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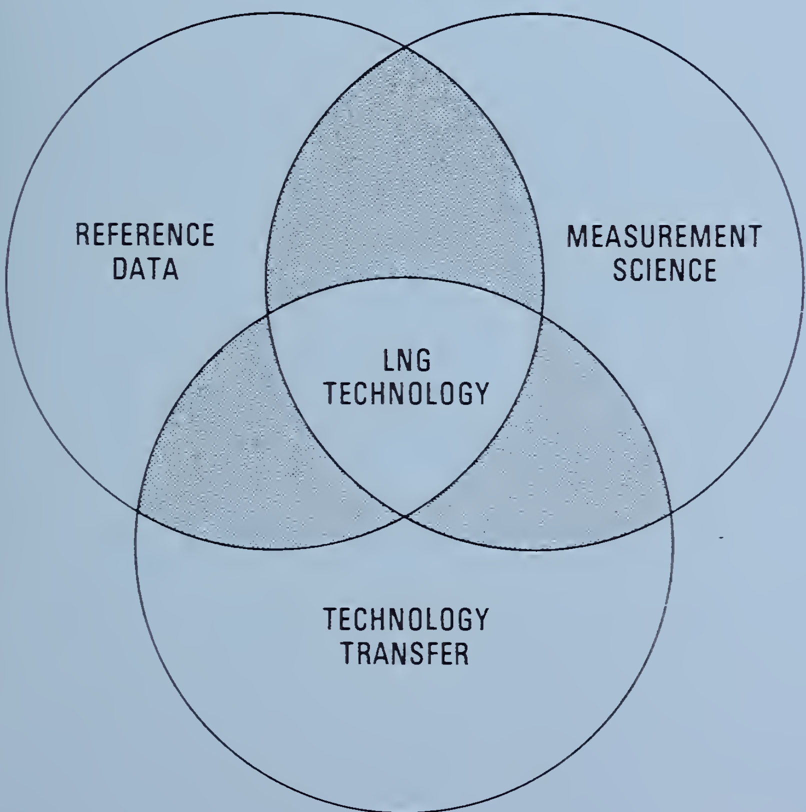
LIQUEFIED NATURAL GAS RESEARCH

at the

NATIONAL BUREAU OF STANDARDS

PROGRESS REPORT FOR THE PERIOD
1 JANUARY–30 JUNE, 1976

D.E. Diller, Editor



CRYOGENICS DIVISION • NBS–INSTITUTE FOR BASIC STANDARDS • BOULDER, COLORADO

NBSIR 76-843

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D.E. Diller, Editor

Cryogenics Division
Institute for Basic Standards
National Bureau of Standards
Boulder, Colorado 80302

Progress Report for the Period
1 January—30 June, 1976

U.S. DEPARTMENT OF COMMERCE, Elliot L. Richardson, Secretary
Edward O. Vetter, Under Secretary
Dr. Betsy Ancker-Johnson, Assistant Secretary for Science and Technology

NATIONAL BUREAU OF STANDARDS, Ernest Ambler, Acting Director

Prepared for:

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LNG Density Project Steering Committee
(in cooperation with the American Gas Association, Inc.)

Pipeline Research Committee
(American Gas Association, Inc.)

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U. S. Department of Commerce
Maritime Administration
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LNG Sampling Measurements Supervisory Committee

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ABSTRACT

Twenty-two cost centers supported by six other agency sponsors in addition to NBS provide the basis for liquefied natural gas (LNG) research at NBS. During this six month reporting period the level of effort was at a 20 man-year level with funding expenditures of over $600,000. This integrated progress report to be issued in January and July is designed to:

1) Provide all sponsoring agencies with a semi-annual and an annual report on the activities of their individual programs.

2) Inform all sponsoring agencies on related research being conducted at the Cryogenics Division of NBS-IBS.

3) Provide a uniform reporting procedure which should maintain and improve communication while minimizing the time, effort and paperwork at the cost center level.

The contents of this report will augment the quarterly progress meetings of some sponsors, but will not necessarily replace such meetings. Distribution of this document is limited and intended primarily for the supporting agencies. <u>Data or other information must be considered preliminary, subject to change and unpublished; and therefore not for citation in the open literature</u>.

Key words: Cryogenics; liquefied natural gas; measurement; methane; properties; research.

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1. Title. THERMOPHYSICAL PROPERTIES DATA FOR PURE COMPONENTS OF LNG MIXTURES

Principal Investigators. R. D. Goodwin, H. M. Roder, and R. Tsumura*.

2. Cost Center Number. 2750574

3. Sponsor Project Identification. American Gas Association, Inc. Project BR-50-10.

4. Introduction. Accurate phase equilibrium, equation of state (PVT), and thermodynamic properties data are needed to design and optimize gas separation and liquefaction processes and equipment. Accurate data for the pure components of LNG mixtures will permit developing comprehensive accurate predictive calculation methods which take into account the dependence of the thermophysical properties of mixtures on the composition, temperature, and density.

This project will provide comprehensive accurate thermophysical properties data and predictive calculation methods for compressed and liquefied hydrocarbon gases to support the development of LNG technology at NBS and throughout the fuel gas industry.

5. Objectives or Goals. The objectives of our work are the determination of comprehensive accurate thermophysical properties data and predictive calculation methods for the major pure components (methane, ethane, propane, butanes, and nitrogen) of liquefied natural gas mixtures at temperatures between 90 K and 300 K and at pressures up to 350 bar (5000 psi). Our goal is to provide a range and quality of data that will be recognized as definitive or standard for all foreseeable low temperature engineering calculations.

6. Background. Liquefied natural gas is expected to supply an increasing percentage of the United States' future energy requirements. It is likely that massive quantities of liquefied natural gas will be imported during the years 1976 - 1990. Ships and importation terminals are being built for transporting, storing, and vaporizing liquefied natural gas for distribution. Accurate physical and thermodynamic properties data for compressed and liquefied natural gas mixtures are needed to support these projects. For example, accurate compressibility and thermodynamic properties data are needed to design and optimize liquefaction and transport processes; accurate data for the heating value, which for liquefied natural gas mixtures depends on the total volume, the density, and the composition, are needed to provide a basis for equitable custody transfer.

Accurate thermodynamic properties data for liquefied gas mixtures must be based on precise compressibility and calorimetric measurements; compressibility data give the dependence of thermodynamic properties on pressure and density (at fixed temperatures); calorimetric data give the dependence of thermodynamic properties on temperature (at fixed pressures and densities). It is impossible, however, to perform enough compressibility and calorimetric measurements directly on multicomponent mixtures to permit accurate interpolation of the data to arbitrary composition, temperatures and pressure. Instead, thermodynamic properties data for multicomponent mixtures usually must be predicted (extrapolated) from a limited number of measurements on the pure components and their binary mixtures.

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*Consejo Nacional de Ciencia y Tecnologia (CONACYT) Mexico City. Currently a guest worker with the Cryogenics Division, National Bureau of Standards, Institute for Basic Standards in Boulder, Colorado.

This project was initiated to provide the natural gas industry with comprehensive accurate data for pure compressed and liquefied methane, the most abundant component in LNG mixtures. We have published National Bureau of Standards Technical Note 653, "Thermophysical Properties of Methane, From 90 to 500 K at Pressures to 700 Bar," by Robert D. Goodwin (April 1974). This report contains the most comprehensive and accurate tables available for the thermophysical properties of pure gaseous and liquid methane, and provides an accurate basis for calculating thermophysical properties data for LNG mixtures. Similar data have now been obtained for compressed and liquefied ethane.

7. Program and Results.

7.1 Ethane, Specific Heat Data -- H. M. Roder

This phase of the program is essentially complete. Two manuscripts describing the results of the research have been submitted for publication:

H. M. Roder, Measurements of the Specific Heats, C_σ and C_V of Dense Gaseous and Liquid Ethane, submitted to J. Res. Nat. Bur. Stand. (US).

H. M. Roder, The Heats of Transition of Solid Ethane, to appear in the August 15 issue of J. Chem. Phys. (1976).

7.2 Ethane, Sound Velocity Data -- R. Tsumura

Measurements of the speed of sound in saturated liquid and compressed fluid ethane have been made at a frequency of 10 MHz using the pulse-echo technique. Measurements were made in the saturated liquid from near the triple point to 280 K and in the compressed fluid along selected isotherms from 100 to 320 K at pressures to about 35 MPa. Preliminary analysis of the internal consistency of these data has been made and the imprecision is estimated to be less than 0.05%.

Near the critical point, where the use of the pulse-echo technique was impossible, a new method, using the alignment of the leading edges of the electrical pulse and the acoustical pulse, was employed, extending the data in the saturated liquid up to 299 K and in the compressed liquid to densities between 10 and 12 mol/l.

Some data were also obtained using the pulse-echo technique at a frequency of 1 MHz; the imprecision in the data is estimated to be less than 0.1%. The agreement with the data at 10 MHz in the saturated liquid in the range 160 to 299 K is within experimental error. However, a systematically increasing disagreement has been observed as the triple point is approached, reaching a maximum of 0.8% near this point.

7.3 Ethane, Thermophysical Properties Data -- R. D. Goodwin

All computational work on the thermophysical properties of ethane has been completed, employing new experimental physical properties data from this laboratory. A manuscript "Thermophysical Properties of Ethane, from 90 to 600 K at Pressures to 700 Bar," has been completed and is being reviewed prior to publication as an NBS Technical Note.

7.4 Propane, Thermophysical Properties Data -- R. D. Goodwin

Many of the available published physical properties data on propane have been acquired via our Cryogenics Data Center from their "Bibliography of References, Thermophysical Properties of Propane in the Solid, Liquid and Gaseous Phases," April 27, 1976. We have recently developed a vapor-pressure equation and formulations for the orthobaric densities of propane based on this data.

8. Problem Areas. None.

9. Funding. January 1 - June 30, 1976.

Man-years expended	1.0
Equipment and/or Services Purchased	5.2K$
Total Reporting Period Cost	71.0K$
Balance Remaining	101.3K$

10. Future Plans.

Objectives and Schedule: Quarter	3	4
Measure, analyze and report ultrasonic velocity data for ethane.	————	————>
Analyze available physical properties data for propane.	————	————
Prepare and performance test PVT apparatus for propane.	————	————

1. Title. FLUID TRANSPORT PROPERTIES

Principal Investigator. Howard J. M. Hanley

2. Cost Center Number. 2750124

3. Sponsor Project Identification. NBS-Office of Standard Reference Data

4. Introduction. Methods for predicting the transport properties of fluid mixtures are unreliable and data are scarce. Prediction methods are needed, however, to supply the necessary design data needed to increase efficiency and reduce costs.

5. Objectives or Goals. The long range or continuing goal of the program is to perform a systematic study of the theories and experimental measurements relating to transport properties, specifically the viscosity and thermal conductivity coefficients, of simple mixtures over a wide range of experimental conditions. The specific objectives of the program include: 1) the systematic correlation of the transport properties of simple binary mixtures and the development of prediction techniques, 2) development of a mixture theory for the dilute gas region and the dense gas and liquid regions, 3) extension of the theory and prediction techniques to multicomponent systems, and 4) suggested guidelines for future areas of experimental work.

6. Background. A continuing program has successfully expanded the state-of-the-art of transport phenomena for pure fluids. Information for pure fluids is required as a prerequisite for mixture studies. The theory of transport phenomena has been developed and applied to produce practical numerical tables of the viscosity, thermal conductivity and diffusion coefficients of simple fluids: Ar, Kr, Xe, N2, O2, F2, He, H_2, CH_4. Recent work has extended this approach to ethane. It has been shown that a successful mixture program can emerge from combining the results for pure fluids with equation of state studies. The equation of state work is being carried out by other investigators in this laboratory.

7. Program and Results. A procedure to predict the transport properties of mixtures has been developed[1,2]. The properties of nitrous oxide have been studied and tabulated values are available[3].

8. Problem Areas. The lack of suitable mixture transport experimental data for comparison purposes is the main problem.

9. Funding. January 1 - June 30, 1976.

Allocation	60.0K$	OSRD
Labor	0.4 MY	24.2K$
Other Costs		1.8K$
Total		26.0K$

10. Future Plans. The transport properties of ethane have been tabulated and will be published. Propane is being investigated. A procedure to calculate the transport properties of mixtures is in process of publication. The procedure will be investigated further.

References

1. H. J. M. Hanley, Cryogenics (In press, 1976).
2. H. J. M. Hanley, AIChE J. (submitted).
3. H. J. M. Hanley, private report to be published. Data available from the Cryogenics Division.

1. Title. PROPERTIES OF CRYOGENIC FLUIDS

Principal Investigators. G. C. Straty, B. J. Ackerson and D. E. Diller

2. Cost Center Number. 2750141

3. Sponsor Project Identification. NBS

4. Introduction. Accurate thermophysical properties data and predictive calculation methods for cryogenic fluids are needed to support advanced cryogenic technology projects. For example, liquefied natural gas is expected to supply an increasing percentage of the United States' energy requirements through 1990. Liquefaction plants, ships and receiving terminals are being constructed to transport and store natural gas in the liquid state (LNG). Accurate thermophysical properties data for LNG are needed to design low temperature processes and equipment. Accurate data will benefit the energy industries and the consumer by providing for safe and efficient operations and reduced costs.

5. Objectives or Goals. The objectives of this project are to provide comprehensive accurate thermodynamic, electromagnetic and transport properties data and calculation methods for technically important compressed and liquefied gases (helium, hydrogen, oxygen, nitrogen, methane, ethane, etc.) at low temperatures. Precise compressibility, calorimetric and other physical property measurements will be performed to fill gaps and reconcile inconsistencies. Definitive interpolation functions, computer programs and tables will be prepared for engineering calculations. The immediate goals of this work are to obtain accurate sound velocity and thermal diffusivity data for compressed and liquefied gases by using laser light scattering spectroscopy techniques. Sound velocity data are useful for testing the consistency of volumetric, calorimetric and thermodynamic properties data, and are potentially useful for density gauging applications. Thermal diffusivity data are required for performing thermodynamic and heat transfer calculations.

6. Background. When light is incident on a perfectly homogeneous fluid, the reradiated (scattered) light field sums to zero in all but the exact forward direction. For a "real" fluid, however, fluctuations, arising through various mechanism, destroy the perfect homogeneity and results in the scattering of light in other directions as well. For example, thermally activated density fluctuations (phonons), propagating with the characteristic velocity of sound, give rise to scattered light Doppler shifted in frequency from the incident light frequency and whose spectrum contains information on the sound velocity and attenuation. Local non-propagating temperature fluctuations, which decay diffusively, give rise to scattered light in a narrow frequency band about the incident light frequency and whose spectrum contains information on the lifetime of fluctuations (thermal diffusivity). Since the frequency shifts are generally very small, it was not until the advent of the lasers with their extremely well defined frequency, that practical experiments using these phenomena were possible.

The application of laser light scattering techniques to obtain thermophysical properties data was initiated to complement and check other measurement methods and to solve measurement problems inherent in more conventional methods. For example, laser light scattering techniques permit measurements of sound velocities for fluids under conditions for which sound absorption is too large to perform ultrasonic measurements; laser light scattering techniques permit measurements of thermal diffusivities under conditions for which convection interferes with measurements of thermal conduction. The feasibility of light scattering experiments to obtain data on binary diffusion coefficients has also been demonstrated.

7. Program and Results. Apparatus has been assembled for laser light scattering spectroscopy on compressed and liquefied gases (76 - 300 K, 350 bars). The apparatus consists of a high pressure optical cell, a cryostat refrigerated by means of liquid nitrogen, an argon ion laser and low-level light detection equipment.

The light scattered from fluctuations in the fluid can be analyzed with either digital autocorrelation techniques for the examination of the very narrow lines associated with scattering from temperature fluctuations (Rayleigh scattering) or with a pressure scanned Fabry Perot interferometer for the measurement of the Doppler frequency shifts associated with the scattering from propagating density (pressure) fluctuations (Brillouin scattering).

Apparatus for photon-counting and digital autocorrelation has been assembled, interfaced with computer facilities and programmed to enable on-line data accumulation and analysis. Apparatus tests on well characterized test fluids have been satisfactory. Measurements of the thermal diffusivity of methane in the critical region are now in progress. The obtained data appear to be consistent with scaled data from other fluids. Extension of these measurements into regions more removed from critical are planned.

8. Problem areas. Light scattered from pure fluids away from critical is very weak. Initial attempts to obtain data in these regions revealed the presence of an extraneous low-level signal previously undetected. We have been unable to adequately treat this signal mathematically and its presence appears to degrade data accuracy excessively. We feel that this extraneous signal is a result of building vibrations which modulate the light scattering signal. We plan to isolate the complete optical system from the building using an air suspension system in an attempt to remedy this problem.

9. Funding. January 1 - June 30, 1976

Man-years expended	0.3
Equipment and/or Services Purchased	4.7K$
Total Reporting Period Cost	17.5K$
Balance Remaining	0.0K$

10. Future Plans.

Objectives and Schedule: Quarter	3	4
Measure, analyze and report thermal diffusivity coefficient data for methane.		

1. Title. PROPERTIES OF CRYOGENIC FLUID MIXTURES

Principal Investigators. M. J. Hiza, W. M. Haynes, A. J. Kidnay (part-time), and R. C. Miller (part-time).

2. Cost Center Numbers. 2750142, 2750145, 2750548, and 2574574

3. Sponsor Project Identification. NBS, NBS (OSRD), NASA, AGA

4. Introduction. Accurate thermodynamic properties data and predictive calculation methods for mixtures of cryogenic fluids are needed to design and optimize low temperature processes and equipment. This project provides new experimental measurements on equilibrium properties and compilations of evaluated equilibrium properties data which are suitable for direct technological use or for the evaluation of predictive calculation methods.

5. Objectives or Goals. The overall objectives of this project are to provide critically evaluated data, original and from other sources, on the phase equilibria and thermodynamic properties of cryogenic fluid mixtures. The program has been divided into the following elements:

a) Preparation of a comprehensive bibliography on experimental measurements of equilibrium properties for mixtures of selected molecular species of principal interest in cryogenic technology.

b) Selection and/or development of methods for correlation, evaluation and prediction of equilibrium properties data.

c) Retrieval and evaluation of experimental data for specific mixture systems selected on the basis of theoretical and/or technological importance.

d) Preparation of guidelines for future research based on the deficiencies noted in (a), (b), and (c).

e) Performing experimental research to alleviate deficiencies and provide a basis for improvement of prediction methods.

6. Background. A physical equilibria of mixtures research project was established in the Cryogenics Division in 1959. The initial effort, based on a bibliographic search and other considerations, was directed toward the acquisition of new experimental data on the solid-vapor and liquid-vapor equilibria and physical adsorption properties for a limited number of binary and ternary mixtures of components with widely separated critical temperatures. Most of the systems studied included one of the light hydrocarbon species -- methane, ethane, or ethylene (ethene) -- with one of the quantum gases -- helium, hydrogen, or neon. The data for these systems led to significant improvements in the predictions of physical adsorption equilibrium and a correlation for the prediction of deviations from the geometric mean rule for combining characteristic energy parameters. In addition, significant new information was obtained for interaction third virial coefficients which was used in a correlation by one of our consultants, J. M. Prausnitz. The approach taken in this work has been as fundamental as possible with the intention of having an impact on a broad range of mixture problems.

