydrates In Oil-Water Systems", Multi-Phase Flow - Proceedings of the 4th International Conference, pp. 15-34
3. Børrehaug, A. and Gudmundsson J.S. (1996): "Gas Transportation in Hydrate Form," EUROGAS 96, 3-5 June, Trondheim, 35-41
4. Boslashrrehaug, A., "Natural Gas Hydrate an Alternative to Liquefied Natural Gas," Norwegian University of Science and Technology, January 1996.
5. GAS-IN-ICE: Formation Rate and Gas Content, Department of Petroleum Engineering and Applied Geophysicists, Norwegian Institute of Technology, University of Trondheim, Technical Report, pp 53
6. Gudmundsson, J.S., Parlaktuna, M and Khokhar, A.A., "Storing Natural Gas as Frozen Hydrate," Society of Petroleum Engineers Production and Facilities, 1994, 69-73
7. Gudmundsson, J.S. , Method for Production of Gas Hydrate for Transportation and Storage, U.S. Patent No. 5,536,893, 1996
8. Gudmundsson, JS and Parlaktuna, M., "Storage of Natural Gas Hydrate at Refrigerated Conditions," AIChE Spring National Meeting, New Orleans, 1992, 27.
9. Gudmundsson, J.S., Hveding, F. and Børrehaug, A., Transport of Natural Gas as Frozen Hydrate, Proceedings of the 5th International Offshore and Polar Engineering Conference, The Hague, June 11-16, Vol. I, 1995, 282-288
10. Gudmundsson, J.S. and A. Boslashrrehaug, FROZEN HYDRATE FOR TRANSPORT OF NATURAL GAS, 2nd International Conference on Natural Gas Hydrate, June 2-6, 1996, Toulouse, France.
<<http://www.ipt.unit.no/~ngh/library/paper2.html>>
11. Gudmundsson, J.S., Korsan, K. and Børrehaug, A., Crude Oil/Gas Hydrate Slurry - Concept Evaluation, Department of Petroleum Engineering and Applied Geophysicists, Norwegian Institute of Technology (now Norwegian University of Science and Technology), Trondheim, 1995

12. Hauge, Janne, NATURAL GAS HYDRATE - Determination of Free Water Using Conductivity Measurements, December 1996
<<http://www.ipt.unit.no/~jsg/studenter/diplom/hauge.html>>
13. Holder, Gerald D., Enick, Robert M., SOLID DEPOSITION IN HYDROCARBON SYSTEMS, Gas Research Institute, Chicago, December 1992
14. Holder, G.D., Hand, J.H., MULTIPLE-PHASE EQUILIBRIA IN HYDRATES FROM METHANE, ETHANE, PROPANE AND WATER MIXTURES, AIChE Journal, Vol. 28, No. 3, pp.440-447
15. Hwang, M.J., Wright, D.A., Kapur, A., Holder, G.D., AN EXPERIMENTAL STUDY OF CRYSTALLIZATION AND CRYSTAL GROWTH OF METHANE HYDRATES FROM MELTING ICE, Journal of Inclusion Phenomena and Molecular Recognition in Chemistry, Vol. 8, pp. 103-116, 1990
16. IMAI Noboru: Crystalline structure of methane hydrate. CHISHITSU NEWS, Geological Survey of Japan, 1997
17. Jamaluddin, A.K.M., Kalogerakis, N., Bishnoi, P.R., HYDRATE PLUGGING PROBLEMS IN UNDERSEA NATURAL GAS PIPELINES UNDER SHUTDOWN CONDITIONS, Journal of Petroleum Science and Engineering, Vol. 5, pp. 323-335, 1991
18. Kalogerakis, Nicholas., Jamaluddin, A.K.M., Dholabhai, P.D., Bishnoi, P.R. EFFECTS OF SURFACTANTS ON HYDRATE FORMATION KINETICS, Society of Petroleum Engineers 25188, Society of Petroleum Engineers International Symposium on Oilfield Chemistry, New Orleans, March 2-5, 1993
19. Kelland, M.A., Svartaas, T.M., Dybvik, L., NEW GENERATION OF GAS HYDRATE INHIBITORS, RF-Rogaland Research, Society of Petroleum Engineers 30695, Society of Petroleum Engineers Annual Technical Conference in Dallas 22-25 October 1995, 529-537
20. Kuuskraa, V.A., et al., "Conceptual models for gas hydrates," DoE/ME/19239-1422, National Technical Information Center, 1995
21. Kuuskraa, V.A. and Hammershaimb, E.C., Handbook of Gas Hydrate Properties and Occurrence, No. DE-AC21-(82Mc19239), Lewin and Associates Inc., 1983
22. Kvamme, Bjørn, AN EXTENDED ABSORPTION THEORY FOR HYDRATE EQUILIBRIUM, Telemark Institute of Technology, Kjoslashnes Ring 56, N-3914 Porsgrunn, Norway
23. Kvenvolden, Keith. A., MARINE GAS HYDRATES - I: GEOCHEMICAL EVIDENCE, U.S. Geological Survey, Menlo Park, California 94025

