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STUDY OF GELLED LNG

Final Technical Report

By

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January 1980

Work Performed Under Contract No. AC03-78EV02057

Aerojet Energy Conversion Company
Sacramento, California

U. S. DEPARTMENT OF ENERGY

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DOE Contract No. EP-78-C-03-2057 (Old)
DE-AC-03-78EV02057 (New)

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Final Technical Report
DOE Contract No. DE-AC-03-78EV02057

STUDY OF GELLED LNG

Report No. DE-AC-03-78EV02057-F

January 1980

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FOREWARD

A program was undertaken at the Aerojet Energy Conversion Company (AECC) under Contract DE-AC-03-78EV02057* with the Department of Energy (DOE), the objectives of which were to obtain basic data to characterize gelled LNG rheology and safety aspects and to conduct an industrial scale gelation system study.

Department of Energy Program Management and Technical Direction was by Dr. Henry F. Walter of the Fossil and Inexhaustible Technologies Branch of the Environmental Control Technology Division. Dr. Myron Gottlieb and Dr. William E. Mott are the respective managers of those organizations.

Aerojet Energy Conversion Company Program Management was by Mark Rudnicki. The experimental work was under the direction of Dr. Gene Vander Wall with Jackie Cabeal and Kent Schaplowsky performing the experiments. Larry Hoffman and Ron Newton were responsible for the preliminary design and economic studies.

Professor Robert C. Reid of Massachusetts Institute of Technology provided a valuable critique of this report.

This document comprises the Final Report under the contract.

* Previous contract number assigned was EP-78-C-03-2057

ABSTRACT

Research conducted under DOE contract DE-AC-03-78EV02057 involved the characterization of gelled LNG (GELNG) with respect to process, flow, and use properties and an examination of the degree of safety enhancement attainable by gelation. The investigation included (1) an experimental examination of gel properties and gel safety characteristics as well as (2) an analytical study involving the economics and preliminary design of an industrial scale gelation system.

The safety-related criterion for successful application of gelled LNG is the substantial reduction of the Maximum Distance to the Lower Flammability Limit, MDLFL. This will be achieved by first, gel-inhibition of the hydrodynamic pooling and spreading of the spill, and second, the suppressed thermal transport properties of the GELNG relative to those of LNG.

Experimental work on this contract revealed the superiority of water over methanol as a gelling agent for LNG on the basis of minimization of gelant required to obtain a given gel structure. Yield stresses were measured over a range of gel conditions and were found to increase with increasing gelant content. Similarly, determinations of rheological characteristics were conducted, revealing effects of gelant concentration in the carrier gas and end product GELNG. Gels flowed easily through flow coils, exhibiting shear thinning with no evidence of gel structure degradation even after repeated shearing. Gel expulsion from tanks was found to be dependent on tank surface area. Expulsion efficiencies greater than 90 percent of those exhibited by LNG were obtained for gels using a tank with a surface area to volume ratio as large as 8.5 ft^{-1} . There was little difference found between boiloff rates of LNG and GELNG under simulated storage conditions of low and moderate heat fluxes; further work in this area is suggested to define the heat flux level at which GELNG shows significant effectiveness. Five gallon unconfined spills showed that gelation significantly increases total spill vaporization times and decreases maximum spill spread areas. Vaporization rates determined from 0.4 gallon confined spills on sand, concrete, and water were also found to be lower for gels than for LNG. Rates were decreased as much as five-fold at some points along the

ABSTRACT (cont.)

vaporization rate vs time curves for sand and concrete spill tests rates were found to decrease by more than two times at some points along water spill vaporization rate curves. It was found that 2 weight % gelant GELNG could not be driven through a simulated crack, even at up to 20 psig driving pressure; LNG was found to flow freely at lower pressures.

The industrial scale gelation study evaluated a design capable of producing 11,000 gallons (LNG tank truck) of gel in two hours. The increased cost of gelation using this equipment was estimated at \$0.23/10⁶ Btu for plants with liquefaction facilities.

The technical results of this study are supportive of the conclusion that gelation of LNG will reduce, relative to ungelled LNG, the hazard associated with a given size spill. Parameters of interest to the LNG facility operator (such as pumpability) are not significantly affected by gelation, and the impact on LNG delivery cost appears to be small, about 5%. Thus, the initial assumption that gelation would provide a practical means to enhance safety is supported by the results of this study. Larger scale, comparative spill tests of LNG and GELNG are now required to confirm the safety aspects of use of the gelled material.

TABLE OF CONTENTS

	<u>Page</u>
1.0 Introduction	1
2.0 Experimental Results and Discussion	3
2.1 Task 1 - Gel Preparation	3
2.1.1 Gel Production	3
2.1.2 Gelant Selection	6
2.1.3 Gel Preparation	6
2.2 Task 2 - Gel Characterization	7
2.2.1 Yield Stress	7
2.2.2 Rheological Characteristics	14
2.2.3 Flow Characteristics Under Simulated Transfer Conditions	50
2.2.4 Expulsion Behavior	55
2.2.5 Gel Aging Characteristics	60
2.2.6 Boil-Off Rates Under Simulated Storage Conditions	62
2.3 Task 3 - Safety Evaluation Tests	70
2.3.1 Task 3.1 - Spill Behavior	72
2.3.2 Task 3.2 - Leakage Behavior	84
2.3.3 Task 3.3 - Boil-off Behavior	93
3.0 Results of Industrial Scale Gelation Process Studies	118
3.1 Task 4 - Preliminary Design of an Industrial Scale Gelation System	118
3.1.1 Preliminary Specification	118
3.1.2 Preliminary Design	119
3.2 Task 5 Preliminary Economic Assessment	121
4.0 Conclusions and Recommendations	126
4.1 Conclusions	126
4.1.1 Gel Preparation	126
4.1.2 Yield Stress	126
4.1.3 Rheological Characteristics	127

TABLES OF CONTENTS (cont.)

	<u>Page</u>
4.1.4 Flow Characteristics Under Simulated Transfer Conditions	128
4.1.5 Expulsion Behavior	128
4.1.6 Gel Aging Characteristics	128
4.1.7 Boil-off Rates Under Simulated Storage Conditions	128
4.1.8 Spill Behavior	129
4.1.9 Leakage Behavior	129
4.1.10 Boil-Off Behavior	129
4.1.11 Preliminary Design of an Industrial Scale Gelation System	130
4.1.12 Preliminary Economic Assessment	130
4.2 Recommendations	130
References	132
Appendix I - Calculation of the Effective Length of Flow Coils and Ancillary Transfer System	133

LIST OF TABLES

<u>Table No.</u>		<u>Page</u>
2.2.1-1	Yield Stress Data for Methane and LNG Gels at 102°K Prepared Using Approximately 25 Vol. % Water Gelant in the Injection Gas Stream	12
2.2.1-2	Yield Stress Data for LNG Gels at 102°K Prepared Using Water and Methanol Gelants	15
2.2.1-3	Yield Stress Data for LNG Gels at 102°K Prepared Using Various Amounts of Water Vapor Gelant in the Injection Gas Stream	16
2.2.2-1	Characteristic Flow Data ¹ for Methane Gels at 102°K Prepared Using 25 Vol. % Water Gelant in the Injection Gas Stream	19
2.2.2-2	Characteristic Flow Data ¹ for LNG A Gels at 102°K Prepared Using 25 Vol. % Water Gelant in the Injection Gas Stream	20
2.2.2-3	Characteristic Flow Data ¹ for LNG B Gels at 102°K Prepared Using Approximately 25 Vol. % Water Gelant in the Injection Gas Stream	21
2.2.2-4	Characteristic Flow Data ¹ for LNG Gels Using Methanol Gelant at 102°K	22
2.2.2-5	Characteristic Flow Data ¹ for LNG A Gels at 102°K Prepared Using 60 Vol. % Water Gelant in the Injection Gas Stream	23
2.2.2-6	Characteristic Flow Data ¹ for LNG A Gels at 102°K Prepared Using 24 Vol. % Water Gelant in the Injection Gas Stream	24
2.2.2-7	Characteristic Flow Data ¹ for LNG A Gels at 102°K Prepared Using 10 Vol. % Water Gelant in the Injection Gas Stream	25
2.2.2-8	Characteristic Flow Data ¹ for LNG A Gels at 102°K Prepared Using 2.5 Vol. % Water Gelant in the Injection Gas Stream	26
2.2.2-9	Characteristic Flow Data for Methane Gels Determined Using a 0.190" I.D. Flow Coil ¹ at 102°K Prepared Using 25 Vol. % Water Gelant in the Injection Gas Stream	27
2.2.2-10	Characteristic Flow Data for LNG A Gels Determined Using a 0.190" I.D. Flow Coil ¹ at 102°K Prepared Using 25 Vol. % Water Gelant in the Injection Gas Stream	28

LIST OF TABLES (cont.)

<u>Table No.</u>		<u>Page</u>
2.2.4-1	Expulsion Efficiencies for Methane and LNG Gels ¹ at 102°K	57
2.2.4-2	Expulsion Efficiencies for Methane and LNG Gels ¹ Using 7 psig Driving Pressure at 102°K	59
2.2.4-3	Expulsion Efficiencies from a High Surface Area to Volume Ratio Vessel ¹ for LNG Gels ² at 102°K	61
2.2.5-1	Aging Characteristics of Methane and LNG Gels ¹ Under Static Storage Conditions at ~112°K	63
2.2.6-1	Static Boil-Off Rates at Low Heat Flux for Methane, LNG, Gelled Methane and Gelled LNG ¹	67
2.2.6-2	Static Boil-off Rates at Moderate Heat Flux for LNG A and GELNG A ¹	71
2.3.1-1	Unconfined Land Spill Test Results	77
2.3.1-2	Unconfined Water Spill Test Results	85
2.3.2-1	Orifice Leakage Behavior of LNG and GELNG ⁽¹⁾	91
2.3.2-2	Crack Leakage Behavior of LNG and GELNG ⁽¹⁾	95
3.1.2-1	GELNG Industrial-Scale System Component List	122
3.2-1	Cost Summary - GELNG Industrial Scale Plant	124

LIST OF FIGURES

<u>Figure No.</u>		<u>Page</u>
2.1.1-1	Gel Production Facility: Interior of Isothermal Gelation Enclosure	4
2.1.1-2	Gel Production Facility: View From Control Room Looking Into The Isothermal Gelation Enclosure	5
2.2.1-1	Yield Stress Spheres	9
2.2.1-2	Weighted Sphere Yield Stress Determination Apparatus	10
2.2.2-1	Characteristic Flow Coils	18
2.2.2-2	Characteristic Flow Curves of Gelled Methane at 120°K Prepared Using 25 Vol. % Water Gelant in the Injection Gas Stream	29
2.2.2-3	Characteristic Flow Curves of Gelled LNG A at 102°K Prepared Using 25 Vol. % Water Gelant in the Injection Gas Stream	30
2.2.2-4	Characteristic Flow Curves of Gelled LNG B at 102°K Prepared Using 25 Vol. % Water Gelant in the Injection Gas Stream	31
2.2.2-5	Characteristic Flow Curves of Gelled LNG A at 102°K Using Methanol Gelant	32
2.2.2-6	Characteristic Flow Curves of Gelled LNG A at 102°K Prepared Using 60 Vol. % Water Gelant in the Injection Gas Stream	33
2.2.2-7	Characteristic Flow Curves of Gelled LNG A at 102°K Prepared Using 24 Vol. % Water Gelant in the Injection Gas Stream	34
2.2.2-8	Characteristic Flow Curves of Gelled LNG A at 102°K Prepared Using 10 Vol. % Water Gelant in the Injection Gas Stream	35
2.2.2-9	Characteristic Flow Curves of Gelled LNG A at 102°K Prepared Using 2.5 Vol. % Water Gelant in the Injection Stream	36
2.2.2-10	Characteristic Flow Curves of Gelled LNG A and Gelled Methane at 102°K Prepared Using 25 Vol. % Water Gelant in the Injection Gas Stream	37
2.2.2-11	Characteristic Flow Curves of Gelled LNG B and Gelled Methane at 102°K Prepared Using Approximately 25 Vol. % Water Gelant in the Injection Gas Stream	38

LIST OF FIGURES (cont.)

<u>Figure No.</u>		<u>Page</u>
2.2.2-12	Characteristic Flow Curves of Gelled LNG A and Gelled LNG B at 102°K Prepared Using Approximately 25 Vol. % Water Gelant in the Injection Gas Stream	39
2.2.2-13	Characteristic Flow Curves of Gelled LNG A Using Water Gelant (10 Vol. % in Injection Gas Stream) or Methanol Gelant (9.6 Vol. % in Injection Gas Stream) at 102°K	40
2.2.2-14	Characteristic Flow Curves of Gelled Methane for Two Flow Coils at 102°K Prepared Using 25 Vol. % Water Gelant in the Injection Gas Stream	41
2.2.2-15	Characteristic Flow Curves of Gelled LNG A for Two Flow Coils at 102°K Prepared Using 25 Vol. % Water Gelant in the Injection Gas Stream	42
2.2.2-16	Laminar Flow Constraint Relationship	47
2.2.2-17	Composite of All Shear Experimental Data	48
2.2.2-18	Shear Diagram for GELNG	49
2.2.3-1A	Temperature versus Time During Transfer of LNG A Through a 0.18-in. I.D. Tube Surrounded by Gaseous Nitrogen	51
2.2.3-1B	Temperature versus Time During Transfer of LNG A Through a 0.18-in. I.D. Tube Surrounded by Gaseous Nitrogen	52
2.2.3-2A	Temperature versus Time During Transfer of Gelled LNG A Through a 0.18-in. I.D. Tube Surrounded by Gaseous Nitrogen	53
2.2.3-2B	Temperature versus Time During Transfer of Gelled LNG A Through a 0.18-in. I.D. Tube Surrounded by Gaseous Nitrogen	54
2.2.6-1	Dewar Boil-off Test Apparatus	65
2.2.6-2	Polystyrene Vessel Boil-off Test Apparatus	66
2.2.6-3	Moderate Heat Flux Boil-off Test Vessel	69
2.3.1-1	Modified M.I.T. Spill Apparatus Testing with LNG A	74
2.3.1-2	Modified M.I.T. Spill Apparatus Testing with Gelled LNG A	75
2.3.1-3	Unconfined LN ₂ Land Spill - Test #1	78
2.3.1-4	Unconfined LNG Land Spill - Test #2	79

LIST OF FIGURES (cont.)

<u>Figure No.</u>		<u>Page</u>
2.3.1-5	Unconfined Gelled LNG Land Spill - Test #3	80
2.3.1-6	Unconfined Gelled LNG Land Spill - Test #4	81
2.3.1-7	Unconfined LN ₂ Land Spill - Test #5	82
2.3.1-8	Unconfined Gelled LNG Land Spill - Test #6	83
2.3.1-9	Unconfined LNG Water Spill - Test #1	86
2.3.1-10	Unconfined Gelled LNG Water Spill - Test #2	87
2.3.2-1	Leakage Vessel	89
2.3.2-2	Leakage Test Apparatus	90
2.3.2-3	A Section of the Leakage Test Crack Magnified 31.5 Times	94
2.3.3-1	Confined Spill Vaporization Apparatus	97
2.3.3-2	Vaporization Rate of Liquid Methane and Methane Gels on Water	98
2.3.3-3	Vaporization Rate of LNG A and LNG B Gels on Water	99
2.3.3-4	Vaporization Rate of LNG B and LNG B Gels on Water	100
2.3.3-5	Vaporization Rate of LNG A Gels on Water	101
2.3.3-6	Vaporization Rate of LNG B Gels on Water	102
2.3.3-7	Vaporization Rate of Liquid Methane and Methane Gels on Silica Sand	104
2.3.3-8	Vaporization Rate of LNG A and LNG A Gels on Silica Sand	105
2.3.3-9	Vaporization Rate of LNG B and LNG B Gels on Silica Sand	106
2.3.3-10	Vaporization Rate of LNG A Gels on Silica Sand	107
2.3.3-11	Vaporization Rate of LNG A and Gelled LNG A on Silica Sand in the Presence of an Ignition Source	109
2.3.3-12	Concrete Spill Basin	110
2.3.3-13	Contained LNG A Spill on Concrete	112
2.3.3-14	Contained LNG B Spill on Concrete	113
2.3.3-15	Vaporization of Methane and Methane Gel on Concrete	114
2.3.3-16	Vaporization of LNG A and LNG A Gel on Concrete	115

LIST OF FIGURES (cont.)