Recent efforts have been directed toward problems associated with systems containing components with overlapping liquid temperature ranges, such as the nitrogen + methane system.

7. Program and Results. The recent progress is summarized as follows:

a) New liquid-vapor equilibrium composition measurements at selected conditions for the methane + ethane and the methane + ethylene systems have been obtained and analyzed. A paper reporting these data has been released for publication and will be submitted to the Journal of Chemical Thermodynamics.

b) Work is continuing on the compilation and evaluation of liquid-vapor equilibrium data, saturated liquid excess volumes, excess Gibbs functions and Henry's constants for the methane + ethane system. A paper discussing this work and the results is being prepared for submission to the Journal of Physical and Chemical Reference Data.

c) An equation of state, recently proposed by Peng and Robinson, is being evaluated as a simple representation of the phase equilibria data over the entire liquid range for systems such as nitrogen + methane and methane + ethane. This equation appears promising in the region where one component is supercritical, as well as the region where both components are subcritical.

8. Problem Areas. None.

9. Funding. January 1 - June 30, 1976

Man-years expended	0.7
Equipment and/or Services Purchased	1.8K$
Total Reporting Period Cost	63.9K$
Balance Remaining	25.0K$

10. Future Plans.

Objectives and Schedule: Quarter	3	4
Evaluate, correlate and report liquid-vapor equilibrium properties data for methane-ethane mixtures.	————	————>
Evaluate and report promising calculation methods for LVE and PVTx properties of methane-nitrogen mixtures.	————	————>
Prepare and performance test PVTx apparatus for methane-nitrogen mixtures.	————	————
Prepare and report graphs of liquid-vapor equilibrium properties data for methane-nitrogen mixtures.		————

1. Title. DENSITIES OF LIQUEFIED NATURAL GAS MIXTURES

Principal Investigators. M. J. Hiza, W. M. Haynes, and R. D. McCarty

2. Cost Center Numbers. 2751574, 2752574

3. Sponsor Project Identification. LNG Density Project Steering Committee; American Gas Association, Inc., Project BR-50-11.

4. Introduction. Accurate density measurements and calculation methods for liquefied natural gas mixtures are needed to provide a basis for custody transfer agreements and for mass, density, and heating value gauging throughout the fuel gas industry.

The basis for the custody transfer of natural gas is its heating value. It is difficult to determine and agree on the heating value of extremely large volumes of natural gas in the liquid state. For example, methods for calculating the heating value of a liquefied natural gas mixture require knowing its density, which in turn depends on its composition, temperature, and pressure. As the compositions of LNG mixtures vary considerably, depending on the sources of the gas and the processing conditions, accurate methods are needed for calculating liquid densities at arbitrary compositions, temperatures and pressures. The accuracy is important because of the extremely large volumes of liquid involved.

5. Objectives or Goals. The objectives of this work are to perform accurate (0.1%) and precise (0.02%) measurements of the densities of saturated liquid methane, ethane, propane, butanes, nitrogen and their mixtures mainly in the temperature range 105-140 K, and to test and optimize methods for calculating the densities of LNG mixtures at arbitrary compositions and temperatures.

6. Background. This project is being carried out at NBS because of the realization that equitable custody transfer agreements could be reached more readily if the density measurements and the evaluation and development of calculation methods were performed by independent professionals of established reputation.

An apparatus incorporating a magnetic suspension technique has been developed for absolute density measurements on liquids and liquid mixtures, particularly at saturation, for temperatures between 90 and 300 K. The estimated imprecision of measurement is less than 0.02% and the estimated inaccuracy is less than 0.1%.

7. Program and Results. Saturated liquid density measurements have been carried out for the following mixtures:

a) 0.30 CH_4 + 0.70 C_3H_8 (105 - 110 K)

b) 0.86 CH_4 + 0.14 C_3H_8 (105 - 130 K)

c) 0.49 CH_4 + 0.51 iC_4H_{10} (110 - 125 K)

d) 0.59 CH_4 + 0.41 nC_4H_{10} (120 - 130 K)

e) 0.30 N_2 + 0.70 CH_4 (100 - 120 K)

f) 0.06 N_2 + 0.94 C_2H_6 (105 - 120 K)

g) 0.02 N_2 + 0.98 C_3H_8 (110 - 115 K)

h) 0.04 N_2 + 0.96 C_3H_8 (105 - 110 K)

i) $0.07\ N_2 + 0.93\ C_3H_8$ (100 - 105 K)

j) $0.34\ N_2 + 0.34\ CH_4 + 0.32\ C_2H_6$ (105 - 115 K)

k) $0.16\ N_2 + 0.67\ CH_4 + 0.17\ C_2H_6$ (105 - 120 K)

l) $0.10\ N_2 + 0.80\ CH_4 + 0.10\ C_3H_8$ (105 - 120 K)

m) $0.80\ CH_4 + 0.10\ C_2H_6 + 0.10\ C_3H_8$ (105 - 120 K)

n) $0.05\ N_2 + 0.85\ CH_4 + 0.05\ C_2H_6 + 0.05\ C_3H_8$ (105 - 120 K)

o) $0.85\ CH_4 + 0.05\ C_2H_6 + 0.05\ C_3H_8 + 0.05\ iC_4H_{10}$ (105 - 125 K)

p) $0.05\ N_2 + 0.80\ CH_4 + 0.05\ C_2H_6 + 0.05\ C_3H_8 + 0.05\ iC_4H_{10}$ (105 - 120 K)

q) $0.85\ CH_4 + 0.05\ C_2H_6 + 0.05\ C_3H_8 + 0.05\ nC_4H_{10}$ (115 - 130 K)

r) $0.05\ N_2 + 0.79\ CH_4 + 0.06\ C_2H_6 + 0.05\ C_3H_8 + 0.05\ nC_4H_{10}$ (105 - 110 K)

s) $0.85\ CH_4 + 0.05\ C_2H_6 + 0.04\ C_3H_8 + 0.03\ iC_4H_{10} + 0.03\ nC_4H_{10}$ (105 - 120 K)

t) $0.04\ N_2 + 0.81\ CH_4 + 0.05\ C_2H_6 + 0.05\ C_3H_8 + 0.025\ iC_4H_{10} + 0.025\ nC_4H_{10}$ (105 - 120 K)

This completes the planned density measurements for binary and multicomponent mixtures. All of the density data are now being used to evaluate and optimize several calculation methods for predicting the densities of multicomponent LNG type mixtures.

A manuscript which discusses the magnetic densimeter and method of measurement in detail has been submitted to the Review of Scientific Instruments for publication. Included is an analysis of the measurement errors and data for pure nitrogen and methane.

8. Problem Areas. None

9. Funding. January 1 - June 30, 1976

2751574 (measurements)

Man-years expended	0.8
Equipment and/or Services Purchased	1.6K$
Total Reporting Period Cost	53.1K$
Balance Remaining	22.7K$

2752574 (calculation methods)

Man-years expended	0.25
Equipment and/or Services Purchased	3.9K$
Total Reporting Period Cost	20.6K$
Balance Remaining	4.0K$

10. Future Plans.

Objectives and Schedule: Quarter	3	4
Analyze and report orthobaric liquid density measurements for binary and multicomponent mixtures of LNG components.	——→	
Evaluate, optimize and report several calculation methods for orthobaric liquid densities of LNG type mixtures.	——→	
Prepare project summary report.	——→	

1. Title. LOW TEMPERATURE MATERIAL BEHAVIOR

Principal Investigators. H. I. McHenry and R. P. Reed

2. Cost Center Number. 2750430

3. Sponsor Project Identification. Maritime Administration Misc. P.O. #400-58074.

4. Introduction. For cryogenic applications, the ASME Boiler and Pressure Vessel Code and the API Standard 620 Appendix Q Code specify the same design allowable stress level for 5Ni steel as for 9Ni steel. Since 5Ni steel costs approximately 20% less than 9Ni steel, significant cost savings could be achieved by using this material for LNG applications. At the present time, 5Ni steel cannot be used in place of 9Ni steel for marine applications because the U. S. Coast Guard has not approved it. The principal reasons that the USCG has delayed approval are lack of service experience in land based tankage and concern that the fracture resistance of the weld heat affected-zone (HAZ) is inadequate.

5. Objectives. This program is being conducted to evaluate the fracture resistance of the heat affected zone of 5Ni steel weldments at room temperature, 111 K and 76 K.

6. Background. This program is a continuation of the program conducted by Reed, et al. to determine the mechanical properties of candidate materials for LNG tankage. The work demonstrated that 5Ni steel plate has adequate mechanical properties for LNG applications. Further work was recommended to verify that the plate properties would be retained in the weld heat affected zone.

7. Program and Results. The program to evaluate the fracture behavior of the heat-affected zone in 5% Ni steel weldments has been completed.

   The fracture properties of the base metal and the heat affected zone (HAZ) of 5% steel weldments were determined at room temperature, 111 K and 76 K; emphasis was placed on tests at 111 K, the minimum boiling point of liquefied natural gas (LNG). The 32 mm-thick test plates, which met the requirements of ASTM A645, were welded using the pulsed-power-gas-metal-arc process at a heat input of 10.6 kJ/cm. The fatigue crack growth rates were determined for cracks growing through the thickness using four-point bend specimens. At 111 K, the rates in the base metal were essentially the same as found by other investigators; however, the rates in the HAZ were up to 10 times faster than previously reported. Fracture toughness tests were conducted under load-controlled conditions using J-integral procedures. At 111 K, the base metal and HAZ toughness values were 30 and 50 percent lower, respectively, than toughness values obtained previously for the same plate of test material under displacement-controlled conditions. Fracture mechanics analyses using the results reported herein indicate that 5% Ni steel is suitable for LNG applications, but more conservative estimates of fatigue life and critical crack size are necessary.

   A complete report of this investigation is presented in a paper entitled "Fracture Behavior of the Heat Affected Zone in 5% Ni Steel Weldments." (See Appendix A.)

8. Problem Areas. None. The program has been completed.

9. Funding. January 1 to June 30, 1976

Expended	$20K
Remaining	0K

10. Future Plans. None. The program has been completed.

1. Title. PROGRAM FOR REDUCING THE COST OF LNG SHIP HULL CONSTRUCTION -- PHASE II SHIP STEEL IMPROVEMENT PROGRAM

Principal Investigators. H. I. McHenry, M. B. Kasen, and R. P. Reed

2. Cost Center Number.

2753430 - LNG Ship Hull Materials (Shipyard Contracts)
2751430 - LNG Ship Construction Materials (Metallurgical Evaluation)
2752430 - LNG Ship Hull Materials (Fracture Properties)

3. Sponsor Project Identification. Maritime Administration Misc. P. O. 400-58073.

4. Introduction. Construction of LNG tankers requires the use of fine grain normalized steels for the part of the hull structure that is cooled by the cargo to temperatures in the range of 0 to -50°F. Several ABS steels have satisfactory base plate properties but extreme care must be exercised during welding to avoid degradation of the steel adjacent to weld (the heat affected zone) to a level of toughness below U. S. Coast Guard requirements. Significant cost problems are being encountered by U. S. shipyards due to the resulting inefficient low-heat-input welding procedures that must be employed to meet the fracture requirements in the heat affected zone.

The feasibility of reducing the cost of LNG ship hull construction was investigated in Phase I of this project, leading to the Phase II program described below.

5. Objective. The objectives of the Phase II program are 1) to have the four major plate producers supply three LNG shipyards with production heats of ABS steels modified to possess improved transverse fracture properties at low temperatures, 2) to have the LNG shipyards evaluate these plates by qualifying optimum welding procedures in accordance with the USCG requirements, and 3) to provide a metallurgical evluation of factors that influence heat affected zone toughness in the improved steels.

6. Background. Early in 1974, the Welding Panel of MarAd's Ship Production Committee recommended that a program be conducted to reduce the cost of ship hull construction. NBS was requested by MarAd to propose such a program to the LNG subcommittee of the Welding Panel at a meeting in Boulder in August. In mid-October, MarAd approved the initial phase of NBS's recommended program, I.E., to survey the problem and the technology available for its solution. On the basis of this survey and as the result of a meeting of the Welding Panel in March, 1975, a coordinated program involving the LNG shipyards, the steel suppliers, and NBS was recommended to MarAd and to the Welding Panel. This program was approved and work started in May 1975.

7. Program and Results. Steel deliveries to the three LNG shipyards started in April 1976 and will be complete by August 1976. The status of the steel shipments is summarized as follows:

Shipyard	Steel Co.	Steel Grade*	Delivery Date
Avondale	Armco	V-062	August 1976
		V-062 (SSC)**	August 1976
General Dynamics	U.S. Steel	CS (SSC)	June 1976
	Bethlehem	ASTM A537A-Mod	April 1976
	Bethlehem	ASTM A537A-Mod	August 1976
Newport News	Bethlehem	V-051 (SSC)	June 1976

* The steel grades V-062, V-051 and CS are American Bureau of Shipping grades.

** SSC. Sulfide Shape Control employed.

The first heat of ASTM-A537-Mod steel delivered to General Dynamics did not meet the specified properties due to inadequate sulfide shape control. This heat was eliminated from the program and a second heat was ordered for replacement. Shipments to Avondale were delayed because of difficulties in disposing of the balance of the two test heats not needed for experimental purposes. The disposition problem was resolved by Armco who sold the balance of the heat for use in construction of an offshore drilling rig.

The properties of the steel delivered to date have been outstanding (ASTM A537A-Mod excepted):

Steel Grade	Steel Co.	Plate	Transverse Charpy Energy (ft lb)
V-051	Bethlehem	1/2 in. thick	240 ft lb avg @ -60°F
		1 in. thick (PC #1)	77 ft lb avg @ -60°F
		1 in. thick (PC #2)	120 ft lb avg @ -60°F
CS	U.S. Steel	1 in. thick	174 ft lb @ -40°F
		1/2 in. thick	124 ft lb @ -40°F

Each of the shipyards plans to start the weld evaluation test program during the next reporting period.

8. Problem Areas. The development work has been delayed because of problems in finalizing the steel orders.

9. Funding. January 1 - June 30, 1976.

Cost Center	Cost to June 30, 1976	Balance
2753430	109K$	36K$
2751430	57K$*	23K$
2752430	42K$	18K$

* Includes Phase I costs.

10. Future Plans. Lukens Steel Company has been asked to submit a proposal for evaluating two heats of higher-strength ship steel meeting the requirements of V-062 with a minimum yield strength of 51 ksi.

1. Title. CUSTODY TRANSFER - LNG SHIPS

Principal Investigators. R. S. Collier, P. J. Giarratano, and J. D. Siegwarth

2. Cost Center Number. 2750460

3. Sponsor Project Identification. Maritime Administration, Misc. P.O. #400-58074, #400-69012.

4. Introduction. In response to a request from the U.S. shipbuilding industry, NBS is conducting an independent design review of the shipboard custody transfer systems under the sponsorship of the Maritime Administration and in cooperation with the major U.S. shipbuilding companies.

5. Objectives. The objectives of this program are to 1) Identify the major technical areas relating to uncertainties in the measurement of total mass and total heating value, 2) Estimate uncertainties in the total mass and total heating value due to these identified factors, 3) Develop a proposed testing program for custody transfer system components, and 4) Investigate improved gauging techniques.

6. Background. Calendar year 1974 funding provided for the initial review of ships designated by MA Design LG8-S-102a MA Hulls 289, 290, 291. The current funding provides for an extension of this program to include ships of other designs which are being built by the major U.S. shipbuilding companies and also to verify tank survey and gauging methods for LNG custody transfer.

7. Program and Results. A. Working relationships with four major U. S. shipbuilders have been initiated. Most of the problem areas which are common to custody transfer systems of all types have been identified and are listed as follows:

1. Density
   - a) accuracy
   - b) rangeability
   - c) stability
2. Tank Strapping (Tank Surveys)
   - a) thermal effects
   - b) loading factors
   - c) measurement techniques
3. Convection (Non-Uniform Density)
   - a) density or composition stratification
   - b) possible isolation of measurement stillwells
4. Tank Weathering
   - a) time changes in composition, stratification, etc.
   - b) composition measurement
   - c) sampling
5. Liquid Level/Total Volume Measurement
6. Pressure and Temperature Measurements (gradients included).
7. Electronic Signal Conditioning, Data Reduction, Analysis and Readout

B. First Quarter - Three different methods for modeling the LNG tank weathering problem were developed. All of these methods assumed an equilibrium or quasi-equilibrium situation within the tank. An actual experimental condition is the only method of testing the validity of this assumption; this should be done in the latter stages of the investigation. For the present, all three models will require extensive computer analysis in order to obtain useful predictions and will also rely on an adequate correlation technique for the mixture phase equilibria. This study should be undertaken as soon as there is sufficient confidence in the validity of the correlation technique.

The draft submitted in the last report relating the density, dielectric constant and temperature for LNG mixtures was reviewed by the editorial board and submitted for publication.

Second Quarter - NBS became involved in the tank survey procedures for obtaining the tank capacity tables for the LNG ships designated in paragraph 6 above. The task for NBS is to estimate the uncertainty in the tank volume which is obtained by a photogrammetric process using multiple station analytical stereotriangulation. The task is divided into three parts. First, the uncertainty in obtaining the coordinates of targets painted on the inside surface of the tank. Second, the uncertainty of numerical integration of the volume using a specified number of target locations; and third, the changes in tank shape due to stress loading and thermal contraction factors.

Design and construction has been started for gauge blocks and rods to be used for verification of coordinate measurements. Also, numerical integration techniques based on spherical harmonics have been obtained for converting the target locations into a volume measurement. Another program based on a least squares technique is in progress. Collaboration with the ship owners and builders is in progress in order to obtain nominal surveys as constraints on the numerical techniques and also to schedule the NBS procedures into the construction schedule for the tanks.

Further work is in progress using the RF gauging technique. A large gas holder, 16 ft in diameter and 18 ft high with a center tube (or tower) has been resonated successfully. Further experiments on a 30 ft diameter sphere are scheduled for late summer. A portable instrumentation package has been designed and constructed and is presently in use. One phase of calculation for RF gauging has been completed for a liquid-gas fill condition.

8. Problem Areas. None.

9. Funding. January 1 - June 30, 1976.

Man-years expended	0.8
Total Cost	47.0K$
Balance Remaining	40.7K$

10. Future Plans.

1. NBS will install gage blocks and gage rods (which are manufactured, targeted, and calibrated at NBS) as one independent check on the accuracy of the photogrammetric coordinate determination.

2. NBS may require 100 additional targets (one per plate). It is clear that four targets per plate is sufficient to determine the tank shape factors (assuming a constant radius of curvature for each plate) but it is also clear that extra (redundant) data is necessary to determine the uncertainties in the shape factors. It is not clear that adding 100 extra target points is the best way to obtain the redundant data; measuring the uncertainty in the radius of curvature of a number of plates in place could be another method.