24. Laider, K.J., Meiser, J.H., Physical Chemistry, The Benjamin/Cummings Publishing Company, Inc., 1982, 919 pp
25. "Lattice relaxation in type I gas hydrates", AIChE J., 37, 1511,1991
26. Lederhos, J.P., Mehta, A.P., Nyberg, G.B., Warn, K.J. and Sloan, E.D.,«Structure H Clathrate Hydrate Equilibria of Methane and Adamantane», AIChE Journal, Vol. 38, No. 7, July 1992, pp 1045-1048
27. Lippman, D., Kessel, D., Rahimian, I., GAS HYDRATE NUCLEATION AND GROWTH KINETICS IN MULTIPHASE TRANSPORT SYSTEMS, Proceedings of the Fifth (1995) International Offshore and Polar Engineering Conference, The Hague, June 11-16 1995
28. Long, J., Lederhos, J., Sum, A., Christiansen, R., Sloan, E.D., KINETIC INHIBITORS OF NATURAL GAS HYDRATES, Proceedings, Annual Convention of the Gas Processors Association, 1994
29. Lundgaard, Lars, Mollerup, Joslashrgen M., INFLUENCE OF GAS PHASE FUGACITY AND SOLUBILITY ON CORRELATION OF GAS HYDRATE FORMATION PRESSURE, Fluid Phase Equilibria, Vol. 70 (1991), pp. 199-213
30. Lundgaard, Lars., Mollerup, Jøslashrgen, CALCULATION OF PHASE DIAGRAMS OF GAS HYDRATES, Fluid Phase Equilibria, 1992
31. MAEKAWA Tatsuo, The physicochemical characteristics of natural gas hydrates determined by laboratory experiments. CHISHITSU NEWS, Geological Survey of Japan, 1997
32. Makogon, Y.F., Hydrates of Natural Gas, PennWell, Tulsa, 1981
33. Makogon, Y.F., 1984, Production from natural gas hydrate deposits, Gazovaya Promishlennost, v. 10, p. 24-26
34. Makogon, Y.F., 1988, Natural gas hydrates - the state of study in the USSR and perspectives for its using: Paper presented at the Third Chemical Congress of North America, Toronto, Ontario, Canada, June 1988, 20 p
35. Makogon, Y.F., 1995, "Hydrates of Hydrocarbons", Japan National Oil Corporation Seminar on the Gas Hydrate Development Technology, September 11 - 13, 1995, Chiba, Japan
36. Mathews, M.A., Logging characteristics of methane hydrate, paper K, in 10th
37. Max, M.D., "Clathrate-Based Fuel Storage and Transport Media: Potential Impact," Fuel Chemistry Symposium on Gas Hydrates, American Chemical Society, April 1997

38. Mehta, A.P. and Sloan Jr., E.D., Structure H Hydrate Phase Equilibria of Methane + Liquid Hydrocarbon Mixtures, Journal of Chemical Engineering Data, Vol. 38, No. 4, 1993, pp 580-582
39. Mehta, A.P. and Sloan, E.D., «Structure H hydrates: the state-of-the-art», Colorado School of Mines, Golden (USA), 2nd International Conference on Natural Gas Hydrates, Toulouse, France, June 2-6, 1996, pp 1-8
40. Mehta, A.P. and Sloan Jr., E.D., Structure H Hydrate Phase Equilibria of Paraffins, Naphthenes and Olefins with Methane, Journal of Chemical Engineering Data, Vol. 39, No. 4, 1994, pp 887-890
41. Mori, T., Mori, Y.H., CHARACTERIZATION OF GAS HYDRATE FORMATION IN DIRECT-CONTACT COOL STORAGE PROCESS, Rev. Int. Froid. Vol. 12, September, 1989
42. NAKAMURA Kazuo: Evaluation of physical properties of methane hydrate by computer simulation. CHISHITSU NEWS, Geological Survey of Japan, 1997
43. Natural Gas Hydrates - Properties, Occurrence and Recovery, ed. Cox, J.L., Butterworths, Woburn, 1983
44. Nerland, B. & Oslo, "Natural Gas Hydrates: Separation and Gas Content," Diploma thesis, Department of Petroleum Engineering and Applied Geophysicists, Norwegian Institute of Technology
45. Ngan, Y., Englezos, P., «Concentration of aqueous solutions by clathrate hydrate formation», 2nd International Conference on Natural Gas Hydrates, Toulouse, France, June 2-6, 1996, pp 467-474
46. Nygaard, H.F., TRANSPORTABILITY OF HYDRATES IN MULTIPHASE SYSTEMS,
47. Perry, R.H. and Green, D., Perry's Chemical Engineers' Handbook, 6th ed., McGraw-Hill, New York, 1984
48. Plummer, P.M.L., Chen, T.S., MOLECULAR DYNAMICS STUDY OF WATER CLATHRATES, Journal of Physical Chemistry, Vol. 87, No. 21, 1983, pp. 4190-4197
49. Rodger, P.M., "Towards a microscopic understanding of Clathrate Hydrates", Annals of the New York Academy of Science, 715, 1994, 207
50. Rodger, P.M., "Computational Studies of Clathrate Hydrates", in Spectroscopic and computational studies of supramolecular systems, J.E.D. Davies (ed.), Kluwer Academic Publishers, 1992