<u>Figure No.</u>		<u>Page</u>
2.3.3-17	Vaporization of LNG B and LNG B Gel on Concrete	116
2.3.3-18	Vaporization of LNG A Gels on Concrete	117
3.1.2-1	Continuous Gelation Plant Schematic, Conversion LNG to GELNG	120

1.0 INTRODUCTION

The projected importation of large quantities of LNG into the U.S., as a result of the domestic natural gas shortage, has generated considerable public concern and resistance because of the potential danger of catastrophic explosion or asphyxiation from vapor clouds formed by the rapid evaporation of accidentally spilled LNG. Projections of LNG imports of about 5 billion cfpd in 1980 and over 10 billion cfpd by 1990 indicate that by 1990 ships will be off-loading at the rate of five ships per day with about 15 LNG carriers in U.S. ports at all times. Therefore, the potential for accidental spills resulting from collision, etc. cannot be considered negligible, and the consequences of a major spill, especially in a populated and/or industrial area, are totally unacceptable.

One characteristic of an LNG spill is its rapid spread over the spill surface, creating a very large heat transfer area and, hence, very rapid evaporation. Preventing the rapid spread of the spill would reduce the overall evaporation rate to a level where natural dispersion could keep cloud concentrations to an acceptable level. If, in addition, a means could be found to reduce the evaporation rate per unit surface area of the spilled LNG, this would reduce the overall evaporation rate even further. A promising method of preventing the rapid spread of spilled LNG and reducing its vaporization per unit surface area is to convert the liquid to a semi-solid (viscoelastic) state by gelation.

A method for gelling methane using water and methanal gelants was developed by Aerojet for utilization with the methane fuel and other hydrocarbons. Aerojet processes are covered by U.S. Pat #4,011,730 and other inventions. The program resulted in the development of methane gels which could essentially prevent the solubilization of nitrogen in the fuel. Subsequent work by Lucile M. Shanes⁽²⁾ at the Massachusetts Institute of Technology was directed towards a fundamental understanding of gelants and gel characteristics.

1.0, Introduction (cont.)

The objective of the investigation considered here was to characterize gelled LNG for process, flow, and use properties and to demonstrate the degree of safety enhancement which can be achieved by gelation. To attain the objective a five task technical program was planned. The tasks were:

Task 1 - Gel Preparation

Task 2 - Gel Characterization

Task 3 - Safety Evaluation Tests

Task 4 - Preliminary Design of an Industrial Scale Gelation System

Task 5 - Preliminary Economic Assessment

The results of the investigation are presented in this report. The report is organized in the following manner: 1.0, Introduction; 2.0, Experimental Results and Discussion; 3.0, Results of Industrial Scale Gelation Process Studies, and 4.0, Conclusions and Recommendations.

2.0 EXPERIMENTAL RESULTS AND DISCUSSION

Experimental work performed on the program was directed toward completion of the first three tasks. Accordingly, the results are presented under the following headings: 2.1, Task 1 - Gel Preparation; 2.2, Task 2 - Gel Characterization, and 2.3, Task 3 - Safety Evaluation Tests.

2.1 TASK 1 - GEL PREPARATION

Performance of the gel preparation task served two distinct functions. It produced gels for the characterization and safety evaluation tasks, and furnished information concerning gelant selection.

2.1.1 Gel Production

The batch gel production facility assembled under this task is shown in Figures 2.1.1-1 and 2.1.1-2. This facility allowed for the preparation and evaluation of approximately four liter quantities of gel. These four liter batches were used for the characterization studies of Task 2 and in most of the safety evaluation testing performed in Task 3. When five gallon quantities of gel were required for unconfined spill testing under Task 3, multiple batch preparations were utilized. A total of approximately 90 gels were prepared for characterization and safety testing.

Methane and two distinct LNG compositions containing heavier hydrocarbons were selected for gelation studies. The two LNG compositions were designated LNG A and LNG B with LNG A containing nominally 93% CH_4 and 7% C_2H_6 and LNG B containing nominally 85% CH_4 , 10% C_2H_6 , and 5% C_3H_8 . Nitrogen was not considered as a compositional variable in this study, since it was believed that small concentrations of nitrogen in LNG would not significantly affect gel behavior. LNG samples used in gelation and baseline testing were prepared by condensing component gases and then mixing liquid volumes corresponding to the desired LNG composition.

Figure 2.1.1-1. Gel Production Facility: Interior of Isothermal Gelation Enclosure

Figure 2.1.1-2. Gel Production Facility: View from Control Room
Looking Into the Isothermal Gelation Enclosure

2.1, Task 1 - Gel Preparation (cont.)

The LNG composition of gels was determined from the known composition of the initial LNG by attributing volume change during gelation to the addition of gelant and the vaporization of methane. Gelant content of gels was obtained by vaporizing a known volume of gel and weighing the remaining gelant.

2.1.2 Gelant Selection

Two gelant candidates, methanol and water, were investigated with respect to properties exhibited by gels produced using each gelant. Gels utilizing each gelant candidate were characterized according to yield stress and rheological characteristics. Data for these determinations is presented under Task 2 in Sections 2.2.1.3 and 2.2.2.1.4. The data show that significantly more gelant was required for methanol gels to obtain the same degree of structure as water gels. Water was the obvious gelant choice for applications requiring a minimum amount of gelant. For this reason, only water gelant gels were investigated in the remaining work performed in this program. (Note the exception of previously cited work reported upon in Sections 2.2.1.3 and 2.2.2.1.4.)

2.1.3 Gel Preparation

The gels prepared under this task involved different concentrations of gelant in the injection gas stream. Gelant injection concentrations were assumed to affect the dispersion of gelant in the liquid to be gelled. Low concentrations would most likely produce the best dispersion.

Gels prepared using a variety of gelant injection stream concentrations were characterized according to yield stress and rheological characteristics. The data for these characterizations are presented in Sections 2.2.1.4 and 2.2.2.1.5, respectively. The trends observed in this

2.1, Task 1 - Gel Preparation (cont.)

set of tests made it evident that gelant injection concentration had an observable effect on gel properties over the range of injection concentrations investigated. Gels required less gelant to attain a given structure when prepared using a lower gelant injection concentration.

A gelant injection stream concentration of 25 volume percent was used for gels prepared throughout the remainder of this work (except Sections 2.2.1.4 and 2.2.2.1.5). This concentration was chosen in order to provide adequate dispersion without requiring excessively long gelation times. It should be kept in mind that conclusions drawn concerning certain gelant content gels in this report are often dependent on gelant dispersion and may therefore vary slightly if other preparation methods are used.

2.2 TASK 2 - GEL CHARACTERIZATION

Physical characteristics of LNG gels and their variation with gelant content, gel composition, gelant type, and method of preparation were examined. Gels were characterized according to six properties: (1) yield stress; (2) rheological characteristics; (3) flow characteristics under simulated transfer conditions; (4) expulsion behavior; (5) gel aging characteristics; and (6) boil-off rates under simulated storage conditions.

2.2.1 Yield Stress

Yield stress measurements were made on approximately 90 gels prepared under Task 1 (Section 2.1) using the weighted sphere method. The method involved the determination of the maximum weight sphere that could be supported by a given gel. Four glass spheres of the same diameter, containing various amounts of mercury to provide a range of weights, were employed.

2.2, Task 2 - Gel Characterization (cont.)

The spheres were calibrated using a series of water-carbapol 940 gels whose yield stresses had been determined with a cone penetrometer. Calibrations showed that support of half of the sphere above the gel surface corresponded to 270 dynes/cm², 771 dynes/cm², 973 dynes/cm², and 1311 dynes/cm² for the four spheres used. Examples of the weighted spheres used for yield stress determinations are shown in Figure 2.2.1-1.

Gels to be tested by the weighted sphere method were first transferred to a 700 cc cylindrical pyrex vessel maintained at 102°K. One of the spheres which had been pre-cooled in liquid nitrogen was then gently lowered onto the gel surface. The region of support within the gel was noted and the sphere was removed. The process was repeated using other spheres until the maximum weight sphere with at least half of its volume supported above the gel surface was determined. Figure 2.2.1-2 shows a yield stress sphere in the structure determination flask as viewed from the interior of the isothermal gelation enclosure.

It is important to note that yield stresses determined by the weighted sphere method actually represent a yield stress range. This range corresponds to yield stress values between the maximum weight supported and the minimum weight which fails to be supported. Since values listed in this report are determined from the maximum supported weight, they represent minimum yield stress values.

Yield stresses for methane and LNG gels were found to vary with gelant content, gel composition, gelant type, and injection gelant concentration.

Figure 2.2.1-1. Yield Stress Spheres

Figure 2.2.1-2. Weighted Sphere Yield Stress Determination Apparatus

2.2, Task 2 - Gel Characterization (cont.)

2.2.1.1 Variation of Yield Stress with Gelant Content

Under the conditions of similar composition and similar preparation methods using a single gelant type, yield stresses for LNG and methane gels were found to increase with gelant content over the range of conditions investigated. This can perhaps best be seen through an examination of each of the three sections of Table 2.2.1-1. Each section of the table presents data for one gel composition type prepared using approximately 25 volume percent water vapor gelant in the injection gas stream. Gelant contents investigated in the table range from 3.8 to 6.5 weight percent for LNG B gels, from 2.2 to 5.5 weight percent for LNG A gels, and from 1.6 to 4.6 weight percent for methane gels. Over these condition ranges the observed yield stress trend was evident with only a few minor exceptions. These exceptions generally occurred at gelant contents corresponding to yield stresses near the extremes of two adjacent sphere test ranges. Measurements made at these gelant contents would be strongly affected by slight deviations in test and preparation conditions. This roughness in the data could be reduced in future testing by using a larger number of weighted spheres.

2.2.1.2 Variation of Yield Stress with Hydrocarbon Composition of the Gel

A comparison between the three sections of Table 2.2.1-1 reveals that yield stresses were less for LNG gels than for methane gels when the gels compared were of similar gelant content with similar preparation histories using a single gelant type. Yield stresses for the two types of LNG gels examined did not differ significantly over the range of conditions investigated. Gel condition ranges in this investigation included a preparation method using approximately 25 volume percent water vapor gelant with gelant contents varying from 3.8 to 4.6 weight percent.

TABLE 2.2.1-1

YIELD STRESS DATA FOR METHANE AND LNG GELS AT 102°K
 PREPARED USING APPROXIMATELY 25 VOL % WATER
 GELANT IN THE INJECTION GAS STREAM

Approximate LNG Composition of Gel (Vol. % as Gas)			Gelant	Volume % Gelant in Injection Gas Stream	Wt. % Gelant	Yield Stress ² (dynes/cm ²)
Methane	Ethane	Propane				
84	11	5	Water	25	3.3	771
85	10	5	Water	25	3.5	771
88	8	4	Water	26	3.8	771
85	10	5	Water	25	4.0	270
85	10	5	Water	25	4.1	771
77	15	8	Water	25	4.3	973
81	13	6	Water	25	4.3	973
84	11	5	Water	25	4.4	973
85	10	5	Water	26	4.6	973
85	10	5	Water	25	6.5	973
93	7	0	Water	24	2.2	<270
90	10	0	Water	25	2.6	<270
91	9	0	Water	24	2.8	<270
93	7	0	Water	25	2.8	<270
89	11	0	Water	25	2.9	270
93	7	0	Water	25	2.9	270
93	7	0	Water	25	3.0	270
93	7	0	Water	25	3.0	270
91	9	0	Water	25	3.1	270
93	7	0	Water	25	3.1	270
93	7	0	Water	25	3.2	270
93	7	0	Water	25	3.5	270
93	7	0	Water	25	3.5	771
93	7	0	Water	25	3.6	771
88	12	0	Water	24	3.7	270
93	7	0	Water	25	3.8	771
93	7	0	Water	25	4.0	270
89	11	0	Water	26	4.1	771
93	7	0	Water	25	4.1	973
85	15	0	Water	24	4.4	771
93	7	0	Water	25	4.6	771
87	13	0	Water	26	4.7	1311
91	9	0	Water	25	4.7	973
93	7	0	Water	25	5.5	973

TABLE 2.2.1-1 (cont.)

Approximate LNG Composition of Gel (Vol. % as Gas)			<u>Gelant</u>	Volume % Gelant in Injection Gas Stream	Wt. % Gelant	Yield Stress ² (dynes/cm ²)
<u>Methane</u>	<u>Ethane</u>	<u>Propane</u>				
100	0	0	Water	25	1.6	≤270
100	0	0	Water	25	1.9	270
100	0	0	Water	25	2.7	270
100	0	0	Water	25	2.9	771
100	0	0	Water	26	3.5	771
100	0	0	Water	25	3.6	771
100	0	0	Water	25	3.7	771
100	0	0	Water	25	3.8	973
100	0	0	Water	25	4.3	973
100	0	0	Water	25	4.3	>1311
100	0	0	Water	25	4.6	1311

2.2, Task 2 - Gel Characterization (cont.)

2.2.1.3 Variation of Yield Stress with Gelant Type

Two gelant candidates, water and methanol, were examined with respect to the yield stresses exhibited by their corresponding LNG A gels. LNG A gelled with methanol required significantly more gelant to achieve yield stresses corresponding to those measured for gels gelled with water. This indicates that yield stresses for methanol gels would be much less than those for water gels when both types of gels were prepared using similar injection gelant concentrations, similar gel compositions, and similar gelant contents. This trend may be derived from the data in Table 2.2.1-2 for gel condition ranges listed in the table. The range of conditions investigated included a composition similar to LNG A, gelant injection stream concentrations varying from 2.5 to just under 10 volume percent, and gelant contents up to 27 weight percent for methanol gels.

2.2.1.4 Variation of Yield Stress with Injection Gelant Concentration

Yield stress measurements were made on gels with differing preparation histories. The specific variation in gel preparation involved changes in the gelant concentration of the injection gas stream. Yield stresses increased with decreasing gelant concentration for gels of similar composition, similar gelant content, and the same gelant type. Table 2.2.1-3 shows this trend for LNG A gels. Specific points of comparison are shown on the table.

2.2.2 Rheological Characteristics

Two types of tests were performed to characterize LNG and methane gels according to their rheological properties. Both types of testing involved flowing gels through coiled tubes under isothermal

TABLE 2.2.1-2

YIELD STRESS DATA FOR LNG GELS AT 102°K
PREPARED USING WATER AND
METHANOL GELANTS

Approximate LNG Composition of Gel (Volume % as Gas)		Gelant	Volume % Gelant in Injection Gas Stream	Wt. % Gelant	Yield Stress ² (dynes/cm ²)
Methane	Ethane				
94	6	Water	2.5	1.2	<270
93	7	Water	2.5	1.3	<270
89	11	Water	2.5	2.0	270
93	7	Methanol	9.6	16	<270
89	11	Methanol	9.6	22	270
86	14	Methanol	2.5	27	270

TABLE 2.2.1-3

YIELD STRESS DATA FOR LNG GELS AT 102°K PREPARED USING VARIOUS
AMOUNTS OF WATER VAPOR GELANT IN THE INJECTION GAS STREAM

Approximate LNG Composition of Gel (Volume % as Gas)		Gelant	Volume % Gelant in Injection Gas Stream	Wt. % Gelant	Yield Stress (dynes/cm ²)
Methane	Ethane				
95	5	Water	60	3.2	270
94	6	Water	60	3.7	270
92	8	Water	60	5.1	771
90	10	Water	25	2.6	270
89	11	Water	25	2.9	270
93	7	Water	24	2.2	270
91	9	Water	24	2.8	270
88	12	Water	24	3.7	270
85	15	Water	24	4.4	771
86	14	Water	19	3.1	270
79	21	Water	19	4.4	973
95	5	Water	10	1.2	270
94	6	Water	10	1.5	270
93	7	Water	10	1.9	270
90	10	Water	10	2.4	805
94	6	Water	2.5	1.2	270
93	7	Water	2.5	1.3	270
89	11	Water	2.5	2.0	270

2.2, Task 2 - Gel Characterization (cont.)

conditions. One test type was designed to provide characteristic flow data by measuring shear rates for gels flowed under selected constant shear stresses, while the other test type involved determinations of the degree of gel structure degradation resulting from repeated flow cycles at high shear rates.