3. Other nominal (spot check) surveys of the inside of the tank will be necessary to provide a first order (mathematical) constraint on the calculation of the tank shape. It has not been decided whether NBS will perform that survey or obtain information from other surveys at the tank site.

4. A system of target identification will be established and that NBS will be apprised of that system at the earliest possible date.

5. NBS will obtain the target coordinate data in a form suitable for independent calculations (data cards).

6. NBS will obtain certain detailed information from the subcontractor for the ship builder concerning the determination of target coordinates from plate coordinates and also in determining tank shape factors from target coordinate data. Also held by the subcontractor for the shipbuilder are some technical publications and their updates which are being requested by NBS.

7. The shipbuilders will supply currently available calculations or technical papers, if any, relating to the calculation of stresses in the tank and the stress-strain relationships caused by tank loading. Outputs from strain gages will also be useful.

8. NBS will also obtain further information concerning the tank thermal contraction coefficients both at and around ambient temperatures and also down to LNG temperatures.

9. We will perform further calculations concerned with LNG tank weathering.

10. We will also perform an RF gauging experiment in a 30 ft. diameter spherical LNG tank.

1. Title. HEATING VALUE OF FLOWING LNG

Principal Investigators. J. A. Brennan and J. M. Arvidson

2. Cost Center Number. 2756579

3. Sponsor Project Identification. Pipeline Research Committee (American Gas Association) PR-50-48.

4. Introduction. This project will test instrumentation for making heating value measurements in actual applications of flowing LNG. Information from projects currently underway by Younglove (cost center 2757574) on densimeters and by Haynes and Hiza (cost center 2751574) on mixture densities will be utilized where appropriate to provide state of the art information.

5. Objectives. The objective of this program is to measure total heating value of LNG flowing in a pipeline by the integration of individual measurements of flow, density and specific heating value. Flow measurement requires determination of flowmeter performance in line sizes larger than presently available calibration facilities. Therefore, a secondary objective is to establish appropriate flowmeter scaling laws.

6. Background. The LNG flow facility at NBS will be utilized to evaluate the response of the individual elements in the heating value measurement. Different compositions of LNG will be prepared to provide a range of densities and temperatures sufficient to determine any dependencies. A limited amount of sampling work is included to determine the relative importance of this parameter to the overall measurement.

Flowmeter scaling is being done utilizing the cryogenic and the water flow facilities at NBS and private LNG peak shaving facilities. This portion of the program is behind schedule because of scheduling problems at the private LNG facilities.

7. Results. A. Three tests of the eight inch flowmeter at the Transco peak shaving plant were completed during this reporting period. The results of those tests and the results from the four inch flowmeter test referred to in the last report are shown in figure 1. As can be seen in this figure, there is a disturbing difference between the data taken during the last test and almost all the previous tests. Although the difference was almost within the experimental error tolerance, the internal consistency strongly suggests something was performing differently during the last test. At the last meeting of the Supervisory Committee several courses of action were suggested to identify the sources of the discrepancy.

One area of concern was the stability of the orifice flowmeter recording instrumentation. This does not appear to be a problem since the recorders were calibrated by Transco measurement personnel between each of the LNG tests. No adjustments were required during any of these calibrations.

It was also suggested that new instrumentation be installed to record the orifice flowmeter data on our data logger. This suggestion was accepted and it was agreed that this additional information could be recorded within the existing project funding. This can be done by reducing the amount of testing on the NBS LNG flow facility.

There is a severe problem of data transmission at the Transco site. The environment is extremely noisy and requires high quality instrumentation if any improvement is to be gained over the existing system. Since there is no available wiring or empty conduits running between the two measurement points (liquid and gas), it is recommended that the data be recorded on separate units. The units can be electrically tied together so that the recordings are synchronized. Using this procedure will result in less interference and less expensive data transmission lines.

To provide new instrumentation and recording equipment will cost between $7000 and $9000. This will provide instrumentation necessary to record the output from two orifice runs. The actual cost will depend on the choice of pressure transducers and recording system. The recommended pressure transducers would cost $3250 and the recommended recording system would be cost shared on an equal basis with another project resulting in an expense of $3450. This recording system would utilize a tape recorder already available at NBS. Approximately $1000 would be needed to install and check out the system for a total estimated expense of $7700.

The cost sharing of the recording system can be accomplished provided NBS is permitted to retain title to the equipment. If this is not possible then the most cost effective procedure is to fabricate a system similar to the one now being used at Transco. This latter arrangement would also utilize the available tape recorder but would cost the project approximately $4700 resulting in a net cost of almost $9000. Both estimates can be reduced by $600 if lower cost pressure transducers are selected.

At the last meeting it was also recommended that the data from Transco's ultrasonic flowmeter be recorded on the existing data logger. The vortex shedding flowmeter has redundant sensing available and this output will also be recorded in the future. The logger has been returned to Boulder and the necessary modifications are being made to record these two additional bits of information.

B. Liquid Nitrogen Tests

a) Flowmeter

The four inch flowmeter tested at Transco was returned to NBS and retested on the nitrogen flow facility. Unlike the first tests, the recent test included the eight by four inch reducers on the flowmeter piping just as it was tested at Transco. The average meter factors measured during these two tests differed by only 0.12 percent. Therefore, there doesn't appear to be any reason to question the stability or the installation of the four inch flowmeter during the LNG tests at Transco.

Tests on the four inch flowmeter were also run using one of the electronic signal conditioners supplied with the eight inch flowmeter presently installed at Transco. This particular signal conditioner had failed during the LNG test last January 18th and had been repaired by the manufacturer. The results obtained from this test indicated a very sensitive dependence on sensor current and might be the cause of the shift in the last LNG test at Transco. The system was set up and adjusted on January 19th by the manufacturer but it is possible that it was slightly out of adjustment during the tests on February 2nd and 3rd. If this problem did, in fact, exist it could explain the change in bias observed during the February tests. It might be possible to check this problem during the next LNG test but due to the nature of the problem the check can't be conclusive.

Additional information on meter factor shifts from water to liquid nitrogen on another two inch flowmeter was also recently obtained. The ratio of the liquid nitrogen meter factor to the water meter factor was 1.0206. On the previous two inch meter the ratio was 1.0156 and on the four inch it was 1.0165. There is almost 0.5 percent difference in the ratio for the two 2-inch flowmeters. Without additional information on other meters there is no way to tell whether the difference is typical or not. The difference is larger than desirable and points out a need for additional information on other meters.

In addition to the information on water to liquid nitrogen meter factor shift, information on water calibrations at NBS Gaithersburg and a private calibration facility was also obtained. There was remarkable agreement between the two facilities. This information is very useful and encouraging since the private facility has a larger capacity than the NBS facility and could be useful to this project in the future.

C. Densitometer

Liquid nitrogen calibration of the densitometer used during the last LNG test at NBS was started and is continuing. This densitometer is a replacement for the one that failed and has had no previous application in cryogenic service. During the first liquid nitrogen test there was an apparent shift in the performance and, according to the manufacturer, shifts can occur in the densitometer performance during the first few cycles to cryogenic temperature.

Additional data is being taken on the densitometer each time the flow facility is operated. This additional data will be used to check the stability of the densitometer for as long as possible before moving it back to the LNG facility.

8. Problem Areas. None

9. Funding. January 1 - June 30, 1976.

Man-years Expended	0.9
Total Reporting Period Costs	58.0K$
Balance Remaining	66.0K$

10. Future Plans. Instrumentation is being prepared for both the future tests at Transco and the NBS LNG facility. Component integration testing of the LNG heating value measurement station will be started in the fall. An existing minicomputer will be used in this work. No major problems are anticipated in completing this phase of the program.

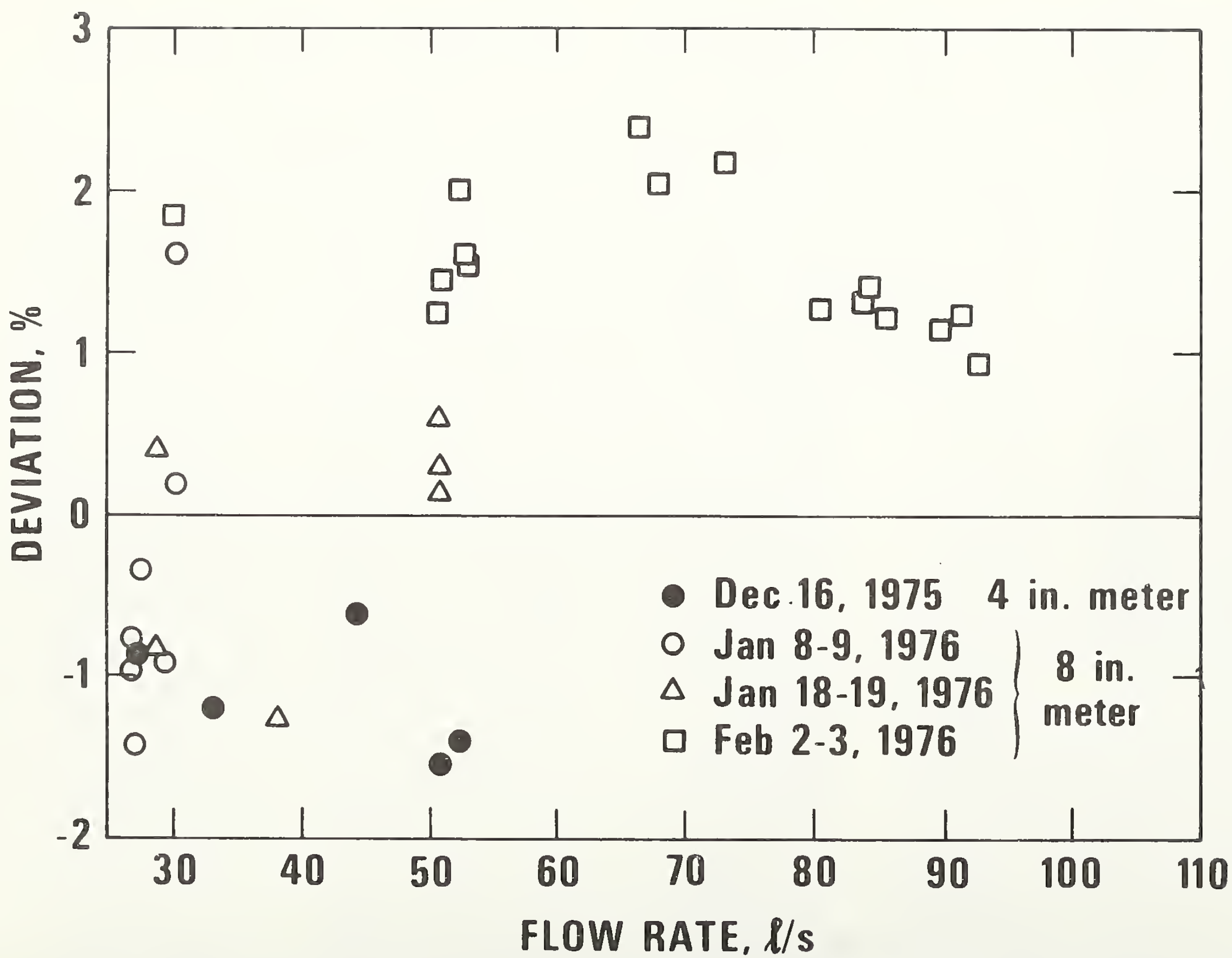

Figure 1. Vortex shedding flowmeter performance in LNG.

1. Title. LNG DENSITY REFERENCE SYSTEM

Principal Investigators. Ben Younglove and John Arvidson

2. Cost Center Number. 2757574, 2750161

3. Sponsor Project Identification. American Gas Association, Inc., Project BR-50-10, National Bureau of Standards

4. Introduction. A density reference system has been developed to evaluate the ability of commercially available instruments to measure densities of LNG directly. Density is an essential measurement in determining the total energy content of natural gas reservoirs. This effort is oriented towards metrology, whereas the output from cost center 2751574 will provide basic reference data on pure liquids and mixtures, to evaluate methods for calculating the density indirectly.

5. Objectives. The objective of this research is to provide a system for evaluating the density measurement capability of commercially available meters. From the commercial meters we will attempt to select one or two capable of performance as transfer standards, in order to provide traceability of accuracy to field density measurement systems.

6. Background. The density reference system project was initiated in 1973. Since that time the reference system has been designed, constructed, and is now in operation, evaluating commercial density metering systems.

7. Program and Results. Data have been accumulated on performance of the vibrating cylinder, vibrating plate, and the capacitance meter in liquid methane, methane + ethane, methane + propane, methane + butane, methane + nitrogen, and also in multicomponent LNG type mixtures.

A draft of a summary report of the results obtained for these meters has been submitted to the sponsor for review; data for the individual meters has been submitted to the respective manufacturers for review. A provisional accuracy statement for the density reference system is also under review. Additional data are being taken on pure methane to increase the confidence of the accuracy statement and to determine a more precise value for the random error associated with the measurement of the apparent weight of the silicon plummet immersed in LNG.

8. Problem Areas. Review of the data shows a small but perceptible drift in the vibrating cylinder data; a zero offset has been found in the Archimedes principle densimeter data, probably due to uncertainties in fluids properties data for methane and nitrogen; an electronic readout parameter change is needed for the capacitance densitometer, particularly in the presence of nitrogen; and a mechanical stability offset occurs periodically with the vibrating plate densimeter.

Also under investigation are small but perceptible shifts in the measurements obtained from the density reference system on each occasion of fluid fill. There is also a problem in determining the composition of the fluid for multicomponent mixtures containing nitrogen (butanes also may give a similar problem) due to lack of accurate liquid-vapor equilibrium data for LNG type mixtures.

9. Funding. January 1 - June 30, 1976

Man-years Expended	0.5
Total Project Cost	32.0K$
Balance Remaining	0.0K$

10. Future Plans. Review and revision of the provisional accuracy statement will be completed during the next reporting period.

1. Title. LNG SAMPLING MEASUREMENT STUDY

Principal Investigator. W. R. Parrish

2. Cost Center Number. 2750575

3. Sponsor Project Identification. LNG-Sampling Measurements Supervisory Committee.

4. Introduction. Composition is used to determine both the heating value and the quantity (through density) of LNG shipments. Thus, any error in composition doubles when calculating the total heating value and dollar value of a LNG tanker cargo. Compositions are determined by sampling LNG, on either a batch or continuous basis, and analyzing the vaporized mixture. Although several sampling techniques exist, none have received widespread acceptance in the LNG industry. Also, a standard technique has not been established for analyzing the vaporized sample.

5. Objectives or Goals. The objectives of this work are to evaluate existing sampling techniques appropriate to LNG systems and to recommend the most accurate analytical technique. Only sampling devices applicable to pipelines are being considered. The sampling techniques are judged on:

   a) representativeness of sample,

   b) insensitivity of results to composition, temperature, pressure, degree of liquid subcooling, flow rate and operator, and

   c) simplicity.

   Initial evaluations will be made in a laboratory-scale apparatus; final evaluation of the most promising sampling techniques will be performed in the LNG flow facility.

6. Background. This work is being performed at NBS because there is a need to determine the best means for obtaining the composition of LNG shipments. Current LNG buying contracts include specifications on when and how many liquid samples are to be taken but omit the sampling technique to be used. The evaluation of sampling techniques by impartial professionals will lead to the acceptance of the most accurate composition determination method by all parties involved in LNG custody transfer.

7. Program and Results. This program has just started and the laboratory apparatus is in the design and building stage. Evaluation of analytical techniques is just underway.

8. Problem Areas. None.

9. Funding. January 1 - June 30, 1976.

Man-years expended	0.2
Total reporting period cost	12.0K$
Balance remaining	13.0K$

10. Future Plans

Objectives and Schedule: Quarter	3	4
Evaluate analytical techniques	——→	
Evaluate sampling techniques in laboratory Scale apparatus	——	————

1. Title. SURVEY OF CURRENT LITERATURE ON LNG AND METHANE
Principal Investigator. Neil A. Olien

2. Cost Center Number. 2759574

3. Sponsor Project Identification. American Gas Association, Inc., Project BR-50-10.

4. Introduction. It is important that all NBS personnel working in LNG, as well as the AGA and others, keep up with what is going on throughout the world in the LNG field. This project is designed to provide the Current Awareness and other information services to allow workers to keep abreast of new research and other developments.

5. Objectives or Goals. We will publish and distribute each April, July, October, and January a listing of all significant papers, reports, and patents relating to methane and LNG properties and technology. The references will be listed under convenient subject headings. The Quarterly will be distributed to all interested AGA member companies and be made available to the general public on a subscription basis. In addition, LNG related information will be entered into the Cryogenic Data Center's Information System for quick retrieval. A continuing awareness of the current publication scene will be maintained for any new periodical to be reviewed cover-to-cover. Finally we will update and make available comprehensive bibliographies on the properties and technology of LNG. There are three bibliographies involved: methane properties, methane mixtures properties, and processes and equipment involving methane and LNG. These three will be updated each October.

6. Background. In 1969 we made a thorough review of the world's publications to determine which periodicals and abstracting services should be scanned cover-to-cover to adequately encompass the LNG field. The result is that we now scan over 300 primary publications and nearly 30 secondary publications. Of these, approximately one-third are directly related to LNG. In addition, within the past two years we have increased our coverage of the energy field to include hydrogen as a future fuel. Much of this information is also pertinent to LNG and as such is listed in our LNG-related publications. Our Current Awareness Service has been published weekly since 1964 (beginning in 1975 the publication became biweekly) and the Liquefied Natural Gas Survey has been published quarterly since 1970.

7. Program and Results. Four issues of the LNG Quarterly are prepared each year and distributed. There are now 121 subscriptions going to AGA Member Companies and 155 to other subscribers.

The three comprehensive bibliographies mentioned in section 5 have been reviewed and shortened, and more selective bibliographies have resulted. The latest versions were completed as of January 1, 1976.

B-1371 THE THERMOPHYSICAL PROPERTIES OF METHANE AND DEUTERO-METHANE IN THE SOLID, LIQUID AND GASEOUS PHASES - A SELECTED BIBLIOGRAPHY. Indexed by property, phase and author, 80 pages (Jan 1976). ($8.00).

B-1372 THE THERMOPHYSICAL PROPERTIES OF METHANE MIXTURES - A SELECTED BIBLIOGRAPHY. Indexed by property, system and author, 140 pages (Jan 1976). ($10.00).

B-1264 PROCESSES AND EQUIPMENT INVOLVING LIQUEFIED NATURAL GAS AND METHANE - A SELECTED BIBLIOGRAPHY. Indexed by subject and author, 76 pages (Feb 1975). ($8.00).

B-1367 Supplement to B-1264, indexed by subject and author, 40 pages (Jan 1976). ($5.00).

Over the past five years we have distributed over 420 copies of these and the comprehensive bibliographies. A bibliography on LNG Patents was supplied to AGA in May, 1975. Two supplements to this were also completed, one in July 1975 and one in January 1976.