51. Ross, Russel G., Andersson, Per, CLATHRATE AND OTHER SOLID PHASES IN TETRAHYDROFURAN-WATER SYSTEM: THERMAL CONDUCTIVITY AND HEAT CAPACITY UNDER PRESSURE, Canadian Journal of Chemistry, Vol. 60, 1982 pp. 881-892
52. Rummelhoff, C.J., Bakke, J., TRANSPORT AND DISTRIBUTION OF NATURAL GAS IN NORWAY, COMPARISON OF ALTERNATIVE TECHNICAL SOLUTION, Kvaeligner Moss Technology a.s
53. Rummelhoff, C.J., HYDRATE AS ENERGY CARRIER, A FEASIBILITY STUDY, A Kvaeligner Report for NTNF, Aug, 2 1991
54. Sassen, R., S.T. Sweet, D.A. DeFreitas, and A.V. Milkov, Exclusion of 2-methylbutane (isopentane) during crystallization of structure II gas hydrate in sea-floor sediment, Gulf of Mexico: Organic Geochemistry, v. 31, November 2000, p. 1257-1262
55. Skovborg, P., Ng, H.J., Rasmussen, P., MEASUREMENT OF INDUCTION TIMES FOR THE FORMATION OF METHANE AND ETHANE GAS HYDRATES, Chemical Engineering Science, Vol. 48, No. 3 pp. 445-453, 1993
56. Sloan, E.D., Clathrate Hydrates of Natural Gases, Marcel Dekker, Inc., New York, 1990, 641 pp
57. Sloan, E. Dendy, HYDRATE NUCLEATION FROM ICE, Proceedings of the Sixty-Eighth Gas Processors Association Annual Convention, Committee Reports, pp. 52-59
58. Sloan Jr., E.D., «Natural Gas Hydrates», Journal of Petroleum Technology, Dec. 1991, pp 1414-1417
59. Smelik, E. A., King, Jr., H. E., "Crystal-growth studies of natural gas clathrate hydrates using a pressurized optical cell," American Mineral, 1997, pp 82, 88-98
60. Smirnov, L.F., NEW TECHNOLOGIES USING GAS HYDRATES, Odessa Technological Institute of the Refrigeration Industry. (Translated from Teoreticheskie Osnovy Khimicheskoi Tekhnologii, Vol. 23, No. 6, pp. 808-822, November-December, 1989) 1990, Plenum Publishing Corp.
61. Soper, A.K. (ISIS), C Koh, R Westacott, J Savidge, "In situ study of gas hydrate formation in aqueous solution," ISIS 97
<<http://www.isis.rl.ac.uk/annualreport/feature4.htm>>
62. Tohdi, B., Burgass, R.W., Danesh, A., Todd, GAS HYDRATE FORMATION AND INHIBITION PREDICTION, Department of Petroleum Engineering, Heriot-Watt University, Edinburgh, EH14 4AS

- 63 Tohidi, B., Danesh, A., Burgass, R.W., Todd, A.C., GAS SOLUBILITY IN SALINE WATER AND ITS EFFECTS ON HYDRATE EQUILIBRIA, Proceedings of the Fifth (1995) International Offshore and Polar Engineering Conference, The Hague, June 11-16 1995
- 64 Westacott, R.E. & P.M. Rodger, "Direct free energy calculations for clathrate hydrates", *Annals of the New York Academy of Science*, 715, 537
- 65 Yakushev, V.S. and Istomin V.A., "Gas-Hydrates Self-Preservation Effect," 136-139, *Physics and Chemistry of Ice*, (ed. N. Maeno and T. Hondoh), Hokkaido Univ. Press, Sapporo, 1992

11 - NOMENCLATURE

A	Angstrom
AS	Australian Standard
ASTM	American Standard Test of Material
Bar.	Barometric Pressure
C	Degree Centigrade
CC	Cubic Centimeter
CNG	Compressed Natural Gas
CP	Centipoise
Cp	Specific Heat at Constant Pressure
Cv	Specific Heat at Constant Volume
g	Gram
gmol	Gram-mole
HFVF	Hydrate Formation Volume Factor
ID	Inside Diameter
JT	Joule-Thomson
K	Degree Kelvin
Kg	Kilogram
KJ	Kilojoule
Kpa	Kilopascal
l	Litre
LNG	Liquified Natural Gas
LPG	Liquid Propane Gas
Mpa	Megapascal
M	Mass
m	Mole
n	Number of Moles
OD	Outside Diameter
Psia	Pound per square inch absolute
ppm	Parts per Million
PSV	Pressure Safety Valve
P&ID	Piping and Instrument Diagram
PVT	Pressure, Volume, Temperature
R	Coefficient
STP	Standard Temperature and Pressure
Sm	Standard Cubic Meter
Sg	Specific Gravity
SLS	Sodium Loryal Sulphate
TS	Toluene Sufonic Acid

12 - APPENDICES

APPENDIX A - Pilot Plant Operation Summary

Operation Summary

This sections outlines the necessary considerations for reading and interpreting the Natural Gas Hydrate Pilot Plant test results. The data is summarized into three tables and described below.

Typical Plant Operation Routine

After completion of a run the vessel and the door is cleaned and a new test bottle is fixed on a stand and placed on the door with the collection funnel on top of the bottle. Note that runs prior to 15/5/01 did not use this process and the hydrates made were manually transferred to the bottle and closed. The flash vessel is closed and gas is injected into the system to purge air from the system. The vessel is then pressurized to the test vessel pressure (700 kPa or 100 psig). The system is allowed to cool to the test vessel temperature (-10 ~ -15 °C). The HP Cylinder is pressurized to the test nozzle pressure (10000 – 14000 kPa or 1300 – 2200 psig). Further, the system tubing is purged with gas through a three-way valve fitted near the nozzle to ensure no water remains in the tubing.

The operation is commenced by taking the initial readings and then opening the high-pressure gas flow into the vessel. The HP cylinder is also open at this point and then the liquor pump switched on. The pressure in the vessel is maintained constantly (700 kPa) by venting the gas from the vessel. When the operation is trouble free the temperature at the vessel top would fall rapidly and remains low and then start to raise, water saturated gas reaches the nozzle at this point of operation.

The up-stream nozzle pressure will drop if the nozzle is not blocked. The operation is continued until the pressure falls to around 1300 psig upstream of the nozzle. The liquor pump is switched off first and then gas is allowed to flow for some time to remove the saturated gas/liquor from the vessel. The final readings are taken at this point.

The vessel is then vented and the door removed. The test bottle arrangement is removed. Typically, some hydrates remain in the funnel surface which are transferred into the bottle, and the volume measurements recorded using a plunger. Note that these measurements were done after 1/6/01. The bottle is sealed and taken for laboratory measurements of the gas and liquid volumes.

Operation Notes:

Liquor Concentration

The liquor used throughout the test contained a concentration 1.24 g TSA in 1-liter tap water. This was seen as the optimum value resulting from the Lab trials on Hydrates.