2.2.2.1 Characteristic Flow Testing

Shear rates were determined in the isothermal gelation enclosure using a flow loop consisting of coiled copper tubing. Flow coils are pictured in Figure 2.2.2-1. After gel preparation, the pyrex gelation vessel was pressurized to a preselected value and a valve was opened to allow flow through the loop. The volume of gel flowing through the tubing was detected by fiducial marks in the 700 cc receiving vessel and was recorded as a function of time.

Shear rate determinations at various shear stresses were used to obtain apparent viscosities and characteristic flow curves for gels tested. Gels varying in gelant content, gel composition, gelant type, and injection gelant concentration were examined. In addition, flow characteristics were determined using two different sized flow coils. Calculations used to determine effective lengths of the two flow coils for use in shear rate determinations are provided in Appendix I.

2.2.2.1.1 General Flow Characteristics

All gels subjected to characteristic flow testing showed shear-thinning (reduction in the slope, on a log-log plot of shear stress versus shear rate, relative to a Newtonian fluid) tendencies. This was true regardless of gelant content of the gel, LNG composition of the gel, gelant type employed, or injection gelant concentration. Data showing this trend are presented in Tables 2.2.2-1 through 2.2.2-10 and Figures 2.2.2-2 through 2.2.2-15.

Figure 2.2.2-1. Characteristic Flow Coils

TABLE 2.2.2-1

CHARACTERISTIC FLOW DATA¹ FOR METHANE GELS AT 102°K PREPARED USING
25 VOL. % WATER GELANT IN THE INJECTION GAS STREAM

Wt. % Gelant	Yield Stress ² (dynes/cm ²)	Flow Velocity (cm/sec)	ΔP (psi)	Shear ² Stress ² (dynes/cm ²)	Shear Rate ¹ (sec ⁻¹)	Apparent ² Viscosity ² (centipoise)	Apparent Reynolds Number ³
2.7	270	33.3	5	54.4	337	16.1	72.7
2.7	270	242	10	109	2457	4.42	1932
2.7	270	500	15	163	5065	3.22	5472
2.9	805	32.3	10	109	327	33.2	34.3
2.9	805	218	15	163	2208	7.39	1041
4.3	>1311	21.9	15	163	222	73.4	10.7

¹Coil 2A, 0.790 cm ID.

²Shear stress and apparent viscosity are based on a calculated flow coil effective length of 1252 cm.

³Apparent Reynolds numbers are calculated using apparent viscosities.

TABLE 2.2.2-2

CHARACTERISTIC FLOW DATA¹ FOR LNG A GELS AT 102°K PREPARED
USING 25 VOL. % WATER GELANT IN THE INJECTION GAS STREAM

Approximate LNG Composition of Gel (Volume % as Gas)		Wt. % Gelant	Yield Stress (dynes/cm ²)	Shear Stress ² (dynes/cm ²)	Shear Rate (sec ⁻¹)	Apparent Viscosity ² (centipoise)	Apparent Reynolds Number ³
Methane	Ethane						
90	10	2.6	<270	32.6	132	24.7	19.5
90	10	2.6	<270	54.4	265	20.5	47.0
90	10	2.6	<270	76.1	896	8.50	384
90	10	2.6	<270	109	1631	6.67	891
89	11	2.9	270	109	792	13.7	211
89	11	2.9	270	163	1701	9.59	650

¹Coil 2A, 0.790 cm ID.

²Shear stress and apparent viscosity are based on a calculated flow coil effective length of 1252 cm.

³Apparent Reynolds numbers are calculated using apparent viscosities.

TABLE 2.2.2-3

CHARACTERISTIC FLOW DATA¹ FOR LNG B GELS AT 102°K
 PREPARED USING APPROXIMATELY 25 VOL. %
 WATER GELANT IN THE INJECTION GAS
 STREAM

Approximate LNG Comp. of Gel (Volume % as Gas)*			Wt. % Gelant	Yield Stress ² (dynes/cm ²)	Shear Stress ² (dynes/cm ²)	Shear Rate ¹ (sec ⁻¹)	Apparent Viscosity ² (centipoise)	Apparent Reynolds Number
<u>Methane</u>	<u>Ethane</u>	<u>Propane</u>						
25 Vol. % Gelant in the Injection Gas Stream								
85	10	5	6.5	973	272	4088	6.65	2380
26 Vol. % Gelant in the Injection Gas Stream								
88	8	4	3.8	771	54.4	243	22.4	40.9
88	8	4	3.8	771	87.0	576	15.1	144
88	8	4	3.8	771	109	1071	10.2	397
88	8	4	3.8	771	131	1770	7.37	904
88	8	4	3.8	771	163	2649	6.16	1619

¹Coil 2A, 0.790 cm ID.

²Shear stress and apparent viscosity are based on a calculated flow coil effective length of 1252 cm.

³Apparent Reynolds numbers are calculated using apparent viscosities.

TABLE 2.2.2-4

CHARACTERISTIC FLOW DATA¹ FOR LNG GELS USING
METHANOL GELANT AT 102°K

Approximate LNG Comp. of Gel (Volume % as Gas)		Wt. % Gelant	Yield Stress (dynes/cm ²)	Shear Stress ² (dynes/cm ²)	Shear Rate ¹ (sec ⁻¹)	Apparent Viscosity ² (centipoise)	Apparent Reynolds Number ³
Methane	Ethane						
9.6 Vol. % Gelant in the Injection Gas Stream							
93	7	16	<270	32.6	303	10.8	108
93	7	16	<270	54.4	799	6.81	452
89	11	22	270	87.0	464	18.8	101
89	11	22	270	109	1323	8.22	654
2.5 Vol. % Gelant in the Injection Gas Stream							
86	14	27	270	54.4	363	15.0	103
86	14	27	270	65.3	490	13.3	157
86	14	27	270	109	906	12.0	321

¹Coil 2A, 0.790 cm ID.

²Shear stress and apparent viscosity are based on a calculated flow coil effective length of 1252 cm.

³Apparent Reynolds numbers are calculated using apparent viscosities.

TABLE 2.2.2-5

CHARACTERISTIC FLOW DATA¹ FOR LNG A GELS AT 102°K PREPARED
USING 60 VOL. % WATER GELANT IN THE INJECTION GAS STREAM

Approximate LNG Comp. of Gel (Volume % as Gas)		Wt. % Gelant	Yield Stress (dynes/cm ²)	Shear Stress ² (dynes/cm ²)	Shear Rate ¹ (sec ⁻¹)	Apparent Viscosity ² (centipoise)	Apparent Reynolds Number ³
Methane	Ethane						
95	5	3.2	<270	54.4	513	10.6	172
95	5	3.2	<270	76.1	1472	5.17	1013
95	5	3.2	<270	109	2812	3.87	2587
94	6	3.7	<270	76.1	282	27.0	37.5
94	6	3.7	<270	109	522	20.8	89.6
94	6	3.7	<270	163	2270	7.18	1132
92	8	5.1	771	141	810	17.4	170
92	8	5.1	771	163	825	19.8	152
92	8	5.1	771	185	1640	11.3	532
92	8	5.1	771	218	3689	5.89	2288

¹Coil 2A, 0.790 cm ID.

²Shear stress and apparent viscosity are based on a calculated flow coil effective length of 1252 cm.

³Apparent Reynolds numbers are calculated using apparent viscosities.

TABLE 2.2.2-6

CHARACTERISTIC FLOW DATA¹ FOR LNG A GELS AT 102°K PREPARED
USING 24 VOL. % WATER GELANT IN THE INJECTION GAS STREAM

Approximate LNG Comp. of Gel (Volume % as Gas)		Wt. % Gelant	Yield Stress (dynes/cm ²)	Shear Stress ² (dynes/cm ²)	Shear Rate ¹ (sec ⁻¹)	Apparent Viscosity ² (centipoise)	Apparent Reynolds Number ³
Methane	Ethane						
93	7	2.2	<270	54.4	355	15.3	82.8
91	9	2.8	<270	54.4	133	40.9	11.8
91	9	2.8	<270	109	546	19.9	99.3
88	12	3.7	270	109	466	23.3	74.2
88	12	3.7	270	163	1129	14.4	290

¹Coil 2A, 0.790 cm ID.

²Shear stress and apparent viscosity are based on a calculated flow coil effective length of 1252 cm.

³Apparent Reynolds numbers are calculated using apparent viscosities.

TABLE 2.2.2-7

CHARACTERISTIC FLOW DATA¹ FOR LNG A GELS AT 102°K PREPARED
USING 10 VOL. % WATER GELANT IN THE INJECTION GAS STREAM

Approximate LNG Comp. of Gel (Volume % as Gas)		Wt. % Gelant	Yield Stress (dynes/cm ²)	Shear Stress ² (dynes/cm ²)	Shear Rate ¹ (sec ⁻¹)	Apparent Viscosity ² (centipoise)	Apparent Reynolds Number ³
Methane	Ethane						
95	5	1.2	<270	32.6	366	8.90	145
95	5	1.2	<270	54.4	607	8.96	238
95	5	1.2	<270	76.1	1406	5.42	913
94	6	1.5	270	54.4	155	35.2	15.6
94	6	1.5	270	109	461	23.6	69.3
94	6	1.5	270	185	2335	7.92	1045
93	7	1.9	270	109	141	76.9	6.59
93	7	1.9	270	163	427	38.2	40.1
93	7	1.9	270	218	1615	13.5	429
90	10	2.4	805	163	182	89.8	7.34
90	10	2.4	805	218	407	53.4	27.6

¹Coil 2A, 0.790 cm ID.

²Shear stress and apparent viscosity are based on a calculated flow coil effective length of 1252 cm.

³Apparent Reynolds numbers are calculated using apparent viscosities.

TABLE 2.2.2-8

CHARACTERISTIC FLOW DATA¹ FOR LNG A GELS AT 102°K PREPARED
USING 2.5 VOL. % WATER GELANT IN THE INJECTION GAS STREAM

Approximate LNG Comp. of Gel (Volume % as Gas)		Wt. % Gelant	Yield Stress (dynes/cm ²)	Shear Stress ² (dynes/cm ²)	Shear Rate ¹ (sec ⁻¹)	Apparent Viscosity ² (centipoise)	Apparent Reynolds Number ³
Methane	Ethane						
94	6	1.2	<270	43.5	393	11.1	126
94	6	1.2	<270	54.4	848	6.41	469
93	7	1.3	<270	43.5	172	25.3	24.3
93	7	1.3	<270	54.4	385	14.1	97.3
93	7	1.3	<270	76.1	1194	6.37	669
89	11	2.0	270	76.1	222	34.4	23.6
89	11	2.0	270	109	547	19.9	100
89	11	2.0	270	163	1476	11.1	488

¹Coil 2A, 0.790 cm ID.

²Shear stress and apparent viscosity are based on a calculated flow coil effective length of 1252 cm.

³Apparent Reynolds numbers are calculated using apparent viscosities.

TABLE 2.2.2-9

CHARACTERISTIC FLOW DATA¹ FOR METHANE GELS USING 25 VOL. % WATER GELANT
IN THE INJECTION GAS STREAM

Wt. % Gelant	Yield Stress (dynes/cm ²)	Flow Velocity (cm/sec)	ΔP (psi)	Shear Stress ² (dynes/cm ²)	Shear Rate ¹ (sec ⁻¹)	Apparent Viscosity ² (centipoise)	Apparent Reynolds Number ³
1.6	<270	58.4	5	28.9	968	2.98	415
1.9	270	38.5	10	57.8	639	9.04	90.5
1.9	270	48.4	12	69.3	802	8.65	119
1.9	270	68.5	15	86.7	1135	7.63	190
2.9	771	22.0	15	86.7	365	23.7	19.8

¹Coil 1A, 0.483 cm ID.

²Shear stress and apparent viscosity are based on a calculated flow coil effective length of 1440 cm.

³Apparent Reynolds numbers are calculated using apparent viscosities.

TABLE 2.2.2-10

CHARACTERISTIC FLOW DATA¹ FOR LNG A GELS
 USING 25 VOL. % WATER GELANT IN
 THE INJECTION GAS STREAM

Approximate LNG Comp. of Gel (Volume % as Gas)		Wt. % Gelant	Yield Stress ² (dynes/cm ²)	Shear Stress ² (dynes/cm ²)	Shear Rate ⁻¹ (sec ⁻¹)	Apparent Viscosity ² (centipoise)	Apparent Reynolds Number ³
Methane	Ethane						
93	7	3.5	270	86.7	1452	5.97	327
93	7	3.5	270	116	2202	5.25	564
93	7	3.5	270	144	3562	4.05	1181

¹Coil 1A, 0.483 cm ID.

²Shear stress and apparent viscosity are based on a calculated flow coil effective length of 1440 cm.

³Apparent Reynolds numbers are calculated using apparent viscosities.

Figure 2.2.2-2. Characteristic Flow Curves of Gelled Methane at 102°K Prepared Using 25 Vol. % Water Gelant in the Injection Gas Stream (Ref. Table 2.2.2-1)

- Gelled LNG A (90 Vol. % CH₄, 10 Vol. % C₂H₆) - 2.6 wt. % water
 ○ Gelled LNG A (89 Vol. % CH₄, 11 Vol. % C₂H₆) - 2.9 wt. % water

Figure 2.2.2-3. Characteristic Flow Curves of Gelled LNG A at 102°K Prepared Using 25 Vol. % Water Gelant in the Injection Gas Stream (Ref. Table 2.2.2-2)

- Gelled LNG B (85 Vol. % CH₄, 10 Vol. % C₂H₆, 5 Vol. % C₃H₈) - 6.5 wt. % water
 ○ Gelled LNG B (85 Vol. % CH₄, 8 Vol. % C₂H₆, 4 Vol. % C₃H₈) - 3.8 wt. % water

Figure 2.2.2-4. Characteristic Flow Curves of Gelled LNG B at 102°K Prepared Using 25 Vol. % Water Gelant in the Injection Gas Stream (Ref. Table 2.2.2-3)

- Gelled LNG A (93 Vol. % CH₄, 7 Vol. % C₂H₆) - 16 wt. % CH₃OH Prepared Using 9.6 Vol. % CH₃OH in Injection Gas Stream
- Gelled LNG A (89 Vol. % CH₄, 11 Vol. % C₂H₆) - 22 wt. % CH₃OH Prepared Using 9.6 Vol. % CH₃OH in Injection Gas Stream
- Gelled LNG A (86 Vol. % CH₄, 14 Vol. % C₂H₆) - 27 wt. % CH₃OH Prepared Using 2.5 Vol. % CH₃OH in Injection Gas Stream

Figure 2.2.2-5. Characteristic Flow Curves of Gelled LNG A at 102°K Using Methanol Gelant (Ref. Table 2.2.2-4)

- △ Gelled LNG A (95 Vol. % CH₄, 5 Vol. % C₂H₆) - 3.2 wt. % water
- Gelled LNG A (94 Vol. % CH₄, 6 Vol. % C₂H₆) - 3.7 wt. % water
- Gelled LNG A (92 Vol. % CH₄, 8 Vol. % C₂H₆) - 5.1 wt. % water

Figure 2.2.2-6. Characteristic Flow Curves of Gelled LNG A at 102°K Prepared Using 60 Vol. % Water Gelant in the Injection Gas Stream (Ref. Table 2.2.2-5)

- $\triangle$ Gelled LNG A (93 Vol. % CH_4 , 7 Vol. % C_2H_6) - 2.2 wt. % water
 $\square$ Gelled LNG A (91 Vol. % CH_4 , 9 Vol. % C_2H_6) - 2.8 wt. % water
 $\circ$ Gelled LNG A (88 Vol. % CH_4 , 12 Vol. % C_2H_6) - 3.7 wt. % water

Figure 2.2.2-7. Characteristic Flow Curves of Gelled LNG A at 102°K Prepared Using 24 Vol. % Water Gelant in the Injection Gas Stream (Ref. Table 2.2.2-6)