8. Problem Areas. None.

9. Funding. January 1 - June 30, 1976.

Labor	4.6K$
Other Costs	0.9K$
Total	5.5K$
Remaining	0.6K$

10. Future Plans. Issue 76-2 was delivered to the printer on July 2, 1976. For the past six months all printing, distribution and subscription fulfillment functions have been handled locally by the NBS-Cryogenic Data Center. This has solved the problems we previously had when dealing with the National Technical Information Service. We feel we can now provide a responsive and responsible service to our customers in the natural gas industry.

1. Title. LIQUEFIED NATURAL GAS TECHNOLOGY TRANSFER

Principal Investigator. D. B. Mann

2. Cost Centers. 2750403, 2751403, 2752403, 2750570, 2754574 and 2758574.

3. Sponsor Project Identification. Maritime Administration Miscellaneous Purchase Order No. 400-69012; American Gas Association, Inc. Project BR 50-10; American Bureau of Shipping letter dated 21 November 1975.

4. Introduction. The liquefied natural gas program at the Cryogenics Division of NBS-IBS/Boulder represents an investment by industry and Government agencies of over $5 million over the past six years. This investment was designed to develop reference quality properties data for both fluids and materials, instrumentation and measurement technology for the use of the LNG and related industries. Information developed under this program must be transmitted to the ultimate user in a timely and useful format. The classical publication methods of NBS most certainly provide the scientist and research engineer information in a form most useful to the academic or near academic community. However, as a result of extensive assessments of user requirements, it was found that an additional effective mode for technology transfer would be an LNG Materials and Fluids Data Book. A complete outline and planned table of contents has appeared in previous semi-annual reports. The Maritime Administration of the Department of Commerce and the American Bureau of Shipping have agreed to sponsor the first year's efforts on the materials section and the American Gas Association, Inc. has agreed to sponsor the section on fluids and fluid mixtures. The project was begun on April 1, 1976.

5. Objectives. The Liquefied Natural Gas Materials and Fluids Data Book will provide a method of quick dissemination of property data and related information for the effective generation, utilization and transportation of LNG. The object is to improve technology transfer from the current NBS Cryogenics Division LNG physical measurements program to the users, including federal agencies, the states and industry. For the purpose of this data book, liquefied natural gas is defined as a cryogenic mixture (at less than approximately 150 K) of hydrocarbons, predominantly methane, with less than a total of 20% of the minor components ethane, propane, iso and normal butane, and nitrogen as an inert contaminant. LNG materials will be those associated with the liquefaction, transport and storage of liquefied natural gas.

6. Background. The Data Book is only one of a number of information dissemination methods used to provide workers in the liquefied natural gas (LNG) industry with properties data of known quality in a format consistent with the requirements of the intended user. In the case of the LNG Data Book, the intended audience is the field engineer, plant manager, ship designer or process engineer interested in a ready reference of assessed quality for data to be used in conceptual design, process monitoring, process analysis, and intercomparisons where precision and accuracy are secondary to specific problem solutions. The hierarchy of accuracy and precision will be defined and traceable through reference to scientific and engineering literature.

Data is classified into three groups by the NBS Cryogenics Division.

Group 1. Data which has been generated experimentally by NBS or has been assessed, evaluated or experimentally verified by NBS.

Group 2. Data which has been assessed and evaluated by NBS.

Group 3. Data available in the scientific engineering literature through the NBS Cryogenic Data Center or elsewhere. No NBS evaluation or assessment has been made at this date.

In general, all data included in the LNG Data Book will be from groups 1 and 2. No new assessments or correlations are anticipated or required for this work.

Data will be presented primarily in graphical form. Tables and analytical expressions will be used only where absolutely necessary. Graphs and charts will be in loose-leaf form for ease of updating and additions. This form will also allow immediate implementation for data already available under the NBS LNG program and will provide a convenient form for the output of data from existing projects. The data book will not be a substitute for traditional publications in the scientific literature where measurement science, technique, precision and accuracy are paramount, but will provide the data and references for the necessary assessment by the user.

7. Program and Results. This publication is designed primarily for user requirements and, therefore, we have requested and received special consideration from NBS in its publication. The publication of both graphical and tabular data will be in a dual system of units. These units will be the traditional LNG industry British system of Btu, pound, degree Fahrenheit and the SI system of joule, kilogram and degree Kelvin. It is the intent to give the equal weight to each system of units. For instance, in a graphical format with dual scales the test will be to recover graphical information in either set of units with equivalent precision.

A three-post expandable post binder has been selected and special graphics have been generated and submitted to sponsors for approval. Section tabbing and graph formats have been fixed for both materials and fluids.

Nine structural metals have been selected with additions possible upon consultation with sponsors. Primary emphasis in the fluids section will be on pure methane, pure nitrogen, and methane-nitrogen mixtures. Over 20% of the material to be put in graphical form as been completed to date.

8. Problem Areas. None.

9. Funding. The program was funded April 1st at 130K$ for a 12-month period.

Labor (Man-years)	0.25
Total to 30 June 1976.	23.4K$

10. Future Plans. Binder and divider tabs will be put on order in August with the printing of groups of graphs to proceed periodically thereafter. It is planned to begin distribution the first quarter of 1977.

1. Title. OIML JOINT SECRETARIAT ON LNG MEASUREMENTS
Principal Investigator. Douglas Mann

2. Cost Center Number. 2750104

3. Sponsor Project Identification. American Gas Association, Inc., NBS-Office of International Standards; and NBS-Cryogenics Division.

4. Introduction. The liquefied natural gas program of the National Bureau of Standards Cryogenics Division has, over the past five years, provided the gas industry and interested Government agencies with properties data on materials and fluids, instrumentation, and measurement assistance in the support of commerce in this significant and growing segment of the supplementary fossil energy supply. Support of this program by the American Gas Association, Inc. and Federal Government agencies such as the Maritime Administration (MarAd), NASA, GSA, Federal Power Commission and the NBS-Office of Standard Reference Data has provided a basis for the national acceptance of the results of the NBS LNG program. Through the U.S. membership in the International Organization of Legal Metrology there exists, at the present time, an opportunity to extend, internationally, the utility of data and measurement practice developed under our joint Government/industry program. We have been requested (by OIML membership) to establish an LNG Measurement Secretariat within OIML which, if implemented, would provide a significant international forum for the results of our joint work. It is believed that a joint Secretariat with the LNG industry would provide the most effective means of accomplishing these objectives.

5. Objectives or Goals. Our objective is to accomplish the following goals within the next three years.

a) To establish U.S. (NBS) thermophysical properties data for LNG as the standard data in international usage.

b) To establish U.S. (NBS) materials property data used in fabrication and construction of LNG facilities (liquefiers, storage, transport) as the standard data in international usage.

c) To establish U.S. (NBS) approved measurement technology and instrumentation as related to LNG (pressure, temperature, density, liquid level, flow) as the standard in international LNG trade. The precedent has been established with the successful completion of the joint NBS-CGA cryogenic flow measurement program which has resulted in the adoption of a cryogenic flow measurement code by the National Conference on Weights and Measures. We wish to extend this code on an international basis.

d) To establish and maintain the leadership of U.S. science, engineering, and industry in the research, technology, manufacture and marketing of instruments and measurement systems for liquefied natural gas.

6. Background. OIML was founded in 1955 to promote intergovernmental cooperation in the field of legal metrology which relates to the compatibility of standards of measurement and the legislation and government regulations which may affect such standards of measurement. OIML recommends uniform international requirements for scientific and measurement instruments used in industry and commerce and works out model laws and regulations for consideration by member nations; and, in addition, serves as a center of documentation and information exchange in legal metrology. At present 43 nations are members of this intergovernmental organization.

The United States joined OIML in 1972 (the Senate by resolution of August 11, 1972 gave its advice and consent to the accession of the U.S. to the convention establishing OIML). The responsibility for managing U.S. participation in OIML was assigned to the Department of Commerce and has since been delegated by the Department to the National Bureau of Standards (NBS). Under the general guidance of the Department of State and the Secretary of Commerce, NBS is directly responsible for formulating and implementing U.S. policy towards OIML. U. S. participation in the organization is deemed important for two reasons: First, to protect and enhance some $1 billion worth of scientific and measurement instruments exported each year by U. S. firms and to insure equity in the trade of commodities measured by these instruments; and second, to maintain the U.S. as the world leader in the field of metrology.

In the spring of 1975 at a meeting in Paris of the International Committee of Legal Metrology, the French and U.S. representatives discussed the possibility of creating a new Reporting Secretariat No. 13 on "Liquefied Natural Gas (LNG) Measurement". The U. S. representative, W. E. Andrus, Jr. of NBS, agreed to explore the possibility with U. S. industry and interested government agencies. These discussions resulted in a decision to propose a joint Secretariat with the American Gas Association and NBS-Cryogenics Division in order to best accomplish the tasks. These conclusions were reached during several meetings extending through the latter part of 1975 and early 1976.

7. Program and Results. During this reporting period, the primary objective of the program has been organizational in nature. Douglas Mann of NBS-Cryogenics Division was assigned as co-technical advisor by the National Bureau of Standards. Mr. D. A. Tefankjian, Superintendent, Measurement Department, Texas Eastern Transmission Corporation (the official A.G.A./OIML representative) has begun the process of selecting an A.G.A. co-technical advisor.

8. Problem Areas. None.

9. Funding. January 1 - June 30, 1976. 10K$

10. Future Plans. A meeting is planned in late August of representatives from the Cryogenics Division (NBS), the Office of International Standards (NBS), and representatives of the American Gas Assocation to define the scope direction and time table for the accomplishment of the objectives.

1. Title. FEDERAL POWER COMMISSION CONSULTATION

Principal Investigators. D. B. Chelton, A. F. Schmidt and T. R. Strobridge.

2. Cost Center Number. 2750404

3. Sponsor. Federal Power Commission - Bureau of Natural Gas -- letter agreement dated 4 June 1973.

4. Goals. The Cryogenics Division will provide consultation and advisory services to the Federal Power Commission on the cryogenic safety and the design aspects of current applications before the FPC for authorization of LNG terminal and storage facilities. These services cover properties of cryogenic environments, insulation systems, cryogenic safety, thermodynamics, heat transfer, instrumentation, and cryogenic processes such as refrigeration and liquefaction.

5. Background. Cost Center initiated July 7, 1973.

6. Program and Results. The status of those facilities presently under the jurisdiction of the Federal Power Commission and subject to our review are outlined in the following table.

   Elements of the facilities that are subject to review are the land-based cryogenic storage tank components, bounded by the tanker or barge, the inlet and distribution pipelines. These include, but are not limited to the transfer lines, the storage tanks, the vaporizers and the process piping as it interacts with the storage tanks. It is essential that the reviews cover the operation, maintenance and emergency procedural philosophies for each terminal. Based upon these studies, reports are submitted to the staff of the FPC setting forth the technical evaluations and conclusions on each proposal.

   Emphasis is placed on the safety aspects of the facilities including their possible interactions with the surrounding areas. The impact of engineering design such as appropriate use of existing technology and material selection for structural integrity must be assessed. The basis of review includes various codes and standards, prior experience, precedent and engineering knowledge. Vapor cloud generation and plume dispersion is considered a subject beyond our area of expertise.

7. Funding.

FY 76	35K$
January 1 - June 30, 1976	20K$
Anticipated Man-years of Effort FY 76	0.5

8. Future Plans. At the present time there are several pending applications, but detailed information is not yet available. It is anticipated that additional facilities will be reviewed as applications are made to the Federal Power Commission.

FPC CONSULTATION - LNG FACILITY REVIEW

Applicant	Location	Type Facility	Storage Facility	Status		
				Site Inspection	Technical Meeting	Review
Distrigas - New York Terminal	Staten Island, NY	Import Terminal	2-900,000 barrel	8/21/73	8/21/73	Complete
Distrigas - Everett Marine Terminal	Everett, MA	Import Terminal	1-600,000 barrel 1-374,000 barrel	8/23/73 4/02/76	8/23/73	Complete
Algonquin LNG, Inc.	Providence, RI	Import Terminal	1-600,000 barrel	8/24/73	8/24/73	Complete
Northern Natural Gas Co.	Carlton, MN	Peak Shaving	1-630,000 barrel 10.8 MMCFD liquefier	10/30/73 7/29/75	10/30/73	Complete
Northwest Pipeline Corp.	Plymouth, WA	Peak Shaving	1-348,000 barrel 6.0 MMCFD liquefier	10/31/73 7/31/75	10/31/73	Complete
East Tennessee Natural Gas Co.	Kingsport, TN	Peak Shaving	1-348,000 barrel 5.0 MMCFD liquefier	6/24/75	11/29/73	Complete
Transco Terminal Co.	Bridgeport, NJ	Import Terminal	3-600,000 barrel	1/23/74	1/23/74	Complete
Southern Energy Co.	Savannah, GA	Import Terminal	4-400,000 barrel	1/24/74	2/06/74	Complete
Alabama-Tennessee Natural Gas Co.	Greenbrier, AL	Peak Shaving	1-117,000 barrel 2.0 MMCFD liquefier	**	2/05/74	Complete
Trunkline LNG, Inc.	Lake Charles, LA	Import Terminal	3-600,000 barrel	2/07/74	5/14/74	Complete
Chattanooga Gas Co.	Chattanooga, TN	Peak Shaving	1-348,000 barrel 10.0 MMCFD liquefier	2/28/74	2/28/74	Complete
Tennessee Natural Gas Co.	Nashville, TN	Peak Shaving	1-290,000 barrel 5.0 MMCFD liquefier	2/27/74	2/27/74	Complete
Northern Natural Gas Co.	Hancock Co., IA	Peak Shaving	1-630,000 barrel 10.8 MMCFD liquefier	*	***	Complete+
Texas Eastern Transmission Company	Staten Island, NY	Peak Shaving/ Import	* 9.0 MMCFD liquefier	*	*	In process
El Paso Alaska Co.	Gravina Pt., Alaska	Export Terminal	4-550,000 barrel	8/19/74	*	Pending
Pacific Alaska LNG Co.	Nikiski, Alaska	Export Terminal	2-550,000 barrel 400 MMCFD liquefier	*	3/02/76	Complete+
Western LNG Terminal Co.	L. A. Harbor, CA Oxnard, CA Pt. Conception, CA	Import Terminal Import Terminal Import Terminal	2-550,000 barrel 2-550,000 barrel 2-550,000 barrel	* 12/09/75 12/10/75	* 12/09/75 *	Pending Complete+ Pending
Northern States Power Co.	Eau Claire, WI	Peak Shaving	1- 78,000 barrel 2.0 MMCFD liquefier	3/30/67	3/30/76	In process
Northern States Power Co.	Wescott, MN	Peak Shaving	1-580,000 barrel 1- 38,000 barrel 10 MMCFD liquefier	3/31/76	*	In process
Northwest Pipeline Corp. LNG-II	Plymouth, WA	Peak Shaving	1-522,000 barrel 10.0 MMCFD liquefier	*	*	In process

* to be determined
** NBS visit not scheduled
*** technical meeting not scheduled
\+ additional review is pending final design.

APPENDIX A

Fracture Behavior of the Heat Affected Zone in 5% Ni Steel Weldments*

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ABSTRACT

The fracture properties of the base metal and the heat affected zone (HAZ) of 5% Ni steel weldments were determined at room temperature, 111 K and 76 K; emphasis was placed on tests at 111 K, the minimum boiling point of liquefied natural gas (LNG). The 32 mm-thick test plates, which met the requirements of ASTM A645, were welded using the pulsed-power gas-metal-arc process at a heat input of 10.6 kJ/cm. The fatigue crack growth rates were determined for cracks growing through the thickness using four-point bend specimens. At 111 K, the rates in the base metal were essentially the same as found by other investigators; however, the rates in the HAZ were up to 10 times faster than previously reported. Fracture toughness tests were conducted under load-controlled conditions using J-integral procedures. At 111 K, the base metal and HAZ toughness values were 30 and 50 per cent lower, respectively, than toughness values obtained previously for the same plate of test material under displacement-controlled conditions. Fracture mechanics analyses using the results reported herein indicate that 5% Ni steel is suitable for LNG applications, but more conservative estimates of fatigue life and critical crack size are necessary.

Key Words: Cryogenic temperature; fatigue crack growth; fracture toughness; heat affected zone; J-integral; nickel steel; weldments.

INTRODUCTION

The international trade in liquefied natural gas (LNG) has created a large market for equipment to transport, store and process LNG. Structural materials used for these applications must have adequate strength and toughness at 111 K, the minimum boiling point of LNG. Presently, 9% Ni steel (ASTM A353 and A553) and 5083-0 aluminum alloy are the most widely used materials for LNG structural applications (1). However, a 5% Ni steel, which is specially heat treated to meet the requirements of ASTM specification A645, offers significant cost savings potential and may be widely used in the future.

Over the past few years, considerable work has been done to characterize 5% Ni steel and its weldments at temperatures down to 76 K (2). The fatigue and fracture properties of the weldments have been evaluated by Sarno, Bruner and Kampschaefer (3), Bucci, Greene and Paris (4) and Murayama, Pense and Stout (5). The fatigue crack growth behavior in the heat affected zone (HAZ) was found (3,4) to be far superior to the corresponding behavior in the base metal. For example, at a stress intensity range, ΔK, of 40 $MPa\sqrt{m}$ (36.1 ksi $\sqrt{in}$), the growth rates of cracks in the base metal were about 10 times faster than that of cracks in the HAZ. The fracture toughness of the HAZ was reported (3,4,5) to range between 88 and 526 $MPa\sqrt{m}$ (79.4 to 475 ksi$\sqrt{in}$) over a thickness range of 6.4 to 38mm; low values occurred in thick-section load-controlled tests (3) and the highest values occured in thin-section displacement-controlled tests. This variation in toughness results in a 36-fold difference in calculations of critical crack lengths.

The present study was undertaken to further investigate and clarify the fracture behavior of 5% Ni steel weldments. Fatigue and fracture tests were conducted on the HAZ and the base metal at room temperature, 111 K and 76 K. Emphasis was placed on determining the relative contributions of material variability and of test-method peculiarities to the range of results previously reported. The questions of principal interest are: (1) Is the fatigue crack growth resistance of the HAZ really that good? and (2) Is the toughness of the HAZ really that unpredictable? To answer these questions, two experimental objectives were established. First, the fatigue crack growth behavior of a crack in the HAZ will be determined as it propagates through the thickness. In addition to being an important practical case, cracks in this orientation do not benefit from the favorable closure effects that may have influenced the previous results as discussed by Bucci et al. (4). Second, the range of fracture toughness in the HAZ will be established under load-controlled conditions. A direct comparison with the displacement-controlled toughness measured by Sarno et al. (3) will be possible because the test weldment was prepared using 5% Ni steel from the same heat and essentially the same welding procedures.

MATERIALS AND PROCEDURES

Test Weldments

Two 32 mm-thick 5% Ni steel plates were welded with Inconel 92* (AWS A 5.14 Class ERNiCrFe-6) filler wire. One of the test plates was oriented with the rolling direction perpendicular to the weld joint. This enabled evaluation of HAZ toughness in both base plate orientations. The chemical composition and mechanical properties of the base plate as reported by Sarno (6) are shown in Table I.