Liquor Pump Flow Rate

The operations conducted during 19/4/01 to 15/05/01 had a liquor pump stroke length set point of 7%. The maximum capacity of the pump is 2 lit/min. Initially the liquor used in the operation was recorded by the magnetic flow meter. The magnetic meter is inaccurate at the smaller flow rate; therefore, the subsequent experiments recorded the volume added from a graduated supply vessel. Therefore the pump flow rate was changed to 3% from 22/05/01.

The pump was operated at 3% stroke length or around this value from this date onwards. (Note that 3% is just an operation mark and the actual rate is shown in the calibration curves). The magnetic flow meter is not used for the measurements as it does not record the flow. A set of calibration curves was produced for the pump for the range of operating pressures. The Calibration curves are given in the Appendix.

Gas Recycling

Gas recycling was attempted during the period 8/5/01 to 11/5/01. This was not possible as the vessel had limited volume and the pressure continued to increase. Further, an error in the recycling meter was observed as it continued to read even when gas flow was isolated, possibly due to the vibration of the compressor.

HP Cylinder readings

The HP cylinder provides the system with a volume reservoir. This allows the system to maintain a high nozzle pressure for an increased operation time. The amount of gas used from this cylinder is measured by taking the pressure difference.

Gas Consumption

The gas meter readings are taken at the point when the system is pressurized to the required operational pressure. The amount of gas consumed during the injection is calculated as shown in the notes following Table 24. A negative value at certain points indicates that there is a certain error in the meters or in the recordings.

Summary for Data given in Table 24

Table 24 gives a set of data after applying certain criteria to identify meaningful results. The criteria included:

- Plant injection times lasting longer than 10 minutes;
- Samples yielding a gas volume of 1 liter or more during the lab tests;
- Samples containing more than 10 ml of liquor during lab tests;
- Samples giving a Hydrate Formation Volume Factor (Volume/Volume) – HFVF (V/V) of more than 25.

Further, this Table shows calculations for Hydrate Formation percentages based on weight and mole. Refer to notes given for Table 1 for clarification.

Summary for Data given in Table 24.

The operations shown in Table 24 are for the data recorded after 1/6/01. The operations were similar but this set of data includes bulk density measurements and other additional calculations showing new parameters for study. Further, this reflects the current plant set up. Refer to notes given for Table 2 for clarification.

APPENDIX B - Calibration Curves for Compressor and Liquor Pump

Tests were carried out to find out actual amounts of liquor and gas flows at the operated range of pressures. This was to develop an understanding of the relationship with flow of liquor or gas throughput with the system operation pressure. Further, the curves demonstrate the compressor flow dependence on the ambient temperature.

Gas Compressor

Gas Compressor throughput tests were carried out by recording the low-pressure supply meter reading of the gas upstream of the compressor. The discharge pressure was recorded at the compressor discharge.

Time (min)	Down-stream Pressure kPa (psig)							
	7000 (1016 psig)		11000 (1595 psig)		13800 (2003 psig)		15000 (2170 psig)	
	Meter (m ³)	Rate	Meter (m ³)	Rate	Meter (m ³)	Rate	Meter (m ³)	Rate
0	259.900		260.432		260.928		261.388	
1	259.998	0.098	260.520	0.088	261.008	0.080	261.467	0.079
2	260.080	0.082	260.610	0.090	261.090	0.082	261.546	0.079
3	260.170	0.090	260.696	0.086	261.170	0.080	261.626	0.080
4	260.260	0.090	260.778	0.082	261.256	0.086	261.708	0.082
5	260.350	0.090	260.866	0.088	261.332	0.076	261.788	0.080
Avg Flow Rate (m³/min)	0.090		0.087		0.081		0.080	

Table 44 Gas Compressor Throughput at 22 °C ambient

Down-stream Pressure kPa (psig)						
Time (min)	9000 (2306 psig)		12000 (1741 psig)		14000 (2032 psig)	
	Meter (m³)	Rate	Meter (m³)	Rate	Meter (m³)	Rate
0	262.810		263.320		263.780	
1	262.896	0.086	263.402	0.082	263.860	0.080
2	262.978	0.082	263.482	0.080	263.940	0.080
3	263.064	0.086	263.566	0.084	264.016	0.076
4	263.146	0.082	263.644	0.078	264.096	0.080
5	263.230	0.084	263.724	0.080	264.172	0.076
Avg Flow Rate (m³/min)	0.084		0.081		0.078	

Table 45 Gas Compressor Throughput at 15 °C ambient

Liquor Pump

Liquor pump throughputs tests were carried out by recording the water pumped at different stroke length set points for flow. The water volume was determined by recording the volume collected in a measuring cylinder with time. The pressure was measured at down-stream of the pump. The pump capacity is 2 lit/min. At 3%, the flow rate should be 0.06 lit/min (60 ml/min), but the tests indicate the pump is discharge pressure dependent.

Setting	Pressure (kPa)	Time (min)	Volume (ml)	Rate (lit/min)
3%	7000	5	130	26.000
	11000	5	43	8.600
	13000		0	0.000
5%	7000	3.633	250	68.814
	11000	4.533	250	55.151
	15000	5.517	250	36.252

Table 46 Water pump Throughput

These tests were carried out as part of the plant maintenance program on 31/05/01.

APPENDIX C - Measuring Hydrate Formation Volume Factor

Objectives

The purpose of this procedure is to:

- Determine the HFVF (hydrate formation volume factor) for low and high pressure hydrate production;
- Investigate the properties of a range of chemical additives associated with the formation of hydrates with high HFVF;
- To demonstrate the capability of the hydrate collection equipment;
- To ensure the experimental work is conducted in a safe manner.