- Gelled LNG A (95 Vol. % CH₄, 5 Vol. % C₂H₆) - 1.2 wt. % water
- △ Gelled LNG A (94 Vol. % CH₄, 6 Vol. % C₂H₆) - 1.5 wt. % water
- Gelled LNG A (93 Vol. % CH₄, 7 Vol. % C₂H₆) - 1.9 wt. % water
- Gelled LNG A (90 Vol. % CH₄, 10 Vol. % C₂H₆) - 2.4 wt. % water

Figure 2.2.2-8. Characteristic Flow Curves of Gelled LNG A at 102°K Prepared Using 10 Vol. % Water Gelant in the Injection Gas Stream (Ref. Table 2.2.2-7)

- △ Gelled LNG A (94 Vol. % CH₄, 6 Vol. % C₂H₆) - 1.2 wt. % water
- Gelled LNG A (93 Vol. % CH₄, 7 Vol. % C₂H₆) - 1.3 wt. % water
- Gelled LNG A (89 Vol. % CH₄, 11 Vol. % C₂H₆) - 2.0 wt. % water

Figure 2.2.2-9. Characteristic Flow Curves of Gelled LNG A at 102°K Prepared Using 2.5 Vol. % Water Gelant in the Injection Gas Stream (Ref. Table 2.2.2-8)

- Gelled LNG A (90 Vol. % CH₄, 10 Vol % C₂H₆) - 2.6 wt. % water
- Gelled LNG A (89 Vol. % CH₄, 11 Vol. % C₂H₆) - 2.9 wt. % water
- ▲ Gelled Methane - 2.7 wt. % water
- Gelled Methane - 2.9 wt. % water
- Gelled Methane - 4.3 wt. % water

Figure 2.2.2-10. Characteristic Flow Curves of Gelled LNG A and Gelled Methane at 102°K Prepared Using 25 Vol. % Water Gelant in the Injection Gas Stream (Ref. Tables 2.2.2-1 and -2)

- Gelled LNG B (88 Vol. % CH_4 , 8 Vol. % C_2H_6 , 4 Vol. % C_3H_8) - 3.8 wt. % water
- Gelled LNG B (85 Vol. % CH_4 , 10 Vol. % C_2H_6 , 5 Vol. % C_3H_8) - 6.5 wt. % water
- ▲ Gelled Methane - 2.7% water
- Gelled Methane - 2.9% water

Figure 2.2.2-11. Characteristic Flow Curves of Gelled LNG B and Gelled Methane at 102°K Prepared Using Approximately 25 Vol. % Water Gelant in the Injection Gas Stream (Ref. Tables 2.2.2-1 and -3)

- Gelled LNG B (88 Vol. % CH₄, 8 Vol. % C₂H₆, 4 Vol. % C₃H₈) - 3.8 wt. % water
- Gelled LNG B (85 Vol. % CH₄, 10 Vol. % C₂H₆, 5 Vol. % C₃H₈) - 6.5 wt. % water
- ▲ Gelled LNG A (90 Vol. % CH₄, 10 Vol. % C₂H₆) - 2.6 wt % water
- Gelled LNG A (89 Vol. % CH₄, 11 Vol. % C₂H₆) - 2.9 wt % water
- Gelled LNG A (88 Vol. % CH₄, 12 Vol. % C₂H₆) - 3.7 wt % water

Figure 2.2.2-12. Characteristic Flow Curves of Gelled LNG A and Gelled LNG B at 102°K Prepared Using Approximately 25 Vol. % Water Gelant in the Injection Gas Stream (Ref. Tables 2.2.2-2, -3, -6)

- Gelled LNG A (95 Vol. % CH₄, 5 Vol. % C₂H₆) - 1.2 wt. % water
- △ Gelled LNG A (94 Vol. % CH₄, 6 Vol. % C₂H₆) - 1.5 wt. % water
- Gelled LNG A (93 Vol. % CH₄, 7 Vol. % C₂H₆) - 1.9 wt. % water
- Gelled LNG A (90 Vol. % CH₄, 10 Vol. % C₂H₆) - 2.4 wt. % water
- Gelled LNG A (93 Vol. % CH₄, 7 Vol. % C₂H₆) - 16 wt. % methanol
- Gelled LNG A (89 Vol. % CH₄, 11 Vol. % C₂H₆) - 22 wt. % methanol

Figure 2.2.2-13. Characteristic Flow Curves of Gelled LNG A Using Water Gelant (10 Vol. % in Injection Gas Stream) or Methanol Gelant (9.6% Vol. % in Injection Gas Stream) at 102°K (Ref. Tables 2.2.2-4 and -7)

△	Gelled Methane - 1.6 wt.% water, Coil 1A	) 0.483 cm ID
□	Gelled Methane - 1.9 wt.% water, Coil 1A	
○	Gelled Methane - 2.9 wt.% water, Coil 1A	
▲	Gelled Methane - 2.7 wt.% water, Coil 2A	) 0.790 cm ID
■	Gelled Methane - 2.9 wt.% water, Coil 2A	
●	Gelled Methane - 4.3 wt.% water, Coil 2A	

Figure 2.2.2-14. Characteristic Flow Curves of Gelled Methane for Two Flow Coils at 102°K Prepared Using 25 Vol. % Water Gelant in the Injection Gas Stream (Ref. Tables 2.2.2-1 and -9)

- Gelled LNG A (93 Vol. % CH_4 , 7 Vol. % C_2H_6) - 3.5 wt. % water, Coil 1A
- Gelled LNG A (90 Vol. % CH_4 , 10 Vol. % C_2H_6) - 2.6 wt. % water, Coil 2A
- Gelled LNG A (89 Vol. % CH_4 , 11 Vol. % C_2H_6) - 2.9 wt. % water, Coil 2A

Coil 1A: 0.483 cm ID

Coil 2A: 0.790 cm ID

Figure 2.2.2-15. Characteristic Flow Curves of Gelled LNG A for Two Flow Coils at 102°K Prepared Using 25 Vol. % Water Gelant in the Injection Gas Stream (Ref. Tables 2.2.2-2 and -10)

2.2, Task 2 - Gel Characterization (cont.)

2.2.2.1.2 Variation of Flow Characteristics with Gelant Content

For a given set of conditions governing gel composition, gelant type, and injection gelant concentration, flow characteristics were found to vary with gelant content according to the following trends:

(a) Apparent viscosity at a given shear rate increased with gelant content. Figures 2.2.2-2 through 2.2.2-4 and accompanying data in Tables 2.2.2-1 through 2.2.2-3 show this trend for methane gels (2.7-4.3 wt. % gelant), LNG A gels (2.6-2.9 wt. % gelant), and LNG B gels (3.8-6.5 wt. % gelant) prepared using 25 volume percent water vapor gelant in the injection gas stream. Data in Figure 2.2.2-5 and Table 2.2.2-4 give evidence of the trend for LNG A gels prepared using methanol gelant at 9.6 volume percent gelant in the injection gas stream (16-22 wt. % total gelant content of gels) and at 2.5 volume percent gelant in the injection gas stream (27 wt. % total gelant content of gel). The trend is also evident in Figures 2.2.2-6 through 2.2.2-9 and accompanying Tables 2.2.2-5 through 2.2.2-8 for LNG A gels prepared using 2.5 to 60 volume percent water vapor gelant in the injection gas stream.

(b) The degree of shear thinning showed a weak tendency to increase with gelant content. The data cited above in (a) is indicative of this but not conclusive.

2.2.2.1.3 Variation of Flow Characteristics with Hydrocarbon Composition of Gels

Flow characteristics were examined for gels belonging to three different categories with respect to hydrocarbon composition. The three categories included gels containing only methane, gels containing methane

2.2, Task 2 - Gel Characterization (cont.)

and ethane (LNG A type gels), and gels containing methane, ethane and propane (LNG B type gels). For a given set of conditions governing gelant content, gelant type, and injection gelant concentration, flow characteristics were found to vary with the hydrocarbon composition of gels according to the following trends:

(a) Methane gels had higher apparent viscosities at low shear rates and exhibited a greater degree of shear thinning than corresponding LNG gels (i.e., gels containing heavier hydrocarbons). Data comparing flow characteristics for methane and LNG gels prepared using approximately 25 volume percent water vapor gelant in the injection gas stream are presented in Figures 2.2.2-10 and 2.2.2-11. The data corroborates the trend for both LNG A type gels and LNG B type gels.

(b) LNG A type gels exhibited higher apparent viscosities at given shear rates than LNG B type gels even when methane mole percentages were similar. This trend is evident from data presented in Figure 2.2.2-12 for LNG gels prepared using approximately 25 volume percent water in the injection gas stream.

2.2.2.1.4 Variation of Flow Characteristics with Gelant Type

Flow characteristics were investigated for two gelant candidates, water and methanol. For a given set of conditions governing gelant content, gel composition, and injection gelant concentration, flow characteristics were found to vary with gelant type according to the following trend:

Apparent viscosities for methanol gelant type LNG gels were significantly lower than those for corresponding water gelant

2.2, Task 2 - Gel Characterization (cont.)

type gels even at much higher gelant contents. This was found to be true for LNG A shear rates at both of the comparable injection stream gelant concentrations investigated (~10 vol. % and 2.5 vol. % gelant). Data illustrating this trend are given in Figure 2.2.2-13 for the 10% volume gelant concentration tests.

2.2.2.1.5 Variation of Flow Characteristics with Injection Gelant Concentration

The preparation variable examined was injection stream gelant concentration. For a given set of conditions governing gelant content, gel composition, and gelant type, flow characteristics were found to vary with method of preparation according to the following trend:

Apparent viscosity at a given shear rate increased with decreasing injection stream gelant concentration. Figures 2.2.2-6 through 2.2.2-9 and the corresponding data in Tables 2.2.2-5 through 2.2.2-8 show this trend for LNG A gels using water gelant.

2.2.2.1.6 Variation of Flow Characteristics with Flow Coil Size

Two different sized flow coils were employed to determine the effect of the flow system on flow characteristics. The majority of the flow measurements were made using a 0.311 in. I.D. flow coil. Measurements for methane gels and GELNG A were performed using a 0.190 in. I.D. coil for comparison purposes. Comparison flow curves obtained for the two coils are presented in Figures 2.2.2-14 and 2.2.2-15 along with accompanying data in Tables 2.2.2-1, 2.2.2-2, 2.2.2-9, and 2.2.2-10. Although data is extremely limited, it seems to indicate that apparent viscosity values at low shear rates are higher and shear thinning occurs to a greater degree

2.2, Task 2 - Gel Characterization (cont.)

for gels tested using larger diameter coils. This is reasonable since flow takes on more turbulence as tube diameter increases.

2.2.2.1.7 Remarks on Characteristic Flow Testing

Care was taken to stay close or within the laminar flow conditions so that the calculation of shear rate, i.e., $8V/D$, would be valid. The limiting relationship for flow tube inside diameter, apparent viscosity, and shear rate is shown in Figure 2.2.2-16. Thus far the shear stress vs shear rate and gelant fraction evaluation has been done in only a limited region; this region is indicated in Figure 2.2.2-17, which is a composite of all of the data obtained to date. Figure 2.2.2-18 shows the regions (shaded) wherein data is needed to fully characterize the GELNG. Resolution of gelant fraction influence has not been satisfactory, as seen from the apparent scatter. Selected Newtonian fluid viscosities, water, linseed oil, LNG, etc., are superimposed in Figure 2.2.2-18 to provide apparent viscosity comparison.

2.2.2.2 Shear Degradation Testing

Shear degradation testing was performed using the characteristic flow test apparatus. Gels were subjected to five flow cycles from the preparation vessel to the receiving vessel and back at shear rates greater than 3000 sec^{-1} . Yield stress measurements were made before and after flowing to determine the degree of gel structure degradation.

Two LNG A gels were subjected to shear degradation testing. One of the gels was a 3.5 weight percent water gel with a yield stress of 270 dynes/cm^2 . The other gel was a 4.7 weight percent water gel with a yield stress of 771 dynes/cm^2 . No evidence of shear degradation was noted for either gel.

Figure 2.2.2-16. Laminar Flow Constraint Relationship

Figure 2.2.2-17. Composite of All Shear Experimental Data

Figure 2.2.2-18. Shear Diagram for GELNG

2.2, Task 2 - Gel Characterization (cont.)

2.2.3 Flow Characteristics Under Simulated Transfer Conditions

Flow characteristics of LNG A and GELNG A were determined under comparable nonisothermal conditions by flowing both substances through a controlled heat transfer apparatus. The apparatus consisted of a sixteen inch long stainless steel tube with a .18 inch inner diameter. The tube was fitted with an external jacket through which a measured, ambient temperature gaseous nitrogen flow was passed. The apparatus was fitted with copper-constantan thermocouples in the following manner. At the entrance of the transfer tube, one thermocouple (TFI-1) was inserted through the wall of the tube to measure the fluid (LNG or GELNG) temperature near the inner wall. At the midpoint, one thermocouple (TO-2) was attached to the outer surface of the transfer tube to measure the outer wall temperature. Near the exit of the tube, three thermocouples were installed: one to measure the outer wall temperature (TO-3), one to measure fluid temperature near the inner wall (TFI-3), and one to measure fluid temperature near the middle of the fluid stream (TF-3). In addition, thermocouples monitored bulk entrance and exit temperatures for nitrogen flowing in the external jacket.

To initiate testing a nitrogen flow of approximately .03 SCFM was set in the external jacket. The valve connecting the preparation vessel with the transfer apparatus was then opened and a driving pressure of 20 psig was applied to the preparation vessel to initiate flow. Elapsed flow time was measured and expelled gel was caught and weighed in a pre-cooled Dewar in order to determine gel flow rates. Thermocouple readings were recorded at one second intervals during testing using a Vidar data acquisition system.

Transfer tests using LNG A and LNG A gel containing 3.5 weight percent water gelant were performed. Temperature profiles for the tests are presented in Figures 2.2.3-1A, 2.2.3-1B, 2.2.3-2A,

Figure 2.2.3-1A Temperature versus Time During Transfer of LNG A Through a 0.18 in. I.D. Tube Surrounded by Gaseous Nitrogen

Figure 2.2.3-1b Temperature versus Time During Transfer of LNG A Through a 0.18 in. I.D. Tube Surrounded by Gaseous Nitrogen

Figure 2.2.3-2A Temperature versus Time During Transfer of Gelled LNG A Through a 0.18 in. I.D. Tube Surrounded by Gaseous Nitrogen

Figure 2.2.3-2B. Temperature versus Time During Transfer of Gelled LNG A Through a 0.18 in. I.D. Tube Surrounded by Gaseous Nitrogen

2.2, Task 2 - Gel Characterization (cont.)

and 2.2.3-2B. The discontinuities in LNG temperature curves are due to a 78 second interruption in pressurization. Flow rates determined from the tests were 2630 cc/min for LNG and 1516 cc/min for the gel. This gel transfer rate is in accord with expected results considering apparent viscosities determined in Section 2.2.2 and the higher temperature conditions involved in these tests.

The thermocouple data was not translatable into meaningful heat flux results; the graphs are included for completeness.

2.2.4 Expulsion Behavior

Three types of tests were conducted to investigate expulsion behavior. One set of tests examined maximum expulsion of gels as a function of yield stress, gelant content, and gel composition. A second test set involved expulsion behavior at a constant driving pressure. The third test type probed the relationship between vessel surface area and expulsion efficiency.

2.2.4.1 Maximum Expulsion Tests

Maximum expulsion tests utilized a transparent pyrex expulsion vessel with a full vessel surface area to volume ratio of 0.28 cm^{-1} . The vessel consisted of a 5000 cc volumetrically calibrated round bottom reaction flask with a cylindrical neck opening. The neck opening was sealed with a cap which had a 0.5 inch O.D. transfer tube and a pressurization port passing through it. Gelation equipment and gel preparation process support paraphernalia were also located in the vessel. The entire apparatus was contained in a thermally controllable enclosure which maintained the equipment at 102°K during testing.

2.2, Task 2 - Gel Characterization (cont.)

Tests were initiated with the preparation of gel in the expulsion vessel. The initial gel volume was noted and expulsion was initiated by pressurizing the vessel with helium. Gel was expelled through the transfer tube to a point outside the environmental enclosure using variable driving pressures up to 20 psig. After expulsion had been completed, the remaining gel was allowed to settle in the expulsion vessel and the final volume was recorded.