Welding was done by the Armco Steel Research Center using the pulsed-power gas-metal-arc process and the parameters summarized in Table II. The weld-joint preparation and the welding sequence are shown in Figure 1.

Charpy impact tests were conducted to verify that the weldment met the toughness requirements established by the U.S. Coast Guard (7) for LNG service. Type A (V-notch) specimens were tested in accordance with ASTM E-23

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*Tradenames are used in this report for clarity; in no way does this imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material is the best available for the purpose.

at 76 K. The specimens were cut transverse to the weld axis with the notches normal to the plate surface. The HAZ specimens were cut such that the notch was in the base plate oriented with the rolling direction parallel to the weld joint. Three specimens were tested for each of the following locations as shown in Figure 2: centered in the weld metal; on the fusion line; and in the HAZ 1, 3 and 5 mm from the fusion line. The results are summarized in Table III.

Fatigue Crack Growth Specimens

The fatigue crack growth tests were conducted using four point bend specimens as shown in Figure 3. This specimen was selected to enable determination of the fatigue crack growth rates in the L T orientation, i.e. the plate is loaded in the transverse direction and the crack propagates through the thickness.

A compliance calibration, needed for crack length measurements in the fatigue tests, was established for the four-point bend specimen. Compliance, C, is the ratio of crack opening displacement, Δ, to applied load, P; and C is a function of crack length, a, specimen geometry, and the elastic modulus of the material, E:

$$C = \frac{\Delta}{P} = \frac{1}{EB} f(\frac{a}{W}) \qquad (1)$$

where B = specimen thickness, W = specimen width, and $f(\frac{a}{W})$ = compliance function. The compliance calibration, EBC vs a/W, was obtained using a single specimen by progressively extending a fatigue crack into the specimen and measuring compliance at growth increments of approximately 1 mm. After each compliance measurement, the ratio of minimum-to-maximum load, R, was changed to either R = 0.1 or R = 0.5. An ASTM E-399 clip gage was used for Δ measurements. At a crack length of 1.81 cm, the specimen was fractured to expose the fatigue bands corresponding to each increment of crack growth. Crack lengths for each compliance measurement point were measured from a photograph, Figure 4, of the fracture surface. An average value of the mid-thickness and two quarter-thickness readings was used as the crack length.

The results of the compliance calibration test are shown in Figure 5. A least-squares best fit analysis of the data yields the following expression:

$$a = W[0.5332 - 1.863(EBC)^{1/6} + 1.641(EBC)^{1/3} - .3525(EBC)^{1/2}], \qquad (2)$$

for $0.2 \leq a/W \leq 0.6$. The agreement of Equation (1) with the experimental data and the theoretical results of Srawley and Gross (9) is shown in Figure 5.

Fatigue Crack Growth Testing

Fatigue crack growth tests were conducted on the base metal and the HAZ in air at room temperature, in nitrogen vapor at 111 K and in liquid nitrogen at 76 K. Two tests at 76 K were also conducted on the weld metal. The LNG temperature of 111 K was maintained within $\pm$ 3 K by adjusting the flow of liquid nitrogen into the test dewar with a hand-operated needle valve. Temperature was monitored with a type E thermocouple taped to the bottom of the test specimen.

Four point bend specimens were mounted in the test fixture shown in Figure 6 for fatigue testing in a 100 kN (22,480 lb) electrohydraulic fatigue machine. Tests were conducted using a 20 Hz sinusoidal load wave at an R of 0.1. All specimens were precracked at room temperature to an initial crack length of 0.611 cm (i.e. 0.311 cm beyond the machined-notch depth) using a maximum load that was less than or equal to the maximum load for the fatigue crack growth tests. The procedures for room and cryogenic testing were the same except for the temperature control provisions.

The compliance method (9) was used for crack length measurements. Compliance measurements were taken at increments where the estimated growth was 0.751 cm. The recorded data were cycle number and compliance. Crack lengths were determined from the compliance calibration, Equation (1). Stress intensity ranges, ΔK, were computed from the K-calibration equation of Gross and Srawley (10):

$$\Delta K = \frac{(P_{max} - P_{min})\sqrt{a}}{BW} Y(a/W) \quad (3)$$

where,

$$Y(\frac{a}{W}) = 1.992 - 2.468(\frac{a}{W}) + 12.97(\frac{a}{W})^2 - 23.17(\frac{a}{W})^3 + 24.8(\frac{a}{W})^4, \quad (4)$$

P_{max} = maximum load in the fatigue cycle and P_{min} = minimum load in the fatigue cycle. Crack growth rates were determined by the central difference method. The results were presented in log-log plots of da/dN vs ΔK.

Fracture Toughness Testing

Fracture toughness tests were conducted on the base metal and the HAZ in nitrogen vapor at 111 K. Additional tests were conducted on the HAZ in air at room temperature and in liquid nitrogen at 76 K. The temperature of 111 K was maintained as in the fatigue tests except that the control thermocouple was mounted on the side of the specimen in the plane of the crack.

Modified compact specimens, Figure 7, were tested in accordance with the J-integral procedures described by Landes and Begley (11). In this method, each specimen is loaded to a predetermined displacement level such that a range of subcritical crack extensions occurs in a given test series. Upon reaching the predetermined displacement level, the specimen is unloaded, heat tinted to mark the region of subcritical crack growth that occurred during the load cycle and subsequently loaded to failure to expose the fracture surfaces for measurements of crack length, a, and crack extension,

Δa. The J-integral value for the test is calculated using the approximation of Rice, Paris and Merkle (12):

$$J = \frac{2A}{B(W - a)}, \qquad (5)$$

where A is the area under the load displacement curve. For a given test series, a curve of J vs Δa is constructed. On the same graph, the line defined by Equation (6) is drawn:

$$J = 2\sigma_{flow}\Delta a, \qquad (6)$$

where $\sigma_{flow} = (\sigma_{ys} + \sigma_{uts})/2$, σ_{ys} = .2% offset yield strength, and σ_{uts} = ultimate tensile strength. The intersection of the J-Δa plot and the $J/2\sigma_{flow}$ line is defined as J_{IC}, the value of J at the onset of crack extension. Apparent crack extension at Δa values less than $J/2\sigma_{flow}$ is attributed to deformation at the crack tip instead of material separation. Begley and Landes (13) have proposed that the plane strain fracture toughness, K_{IC}, is related to J_{IC} as follows:

$$K_{IC}(J) = \left(\frac{J_{IC} \cdot E}{1 - \nu^2}\right)^{1/2}, \qquad (7)$$

where E = Young's modulus and ν = Poisson's ratio.

Tests were conducted in two electrohydraulic fatigue machines, each with 100 kN (22,480 lb) capacity. One machine employed the cryostat described by Fowlkes and Tobler (14), and the other a dewar equipped with the mechanical feedthrough shown in Figure 8. The specimens were loaded at 0.5 kN/s (111 lb/s) under load control. Loading was continued until either failure, crack extension due to pop-in, or a predetermined displacement was reached. The specific test termination point for each test is noted in the results. Specimens unloaded prior to failure were heat tinted and subsequently loaded to failure at 76 K to expose the fracture surface. Tinting was accomplished by heating the specimens in a 813 K furnace for 15 minutes. The fractured surfaces were visually examined under 35X magnification for evidence of subcritical crack extension.

RESULTS AND DISCUSSION

Fatigue Crack Growth

The fatigue crack growth test results on 5% Ni steel weldments at room temperature, 111 K and 76 K are summarized in Figures 9, 10 and 11, respectively. The Paris power law (15), Equation (8), is used as the basis for empirical analysis of the data:

$$\frac{da}{dN} = C(\Delta K)^n, \tag{8}$$

where C is the intercept and n is the slope of a log-log plot of da/dn vs ΔK. A least-squares regression analysis was used to obtain a statistical fit of the crack growth data. For each test condition, values of C and n are included in the appropriate plot of the results, Figures 9 to 11.

In all cases, the fatigue cracks propagated in a direction perpendicular to the bending stress, i.e. local properties within the HAZ did not influence the path followed by the fatigue crack. The location of the crack tip varied from the fusion line to a distance about 7 mm from the fusion line as the crack propagated through the thickness.

The fatigue crack growth data for the base metal and the HAZ at room temperature are summaried in Figure 9. The growth rates are essentially the same in both cases and coincide with the base metal data of Bucci et al. (4) and of Tobler, Mikesell, Durcholz and Reed (16).

The fatigue crack growth data for the base metal and the HAZ at 111 K are summarized in Figure 10. The base metal data are in good agreement with the data of previous investigations (3,14,16). However, in contrast with previous results (3,4) where the HAZ exhibited reduced growth rates, the growth rates in the HAZ are approximately 1.5 times faster than the corresponding rates in the base metal. The principal difference between the present and previous investigations was crack orientation. In this study, growth rates were measured as the crack propagated through the thickness; in the previous studies, through-thickness cracks were propagated in the rolling direction. The difference in crack orientation did not appear to influence the base metal results - which were equivalent in all cases (3,14,16). However, in the previous (3,4) HAZ tests, through-thickness cracks were partially located (i.e. near both surfaces) in ductile weld metal. Apparently, deformation of the weld metal limited the range of crack-opening-displacements in these tests and resulted in reduced growth rates as discussed by Bucci et al. (4).

The fatigue crack growth data for the base metal, the HAZ and the weld metal at 76 K are summarized in Figure 11. The base metal data overlap the results of Tobler et al. (16), but have a slightly greater slope than the results of Bucci et al. (4). The crack growth rate in the HAZ was significantly faster than that observed in the base metal. The weld metal had the greatest resistance to fatigue crack growth at 76 K - the only temperature where the crack growth behavior of the weld metal was determined. The crack growth rates in the weld metal at low ΔK levels exhibited more scatter than observed in the higher ΔK tests; however, growth was observed at ΔK levels down to 15 $MPa\sqrt{m}$ (13.5 $ksi\sqrt{in}$). The lowest values of ΔK employed in the weld metal tests of Sarno et al. (3) were approximately 30 MPa$\sqrt{m}$ (27.1 ksi $\sqrt{in}$); difficulties were encountered in getting uniform crack growth along the crack front at lower stress intensities. Similarly, Bucci et al. (4) found it difficult to sustain crack growth in the weld metal at ΔK levels less than 40 MPa$\sqrt{m}$ (36.1 ksi$\sqrt{in}$).

The temperature dependence of fatigue crack growth in 5% Ni weldments is summarized in Figure 12. The room temperature and 111 K data tend to be approximately the same. A significant increase in growth rates occurred at 76 K, particularly in the HAZ tests. The relatively strong temperature dependence between 111 and 76 K may be due to the large decrease in fracture toughness that occurs over this same temperature range (16).

Some crack growth retardation was observed in the present study. In each of the HAZ tests conducted at a maximum load of 6 kN (1350 lb) (specimens 8, 4, 5 and 6), retardation was exhibited at stress intensity levels of over 30 MPa$\sqrt{m}$ (27.1 ksi$\sqrt{m}$), i.e. at crack lengths in excess of a/W = 0.5. Examination of the load-displacement curves for these data points suggest that the reduced growth rates may have been due to crack closure effects. The data points that may have been influenced by closure effects are plotted in Figure 9 to 11; however, these data were not included in the regression analysis to determine C and n values. Similar retardation effects were not observed in the higher load tests (P_{max} > 6 kN), probably because net section yielding tended to separate the fracture surfaces at crack depths greater than a/W = 0.5.

Fracture Toughness

The fracture toughness data for 5% Ni steel weldments at room temperature, 111 K and 76 K are summarized in Table IV. Tests at room temperature and 76 K were conducted on the HAZ in the transverse (TL) orientation. Tests at 111 K were conducted on the base metal in the TL orientation and on the HAZ in both the longitudinal (LT) and TL orientations. Tests were not conducted on the nickel-base weld metal because it was assumed to be tougher than the parent metal or the HAZ on the basis of the Charpy impact results of Table III.

Emphasis was placed on determining the range of fracture toughness characteristic of the HAZ at 111 K. The upper-bound was established by the base metal toughness which averaged 159 MPa$\sqrt{m}$ (144 ksi$\sqrt{in}$) in the two specimens that were loaded to failure; the specimens unloaded prior to failure are discussed below. A lower bound was established by measuring the fracture toughness at pop-in. Pop-in is an abrupt sub-critical crack extension that causes a discontinuity in the load-displacement curve - usually a sudden increase in displacement at a fixed or decreasing load. Three TL specimens exhibited pop-in at an average toughness of 108 MPa$\sqrt{m}$ (97.5 ksi$\sqrt{in}$) and one LT specimen exhibited a pop-in at 136 MPa$\sqrt{m}$ (123 ksi$\sqrt{in}$). In each test where pop-in occurred, the specimen was unloaded immediately after pop-in, heat tinted, fractured and visually examined to identify the location in the HAZ where pop-in occurred. The fracture surfaces of the four specimens that exhibited pop-in are shown in Figure 13. In each case, pop-in occurred along the crack front from the fusion line to a location approximately corresponding to the 5 mm line of Figure 2. Thus, the lowest toughness region of the weldment was identified as the HAZ, but within the HAZ the location of minimum toughness could not be identified. The HAZ toughness was greater in the LT orientation, averaging 155 MPa$\sqrt{m}$ (140 ksi$\sqrt{in}$) than in the TL orientation which averaged 131 MPa$\sqrt{m}$ (118 ksi$\sqrt{in}$).

The HAZ of 5% Ni weldments exhibited relatively brittle behavior at 76 K and very tough behavior at room temperature. The toughness at 76 K averaged 77 MPa$\sqrt{m}$ (69.5 ksi$\sqrt{in}$). Three of the five tests at 76 K satisfied the thickness requirements of ASTM Standard E-399 for valid K_{IC} measurements.

The toughness of the HAZ at room temperature could not be estimated on the basis of the four tests conducted because subcritical crack growth occurred in only one test. The results do suggest that the HAZ toughness is at least as good as the base metal toughness of 220 $MPa\sqrt{m}$ (200 $ksi\sqrt{in}$) reported by Tobler et al. (16) for a test plate from the same heat of 5% Ni steel.

In the fracture toughness tests, efforts were made to obtain J-Δa data for $K_{IC}(J)$ calculations as described in the procedure section. However, subcritical crack extension was not detected (except in room temperature test 3-1) prior to pop-in or fracture despite repeated efforts to find it. In Table IV, each specimen with the note "-unloaded, no Δa-" was loaded to the J level given, unloaded, heat tinted, fractured, and visually examined at 35X for evidence of subcritical crack extension; in each test as noted, no crack extension was observed. Apparently 5% Ni Steel (base metal and HAZ) does not exhibit the slow tearing type of subcritical crack extension at temperatures of 111 K and 76 K unless tested by the displacement-controlled R-curve method used by Sarno et al. (3). Tobler et al. (16) did obtain J-Δa curves at room temperature and 195 K, but did not report subcritical crack growth in the 111 K and 76 K tests.

The plane of the notch in the HAZ specimens is shown in the sketch of the fracture toughness specimen, Figure 7. The fatigue precrack did not propagate uniformly in the HAZ, growing faster on the outside than in the center. The characteristic shape of the precrack, as shown in Figure 13, was essentially the same in all HAZ tests. Crack lengths for fracture toughness calculations were arbitrarily defined as the average of the two maximum lengths at the outside and the minimum length in the center. The precracks in the base metal tests were uniform, and the length was computed as the average of the 1/4, 1/2 and 3/4 thickness values.

Care must be taken in comparing the present results with those obtained by Sarno et al. (3) because of the differences in both the test method and the definition of fracture toughness. Consider, for example, the 111 K test results. In the present investigation, fracture toughness was determined for crack initiation conditions. For the base-metal, specimen failure occurred prior to pop-in and the measured toughness is clearly indicative of the fracture resistance of the material under load-controlled conditions. However, in the HAZ tests, pop-in generally occurred and the load and displacement at pop-in were used to determine the fracture toughness. In contrast, Sarno et al. measured fracture toughness under displacement-controlled conditions in accordance with the ASTM proposed R-curve procedure (17). Using these procedures, stable crack extension readily occurs prior to fracture and toughness is measured after considerable crack extension has occurred. Since toughness increases following the initial increments of crack extension, the fracture toughness values determined by this method are higher. In the HAZ tests on 38 mm plate, Sarno (18) observed pop-in at approximately 110 $MPa\sqrt{m}$ (100 $ksi\sqrt{in}$) which is essentially the same as the value reported herein. However, the test was continued until the full fracture resistance curve was developed and a higher value of fracture toughness (217 $MPa\sqrt{m}$) was reported. Thus, the differences in fracture toughness results are attributable primarily to test method and not to material variability. Comments on the significance of these differences from a design standpoint are included in the next section.

IMPLICATIONS OF THE TEST RESULTS

The test data generated in this program indicate that for the conditions evaluated the fracture resistance of 5% Ni steel weldments may be significantly lower than expected on the basis of previous investigations (3,4). In this section, the significance of the present results relative to LNG applications is assessed.

The fatigue crack growth rates in the HAZ for cracks growing through the thickness are 3 to 10 times faster than the rates reported by Sarno et al. (3) for through-thickness cracks growing in the rolling direction. Consideration is given here to how these results influence life assessments based on fracture mechanics analysis. McCabe, Sarno and Feddersen (19) computed the number of fatigue cycles required to propagate an initial surface crack (semi-elliptical shape, 4 mm deep and 16 mm long) through the thickness of a 16 mm thick plate of 5% Ni steel at 103 K. The fatigue cycling conditions and the stress levels were appropriate for a semi-membrane tank in an LNG ship. Their analysis used the best-fit data of Sarno et al. (3) for the base metal at 103 K as shown in Figure 10. The results indicated that, assuming no crack growth retardation, the fatigue life of the initial flaw prior to leakage was approximately 192 years. In this analysis, it was appropriate to use base metal data, because the crack growth rates were lower in the HAZ. The present results indicate that the growth rates are greater in the HAZ than in the base metal; however, the average rates in the HAZ still fall within the scatterband for the base metal defined by Sarno et al. (3) and within the variability normally found in fatigue crack growth testing (20). The upperbound line of Sarno et al. (3) is a factor of 2.5 greater than the best-fit line used in the analysis (19), i.e. the slope n of equation (8) is the same but the C value is 2.5 times greater. Use of the upper-bound crack growth data would conservatively account for the increased growth rates observed in the HAZ in the present study. Since life scales linearly with C, a conservative estimate of life based on the analysis of McCabe et al. (19) but using the present HAZ crack growth rates would be 77 years. Clearly, this life is sufficient for safe operation of LNG ships for their intended period of use is less than 30 years.

At 111 K the fracture toughness of the HAZ in the present study averaged 108 MPa$\sqrt{m}$ at pop-in. In contrast, the HAZ toughness reported by Sarno et al. (3) under displacement-controlled conditions was 217 MPa$\sqrt{m}$ (196 ksi$\sqrt{in}$) for 38 mm thick plate. The displacement-controlled toughness should be appropriate for redundant structures, but not for single load path structures such as storage tanks and the spherical shipboard tanks of the Moss-Rosenberg (21) design. The displacement-controlled toughness is a factor of 2 greater than the load-controlled toughness. Since critical crack size scales as the square of fracture toughness, a four-fold decrease in critical crack size occurs under load-controlled conditions. Thus, the critical crack size of 102 cm calculated by Sarno et al. (3) for a stress of 163 MPa (23.7 ksi) would be reduced to 25 cm for the present results. Measurements by Tenge and Solli (22) indicate that leaks are detectable at crack lengths of 2 to 4 cm on the penetrating side. Thus, there appears to be a reasonable margin of safety on critical crack size for the load-control case.