Method

Before starting the refrigeration system the following should be observed:

1. Pilot plant pressure vessel is initially cleaned internally with a wire brush to remove any unwanted rust on the wall internals.
2. Coat the O-ring seal of the removed door with grease.
3. Place the hydrate measuring apparatus (figure 27) on the hydrate module vessel door, along with the cylinder cap and close the vessel.
4. Allow the pressure vessel to cool to the desired operation temperature of $-10\text{ }^{\circ}\text{C}$ or lower.
5. Produce sufficient hydrates to fill the vessel (more than 2 lit), and then allow the hydrate temperature to stabilize for 15 minutes.

Note: Protective gloves **MUST** be worn when handling Test Cylinders at freezing temperatures. Vent excess gas and immediately open the module door and remove the hydrate measuring apparatus. Immediately remove the cone, and check to see if enough hydrate was made to completely fill the experimental pressure cylinder.

Note: if not enough hydrate was produced to completely fill the experimental pressure cylinder to the top, use a marker on the cylinder to indicate the hydrate fill level.

If excess hydrate has been formed tap the cylinder gently and then scrape the excess away, screw the cylinder cap on the experimental pressure cylinder with two full turns ASAP. Remove the cylinder holder, place the experimental pressure cylinder in a vice, and completely cap the cylinder off.

Note: during the tightening process of the cylinder cap, the cap valve must be left open to allow ease of closing the cylinder.

Once the experimental pressure cylinder has been capped, remove the cylinder from the vice and place in a water bath. Allow sufficient time (about 1.5 hrs) for the hydrates in the cylinder to melt. Note: check the cylinder temperature after 1.5 hrs using the digital temperature indicator. Remove the cylinder only when the temperature of the cylinder is the same as that of the water bath.

Once the temperature of the cylinder is the same as that of the cylinder bath, remove and towel dry. Connect a pressure gauge to the cylinder valve, slowly open cylinder valve to obtain the cylinder pressure reading (record cylinder pressure reading in table 1). Then, close the cylinder valve and remove the cylinder gauge.

Measuring Evolved Hydrate Gas Volume

6. Check the Horizontal level of the Test Gas Meter is centralised, ensure that there is no water in the ballast and the water level inside the Wet Test Gas Meter is at the appropriate height.
7. Connect the Test Cylinder to the Wet Test Gas Meter with high-pressure tubing via a Liquid Knock-out bottle.
8. Rest the Test Cylinder at an angle against a secured block to keep the fluid away from the "Gas" valve connected to the Wet Test Gas Meter.
9. Record the initial reading of the volume of gas (L) on the face of the Wet Test Gas Meter in table 1.

10. Very slowly, open the elevated valve on the Test Cylinder. Gas must not be vented into the Wet Test Gas Meter any faster than 2 lit/sec.
11. As the gas flow into the Wet Test Gas Meter slows the cylinder gas valve can be used to adjust gas flow through the meter.
12. When no flow is recorded into the Wet Test Gas Meter, close the valve on the Test Cylinder and carefully roll the cylinder sideways 3-4 times. Open the Test Cylinder valve to the Wet Test Gas Meter. If there is additional gas flow from the Test Cylinder repeat this process until no further gas evolves.
13. Close the Test Cylinder valve and record the final volume of gas (L) on the face of the Wet Test Gas Meter in table 1.
14. Disconnect the high-pressure tubing from the Test Cylinder valve and remove the Test Cylinder for cleaning.
15. Place the Test Cylinder in a bench mounted vice on an angle of 50-60 degrees. Open the high side valve and remove the plug end from the Test Cylinder.
16. Using paper hand towel wipe excess grease from the thread and O-ring seal of the plug end and the Test Cylinder.
17. Unclamp the Test Cylinder and carefully empty all liquor into a measuring cylinder and record volume of liquor in table 1.
18. The liquor is to be disposed of by incinerating in the equipment provided.

Note: All the measurements must be recorded in table 1.

Cleaning Experimental Cylinders

19. Fill Test Cylinder with water and 10 ml of Quantum clean (laboratory glass cleaner).
20. Using a long handled brush with a bristle diameter at least 1 cm greater than the internal diameter of the Test Cylinder clean the inside of the test Cylinder, paying special attention to the seal and thread of the open end.
21. To conserve cleaning fluid, pour the contents of the test Cylinder into the next Test Cylinder waiting to be cleaned.
22. Rinse the cleaned Test Cylinder thoroughly with tap water.
23. When satisfied that no cleaning fluid remains in the Test Cylinder leave inverted on a piece of paper hand towel to allow the excess water to drain.
24. Clean the removed plug end and valve with a small amount of the cleaning solution and rinse thoroughly with tap water. Flow water through the open valve.
25. Place the cleaned plug end beside the cleaned Test Cylinder to dry.

APPENDIX D - Hydrate Bulk Density Measuring Procedure

Methodology

Hydrates are collected directly into the sample bomb, measuring container. The hydrates are directed into the sample container using the stainless steel collection funnel.

To ensure sufficient hydrate sample is collected the pilot plant is operated for a minimum period of 40 minutes (note top of the vessel temperature must be maintained below -4°C and nominally 500 ml of water and additive must be injected). Inlet pressure, vessel pressure and injection rate to be maintained at constant conditions for run duration.

Measurement procedure

The volume of collected hydrates is measured in the container. A piston plunger (same internal diameter as sample bomb) is inserted into the chamber until it rests firmly against the hydrate sample. The length of insertion is measured and recorded in millimetres on the production run log sheet. Next the sample is compressed by pressing down on the piston until no further travel is observed. Again the insertion length is measured. Next the gas formation volume factor is measured as per the nominated test procedure. The liberated volume of water and additive are recorded. To determine the bulk and compacted densities the following calculation is performed.

Hydrate Weight

The liquor volume is taken as the mass of hydrate (in grams). Note this assumption can be used as the density of gas is significantly less than that of water.