Expulsion efficiencies were calculated relative to LNG under the same expulsion conditions. Efficiency values were also adjusted to compensate for variation among gel volumes used in the tests. The non-expelled gel volume per unit of initial exposed vessel surface area was calculated for each test. This factor was used to extrapolate remaining gel volumes to those expected for expulsion from a full vessel. Efficiencies were then calculated on a full vessel basis.

Results of maximum expulsion testing are presented in Table 2.2.4-1. The data shows that expulsion efficiencies for gels are slightly lower than those for LNG. In addition, expulsion efficiencies decrease slightly with increasing gelant content and with increasing yield stress for gels with similar LNG compositions. Currently available data is too limited to determine anything of significance about the effects of gel composition on expulsion efficiencies. In examining the expulsion efficiency data for trends, it should be kept in mind that the ability to determine volumetric readings limits the accuracy of listed expulsion efficiencies to $\pm 3\%$.

2.2.4.2 Constant Pressure Tests

Constant pressure expulsion tests were performed using the same test apparatus and basically the same procedure as maximum expulsion tests (Section 2.2.4.1). Constant pressure tests differed by utilizing a

TABLE 2.2.4-1
EXPULSION EFFICIENCIES FOR METHANE AND LNG
GELS¹ AT 102°K

Approximate LNG Composition of Gel (Volume % as Gas)			Wt. % Gelant	Yield Stress (dynes/cm ²)	Expulsion Efficiency ^{2,3} (%)
<u>Methane</u>	<u>Ethane</u>	<u>Propane</u>			
100	0	0	3.7	771	98
100	0	0	3.8	973	94
100	0	0	4.3	973	94
100	0	0	4.6	1311	95
93	7	0	3.5	771	99
85	10	5	3.5	771	95
85	10	5	4.0	270	95
77	15	8	4.3	973	94
84	11	5	4.4	973	86

¹All gels were prepared using approximately 25 volume percent water vapor gelant in the injection gas stream.

²Gels were expelled from a 5000 cc vessel with a surface area to volume ratio equal to 0.28 cm⁻¹ at driving pressures up to a maximum of 20 psig.

³

Listed expulsion efficiencies are relative to LNG under similar expulsion conditions. In addition, values have been corrected to eliminate discrepancies arising from differing volumes of gel used in the tests. A non-expelled volume per exposed vessel surface area factor was used to extrapolate expulsion values to the listed expulsion efficiencies for a full vessel.

2.2, Task 2 - Gel Characterization (cont.)

constant driving pressure of 7 psig to expel the gel rather than a variable pressure. Expulsion efficiencies were calculated in the same manner for both types of test.

Table 2.2.4-2 gives the data for constant pressure expulsion tests. These results seem to indicate lower expulsion efficiencies for gels driven by a constant 7 psig pressure than for similar gels expelled using a variable driving pressure up to 20 psig. This trend, however, seems to warrant further investigation, since pressurization of gel remaining after constant pressure expulsion tests resulted in no further gel expulsion even at driving pressures up to 20 psig.

2.2.4.3 Increased Surface Area Tests

Increased surface area expulsion tests were conducted using a 700 cc transparent pyrex expulsion vessel with a full vessel surface area to volume ratio equal to 0.89 cm^{-1} . The vessel was a volumetrically calibrated, 3 inch I.D. cylindrical flask with a rounded bottom. A 0.5 inch O.D. transfer tube and a pressurization port passed through the cap which sealed the top of the vessel. The apparatus was contained in a thermally controllable enclosure which maintained the equipment at 102°K during testing.

To initiate testing gel was transferred from a preparation vessel to the expulsion vessel. The initial gel volume in the expulsion vessel was recorded and expulsion was started by pressurizing the vessel with helium. Gel was expelled through the transfer tube to another vessel within the isothermal enclosure using varying driving pressures up to 20 psig. After gel expulsion was completed, the gel remaining in the expulsion vessel was allowed to settle and the final gel volume was noted.

TABLE 2.2.4-2

EXPULSION EFFICIENCIES FOR METHANE AND LNG

GELS¹ USING 7 PSIG DRIVING PRESSURE

AT 102°K

Approximate LNG Composition of Gel (Volume % as Gas)			Wt. % Gelant	Yield Stress (dynes/cm ²)	Expulsion Efficiency ^{2,3} (%)
Methane	Ethane	Propane			
100	0	0	3.6	771	88
93	7	0	3.2	270	96
84	11	5	3.3	771	81

¹All gels were prepared using approximately 25 volume percent water vapor gelant in the injection gas stream.

²Gels were expelled from a 5000 cc vessel with a surface area to volume ratio equal to 0.28 cm⁻¹ at a constant driving pressure of 7 psig.

³Listed expulsion efficiencies are relative to LNG under similar expulsion conditions. In addition, values have been corrected to eliminate discrepancies arising from differing volumes of gel used in the tests. A non-expelled volume per exposed vessel surface area was used to extrapolate expulsion values to the listed expulsion efficiencies for a full vessel.

2.2, Task 2 - Gel Characterization (cont.)

Expulsion efficiencies relative to the LNG were calculated using the same type of surface area correction factors used to correct for differing volumes in maximum expulsion tests (Section 2.2.4.1). These correction factors were also used to extrapolate the results to expulsion efficiencies based on a full 5000 cc expulsion vessel with a surface area to volume ratio equal to 0.28 cm^{-1} .

Results of increased surface area expulsion tests are presented in Table 2.2.4-3. Expulsion efficiencies listed in the table are much lower than might be expected on the basis of maximum expulsion test results. Extrapolated expulsion efficiencies, however, are comparable to maximum expulsion test results listed in Table 2.2.4-1. Since the extrapolated efficiencies are based on surface area corrections, this correlation suggests that expulsion efficiencies for LNG gels are strongly dependent on vessel surface area exposed to the gel. It is probable that tanks with smaller surface area to volume ratios than those used in these expulsion tests would have expulsion efficiencies even more comparable to those of LNG.

2.2.5 Gel Aging Characteristics

Two sets of gel aging tests were conducted. Each set involved the static storage of three compositionally different gels under isothermal conditions near their boiling points. A methane gel, an LNG A gel, and an LNG B gel, were selected for storage in each test set. The first test set was monitored for slightly over 24 hours, while the second set had a test duration slightly in excess of 100 hours.

Each gel prepared for storage was tested for gelant content and yield stress before being transferred to the storage apparatus. The storage apparatus consisted of three volumetrically calibrated, 650 cc

TABLE 2.2.4-3

EXPULSION EFFICIENCIES FROM A HIGH SURFACE AREA
TO VOLUME RATIO VESSEL¹ FOR LNG GELS² AT 102 °K

Approximate LNG Composition of Gel (Volume % as Gas)		Volume % Gelant In Injection Gas Stream	Wt. % Gelant	Yield Stress (dynes/cm ²)	Expulsion Efficiency ³ (%)	Extrapolated Expulsion Efficiency ⁴ (%)	Std. Dev. of Extrapolated Expulsion Efficiency Determinations (%)
Methane	Ethane						
94	6	10	1.5	270	82	94	0.4
93	7	10	1.9	270	74	91	2.7
90	10	10	2.4	805	49	83	0.0 ⁵
93	7	2.5	1.3	<270	87	96	1.3
89	11	2.5	2.0	270	76	92	2.2

¹ Gels were expelled from a 700 cc vessel with a surface area to volume ratio equal to 0.89 cm⁻¹ at driving pressures up to a maximum of 20 psig.

² All gels were prepared using water gelant.

³ Listed expulsion efficiencies are relative to LNG under similar expulsion conditions.

⁴ Expulsion efficiencies in this column have been extrapolated to comparable values for expulsion from a full 5000 cc vessel with a surface area to volume ratio equal to 0.28 cm⁻¹ using a surface area correction factor.

⁵ Expulsion efficiency value based on one determination.

2.2, Task 2 - Gel Characterization (cont.)

pyrex storage vessels contained in a thermally controlled enclosure. After gel transfer, storage vessels were capped to seal them from the atmosphere. Storage vessels were maintained at temperatures from 104°K to 112°K throughout the storage periods. A plexiglass window in the environmental enclosure allowed for visual inspection of storage samples. Observations were made at approximately 24 hour intervals.

No visual changes were noted in any of the gel samples over any of the monitored test periods. Results of the gel aging characteristics testing are summarized in Table 2.2.5-1.

2.2.6 Boil-Off Rates Under Simulated Storage Conditions

Comparative boil-off rates for LNG and corresponding gels were examined in two distinct heat flux regimes. The two regimes will be designated as low heat flux and moderate heat flux levels.

2.2.6.1 Low Heat Flux Tests

In order to evaluate boil-off rates for LNG gels under conditions simulating those in storage containers, two sets of vaporization tests were conducted. Test sets differed in the type of storage vessel used. This variation in vessel type enabled boil-off rates to be determined at two different, very low heat fluxes.

Tests in Set #1 were conducted using two 1000 cc shielded glass Dewar boil-off vessels. Dewars which had been precooled with liquid nitrogen were filled with the substance to be tested, capped with a polystyrene plug and placed on a triple beam balance. Weight and elapsed time were recorded at regular intervals for test durations ranging

TABLE 2.2.5-1

AGING CHARACTERISTICS OF METHANE AND LNG GELS¹
 UNDER STATIC STORAGE CONDITIONS AT ~112 °K

Approximate LNG Composition of Gel (Volume % as Gas)			Wt. % Gelant	Initial Yield Stress (dynes/cm ²)	Volume of Gel Stored (cc)	Total Storage Time (hours)	Observations
Methane	Ethane	Propane					
100	0	0	3.7	771	520	24	No visible changes in gel volume or homogeneity
93	7	0	3.5	771	475	27	No visible change in gel volume or homogeneity
85	10	5	3.5	771	510	32	No visible change in gel volume or homogeneity
100	0	0	3.6	771	510	109	No visible change in gel volume or homogeneity
93	7	0	4.6	771	425	113	No visible change in gel volume or homogeneity
84	11	5	3.3	771	540	116	No visible change in gel volume or homogeneity

¹ All gels were prepared using approximately 25 volume percent water vapor gelant in the injection gas stream.

2.2, Task 2 - Gel Characterization (cont.)

from 5 to 28 hours. The Dewar boil-off test apparatus is shown in Figure 2.2.6-1. Two boil-off rate calibration runs using liquid nitrogen were made in each of the two vessels prior to making determinations using LNG in one of the vessels and GELNG in the other.

Static boil-off rates in Set #2 were determined using ~1060 cc cylindrical storage vessels with 3 in. thick polystyrene bead board (1 lb density) walls and a 1/16 in. polyethylene liner. Samples about 500 cc in volume were placed in a precooled storage vessel and allowed to boil-off through a mercury bubble-off. Weight changes were recorded at approximately 15 minute intervals for test durations varying from 2.5 to 8 hours. Figure 2.2.6-2 shows the polystyrene vessel boil-off test apparatus. Relative calibrations for the storage vessels were determined from runs with liquid methane.

Weight versus time data for tests in both sets were fitted to simple exponential expressions. These expressions were used to extrapolate data to initial rates in a full storage vessel. The weight versus time expression derivatives listed in Table 2.2.6-1 (i.e., boil-off rates (g/min)) were evaluated at the full storage vessel condition to obtain boil-off rates. Within each test set, rates were corrected for differences in storage vessels using data from calibration runs. Corrected initial boil-off rates for LNG and GELNG in a full vessel are listed in Table 2.2.6-1 along with accompanying heat fluxes. The data shows very little difference in the boil-off rates of LNG and GELNG under these low heat flux conditions.

Figure 2.2.6-1. Dewar Boil-Off Test Apparatus

Figure 2.2.6-2. Polystyrene Vessel Boil-Off Test Apparatus

TABLE 2.2.6-1

STATIC BOIL-OFF RATES AT LOW HEAT FLUX FOR METHANE, LNG,
GELLED METHANE AND GELLED LNG¹

Approximate LNG Composition of Gel (Vol. % as Gas)		Wt. % Gelant	Yield Stress (dynes/cm ²)	Boil-Off Rate ² (g/min)	Initial Boil-Off Rate ³ in Full Vessel (g/min cm ²)	Initial Heat Flux in Full Vessel (BTU/hr ft ²)
Methane	Ethane					
Set #1						
94	6	0	-	.3235 e ^{-0.0008889t}	6.7 x 10 ⁻⁴	18
91	9	3.1	270	.3720 e ^{-0.0008219t}	6.5 x 10 ⁻⁴	17
Set # 2						
100	0	0	-	.7445 e ^{-0.003441t}	2.6 x 10 ⁻³	70
100	0	3.5	771	1.100 e ^{-0.002691t}	2.5 x 10 ⁻³	67
89	11	4.1	771	.9161 e ^{-0.002884t}	2.5 x 10 ⁻³	67
87	13	4.7	1311	.9254 e ^{-0.003265t}	2.8 x 10 ⁻³	75

¹ All gels were prepared using approximately 25 volume percent water vapor gelant in the injection gas stream.

² Boil-off rates in this column are dependent on vessel characteristics.

³ Rates within each data set in this column are corrected for vessel differences using LN₂ or LCH₄ extrapolated to initial rates in a full vessel.

2.2, Task 2 - Gel Characterization (cont.)

2.2.6.2 Moderate Heat Flux Testing

Three sets of tests were conducted to compare the boil-off rates of LNG A and GELNG A under static storage conditions at moderate heat fluxes. A storage vessel whose insulating properties could be easily varied over the desired range was used in the tests. Boil-off rates and corresponding heat fluxes were determined for LNG A and GELNG A under identical conditions in each of three different insulating regimes.

The storage vessel used in the tests was a 4.75 cm inner diameter 304 stainless steel cylinder with a length of 41.28 cm. The vessel was capped at the top with a 7.62 cm thick polystyrene plug and surrounded on all other sides by a 52.07 cm long, 8.56 cm inner diameter cylindrical stainless steel jacket. Two 0.45 cm diameter ports in the jacket allowed access to the enclosed space between the jacket and the storage vessel. By introducing different very low pressures of helium into the enclosed space through the jacket ports, the insulating properties of the storage vessel could be varied to allow the moderate range of heat fluxes desired. Figure 2.2.6-3 is a photograph of the moderate heat flux boil-off apparatus.

In preparation for testing, the enclosed space in the storage vessel was purged with helium. The space was then pumped down to the desired pressure as determined by a McCleod gauge and sealed off. The entire vessel was then placed inside a nitrogen purged glove bag in order to prevent the condensation of atmospheric moisture on the vessel during vaporization of the cryogen. The vessel was precooled with liquid nitrogen just prior to testing.

To initiate testing the precooled boil-off apparatus was placed on a triple beam balance and filled with the cryogen to be tested.

Figure 2.2.6-3. Moderate Heat Flux Boil-Off Test Vessel

2.2, Task 2 - Gel Characterization (cont.)

The cryogen was allowed to boil-off through a light oil bubble-off via a .635 cm inner diameter tube. Weight and elapsed time were recorded at various intervals for test durations varying from 0.5 to 2 hours.

One test each using LNG A and GELNG A were conducted at three different enclosed space helium pressures. The three helium pressures used corresponded to 0.1 mm Hg, 1.0 mm Hg, and 2.5 mm Hg. Initial weight versus time data for these six tests were fitted to simple exponential expressions. These expressions were extrapolated to full vessel weights. Times corresponding to full vessel weights were then used in boil-off rate expressions to determine initial boil-off rates in a full vessel. These initial boil-off rates in a full vessel, their corresponding heat fluxes, and rate expressions are given in Table 2.2.6-2.

From the data in the table, it is evident that GELNG A has a slightly higher boil-off rate than LNG A under the three sets of conditions investigated. Since gels are known to exhibit significantly lower vaporization rates than LNG under contained spill conditions at higher heat fluxes (Section 2.3.1), it appears that the mechanism responsible for decreased vaporization rate in gels is not apparent at the heat fluxes examined in this moderate heat flux study. Further investigations at higher heat fluxes should be conducted to fully elucidate factors involved in comparative vaporization rates of LNG and gels.

2.3 TASK 3 - SAFETY EVALUATION TESTS

Safety evaluation tests were directed toward defining the relative safety characteristics of GELNG with respect to those of LNG. The three types of tests selected to achieve this goal were spill behavior tests, leakage behavior studies, and boil-off behavior determinations.