The preceding discussion suggests that the failure resistance of 5% Ni steel weldments is satisfactory for LNG applications. This is true for the uniform stress conditions evaluated. Further analyses are required to demonstrate structural safety for cases of combined membrane plus bending stresses. For combined loading, stress levels as high as 378 MPa (55 ksi) are permitted by the U.S. Coast Guard (23). These higher stresses will result in faster crack growth rates and shorter critical sizes. In addition, the bending component will cause cracks to grow preferentially along the high tension surface, resulting in cracks that are much longer at the time of initial leakage. Assuming leakage still occurs prior to fracture, there is less time available for detecting the leak and taking preventive action than there would be for shorter cracks.

The results of the present investigation are also useful in deciding whether or not to substitute 5% Ni steel for 9% Ni steel. Substitution appears to be satisfactory for LNG applications where the service temperature is approximately 111 K. However, in liquid nitrogen at 76 K, the 5% Ni steel weldments exhibit brittle behavior and should not be used in place of 9% Ni steel which retains a higher level of toughness (1,5,16). Since the scope of the current study was limited to evaluation of a single weldment of 32 mm plate, care should be taken in using these data to justify selection of 5% Ni steel.

SUMMARY AND CONCLUSIONS

The fatigue crack growth behavior and the fracture toughness of 32 mm-thick 5% Ni steel weldments have been determined at room temperature, 111 K and 76 K.

The fatigue crack growth rates were determined for cracks propagating through the thickness. In this orientation the crack growth rates in the base metal are essentially the same as previously reported for through-thickness cracks growing in the rolling direction. However, in contrast to previous results, the crack growth rates are faster in the HAZ than in the base metal, particularly at the lower temperatures.

Fracture toughness tests were conducted under load-controlled conditions using test material from the same heat of 5% Ni steel previously evaluated using controlled-displacement test conditions. In this investigation, the fracture toughness of the base metal at 111 K in the TL orientation averaged 159 $MPa\sqrt{m}$ (144 $ksi\sqrt{in}$), as compared to a value of 226 $MPa\sqrt{m}$ (204 $ksi\sqrt{in}$) measured at 103 K in the controlled-displacement tests. The fracture toughness of the HAZ ranged from 103 to 145 $MPa\sqrt{m}$ (93 to 131 $ksi\sqrt{in}$)

at 111 K, as compared to a value of 216 $MPa\sqrt{m}$ (195 $ksi\sqrt{in}$) in the controlled displacement test. The differences in toughness were attributed to differences in the test methods employed and not to material variability.

The fatigue and fracture results reported herein suggest that 5% Ni steel is suitable for LNG applications, but more conservative estimates of life and critical crack size are in order. For the case of a semi-membrane tank subject to uniform membrane stresses, the estimated life prior to leakage and critical crack size are reduced by factors of 2.5 and 4, respectively, from values previously reported.

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REFERENCES

1. Properties of Materials for Liquefied Natural Gas Tankage, ASTM STP 579, American Society for Testing and Materials 1975.

2. Pense, A. W. and Stout, R. D., "Fracture Toughness and Related Characteristics of the Cryogenic Nickel Steels," WRC Bulletin No. 205, Welding Research Council, May 1975.

3. Sarno, D. A., Bruner, J. P. and Kampschaefer, G. E., "Fracture Toughness of 5% Nickel Steel Weldments," Welding Journal, Vol. 53 (11), Nov. 1974, Res. Suppl. pp. 486-s to 494-s.

4. Bucci, R. J., Greene, B. N. and Paris, P. C., "Fatigue Crack Propagation and Fracture Toughness of 5 Nickel and 9 Nickel Steels at Cryogenic Temperatures," Progress in Flaw-Growth and Fracture Toughness Testing, ASTM STP 536, 1973, pp. 202-228.

5. Murayama, N., Pense, A. W. and Stout, R. D., "The Fracture Toughness of Cryogenic Steels," Advances in Cryogenic Engineering, Vol. 22, 1976.

6. Sarno, D. A., Chemical, Mechanical Property and Weldability Data of Armco CRYONIC 5 Steel, Armco Steel Company, June 1973.

7. Anon, U.S. Coast Guard Marine Engineering Regulations, Subchapter F, CG-115, July 1970.

8. Srawley, J. E. and Gross, B., "Stress Intensity Factors for Bend and Compact Specimens," Engineering Fracture Mechanics, Vol. 4, 1972, pp. 587-589.

9. McHenry, H. I., "A Compliance Method for Fatigue Crack Growth Studies at Elevated Temperatures," Journal of Materials, Vol. 6 (4), 1971, pp. 862-873.

10. Gross, B., Srawley, J. E. and Brown, W. F., Jr., "Stress Intensity Factors for a Single-Edge-Notch Tension Specimen by Boundry Collocation of a

Stress Function," Technical Note D-2395, NASA, August 1964.

11. Landes, J. D. and Begley, J. A., "Test Results from J-Integral Studies - An Attempt to Establish a J_{IC} Testing Procedure," Fracture Analysis, ASTM STP 560, 1975, pp. 170-186.

12. Rice, J. R., Paris, P. C. and Merkle, J. G., "Some Further Results of J-Integral Analysis and Estimates," Progress in Flaw-Growth and Fracture Toughness Testing, ASTM STP 536, 1973, pp. 231-245.

13. Begley, J. A. and Landes, J. D., "The J-Integral as a Fracture Criterion," Fracture Toughness, ASTM STP 514, 1972, pp. 1-20.

14. Fowlkes, C. W. and Tobler, R. L., "Fracture Testing and Results for a Ti-6Al-4V Alloy at Liquid Helium Temperature," Engineering Fracture Mechanics, in Press.

15. Paris, P. C., "The Fracture Mechanics Approach to Fatigue," Proceedings, Tenth Sagamore Army Materials Research Conference, Syracuse University Press, Syracuse, NY, 1964, pp. 107-127.

16. Tobler, R. L., Mikesell, R. P., Durcholz, R. L. and Reed, R. P., "Low Temperature Fracture Behavior of Iron-Nickel Alloy Steels," Ref. 1, pp. 261-287.

17. Anon., Proposed Recommended Practice for R-Curve Determination, 1974 Annual Book of ASTM Standards, American Society for Testing and Materials, Philadelphia, PA, 1974.

18. Sarno, D. A., Armco Steel Corporation, Middletown, OH, Private communication, 1976.

19. McCabe, D. E., Sarno, D. A. and Feddersen, C. E., "Fatigue Crack Growth Rate Studies of Partial Thickness Cracks in ASTM Method A645-74 5 Percent Nickel Steel," Ref. 1, pp. 238-260.

20. Clark, W. G., Jr. and Hudak, S. J. Jr., "Variability in Fatigue Crack Growth Rate Testing," Scientific Paper 74-1E7-MSLRA-P2, Westinghouse Research Laboratories, Pittsburgh, PA, September 18, 1974.

21. Howard, J. L., "LNG Marine Carrier Construction," Marine Technology, Vol. 9 (3), 1972, pp. 281-291.

22. Tenge, P. and Solli, O., "Fracture Mechanics in the Design of Large Spherical Tanks for Ship Transport of LNG," Norwegian Maritime Research, Vol. 1 (2), 1973, pp. 1-18.

23. Henn, A. E. and Dickey, T. R., "New Regulations for Liquefied Gas Carriers," paper presented at GASTECH 75, Paris, 1975.

24. Weston, W. F., Naimon, E. R. and Ledbetter, H. M., "Low Temperature Elastic Properties of Aluminum 5083-0 and Four Ferritic Nickel Steels," Ref. 1, pp. 397-420.

LIST OF FIGURES

Table I. Properties of the 5% Ni steel base plate

Chemical Composition[6]

		C	Mn	P	S	Si	Ni	Mo	Al	N
ASTM-A645	Min	---	.30	----	----	.20	4.75	.20	.05	----
	Max	.13	.60	.025	.025	.35	5.25	.35	.12	.02
Heat Analysis		.08	.60	.010	.009	.25	5.03	.30	.08	.010

Tensile Properties[6]

Temperature K	Orientation	Yield MPa	Strength ksi	Ultimate MPa	Strength ksi	Elongation %	Reduction of Area %
297	Longitudinal	514	74.6	676	98.1	33	74
297	Transverse	507	73.6	678	98.4	33	77
144	Transverse	563	81.7	930	135.0	30	72
76	Transverse	772	112.0	1137	165.0	34	66

Charpy Impact Toughness[6]

Temperature K	Orientation	Individual Values J	J	J	Average J	Ft lb
111	Longitudinal	114	144	124	128	94
111	Transverse	84	91	97	91	67
103	Longitudinal	82	72	---	77	56
103	Transverse	79	79	---	79	58
76	Longitudinal	50	46	60	52	38
76	Transverse	48	49	31	42	31

Elastic Properties[24]

Temperature K	Young's Modulus, E GPa	10^6 psi	Poisson's Ratio, ν
297	198	28.7	.288
111	208	30.2	.282
76	209	30.3	.281

Table II. Welding Procedures

Weld position	Horizontal
Plate thickness	32 mm
Joint design	Double vee (See Figure 1)
Shielding gas	75He-25Ar at 39 l/s
Interpass temp	38 C°max.
No. of passes	21
Wire diameter	1.1 mm

Parameters:	Pass 1	Pass 2	Passes 3-21
Current, DCRP, A	110	140	140
Voltage, V	30	32	32
Travel, mm/sec (ipm)	3.4(8)	5.1(12)	4.2(10)
Heat input, kJ/cm (kJ/in)	9.8(24.8)	8.8(22.4)	10.6(26.9)

Table III. Results of the Charpy V-notch impact tests

Notch Location (See Figure 2)	Absorbed Energy Individual Tests J	Average J (Ft lb)
Weld metal	Failed to break (FTB)	FTB
Fusion line	109, 91, 91	97(71)
HAZ, 1 mm	159, 91, 126	125(92)
HAZ, 3 mm	113, 31, FTB	88(65)
HAZ, 5 mm	84, 54, 94	77(57)

Table IV. Fracture Toughness of 5% Ni steel weldments

Temperature	Specimen			J		$K_{Ic}(J)$		Notes
K	No.	Type	Orientation	kJ/m^2	$in\text{-}lb/in^2$	$MPa\sqrt{m}$	$ksi\sqrt{in}$	
297	1-1	HAZ	T L	113.0	644	--	--	Unloaded, no Δa
	2-1			783.0	4468	--	--	Unloaded, no Δa
	3-1			357.0	2040	--	--	Δa = 0.457 mm
	4-1			227.0	1295	--	--	Unloaded, no Δa
111	1-4	HAZ	L T	80.7	461	--	--	Unloaded, no Δa
	2-4			85.6	489	--	--	Unloaded, no Δa
	3-4			121.0	691	--	--	Unloaded, no Δa
	4-4			109.0	620	158.0	143.0	Pop-in
	5-4			104.0	595	155.0	140.0	Pop-in
111	1-3	HAZ	T L	53.9	308	112.0	101.0	Pop-in
	2-3			87.2	498	--	--	Unloaded, no Δa
	3-3			91.1	520	145.0	131.0	Load to failure, no pop-in
	4-3			51.0	291	108.0	97.7	Pop-in
	5-3			45.9	262	103.0	92.7	Pop-in
	6-3			61.6	352	118.0	107.0	Load to failure, no pop-in
76	1-2	HAZ	T L	26.4	151	77.9	70.4	Pop-in
	2-2			19.3	110	66.6	60.2	Pop-in
	3-2			30.5	174	83.7	75.6	Load to failure, no pop-in
	4-2			20.1	115	68.1	61.5	Pop-in
	5-2			34.1	195	--	--	Unloaded, no Δa
111	3-A	Base Metal	T L	99.1	566	--	--	Unloaded, no Δa
	3-B			66.7	381	--	--	Unloaded, no Δa
	3-C			135.0	770	--	--	Unloaded, no Δa
	3-D			112.0	641	161.0	145.0	Load to failure, no pop-in
	3-E			56.4	322	--	--	Unloaded, no Δa
	3-F			108.0	619	157.0	142.0	Load to failure, no pop-in

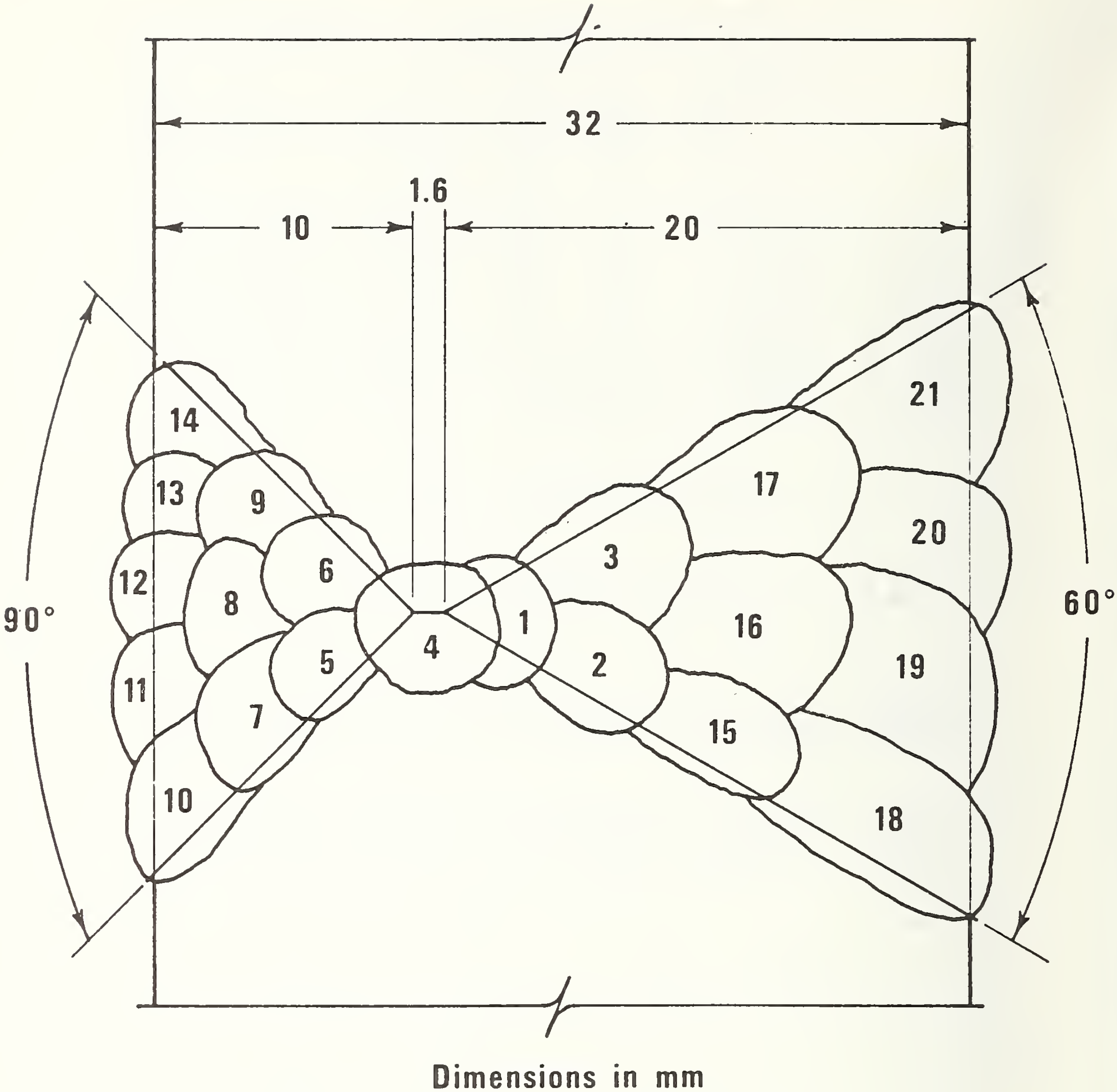

Fig. 1. Weld joint preparation and welding sequence.

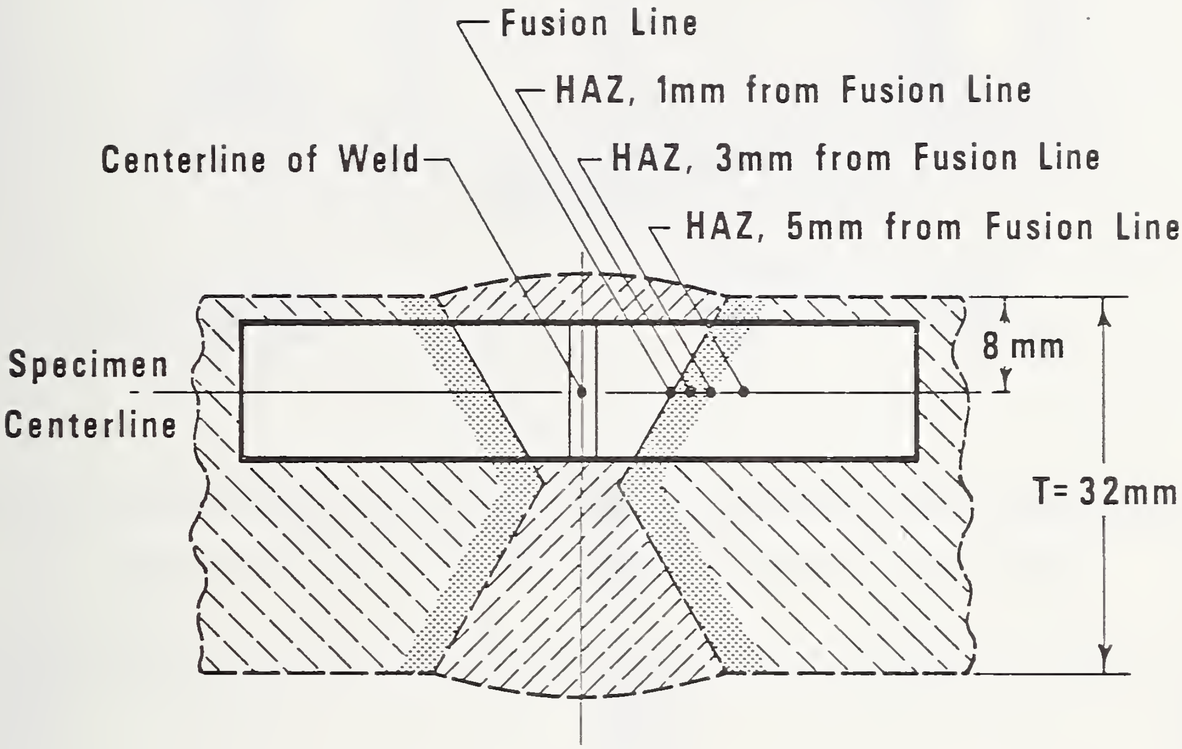

Fig. 2. Notch locations for Charpy impact specimens.