Hydrate Volume

The hydrate volume is calculated as follows:

Determine volume of hydrates by multiplying cross-sectional area of cylinder by length of hydrates collected. Note the length of hydrates is insertion distance in millimetres is subtracted from 400 mm (depth of cylinder). Cylinder diameter is 55 mm.

APPENDIX E – NGH Pilot Plant Test Record Sheet

APPENDIX F – NGH Pilot Plant Monthly Plant Inspection Log

APPENDIX F – NGH Pilot Plant Monthly Plant Inspection Log

For the Month: _____

No	ITEM	PLANT ID	REMARKS	CHECKED BY
1	Temp Gauges	TI-01...15		
2	Pressure Gauges	PI-01...15		
3	Flow Meters	MT-01,2,3,4		
4	Instrument Panel			
5	Level Controller	LI-01		
6	Liquor Storage Vessel	T-002		
7	Production Vessels	V-002, 3		
8	Nozzles	N-001, 2		
9	Gas Storage Cylinders	V-004, 5, 6		
10	Knock-Out Vessel	V-001		
11	Filters	F-001,2,3,4,5		
12	Pressure Regulators	HPR-1,2 LPR-1,2,3		
13	PSVs			
14	Rupture Discs			
15	Compressor Unit	C-001		
16	Liquor Pump	P-002		
17	Refrigeration Unit			
18	Nozzle Heating Unit			
19	Mixer	MX-001		
20	General Valves			
21	Non-Return Valves			
22	Connections and Lines			
23	Quick Closure Doors			

General Overview:

SUPERVISOR

DATE

APPENDIX G - Instrumentation Schedule

a) Instrumentation

Temperature

Item	Location/ Description
TI-01	HP Gas line passing the 4-way junction
TI-02	Liquor outlet from the water pump
TI-03	Bare wire Thermocouple on Right vessel (V-002)
TI-04	Bare wire Thermocouple on Left vessel (V-003)
TI-05	Bare wire Thermocouple on Hot water Inlet on nozzle - Left vessel (V-003)
TI-06	Bare wire Thermocouple on Hot water Outlet on nozzle - Left vessel (V-003)
TI-07	Magnetic base Thermo coupler
TI-08	Temperature indicator - Left Vessel V-002 Bottom
TI-09	Bare wire thermocouple on Vent line from top of left Vessel V-002
TI-10	Bare wire thermocouple on liquor supply line to left Vessel V-002
TI-11	Not Used
TI-12	Temperature transmitter on of flow meter MT-03
TI-13	Temperature transmitter on flow meter MT-01
TI-14	Temperature transmitter on flow meter MT-02

Pressure

PI-01	HP Gas line from the Cylinder V-004
PI-02	HP Gas line from the Compressor
PI-03	Not used
PI-04	Vent line from Right Vessel before the PSV
PI-05	Vent line from the Left Vessel before the PSV
PI-06	Vent line from the Left Vessel after the PSV
PI-07	Vent line from Right Vessel after the PSV
PI-08	Liquor outlet line after the Liquor Pump
PI-09	Liquor/Gas line after the Mixer MX-001

PI-10	Pressure indicator in left Vessel V-003
PI-11	Pressure indicator in right Vessel V-002
PI-12	Pressure transmitter on flow meter MT-03
PI-13	Pressure transmitter on flow meter MT-01
PI-14	Pressure transmitter on flow meter MT-02

Flow

MT-01	LP Gas inlet line
MT-02	Recycled Gas line entering the compressor
MT-03	Venting line
MT-04	Liquor inlet line

Level

LI-01	Liquor Tank T-002
--------------	-------------------

b) Equipment

Filters

F-001	Recycled Gas Line entering the compressor
F-002	Liquor Inlet line entering the Pump
F-003	LP Gas inlet line
F-004	Recycled Gas line
F-005	Controlled Venting line

Vessels

V-001	Liquid knock-out Vessel for Recycled Gas
V-002	Right Vessel for HP Hydrate Production
V-003	Left Vessel for LP Hydrate Production
V-004	HP Cylinder for Pressure adjustment
V-005	Storage cylinder for controlled vent
V-006	Storage cylinder for PSV vent

Pumps

P-001	Not used
P-002	Liquor Pump

Compressor

C-001	HP compressor
-------	---------------

Motor

M-001	Electric motor for compressor
-------	-------------------------------

Mixer

MX-001	Liquor / HP Gas mixer
--------	-----------------------

Tanks

T-001	Cooling Water Tank
T-002	Liquor Tank

Low Pressure Regulators

LPR-1	Recycled Gas line entering Compressor
LPR-2	Controlled vent system
LPR-3	Controlled vent system

High Pressure Regulators

HPR-1	Recycled Gas line passing V-001
HPR-2	Gas/Liquor line passing the Mixer MX-001

Non-Return Valves

CHS4-1	Controlled Vent line from Left Vessel
CHS4-2	Controlled Vent line from Right Vessel
CHS6-1	Liquor inlet line after the pump
CHS6-2	HP Gas cooling line from the Tank T-001
CHS6-3	HP Gas line approaching Liquor line
CHS8-1	Liquor/Gas line approaching Left Vessel
CHS8-2	Liquor/Gas line approaching Right Vessel
NRV-002	Main gas supply line
NRV-003	Recycled gas supply from Vessel V-001

Pressure Relief Valves

4R3A1-1	Controlled Vent line from Left vessel
4R3A1-1	Controlled Vent line from Right vessel
PSVV-1	Direct vent line from Left vessel
PSVV-2	Direct vent line from Right vessel
PSVC-1	HP Gas vent passing the Compressor
R3AE-1	Liquor recycle line