TABLE 2.2.6-2

STATIC BOIL-OFF RATES AT MODERATE HEAT FLUX
FOR LNG A AND GELNG A¹

Approximate LNG Composition of Gel (Vol. % as Gas)		Wt. % Gelant	Yield Stress (dynes/cm ²)	Boil-Off Rate (g/min)	Initial Boil-Off Rate In a Full Vessel (g/min cm ²)	Initial Heat Flux In a Full Vessel (Btu/ft ² hr)
Methane	Ethane					
				Set #1 - 0.1 mm Hg		
93	7	0	--	2.568 e ^{-0.008238t}	4.1 x 10 ⁻³	114
93	7	3.2	270	3.423 e ^{-0.01054t}	5.5 x 10 ⁻³	148
				Set #2 - 1.0 mm Hg		
93	7	0	--	6.140 e ^{-0.02217t}	1.1 x 10 ⁻²	308
93	7	2.8	270	8.121 e ^{-0.02667t}	1.4 x 10 ⁻²	375
				Set #3 - 2.5 mm Hg		
93	7	0	--	3.583 e ^{-0.02283t}	1.2 x 10 ⁻²	317
93	7	2.8	270	8.706 e ^{-0.03005t}	1.6 x 10 ⁻²	422

¹All gels were prepared using approximately 25 volume percent water vapor gelant in the injection gas stream.

2.3, Task 3 - Safety Evaluation Tests (cont.)

2.3.1 Task 3.1 - Spill Behavior

Three types of tests were used to evaluate spill behavior. Simulated one dimensional spills, unconfined land spills, and unconfined water spills were performed using both LNG A and GELNG A.

2.3.1.1 Simulated One Dimensional Spill Tests

Simulated one dimensional spill tests were conducted using a modified version of a spill apparatus designed under the direction of Professor R. C. Reid at M.I.T. The apparatus provided a controlled, virtually one dimensional environment for investigating small scale spills on water. It consisted of a 10 foot long section of clear Pyrex pipe with a 6 inch internal diameter. The pipe was supported horizontally on top of a wood base by polystyrene wedges and enclosed on the sides and top by a Plexiglas safety shield. Aluminum flanges were used to seal the two ends of the pipe. A 15 inch long section of 2 inch inner diameter PVC pipe was attached at a 45° angle to one of the flanges to provide a sample entry port. The other flange was provided with a port for venting evolved gases. A 1/4 inch purge line entering through one end of the wood base provided a dry nitrogen atmosphere in the space between the pipe and the Plexiglas shield.

Before initiating testing, the pipe was half filled with deionized water. Approximately one quart of the test sample was then introduced into the system through the entry port. Any of the sample remaining on the entry port walls was dislodged and pushed into the system using a piston-type cleaning rod. The entry port was then sealed and the sample boil-off and spread behavior were documented both photographically and thermally. Thermal documentation was accomplished through the use of nine thermocouples located along the length of the pipe both in the water and in the vapor space. Thermocouple outputs were scanned and recorded at regular intervals using a Vidar data acquisition system.

2.3, Task 3 - Safety Evaluation Tests (cont.)

Small scale water spills using liquid nitrogen, LNG, and GELNG were conducted. The composition of the LNG involved in the tests was 94% by volume CH_4 and 6% by volume C_2H_6 . The gel used in the spills contained 3.0 weight percent water gelant and had an LNG content of 93% CH_4 and 7% C_2H_6 by volume. Testing on each of the three sample types was performed in triplicate. Both liquid nitrogen and LNG spills produced vapor clouds which were visible for less than 2 minutes. In contrast, GELNG samples showed evidence of gas evolution eight minutes after the spill. Photographic documentation of the spill testing is presented in Figures 2.3.1-1 and 2.3.1-2. The thermocouple data was inconclusive.

2.3.1.2 Unconfined Land Spill Tests

Land spill tests were conducted at a relatively level site large enough to provide for unconfined spills of five gallon quantities of LNG or LNG gels. The site was marked with concentric circles centered at the spill point with radii of 5, 10, 15, 20, and 25 feet. The spill area was instrumented with thermocouples at eight locations. One thermocouple was located 2 inches below ground level at the spill point while a second was placed just below ground level five feet east and north of the spill point. All thermocouple outputs were fed into a Vidar scanner for thermocouple channel sampling and temperature data recording. A wind speed and direction indicator and a relative humidity recorder were located at the site to monitor local weather conditions during spills.

Prior to testing, batches of LNG or GELNG to be spilled were transferred from the gel preparation facility to a small environmental box for transportation to the spill site. Once at the site, the substance to be spilled was transferred to a spill container, which has been pre-cooled with liquid nitrogen. The spill container was an aluminum can 24 inches in height and 10 inches in diameter. The can was surrounded by a

Initial 35 Seconds of Testing at 5 Second Intervals

After 2 min.

Figure 2.3.1-1. Modified M.I.T. Spill Apparatus Testing with LNG A

Initial 3 Minutes of Testing at 30 Second Intervals

After 6 min.

Figure 2.3.1-2. Modified M.I.T. Spill Apparatus Testing with Gelled LNG A

2.3, Task 3 - Safety Evaluation Tests (cont.)

minimum of 6 inches of polystyrene bead board insulation on all sides and fitted with a polystyrene bead board cap. The insulated container fitted into an aluminum frame which provided a pivot axis for tipping the container to initiate the spill. Once the substance had been transferred to the spill container, the container and its contents were weighed. The container was then bolted by its frame to a 25 foot boom and lowered into place over the spill point to provide a spill height of approximately two feet. The container cap was then removed and the container was tipped remotely to initiate the spill. Spills were documented photographically from overhead and from the side. Thermocouples were scanned and temperatures were recorded at five second intervals during the spill.

Six unconfined land spills were conducted. These tests included two liquid nitrogen equipment check out spills, one LNG A spill, and three GELNG A spills. Gels involved in the spills varied in gelant content from 3.1 weight percent to 5.5 weight percent. All gels tested showed a significant increase in total vaporization time and a decrease in maximum spill spread area. This is evident from the spill test results given in Table 2.3.1-1. A qualitative view of vapor cloud dispersion behavior and spill vaporization rates is provided by the time sequenced photographs of land spill testing presented in Figures 2.3.1-3 through 2.3.1-8. Differing ground and weather conditions should be kept in mind when comparing spill data for LNG and corresponding gels.

2.3.1.3 Unconfined Water Spill Tests

Unconfined spills on water were performed using the same apparatus and procedures employed for unconfined land spills (Section 2.3.1.3). The spill site was a sixty foot by eighty foot rectangular pond filled with water to a depth of approximately two feet. Markers were located along two sides of the pond at five foot intervals from the spill point to provide a reference for spill spread distances.

TABLE 2.3.1-1

UNCONFINED LAND SPILL TEST RESULTS

Parameter	1	2	3	4	5	6
Test Number						
Substance Spilled	LN ₂	LNG ⁽²⁾	GELNG ^{(1),(3)}	GELNG ^{(1),(4)}	LN ₂	GELNG ^{(1),(5)}
Mass Spilled (lbs)	36.5	21.5	6.0	18	30	21.5
Volume Spilled (gal)	5.4	5.8	1.6	4.9	4.4	5.6
Wind Direction	SW	SW	NE	SSE	SSE	WNW
Wind Speed (mph)	2.5-3	2	2-3	5-10	5-10	0.5
Average Ambient Temperature (°F)	59	59	51	54	54	70
Relative Humidity (%)	45	45	80	65	65	45
Approx. Maximum Spill Spread Area (sq. ft.)	41	67	13	44	50	49
Approx. Spill Vaporization Time (min.)	0.3	0.2	(10.7) ⁽⁶⁾	(5.8) ⁽⁷⁾	0.3	(7.0) ⁽⁸⁾
Visible Vapor Cloud Dissipation Time (min.)	1.8	1.4	(7.5) ⁽⁶⁾	(4.3) ⁽⁷⁾	1.4	5.5
Ground Conditions	Dry	Dry	Moist	Wet	Wet	Dry

- (1) All gels were prepared using approximately 25 volume percent water vapor gelant in the injection gas stream.
- (2) The LNG composition as volume % gas was 93% CH₄ and 7% C₂H₆.
- (3) The LNG gel used was a 5.5% by weight water gel with a yield stress of ~973 dynes/cm². The LNG composition of the gel as volume % gas was 93% CH₄ and 7% C₂H₆.
- (4) The LNG gel used was a 3.1% by weight water gel with a yield stress of ~270 dynes/cm². The LNG composition of the gel as volume % gas was 93% CH₄ and 7% C₂H₆.
- (5) The LNG gel used was a 3.5% by weight water gel with a yield stress of ~270 dynes/cm². The LNG composition of the gel as volume % gas was 93% CH₄ and 7% C₂H₆.
- (6) The spilled gel was ignited after 7.5 minutes and burned for an additional 3.2 minutes.
- (7) The gel was ignited after 4.3 minutes and burned for an additional 1.5 minutes.
- (8) The remaining gel was ignited after 7.0 minutes and burned less than 0.1 minutes.

INITIAL 20 SECONDS OF TESTING AT 2 SECOND INTERVALS

Figure 2.3.1-3. Unconfined LN₂ Land Spill - Test #1

INITIAL 18 SECONDS OF TESTING AT 2 SECOND INTERVALS

Figure 2.3.1-4. Unconfined LNG Land Spill - Test #2

INITIAL 14 SECONDS OF TESTING AT 2 SECOND INTERVALS

After 7.5 min.

After Ignition

Figure 2.3.1-5. Unconfined Gelled LNG Land Spill - Test #3

INITIAL 16 SECONDS OF TESTING AT 2 SECOND INTERVALS

After 4 min.

Figure 2.3.1-6. Unconfined Gelled LNG Land Spill - Test #4

INITIAL 20 SECONDS OF TESTING AT 2 SECOND INTERVALS

Figure 2.3.1-7. Unconfined LN_2 Land Spill - Test #5

INITIAL 16 SECONDS OF TESTING AT
2 SECOND INTERVALS

AFTER 1 MIN.

AFTER 7 MIN.

Figure 2.3.1-8. Unconfined Gelled LNG Land Spill - Test #6

2.3, Task 3 - Safety Evaluation Tests (cont.)

One LNG A spill and one GELNG A spill were conducted on water. Data for the two tests is given in Table 2.3.1-2 and Figures 2.3.1-9 and 2.3.1-10. Total vaporization times were nearly the same for both unconfined water spills. The gel, however, exhibited a decrease in maximum spill spread area compared to that for LNG.

Review of the spill technique and results of the water spill tests leads to the conclusion that the test series should be redone using less violent spilling onto the water surface. Instead of suddenly dumping 0.02 m^3 of material from a height of 0.61 meters onto the water, it should be gently introduced onto the water surface with essentially zero kinetic energy. This would be more nearly representative of marine spill scenarios.

2.3.2 Task 3.2 - Leakage Behavior

Two categories of leakage tests were conducted using both LNG and GELNG. One test type involved the determination of leakage rates through orifices, while the second test type examined leakage through a crack in a fitting.

2.3.2.1 Leakage Through Orifices

Leakage rates through two different orifices at a driving pressure of approximately 10.5 psig were determined. The orifices involved in the tests were a .128 inch diameter round orifice and a square orifice .132 inch on a side. Both orifices were tested in three different leakage environments. Testing environments included air, water, and the air-water interface.

TABLE 2.3.1-2

UNCONFINED WATER SPILL TEST RESULTS

<u>Parameter</u>	1	2
Test Number		
Substance Spilled	LNG ⁽¹⁾	GELNG ⁽²⁾
Mass Spilled (lbs)	19	19
Volume Spilled (gal)	5.1	4.9
Wind Direction	SW	NW
Wind Speed (mph)	2	0.5
Average Ambient Temperature (°F)	90	86
Relative Humidity (%)	26	21
Approx. Maximum Spill Spread Area (sq. ft.)	960 ⁽³⁾	710
Approx. Spill Vaporization Time (min.)	1.2	1.3
Visible Vapor Cloud Dissipation Time (min.)	1.5	2.0
Water Temp. (°F)	81	85

(1) The LNG composition as volume % gas was 93% CH₄ and 7% C₂H₆.

(2) The GELNG spilled was a 3.5% by weight water gel with a yield stress of ~771 dynes/cm². It was prepared using ~25 volume percent gelant in the injection gas stream. The LNG composition of the gel as volume % gas was 93% CH₄ and C₂H₆.

(3) Spill spread was slightly confined on two sides by the sides of the spill pond. The estimated spill spread area assuming circular symmetry would have been 1260 sq. ft.

INITIAL 16 SECONDS OF TESTING AT
2 SECOND INTERVALS

AFTER 30 SEC

AFTER 1.2 MIN.

Figure 2.3.1-9. Unconfined LNG Water Spill - Test #1

INITIAL 16 SECONDS OF TESTING AT
2 SECOND INTERVALS

AFTER 1 MIN.

AFTER 1.3 MIN.

Figure 2.3.1-10. Unconfined Gelled LNG Water Spill - Test #2

2.3, Task 3 - Safety Evaluation Tests (cont.)

The leakage apparatus was a 2 liter stainless steel tank insulated with a 3 inch blanket of Kaowool insulation. The insulated tank is shown in Figure 2.3.2-1. A .18 inch I.D., pressure regulated nitrogen pressurization line and a .305 inch I.D. vent line entered the top of the tank. In addition, the top of the tank contained a sealable opening for filling the tank and a port for transmitting tank pressure to a 20 psi transducer via a .18 inch I.D. line. The tank exit was a .18 inch I.D. stainless steel tube extending from the bottom of the tank. One of the two interchangeable exit orifices was placed near the downstream end of the exit tube. During testing, the entire apparatus was suspended from a 100 pound capacity load cell. Outputs from both the load cell and the tank pressure transducer were fed to a Varian 9176 recorder to obtain continuous mass vs time relationships. Figure 2.3.2-2 shows the leakage test apparatus.

Prior to beginning a test, the leakage tank was cooled by filling it with liquid nitrogen. A cork was placed in the exit tube just downstream of the orifice to prevent leakage prior to tank pressurization. After removal of the liquid nitrogen, the tank was filled with the LNG or GELNG to be tested. The fill port was sealed and the apparatus was suspended from the load cell with the exit orifice being located in the proper test environment (i.e., in the air, one inch below the surface of the water, or at the air-water interface). The tank vent was then closed and pressurization of the tank with nitrogen was begun. The onset of pressurization forced the cork from the exit tube initiating leakage of the test material. Mass, tank pressure, and time data were continuously recorded.

Leakage behavior test results are given in Table 2.3.2-1. The accuracy of mass determinations in the tests limits the accuracy of listed leakage rates to ± 80 g/min (± 180 cc/min). Keeping these accuracy limits in mind, the following trends are evident from the data:

Figure 2.3.2-1. Leakage Vessel

Figure 2.3.2-2. Leakage Test Apparatus

TABLE 2.3.2-1

ORIFICE LEAKAGE BEHAVIOR OF LNG AND GELNG⁽¹⁾

Approximate LNG Composition of Test Sample (Vol % as Gas)		Wt. % Gelant	Yield Stress (dynes/cm ²)	Leakage Orifice Type	Hydraulic Radius of Leakage Orifice (cm)	Driving Pressure (psig)	Leakage Orifice Location	Leakage Rate (g/min)	Leakage Rate (cc/min)
Methane	Ethane								
93	7	0	-	Round	.0816	10.5	Air	1040	2340
93	7	3.2	270	Round	.0816	10.5	Air	1360	3020
93	7	0	-	Square	.0838	10.5	Air	2390	5380
93	7	4.0	270	Square	.0838	10.5	Air	2030	4470
93	7	0	-	Round	.0816	10.5	Air/Water	550	1240
93	7	4.0	270	Round	.0816	10.5	Air/Water	870	1930
93	7	0	-	Square	.0838	10.4	Air/Water	1550	3480
93	7	4.7	771	Square	.0838	10.4	Air/Water	1390	3060
93	7	0	-	Round	.0816	10.5	Water	530	1190
93	7	4.7	771	Round	.0816	10.5	Water	840	1850
93	7	0	-	Square	.0838	10.5	Water	540	1220
93	7	4.0	270	Square	.0838	10.0	Water	1260	2790

(1) All gels were prepared using approximately 25 volume percent water vapor gelant in the injection gas stream.