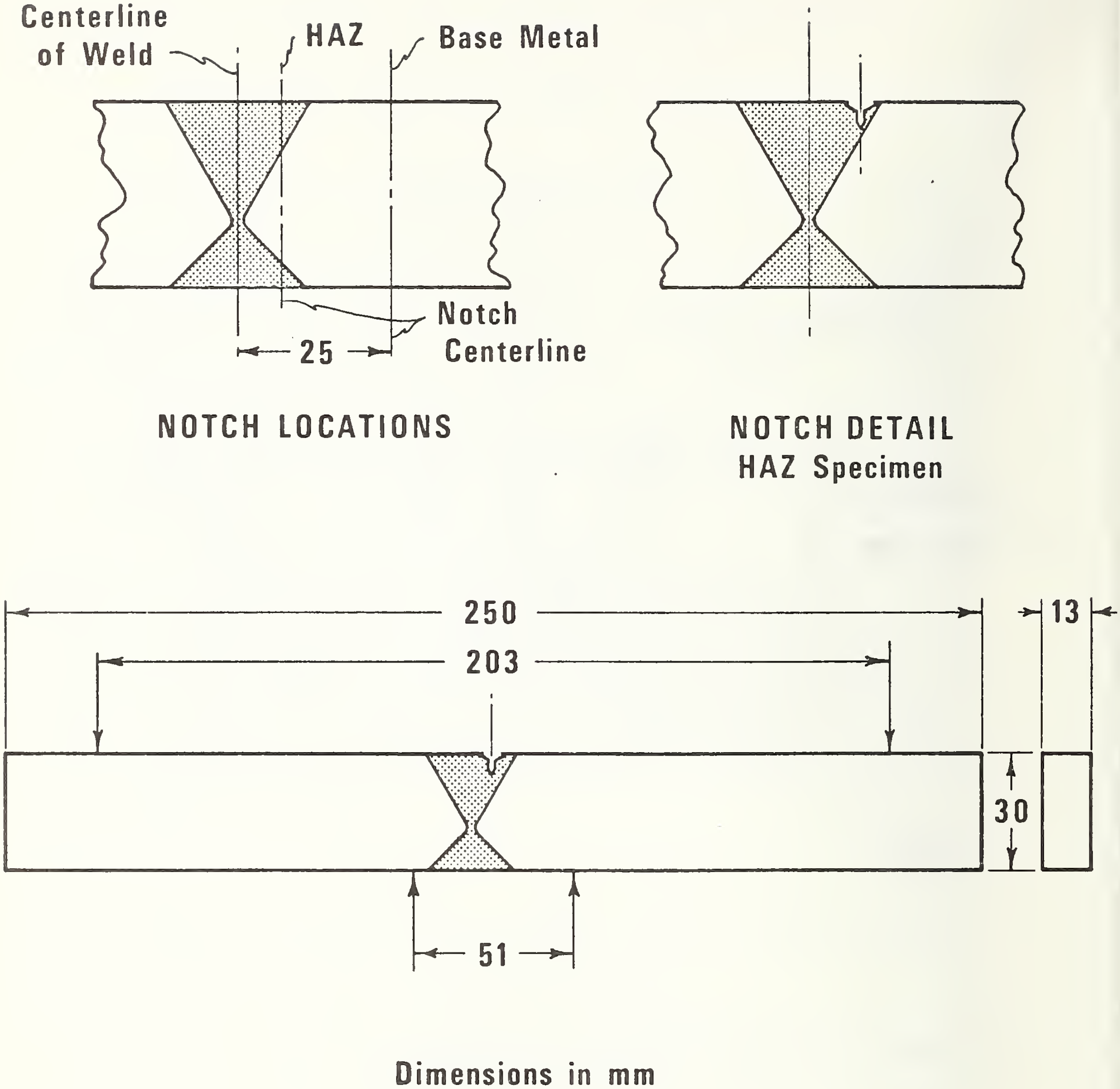

Fig. 3. Four point bend specimen for fatigue crack growth tests.

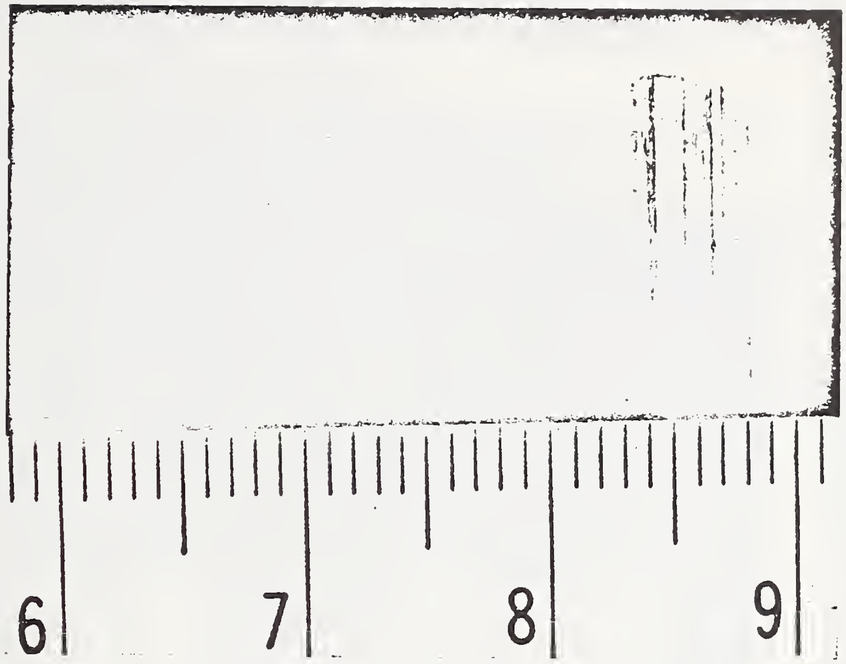

Fig. 4. Fracture surface of the compliance calibration specimen. (Scale in cm)

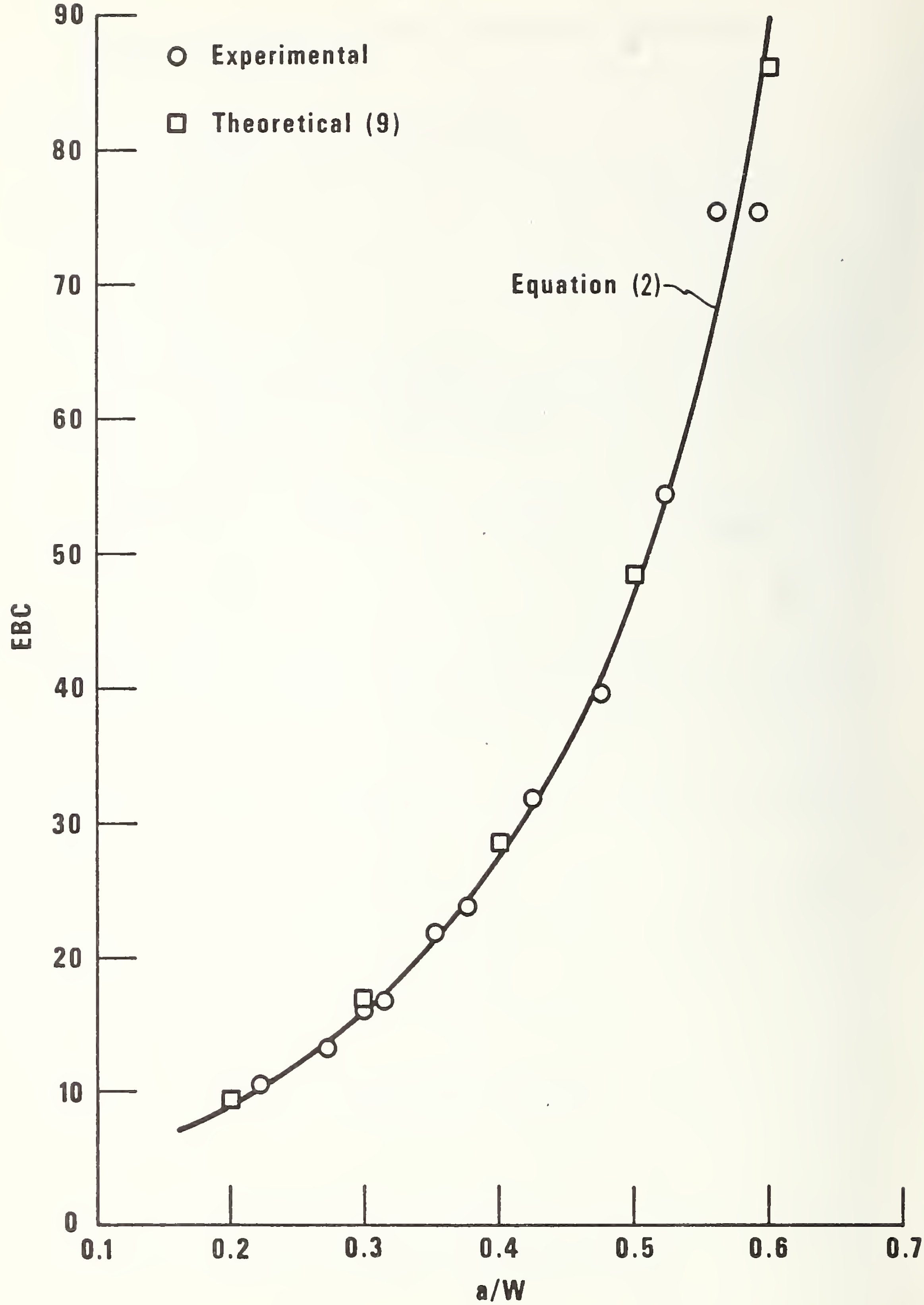

Fig. 5. Compliance calibration of the four point bend specimen.

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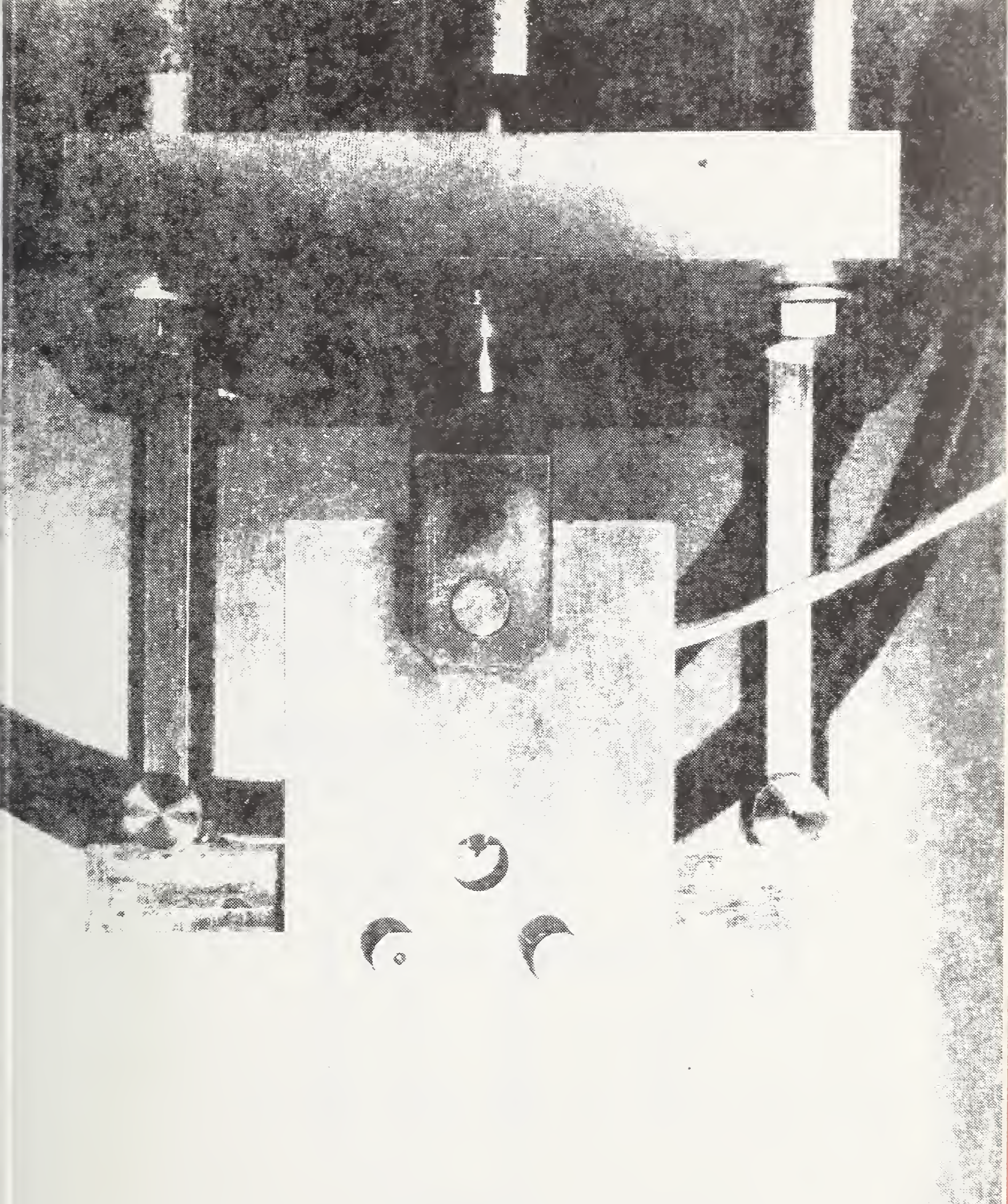
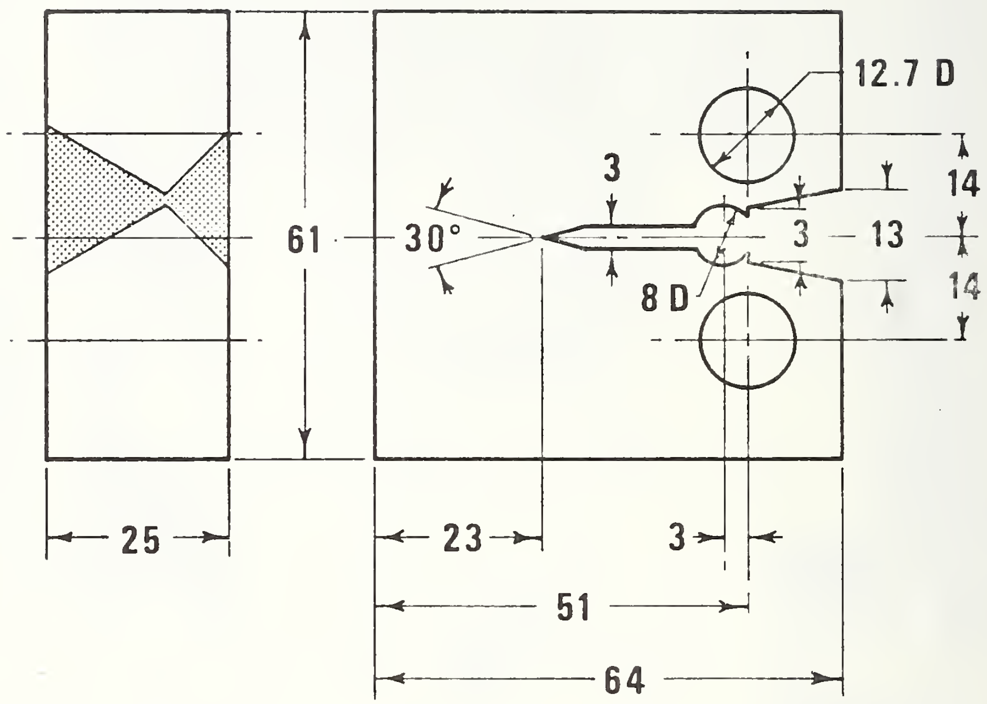


Fig. 6. Four point bend test fixture.



Dimensions in mm

Fig. 7. Modified compact specimen showing notch location for HAZ tests.

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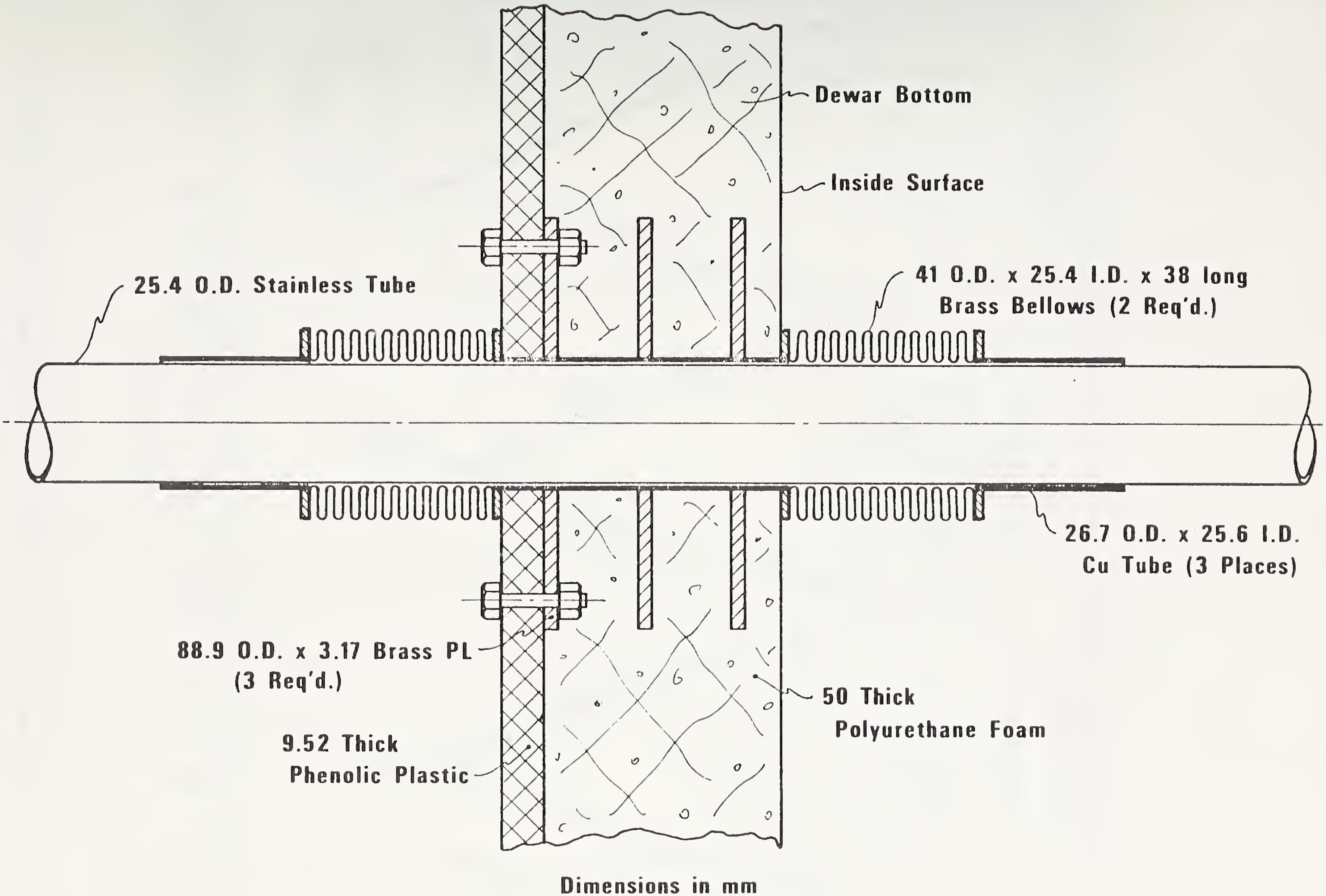

Fig. 8. Mechanical feedthrough for test dewar.