Miscellaneous Valves

18RF8-1	Gas/Liquor line approaching Left vessel
18RF8-2	Gas/Liquor line approaching Right vessel
44S6-1	Recycle Gas line entering Filter F-001
44S6-2	Recycled Gas cooling line approaching the 4-way junction
44S6-3	HP Gas line By-pass cooling
44S6-4	HP Gas line approaching Mixer MX-001 prior to vent line
44S6-5	HP Gas line approaching Mixer MX-001 passing vent line
44S6-6	Liquor inlet line prior to recycle line
44S6-7	Liquor inlet line passing recycle line
45F8-1	Left Vessel adjoining PI-10
45F8-2	Right Vessel adjoining PI-11
4P4T-1	Right Vessel
4P4T-2	Left Vessel
4P4T-3	Knock-out Vessel bottom line
4P4T-4	Controlled Venting System adjoining LPR-2
4P4T-5	Controlled Venting System adjoining LPR-2
4P4T-6	Controlled Venting System adjoining LPR-3
4P4T-7	Controlled Venting System adjoining LPR-3
4P4T-8	Last valve Controlled Venting line
4P4T-9	Last valve Direct Venting line
4P4T-10	V-003 Vessel vent valve
4P4T-11	V-002 Vessel vent valve
1VS4-1	HP Gas line from Cylinder V-004 connecting Vent line from V-003
1VS4-2	HP Gas line from Cylinder V-004 connecting Vent line from V-002
1VS6-1	HP Gas Vent line
1VS6-2	Liquor Recycle line

APPENDIX H - Prestart Plant Alignment and Purge

IF IN DOUBT STOP PROCEDURE AND ASK		
CHECKLIST 1 PRE START PLANT ALIGNMENT AND PURGE		
ITEM	TASK DESCRIPTION	COMMENTS
1.0	Check for Plant integrity	Check for leaks/Mechanical Damage etc
2.0	Check gas Detector	Ensure portable gas detector present and operational
3.0	Plant Purging	-
3.1	<i>Vessel Purging Valves</i>	Pilot plant is purged with NG to expel all air
	Check vessel bottom flanges	Ensure these flanges are secure
	Open 18RF8-1	Located on top of vessel V-003
	Open 18RF8-2	Located on top of vessel V-002
	Open APDGF4-1	Located on vent line form V-003
	Open APDGF4-2	Located on vent line from V-002
3.2	<i>Line Purging Valves</i>	-
	Close main gas valve USBV40 -1	This is located on the floor against the wall of the shed
	Close 4P4T-3	This valve should always be closed during purge
	Open 44S6-1	-
	Close 44S6-2	-
	Open 44S6-3	-
	Open 44S6-4	-
	Open 44S6-5	-
	Close IVS6-1	-
	Close IVS6-2	Gas Lines are now Purged to CHS6-1 and IVS6-2
	Open HPR-2	-
	Open 4P4T-4	-
	Open 4P4T-5	-
	Open 4P4T-6	-
	Open 4P4T-7	-
	Open 4P4T-8	-
	Open IVS4-1	-
	Open IVS4-2	-
3.3	Commence Purging	Purging pressure should be less than 350 kPa
	Open 44S6-HV 043	Purging is done using HP gas cylinder V-004.
	Check PI-02 = PI-09	Max purge duration 60 seconds
	Inspect pipe connections around plant	Check for any gas odour on plant
3.4	Resetting Valves	-
	Close 44S6-HV 043	-
	Close IVS4-1	-
	Close IVS4-2	-
	Close APDGF-1	-
	Close APDGF-2	-
	Close HPR-2	-
	Close 18RF8-1	-
	Close 18RF8-2	-
	Check PI-02 and PI-09	These should be at atmospheric pressure

APPENDIX I - High Pressure Production, Shutdown & Hydrate Removal

(Page 1 of 3)

IF IN DOUBT STOP PROCEDURE AND ASK		
CHECKLIST 3 – HP HYDRATE PRODUCTION, SHUT DOWN AND HYDRATE REMOVAL		
ITEM	TASK DESCRIPTION	COMMENTS
1.0	Check for completion of CHECKLIST 1	Plant should be purged before production begins
2.0	Identify vessel V- 002	Vessel V-002 should only be used for HP hydrate prod
3.0	Switch On Instrumentation Power	Located on switch board in cubicle
4.0	Refrigeration Settings	-
4.1	Switch on refrigeration system at main board	Main switch board in cabinet - outside Shed
4.2	Switch on refrigeration system local to PP	Located on local control consule on PP
4.3	Switch On refrigertaion control system	Control Board in cabinet outside shed
4.4	Set LEFT vessel to -20 deg C	On control baord
4.5	Set RIGHT vessel to +10 deg C	On control board
5.0	EG Nozzel Heating Settings	-
5.1	Switch On nozzle heating system	Located on control panel in cabinet
5.2	Set Pump Temperature Controller to 40 C	On control panel
5.3	Open GS-1	-
5.4	Close GS-2	-
6.0	HP Hydrate Production	-
6.1	Allow 4-6 hours for the Vessels to stabalise.	Vessels need to be cooled to set+D42 temperature
6.2	Check TI-3	This should be - 10 C
6.3	Check Temp on hot water pump	This should be 40 C
6.4	Valve Settings	-
	Close ORS2-1	-
	Close 4P4T-9	-
	Open 44S6-1	-
	Close HV 44S6-2	-
	Close 44S6 HV 043	-
	Close IVS6-1	-
	Close IVS6-2	-
	Open 44S6-3	-
	Close APDGF4-1	-
	Close APDGF4-2	-
	Close 4P4T-3	-
	Close 4P4T-4	-
	Close 4P4T-7	-
	Open 44S6-4	-
	Open 44S6-5	-
	Close IVS6-1	-
	Close 4P4T-8	-
	Close 4P4T-11	3HNK-1 is a parallel valve to 4P4T-11
	Open 44S6-6	-
	Open 44S6-7	-