2.3, Task 3 - Safety Evaluation Tests (cont.)

- ° Gelation had no significant effect on orifice leakage rate for the conditions listed.
- ° Within each of the two test material groups examined (i.e., the LNG group and the GELNG group), leakage rates showed a dependence on leakage orifice environment. Rates increase for water, air-water, and air environments in the order listed.
- ° Within each of the two test material groups studied, leakage rates showed a dependence on orifice type. Rates were faster for the square orifice with a hydraulic radius of .0838 cm than for the round orifice with a hydraulic radius of .0816 cm regardless of the environment.

2.3.2.2 Crack Leakage Behavior

Leakage behavior of LNG and GELNG through a crack was investigated using an experimental setup very similar to that used for orifice leakage determinations. For crack leakage behavior, however, exit orifices were replaced by a cracked, 1/4-inch brass pipe fitting.

The crack was formed by notching a brass pipe fitting and then stress cracking it along the notch by over-torquing a threaded pipe into the fitting threads. One end of the fitting was then sealed shut by silver soldering a pipe plug in place. The other end of the cracked fitting

2.3, Task 3 - Safety Evaluation Tests (cont.)

was used for attachment to the tank exit line. A section of the crack as it appeared under a microscope is shown in Figure 2.3.2-3. Microscopic examination showed the crack to be a very irregular opening with an approximate length of 0.38 cm and a maximum width of .060 cm.

To begin testing, the precooled leakage tank was filled with the LNG or GELNG to be tested. Teflon thread tape was wrapped around the cracked fitting to prevent leakage while filling. Next the leakage tank fill port was sealed and the tank was suspended from the load cell. The tape was unwrapped from the fitting and the tank was pressurized to the predetermined pressure with nitrogen. Mass, tank pressure, and time data were continuously recorded.

Table 2.3.2-2 gives crack leakage behavior test results for five tests. These tests included one using LNG A and four using LNG A gels of three different gelant contents. The table shows the LNG A flowed through the crack at a rate of 964 g/min at a driving pressure of 10.5 psig, while gels with gelant content as low as 2.0 weight percent showed no detectable flow through the crack at the same driving pressure. In addition, a 2.0 weight percent gel showed no detectable flow at a driving pressure of 20 psig. The lower limit for flow detection in these tests was approximately 2 g/min. All gel tests in this set showed a small initial flow of material through the crack upon tank pressurization. This initial flow was followed immediately by flow cessation.

2.3.3 Task 3.3 - Boil-off Behavior

Boil-off rate testing was conducted using methane, LNG A, LNG B, methane gels, LNG A gels, and LNG B gels. Boil-off rates for contained spills of various sizes were examined under four different sets of

Figure 2.3.2-3. A Section of the Leakage Test Crack Magnified 31.5 Times

TABLE 2.3.2-2

CRACK LEAKAGE BEHAVIOR OF LNG AND GELNG (1)

Approximate LNG Composition of Test Sample (Vol. % as Gas)		Wt. % Gelant	Yield Stress (Dynes/cm ²)	Driving Pressure (psig)	Leakage Rate (g/min.)	Leakage Rate (cc/min)
Methane	Ethane					
93	7	0	-	10.5	964	2170
93	7	3.0	270	10.5	0	0
93	7	2.3	<270	10.5	0	0
93	7	2.1	<270	10.5	0	0
93	7	2.1	<270	20.0	0	0

(1) All gels were prepared using approximately 25 volume percent water vapor gelant in the injection gas stream.

2.3, Task 3 - Safety Evaluation Tests (cont.)

spill conditions in order to obtain comparative data for gelled and ungelled material under each set of conditions. The four spill types employed were contained spills on water, contained spills on land, contained spills on land in the presence of an ignition source, and contained spills on concrete.

2.3.3.1 Contained Spills on Water

Boil-off rate determinations for contained spills on water were performed using a 4 inch deep, 20 inch by 19.5 inch rectangular aluminum spill pan suspended from a 100 pound capacity load cell. The spill pan was filled with 30 pounds of water. The cryogen to be spilled was transferred from the preparation facility to a precooled 6 liter Dewar and weighed. The cryogen was then poured into the spill pan and the Dewar weighed again to determine spill size. During vaporization, the output of the load cell was continuously recorded using a Varian 9176 recorder in order to determine mass versus time relationships. The contained spill apparatus is shown in Figure 2.3.3-1.

Sixteen water spill tests were conducted. These included two liquid methane tests, one gelled methane test, four LNG A tests (93 mole % CH_4 , 7 mole % C_2H_6), three GELNG A tests, three LNG B tests (85 mole % CH_4 , 10 mole % C_2H_6) and 5 mole % C_3H_8) and three GELNG B tests. The results of these tests are presented as vaporization rate versus time plots in Figures 2.3.3-2 through 2.3.3-6. Plots in these figures are terminated at points corresponding to a residual cryogen height of .2 cm. This is the point at which surface tension would cause pool break up in the liquid cryogens resulting in incomplete coverage of the water surface.

General characteristics of the methane and LNG vaporization curves are similar to those observed by Shanes.² Vaporization

Figure 2.3.3-1. Confined Spill Vaporization Apparatus

Figure 2.3.3-2. Vaporization Rate of Liquid Methane and Methane Gels on Water

Figure 2.3.3-3. Vaporization Rate of LNG A and LNG A Gels on Water

Figure 2.3.3-4. Vaporization Rate of LNG B and LNG B Gels on Water

Figure 2.3.3-5. Vaporization Rate of LNG A Gels on Water

Figure 2.3.3-6. Vaporization Rate of LNG B Gels on Water

2.3, Task 3 - Safety Evaluation Tests (cont.)

rates, however, are lower than those observed by Shanes and also slightly lower than those given by Drake, et al.³ Both Shanes and Drake noted that the addition of heavier hydrocarbons to methane increased the vaporization rate. This trend is also evident in this study. In her examination of methane-methanol and LNG-methanol gels, Shanes noted vaporization curves which were much flatter than corresponding curves for methane and LNG. The methane-water and LNG-water gels in this study show the same tendency, but again show slightly lower vaporization rates than the methanol gels in Shanes' work.

There are two important points to be noted from Figures 2.3.3-2 through 2.3.3-6. First from Figures 2.3.3-2, 2.3.3-3, and 2.3.3-4 it is evident that gelation significantly reduces the confined water spill vaporization rates of methane, LNG A, and LNG B. Second, Figures 2.3.3-5 and 2.3.3-6 indicate that gels prepared by methods used in this study require greater than 4.4 weight percent water gelant to significantly reduce LNG vaporization rates for contained water spills.

2.3.3.2 Contained Spills on Land

The apparatus employed for confined water spill testing (Section 2.3.3.1) was also used for confined land spill boil-off rate determinations. Instead of water, the aluminum pan was filled with 50 pounds of silica sand.

Land spill vaporization curves are shown in Figures 2.3.3-7 through 2.3.3-10. The figures represent data from four methane spills, one methane gel spill, three LNG A spills, three GELNG A spills, one LNG B spill, and one GELNG B spill. For these land spills, as was the case for water spills, it is evident that gelation significantly reduces the

Figure 2.3.3-7 Vaporization Rate of Liquid Methane and Methane Gels on Silica Sand

Figure 2.3.3-8. Vaporization Rate of LNG A and LNG A Gels on Silica Sand

Figure 2.3.3-9. Vaporization Rate of LNG B and LNG B Gels on Silica Sand

Figure 2.3.3-10. Vaporization Rate of LNG A Gels on Silica Sand

2.3, Task 3 - Safety Evaluation Tests (cont.)

vaporization rates of methane, LNG A, and LNG B. This is seen in Figures 2.3.3-7, 2.3.3-8, and 2.3.3-9. Figure 2.3.3-10 shows that in contrast to water spills, land spill vaporization rates are effectively reduced for even the lowest water content gel tested (2.8 weight percent).

2.3.3.3 Contained Land Spills with Ignition

Boil-off rate tests for confined land spills in the presence of an ignition source were conducted in the same manner as confined land spill tests (Section 2.3.3.2) except that an ignition source was placed in the vicinity of the spill.

Data for one LNG A and one GELNG A land spill vaporization test in the presence of an ignition source are plotted in Figure 2.3.3-11. The plot shows that ignition increases the length of time that both LNG A and GELNG A exhibit high land spill vaporization rates. In addition, the figure makes it evident that gelation significantly reduces confined land spill vaporization rates for LNG A even when a spill ignition source is present.

2.3.3.4 Contained Spills on Concrete

An apparatus similar to the one used for boil-off rate determinations on water (Section 2.3.3.1) was employed to obtain vaporization rates on concrete. A rectangular concrete spill basin replaced the water spill surface in this set of tests. The concrete was cast in the suspended aluminum pan to form a basin 39.84 cm long, 39.53 cm wide, and 3.81 cm deep. The concrete spill basin is shown in Figure 2.3.3-12. The weight of the concrete necessitated the replacement of the 100 pound load cell with a 200 pound capacity load cell. The test method was the same as

Figure 2.3.3-11. Vaporization Rate of LNG A and Gelled LNG A on Silica Sand in the Presence of an Ignition Source

Figure 2.3.3-12. Concrete Spill Basin

2.3, Task 3 - Safety Evaluation Tests (cont.)

that used for vaporization rate determinations on water. The picture sequence in Figure 2.3.3-13 provides a time lapse view of a contained LNG A spill test on concrete. Figure 2.3.3-14 shows a similar view of a GELNG B test.

Figures 2.3.3-15 through 2.3.3-18 represent data for fifteen vaporization rate determinations on concrete. These determinations include four methane tests, one gelled methane test, four LNG A tests, four GELNG A tests, one LNG B test, and one GELNG B test.

Vaporization curves for liquids and gels on concrete show trends which differ from those for vaporization curves of liquids on sand and vaporization curves of liquids and low gelant content gels on water. Unlike the curves for sand and water vaporization, which achieve a maximum vaporization rate at times between 12 and 25 seconds, curves for vaporization on concrete show maximums at initially measured elapsed test times less than 8 seconds. These maximum vaporization rates are only slightly higher for methane and methane gels on concrete than for corresponding spills of methane and methane gel on sand or on water. The addition of heavier hydrocarbons to methane, however, significantly increases maximum vaporization rates for liquids and gels on concrete as compared to rates for similar spills on sand or water.

Two important points about the vaporization of gels should be noted from Figures 2.3.3-15 through 2.3.3-18. First, from Figures 2.3.3-15, 2.3.3-16, and 2.3.3-17, it can be seen that gelation significantly reduces concrete spill vaporization rates for methane, LNG A, and LNG B. Second, Figure 2.3.3-18 shows that all LNG A gels tested exhibited reductions in vaporization rate over LNG A even at gelant contents as low as 1.9 weight percent. The figure also indicates that vaporization rates for gels increased with decreasing gelant content.

Figure 2.3.3-13. Contained LNG A Spill on Concrete

a) Initial 30 seconds of testing at 5 second intervals

b) After 1. minute

c) After 5. minutes

d) After 15. minutes

Figure 2.3.3-14. Contained GELNG B Spill on Concrete

Figure 2.3.3-15. Vaporization of Methane and Methane Gel on Concrete

Figure 2.3.3-16. Vaporization of LNG A and LNG A Gel on Concrete

Figure 2.3.3-17. Vaporization of LNG B and LNG B Gel on Concrete

Figure 2.3.3-18. Vaporization of LNG A Gels on Concrete

3.0 RESULTS OF INDUSTRIAL SCALE GELATION PROCESS STUDIES

Industrial scale gelation studies were performed to obtain preliminary assessments concerning the feasibility and costs of the LNG gelation process on a large scale. The results constitute work conducted under Tasks 4 and 5 of the program and are presented under the following headings: 3.1, Task 4 - Preliminary Design of an Industrial Scale Gelation System and 3.2, Task 5 - Preliminary Economic Assessment.

3.1 TASK 4 - PRELIMINARY DESIGN OF AN INDUSTRIAL SCALE GELATION SYSTEM

The system designed in this task consists of the equipment required to convert LNG to the gelled form, GELNG. Auxiliary equipment (e.g., regasification gelant removal) for integrating the gelation system into an overall LNG facility is not covered in the design, although such factors are considered in the subsequent economic evaluation.

Water is used as the gelant in the design. The selection of gelant concentration is based upon the results of the characterization work of Tasks 1, 2 and 3. A relatively stiff gel is chosen to provide a conservative design and economic evaluation. A final selection of gelant concentration will ultimately depend upon results of large-scale relative spill tests using LNG and GELNG.

3.1.1 Preliminary Specification

The GELNG output capacity of the system is chosen to provide filling of an 11,000 gallon LNG truck in less than two hours. The specific design point chosen is 6800 gallons/hour. For application to a peak shaving plant, this converts to just over 600 M³ per day produced for storage. This design point maximum capacity converts to the following units, provided for convenience:

3.1, Task 4 - Preliminary Design of an Industrial Scale Gelation System (cont.)

10.8 Metric tons/hour

12.8 MMSCF/day

535 MSFC/hr

25.7 Cubic meters/hr

The required GELNG properties are stated in terms of the gelant (water) content of 5%. Data from small-scale spill tests indicates that a 5% gelant concentration will give good relative vaporization performance for GELNG in both land and water spills. It is anticipated that it will be possible to reduce the gelant content to perhaps 2 to 3% as additional data is gathered and the methods of GELNG production are refined.

3.1.2 Preliminary Design

The basic continuous gelation concept selected is for the direct injection of a gaseous gelant feed stream into the LNG as it is transferred to the LNG truck or peak shaving storage tank. The continuous gelation plant schematic is shown in Figure 3.1.2-1. LNG is transferred to a pre-process surge tank at a rated input of 10,000 gal/hr. An LNG pump raises the process stream pressure to overcome system losses.

The pumped LNG then flows through the preconditioner unit to achieve the necessary conditions for the gelation step.

The control point for the process stream occurs at the output of the preconditioner. The preconditioning of the LNG is monitored and controlled by the sensors and valves through the main process control panel.

The conditioned LNG then enters the gelator/separator unit. The gelant is dispersed in the LNG in a continuous manner, producing GELNG (6800 gallons/hour rated capacity) and natural gas vapor. The latter, saturated and at atmospheric conditions, constitutes 32% of the input to the

Figure 3.1.2-1 Continuous Gelation Plant Schematic, Conversion of LNG to GELNG

3.1, Task - Preliminary Design of an Industrial Scale Gelation System (cont.)

gelation plant for the worst case example shown; it is returned for re-liquifaction.

A list of major components and their top level requirements is given in Table 3.1.2-1.

3.2 TASK 5 - PRELIMINARY ECONOMIC ASSESSMENT

A preliminary economic assessment has been made based upon the gelation plant design evolved in Task 4. Included are capital and operating costs for the gelation plant as well as the major economic impacts on the overall processing of GELNG (e.g., reliquefaction of gelator-produced natural gas).

The objective of the economic assessment is to calculate merely the increment of cost to each unit of gas delivered for a plant incorporating gelation relative to that of an unmodified LNG plant. Thus, much simplification of the calculation is valid. All cost figures used are 1977 first quarter U.S. dollars to take advantage of data presented in Reference (4). Personnel (shift foreman and 2 operators) requirements for estimating operating costs are based on engineering judgment. Not included in the capital cost estimates are financing charges during construction, cost of land, working capital, and startup expenses. Other indirect costs, such as engineering and project management costs, permits, fees, are also excluded. No contingency or escalation was used. All of this is consistent with the cost factors obtained from the Reference (4) source.

The estimation of impacts on the existing facility requires some assumptions about how the integration of the gelation plant would be accomplished. For simplicity, it is assumed that a liquefaction facility exists with sufficient capacity to handle the 32% return of gas from the

TABLE 3.1.2-1

GELNG INDUSTRIAL-SCALE SYSTEM COMPONENT LIST

Pre-process surge tank, approximate volume 1 m^3

LNG pump, maximum 200 gpm, 50 psid., 15 shp motor

Preconditioner Unit, 200 gpm tube-side/ $\Delta P = 0.5$ psid, 50 cfs
shell-side/ $\Delta P = 0.15$ psid.

Gelant generator, maximum 0.5 lbm/sec, 400°F, 22. psia, 600. Btu/sec.,
0.5 shp feed pump

Gelator/separator unit

Air filtration unit, maximum 50 cfs., 0.05 psid., 2μ absolute

Air dryer columns unit, maximum 50 cfs, 0.12 psid, 0.1ppm H_2O

Process air blower, maximum 50 cfs, 0.25 psid., 10 shp motor

Electrical control valve actuators

Main process control console

Lines, valves, fittings, wiring, conduit

Thermal insulation

3.2, Task 5 - Preliminary Economic Assessment (cont.)

gelation plant. The associated reliquefaction costs are thus attributed to extra energy costs. It is necessary to provide for gelant removal in the eventual revaporization of GELNG. A capital item has been included to account for this; it is assumed that no additional operating costs of significance are incurred by this addition.

The per unit cost increase in NG due to the gelation plant was obtained by using a fixed annual charge rate of 10% to convert capital cost to yearly plant costs. The fixed annual charge rate represents for the investor the insurance, taxes, bonds interest, and capital recovery that is charged on a yearly basis against the plant capital cost. This annual charge rate would be consistent with a 30-year project life and 10% rate of return. The per unit cost increase is due to the sum of the yearly plant costs and the annual operating costs.

The capital and operating cost estimates are summarized in Table 3.2-1. These are preliminary study cost estimates. The costs can be projected from first quarter 1977 dollars to the present or future by using the Chemical Engineering Plant Index for the capital costs. The annual operating costs can be projected by using 0.5% per month increase.

The capital cost of equipment (\$1,040,000) converts to a yearly plant cost equivalent of \$11.80/hour, as contrasted to the much larger operating cost of \$116/hour. The combined effect is an incremental cost in the delivery of natural gas of $\$0.23/10^6$ Btu, mostly attributed to operating costs. This can be compared to the basic cost of NG at the distribution point of about $\$4.25/10^6$ Btu. Thus, the added cost of gelation would be just over 5% for the conditions and assumptions of this study. The addition of liquefaction capacity, if required, would have a minor impact on this result.

TABLE 3.2-1

COST SUMMARY - GELNG INDUSTRIAL SCALE PLANT

CAPITAL EQUIPMENT COSTS (1977 dollars)

GELATION PLANT		<u>640,000</u>
Equipment		<u>427,000</u>
Pre-process surge tank	7,000	
LNG pump	30,000	
Preconditioner Unit	60,000	
Gelant generator	110,000	
Gelator/separator unit	85,000	
Air filtration unit	20,000	
Air dryer columns unit	35,000	
Process air blower	5,000	
Electrical control valve actuators	25,000	
Main process control console	18,000	
Lines, valves, fittings, wiring, conduit	24,000	
Thermal insulation	8,000	
<u>Installation (50% equipment costs)</u>		<u>213,000</u>
EXISTING SYSTEM MODIFICATION		<u>400,000</u>
Gelant removal system (revaporization)		
INCREMENTAL CAPITAL COST		<u>\$1,040,000</u>

OPERATING COST (1977 \$'s/hr)

GELATION PLANT		<u>83*</u>
Energy Cost		<u>0.6</u>
Shaft power	0.1	
Thermal power	0.5	
Manpower		<u>82</u>
RELIQUEFACTION ENERGY COST		<u>33</u>
Shaft power	32	
Thermal power	1	
INCREMENTAL OPERATING COST		<u>\$116/hour</u>

*rounded off

3.2, Task 5 - Preliminary Economic Assessment (cont.)

It is a major conclusion of this cost study that the operating costs are the dominant cost factor in the increase in per-unit cost. Trade-offs which decrease the annual operating cost for increased initial capital costs would seem justified in future design/economic studies.

4.0 CONCLUSIONS AND RECOMMENDATIONS

4.1 CONCLUSIONS

A diverse examination of GELNG was conducted including gel characterization, safety tests, and a preliminary assessment of an industrial scale gelation process. A summary of major conclusions which can be drawn from the data are presented in accordance with the type of investigation performed.

4.1.1 Gel Preparation

Water was found to be superior to methanol as a gelant choice for applications requiring gel structure with a minimum amount of gelant. Minimization of gelant concentration in the injection gas stream also provided improved gel structure with decreased gelant content.

4.1.2 Yield Stress

Yield stress was investigated with respect to gelant content, hydrocarbon composition of the gel, gelant type, and injection gelant concentration. With each of the other three variables set, gel yield stress was affected by the four individual conditions as follows over the ranges investigated:

- (1) Yield stress increased with increasing gelant content.
- (2) Yield stresses were higher for methane gels than for corresponding LNG gels.
- (3) Yield stresses were higher for gels using water gelant than for corresponding gels using methanol.

4.1, Conclusions (cont.)

- (4) Yield stress increased with decreasing gelant concentration in the injection gas stream.

4.1.3 Rheological Characteristics

The investigation of rheological characteristics involved their variation with gelant content, hydrocarbon composition of the gel, gelant type, and gelant concentration in the injection gas stream. Holding each of the other three variables constant, rheological characteristics for gels over the ranges investigated were found to vary with the four individual conditions as follows:

- (1) Apparent viscosity at a given shear rate increased with increasing gelant content.
- (2) Methane gels had higher apparent viscosities at low shear rates and exhibited a greater degree of shear thinning than corresponding LNG gels. In addition, LNG A type gels showed higher apparent viscosities at given shear rates than LNG B type gels even when methane mole percentages were similar.
- (3) Apparent viscosity at a given rate of shear was significantly higher for LNG gels using water gelant than for corresponding gels using methanol.
- (4) Apparent viscosity at a given shear rate increased with decreasing gelant concentration in the injection gas stream.

All gels tested exhibited shear thinning tendencies with no indication of gel structure degradation even after repeated shearing.

4.1, Conclusions (cont.)

4.1.4 Flow Characteristics Under Simulated Transfer Conditions

No problems were encountered flowing gels under simulated transfer conditions.

4.1.5 Expulsion Behavior

Gel expulsion from tanks was found to be dependent on tank surface area. Expulsion efficiencies greater than 90 percent of those exhibited by LNG were obtained for gels using a tank with a surface area to volume ratio as large as 8.5 ft^{-1} . Expulsion efficiency was found to decrease slightly with increasing gelant content of the gel.

4.1.6 Gel Aging Characteristics

No visual changes were noted in methane or LNG gels subjected to static storage near their boiling point for periods of 24 and 100 hours.

4.1.7 Boil-off Rates Under Simulated Storage Conditions

No significant difference was observed between boil-off rates for LNG and those for LNG gels under static storage conditions at low heat fluxes corresponding to approximately $18 \text{ Btu/ft}^2 \text{ hr}$ and 70 Btu/ft^2 . At three distinct insulating regimes corresponding to LNG heat fluxes between $114 \text{ Btu/ft}^2 \text{ hr}$ and $317 \text{ Btu/ft}^2 \text{ hr}$, gels tested were found to have slightly higher boil-off rates than LNG. This is counter to the trend seen during spills, in which high heat fluxes are encountered. The mechanisms involved in this result are not known at this juncture.

4.1, Conclusions (cont.)

4.1.8 Spill Behavior

Five gallon unconfined land spill tests showed that gelation increases total spill vaporization times and decreases maximum spill spread areas. Similar spills on water exhibited a spill spread decrease for GELNG over LNG with no significant increase in total spill vaporization time.

4.1.9 Leakage Behavior

No significant decrease in orifice leakage rates for gels was noted compared to those for LNG. Leakage was examined at the air-water interface, into air, and into water through two different shaped orifices at driving pressures near 10.5 psig. A crack constructed for leakage rate testing allowed substantial LNG flow at a driving pressure of 10.5 psig, but would not allow the flow of LNG gels with gelant contents as low as 2.0 weight percent even at driving pressures of 20 psig.

4.1.10 Boil-Off Behavior

Confined spill vaporization rates determined from approximately 0.4 gallon spills on land and water were found to be dependent on the elapsed time since spill initiation. Gels showed as much as a five fold decrease over LNG in land spill vaporization rates on sand or concrete at times corresponding to maximum differences in the two rates. Water spill vaporization rates were slightly over two times less for gels than for LNG at times of maximum rate difference when gels contained a minimum of 4.3 weight percent gelant.

4.1, Conclusions (cont.)

4.1.11 Preliminary Design of an Industrial Scale Gelation System

A design for a portable gelation system capable of producing 600 m³ per day was evaluated.

4.1.12 Preliminary Economic Assessment

The increased cost of gelation using the equipment evaluated under Task 4 was estimated at \$0.23/10⁶ Btu for plants with existing liquefaction facilities, a 5% increase in gas delivery cost.

4.1.13 Safety/Economic Implications

The technical results summarized above are supportive of the conclusion that gelation of LNG will reduce, relative to ungelled LNG, the hazards associated with a given spill size. The reduced spread areas and reduced boiling rates (by factors of between 2 and 5) work to inhibit the release rate of natural gas vapor. At the same time, pertinent parameters of interest to the LNG facility operator (such as pumpability) are not significantly affected by gelation. Further, the impact of gelation on delivered gas cost appears small, about 5 percent. While the flow of GELNG through an orifice has been observed to be essentially the same as that for LNG, the former displays a tendency to seal cracks. Thus, the initial assumption that gelation would provide a practical means to enhance LNG safety seems to be supported by the results of this study.

4.2 RECOMMENDATIONS

The following recommendations are made for further work:

- (1) Comparative evaluation of GELNG versus LNG in large-scale (40 M³) tests at NWC, China Lake or other test site.

4.2, Recommendations (cont.)

- (2) Extending the evaluation of rheological characteristics to both higher and lower shear rates.
- (3) Conducting leakage tests with perforation-type orifices.
- (4) Further examination of crack leakage to establish conditions under which GELNG will flow through a crack (crack size, driving pressure).
- (5) A comparative spill, spread, burn, and extinguish test series for LNG and GELNG at Brooklyn Union Gas Company's Hellsgate Firefighting school in conjunction with the New York Municipal Fire Department; 40 M³ is recommended.
- (6) Unconfined water spill tests in which the cryogen is introduced gently onto the water surface to more nearly represent the marine spill scenario.
- (7) Further testing at increased heat flux to establish conditions under which GELNG begins to demonstrate superiority over LNG.
- (8) Additional, controlled unconfined land spill rate tests.

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APPENDIX I
CALCULATION OF THE EFFECTIVE LENGTH OF FLOW COILS
AND ANCILLARY TRANSFER SYSTEM

A. L/D FOR FLOW SYSTEM TUBING AND VALVE

Description: 3/8" OD by .035" wall - Straight: 52.5"
 90° (1 1/8" radius) bend: 3
 45° (1 1/8" radius) bend: 3
 90° fitting: 2
 1/2" OD by .049" wall - Straight: 20.5"
 90° (1 3/4" radius) bend: 2
 90° fitting: 3
 180° (1 3/4" radius) bend: 1
 3/4" Globe Valve ($C_v = 6.0$; orifice = .590")
 3/8" Sections: $L/D \text{ Straight} = \frac{52.5}{.305} = 172.13$
 $L/D \text{ 90° bend} = 3 (13.4) = 40.2$
 $L/D \text{ 45° bend} = 3 (6.7) = 20.1$
 $L/D \text{ 90° fitting} = 2 (57) = 114$
 1/2" Sections: $L/D \text{ Straight} = \frac{20.5}{.402} = 51.00$
 $L/D \text{ 90° bend} = 2 (14.0) = 28$
 $L/D \text{ 90° fitting} = 3 (57) = 171$
 $L/D \text{ 180° bend} = 6.5 + \frac{7.2}{2} + 14.0 = 24.1$
 Globe Valve: $L/D = \frac{891 (d)^4}{f (C_v)^2} = \frac{891 (.590)^4}{f (6.0)^2}$
 for $R_e = 1500$, $f = \frac{64}{1500} = .04267$
 $L/D = 70.28$

For flow system tubing plus valve:

$$L/D = 172.13 + 40.2 + 20.1 + 114 + 51 + 28 + 171 + 24.1 + 70.28$$

$$= 690.81$$

B. COIL 1A (1/4")

Description: 1/4" O.D. copper coil with 0.030" wall containing 24 coils with coil radius of curvature (to coil tube center) equal to 1.875" ($= \frac{3.5 + 0.250}{2}$). Coil section also contains 11-1/2" of straight tubing and 4 90° bends.

Effective Length: Coiled Section:

$$\frac{r}{d} = \frac{1.875}{0.190} = 9.87$$

$$L = \{[4 (24) - 1] (15.5 + 7) = 29.5\} .190 = 412"$$

Other bends and lengths:

$$L = 11-1/2 + 4 (16) .190 = 24"$$

Total Coil 1A = 436"

Effective length of flow system tubing + valve = 131"

$$\text{line} + \text{coil 1A} = 131" + 436" = 567" = \underline{\underline{1440 \text{ cm}}}$$

C. COIL 2A (3/8")

Description: 3/8" O.D. copper coil with 0.032" wall containing 13-1/2 coils with coil radius of curvature (to coil tube center) equal to 1.9375" ($= \frac{3.5 + 0.325}{2}$). Coil section also contains 15-1/2" of straight tubing, 3 90° bends, and 2 45° bends.

Effective Length: Coiled Section:

$$\frac{r}{d} = \frac{1.9375}{0.311} = 6.23$$

$$L = \{ [4 (13.5) - 1] (9.8 + 4.9) + 19.0 \} 0.311 = 248''$$

Other bends and lengths:

$$L = 15 - 1/2 + 3 (12)(.311) + 2 (61)(.311) = 30''$$

$$\text{Total Coil 2A: } 30'' + 248'' = 278''$$

Effective length of flow system tubing + valve = 214''

$$\text{line + coil 2A} = 215'' + 278'' = 493'' = \underline{\underline{1252 \text{ cm}}}$$

To use L/D values directly from the Crane Handbook, it is necessary that

$R_e > 1000$. For the criterion of laminar flow in this expt., $R_e < 2000$.

Thus, $1000 < R_e < 2000$.

$$R_e = 123.9 \frac{dv \rho}{\mu}$$

for the 1/4" coil (at 25°C):

$$2000 = 123.9 \frac{(.190) v (62.24)}{.8937}; \quad v = 2231 \text{ cm/min}; \quad q = 408 \text{ cc/min}$$

$$204 \text{ cc/min} < q < 408 \text{ cc/min}$$

For the 3/8" coil (at 25°C):

$$2000 = 123.9 \frac{(.311) v (62.24)}{.8937}; \quad v = 1362 \text{ cm/min}; \quad q = 668 \text{ cc/min}$$

$$334 \text{ cc/min} < q < 668 \text{ cc/min}$$

TABLE A-I

COIL 1A (1/4")
WATER CALIBRATION

Driving Press. (psig)	h_g Start-end (in. H ₂ O)	Avg. h_g (psig)	Avg. ΔP (psi)	Avg. q (cc/min)	Avg. q (ft ³ /sec)	Temp. (°F)	μ (cp)	Effective Length (ft)
1.00	2 - 5	0.13	0.87	302	1.775×10^{-4}	74.5	.9226	56.5
1.00	2 1/2 - 5 1/2	0.14	0.86	292	1.716×10^{-4}	74.5	.9226	57.8
1.00	1/2 - 4	0.08	0.92	318	1.874×10^{-4}	74.5	.9226	56.6
1.00	1 1/4 - 5	0.11	0.89	308	1.814×10^{-4}	74.5	.9226	56.6
1.08	1/2 - 4 1/4	0.09	0.99	348	2.047×10^{-4}	74.5	.9226	55.8
1.00	1/2 - 4 1/4	0.09	0.11	330	1.943×10^{-4}	74.5	.9226	54.0
0.80	4 - 6	0.18	0.62	239	1.408×10^{-4}	74.5	.9226	50.8
0.75	1/2 - 2 1/2	0.05	0.70	267	1.570×10^{-4}	74.5	.9226	51.4
0.75	1/2 - 2 1/2	0.05	0.70	272	1.599×10^{-4}	74.5	.9226	50.5
0.75	1/2 - 2 1/2	0.05	0.70	270	1.586×10^{-4}	74.5	.9226	50.9

Avg. Effective Length = 54.1' (Theor. Effective Length = 47.3')

Std. Dev. $\pm 2.9'$