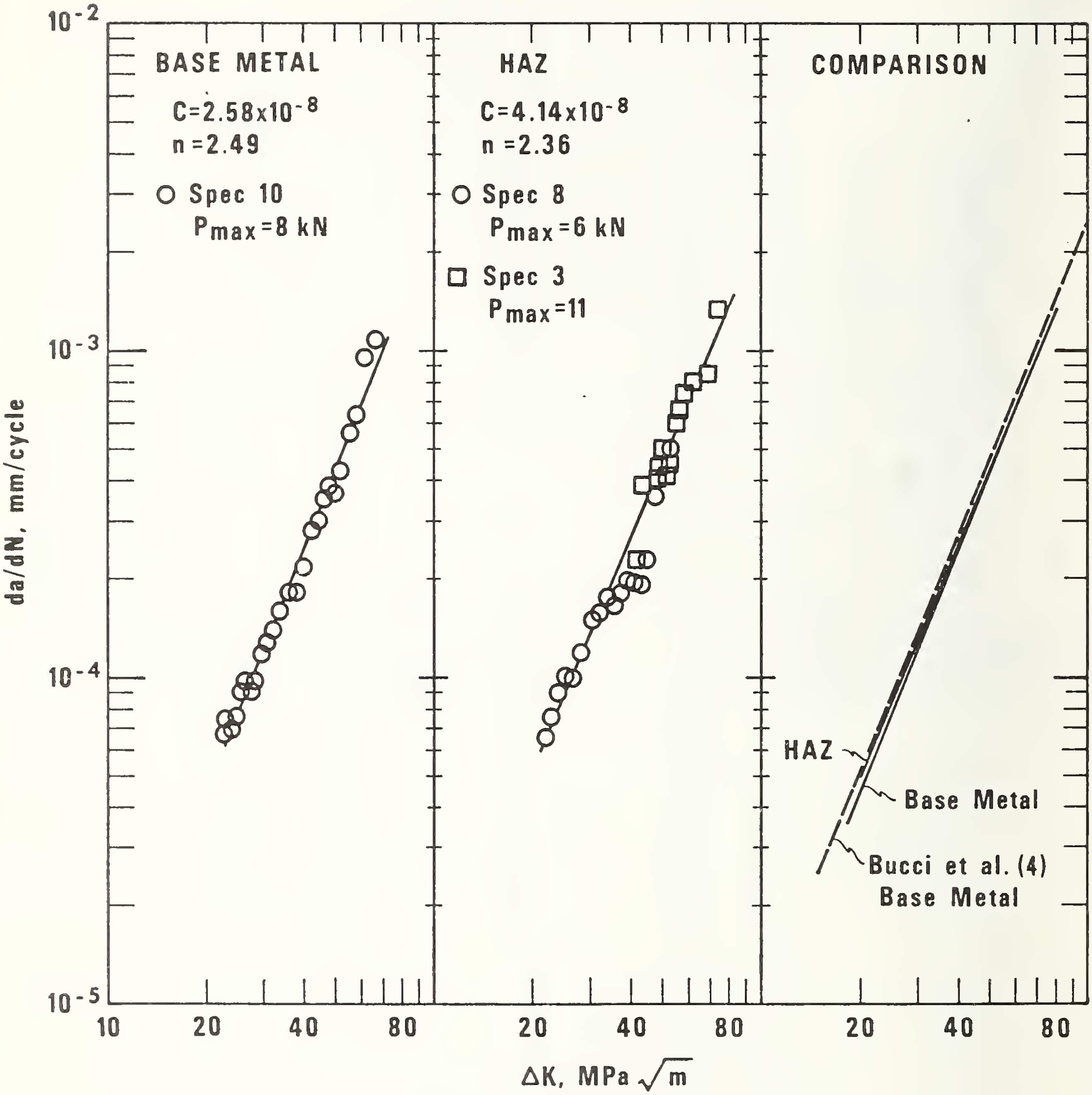

Fig. 9. Fatigue crack growth behavior of 5% Ni steel weldments at room temperature.

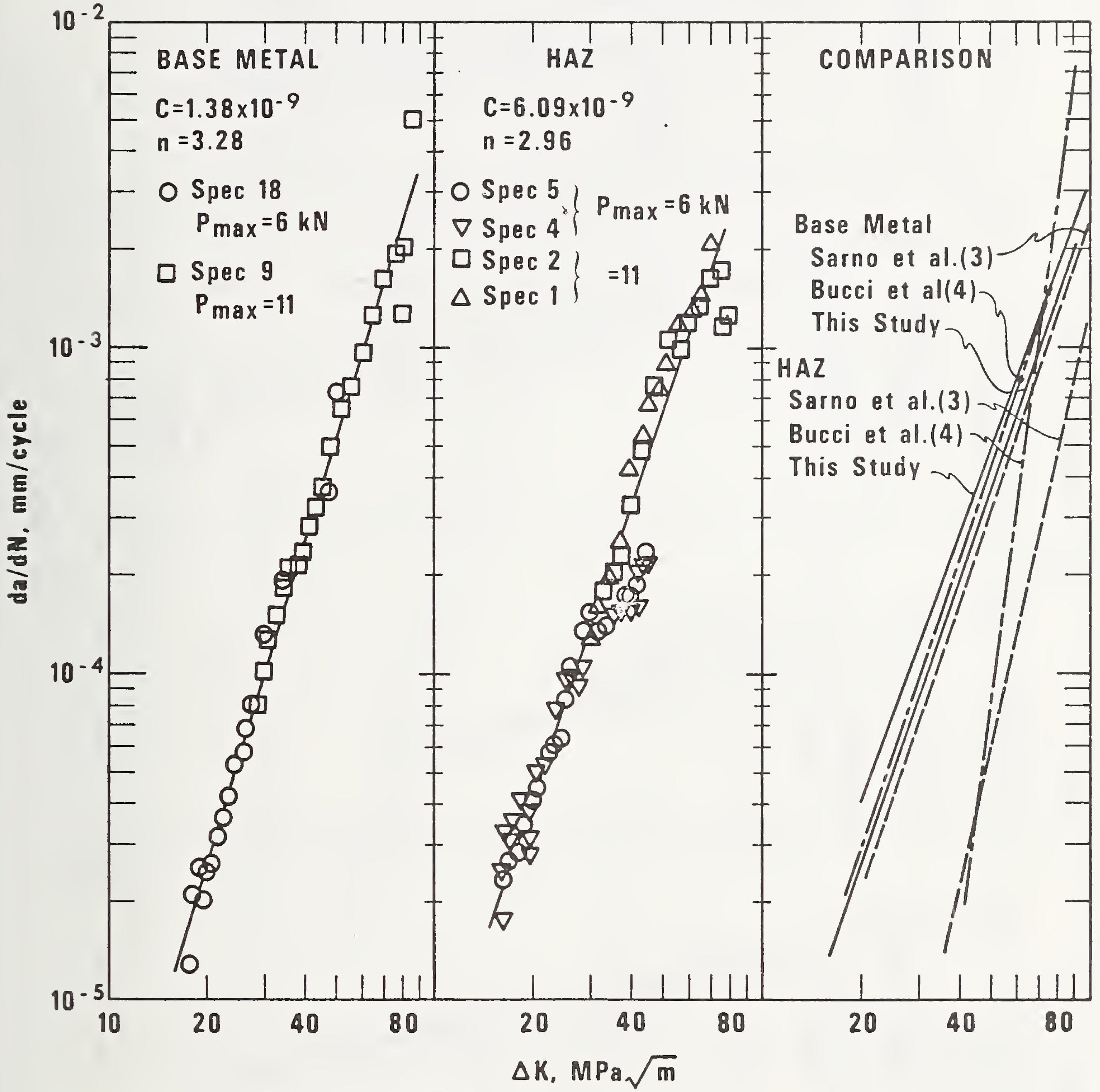

Fig. 10. Fatigue crack growth behavior of 5% Ni steel weldments at 111 K.

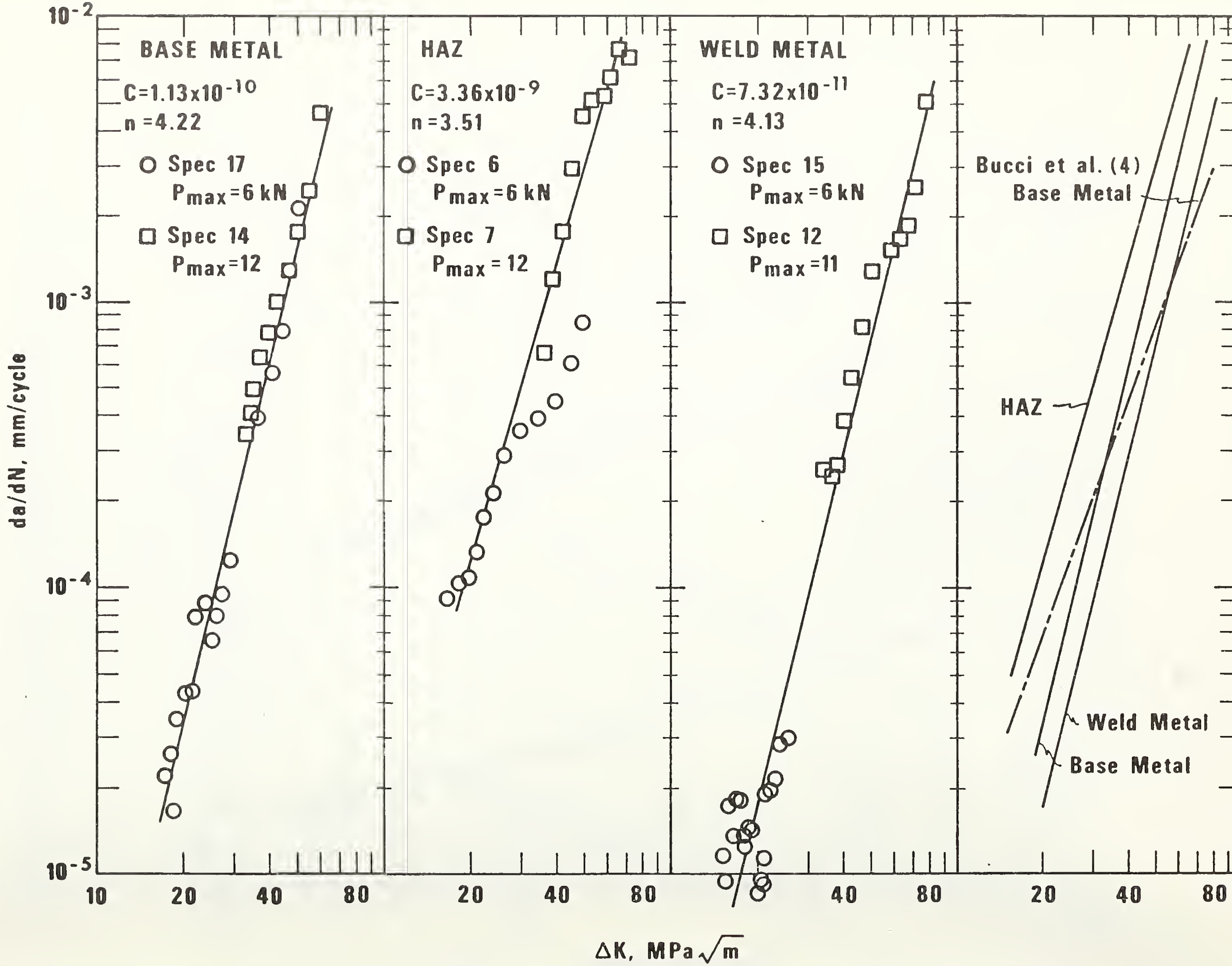

Fig. 11. Fatigue crack growth behavior of 5% Ni steel weldments at 76 K.

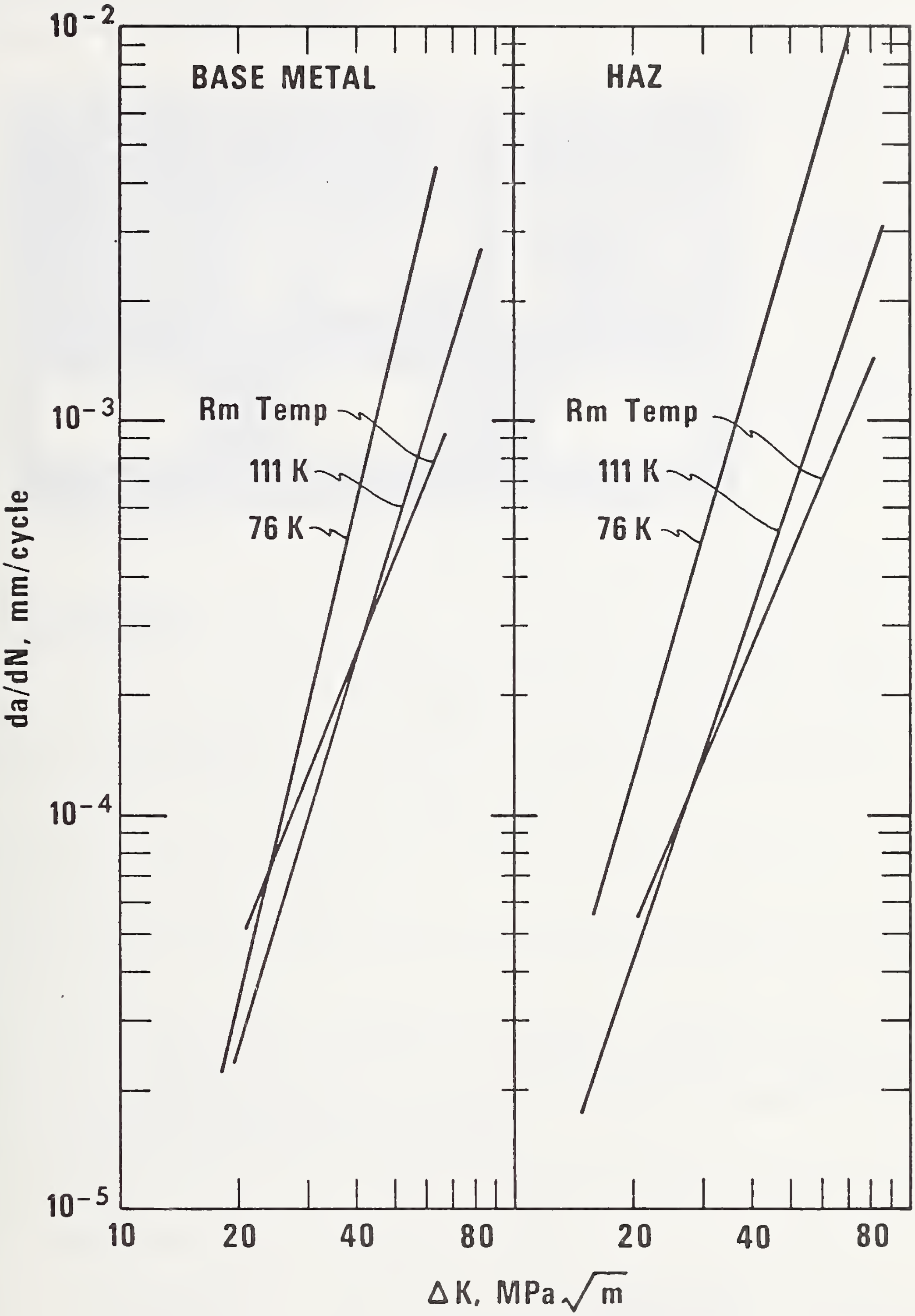

Fig. 12. Effect of temperature on the fatigue crack growth rates in 5% Ni steel weldments.

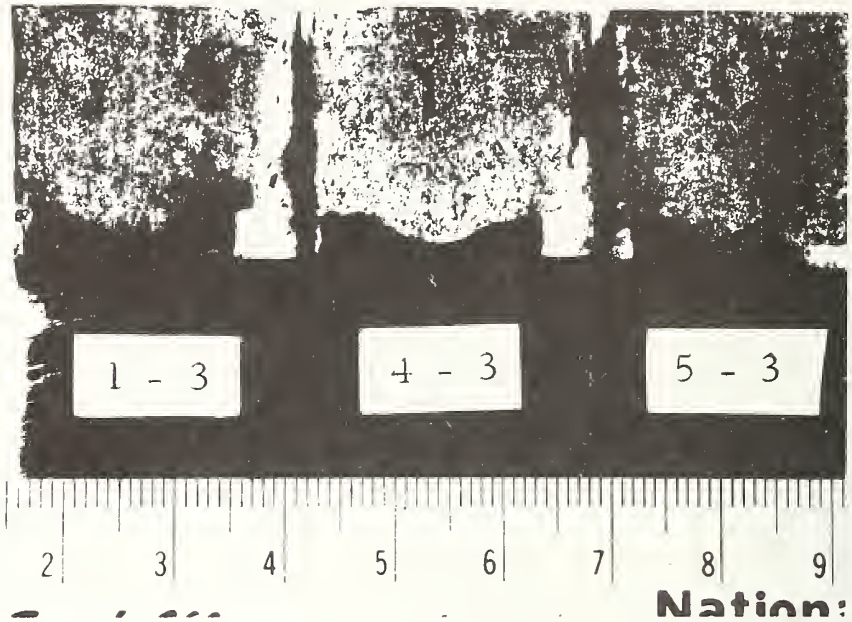

Fig. 13. Fracture surfaces of the HAZ specimens that exhibited pop-in at 111 K.

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15. SUPPLEMENTARY NOTES

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

Twenty-two cost centers, supported by six other agency sponsors in addition to NBS, provide the basis for liquefied natural gas (LNG) research at NBS. During this six month reporting period the level of effort was at a 20 man-year level with funding expenditures of over $600,000. This integrated progress report to be issued in January and July is designed to:

1) Provide all sponsoring agencies with a semi-annual and annual report on the activities of their individual programs.

2) Inform all sponsoring agencies on related research being conducted at the Cryogenics Division of NBS-IBS.

3) Provide a uniform reporting procedure which should maintain and improve communication while minimizing the time, effort and paperwork at the cost center level.

The contents of this report will augment the quarterly progress meetings of some sponsors, but will not necessarily replace such meetings. Distribution of this document is limited and intended primarily for the supporting agencies. Data or other information must be considered preliminary, subject to change and unpublished; and therefore not for citation in the open literature.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

Cryogenics; liquefied natural gas; measurement; methane; properties; research.

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