ITEM	TASK DESCRIPTION	COMMENTS
	Close IVS6-02	-
	Close HPR-2	-
	Close 18RF8-1	-
	Open 18RF8-2	-
	Close 4P4T-1	-
	Close 4P4T-2	-
	Close 45F8-1	-
	Close 45F8-2	-
	Close 43S4	-
	Close 4P4T -10	-
6.5	Open OTBV40-1	-
6.6	Compressor/Liquor Pump Operation	-
	Energise liquor pump P-002 remotely	Located on main switch board in cabinet
	Energise compressor C001/M001 remotely	Located on main switch board in cabinet
	Check for gas	Check portable gas sensor
	Start the compressor C001/M001 locally	Located on control console of PP
6.7	Allow Pressure build-up for 3-4 min	-
	Check PI-09 and PI-01	Indicators should read 12,000 to 15,000 kPa
6.8	Start the liquor pump P002 locally	Located on control console of PP
	Set Pump Capacity to control liquor flow	Setting knob located on pump
	Check PI-08	Indicators should read 12,000 ~15,000 kPa (See note 1)
6.9	Open HPR-2	Note if PI-08 exceeds 0 C stop Liquor pump P-002
6.10	Open ADPGF4-2 (Recycle path)	This will recycle gas and control vessel pressure V001
6.11	Check 4P4T-8 Close	Gas Recycled
6.12	Initiate Experimental Readings	Refer Spreadsheet EXSH -1
6.13	Production time 30 min	Time based on producing approx 3 litres of Hydrates
7.0	Controlled plant shut down	Production should never exceed 5 litres due to
7.1	Stop Water Pump locally	Potential consequences of ice build up in vessel
7.2	Operate the Compressor for 2~3 min	-
7.3	Stop Compressor in locally	-
7.4	Valve Settings	-
	Close OT58BV40-1	Main gas supply to plant
	Close HPR-2	-
	Open IVS6-1	-
	Close 18RF8-2	-
	Open APDGF4-2	-
	Open 4P4T-8	-
	If Meatering Vent Gas	-
	Open 4P4T-7	-
	Set LPR-3	High Pressure Gas control
	Open 4P4T-8	-
	If not meatering	-
	Open 4P4T-11	-
	Open 3HNR-1	-

(Page 3 of 3)

ITEM	TASK DESCRIPTION	COMMENTS
	Open 4P4T-9	-
	Open 4P4T-1	-
8.0	Hydrate Product Removal	Read Section 6.0 of plant procedures
	Open the Bottom flange lock	-
	Open bottom Flange	-
	Breakup ice on bottom of vessel V-002	Achieved by gently forcing steel bar through
<p>Note 1: Indicators PI-04 and PI-05 may be subject to overpressure under certain operating conditions. Consequently these indicators should be isolated. If pressure indication is required the excess pressure should be vented using the bleed valve provided.</p>		

APPENDIX J - Plant Make Safe (Page 1 of 2)

IF IN DOUBT STOP PROCEDURE AND ASK		
CHECKLIST 4 – PLANT MAKE SAFE		
ITEM	TASK DESCRIPTION	COMMENTS
1.0	Check the Controlled Plt Shut Down Checklist	This needs to be completed
2.0	System Pressurising	-
2.1	Vessel Sealing	-
	Check V-004 has Min. Pressure of 100 psi	-
	Ensure bottom flanges on V-002, V-003 are closed.	-
	Close main cylinder valves on V-005 and V-006	-
2.2	Valve Settings	-
	Close 44S6 HV 043	-
	Close 4P4T-8	-
	Close 4P4T-9	-
	Close OT58BV40-1	Main gas supply valve
	Close 44S6-2	-
	Close 4P4T-3	-
	Close 4P4T-4	-
	Close 4P4T-5	-
	Close 4P4T-6	-
	Close 4P4T-7	-
	Close IVS4-1	-
	Close IVS4-2	-
	Close IVS6-1	-
	Close IVS6-2	-
	Close 4P4T-2	-
	Close 45F8-1	-
	Close 4P4T-10	-
	Close 4P4T-1	-
	Close 45F8-2	-
	Close 4P4T-11	-
	Open 44S6-1	-
	Open 44S6-3	-
	Open 44S6-4	-
	Open 44S6-5	-
	Open 44S6-7	-
	Open 44S6-8	-
	Open 18RF8-2	-
	Open 18RF8-1	-
	Open HPR-2	-
	Open APDGF4-1	-
	Open APDGF4-2	-
2.3	Pressurizing	-
	Open 4456 HV 043	-
	Check PI-09	This should be around 700 kPa
	Close 44S6 HV 043	-
	Check PI-09	This should still be around 700 kPa

(Page 2 of 2)

ITEM	TASK DESCRIPTION	COMMENTS
	Check PI-10 = PI-09	Check to ensure no liquor left in MX-001
3.0	Nozzle Hot Water System	-
	Switch off system	Located in main cubicle
	Check Glychol tank	This should be left full
4.0	Electrical System	-
	Switch off system locally	Located on control console
	Switch Off Emergency Switch	Located on control console
	Switch Off system	Located on main switch board in cubicle
	Switch of Refrigeration in the Control Panel	Located on main switch board in cubicle
	Switch Off Instrumentation system	Located on main switch board in cubicle
5.0	Visual inspection of plant periodically	Min 48 hour period

APPENDIX K - Natural Gas Hydrate Project

ENGINEERING CHANGE REQUEST

Date: _____ **Change Request No :** _____

1. Proposal Definition:

2. Is the Proposal a change to the existing facility?

3. Establish a cost estimate:

Description	Cost

4. Review and Approval of Change Request:

Curtin University	Woodside

5. Details of funds available for this Proposal?

6. Action: Detail Design, Procurement, Contracting, Fabrication, Installation, Commissioning, Handover, Job close out.

<i>Action</i>	<i>In charge</i>

7. Close out Project files, Archives documents:
