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Evaluation of the Effects of Natural Gas Contaminants on Corrosion in Compressed Natural Gas Storage Systems—Phase II

Fred F. Lyle, Jr.

Report Prepared by
Southwest Research Institute
6220 Culebra Road
San Antonio, Texas 78284

under

Subcontract 86X-22025C

for

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
operated by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
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OFFICE OF TRANSPORTATION SYSTEMS
ALTERNATIVE FUELS UTILIZATION PROGRAM

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ALTERNATIVE FUELS UTILIZATION PROGRAM

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ABSTRACT

This report describes a research program that was conducted to define natural gas contaminant levels necessary to insure that internal corrosion of compressed natural gas (CNG) cylinders does not constitute a hazard over the lifetimes of the cylinders. A literature search was performed and companies in the natural gas transmission and distribution industries were contacted: to identify and determine the composition ranges of contaminants in natural gases; and to obtain information regarding corrosion damage of CNG cylinders and cylinder materials. Corrosion and stress corrosion cracking (SCC) tests were performed on the cylinder materials most widely used in CNG cylinders in the United States (4130X and 15B30 steels and 6061-T6 aluminum alloy). Tests were conducted in: natural gases from several producing wells and from an interstate pipeline; and in aqueous solutions saturated with varying concentrations of natural gas contaminants. Also, metallurgical analyses of nine (eight steel and one aluminum) used CNG cylinders were performed.

Limiting concentrations of hydrogen sulfide (H_2S), carbon dioxide (CO_2), and other CNG contaminants necessary to prevent internal corrosion of CNG fuel and storage cylinders were defined. This knowledge will minimize potential hazards of using CNG as a vehicle fuel. It should also lead to reduced costs of CNG use, since it has been shown that reduction of contaminants to the very low levels currently specified by the U.S. Department of Transportation (DOT) and the Canadian Transport Commission (CTC) is not necessary. A gas-quality standard based on program results is recommended. The National Fire Protection Association (NFPA) has adopted the recommended gas-quality standard.

EXECUTIVE SUMMARY

Natural gas suppliers, natural gas vehicle operators, and various local, state, and federal government agencies are concerned about safe operation of CNG vehicles, in particular with regard to the potential of contaminants in natural gas to cause corrosion damage to internal surfaces of CNG cylinders. In view of the possibility that significant corrosion damage to CNG fuel cylinders could occur, however small that possibility might be, a committee of the National Fire Protection Association (NFPA) attempted in 1984 to define allowable contaminant levels for CNG which are necessary to prevent significant internal corrosion of CNG fuel cylinders and storage cylinders. After investigating existing data and codes, the NFPA committee concluded that sufficient technical data upon which to base gas-quality standards did not exist.

This report describes a research project conducted at Southwest Research Institute (SwRI) to provide the data needed to develop a gas-quality standard for natural gases used as CNG. The project was conducted in two parts. Phase I was jointly sponsored by the New York State Energy Research and Development Authority (NYSERDA), Albany, NY, and the New York Gas Group (NYGAS), New York, NY, an association of gas companies operating in New York State. Phase II work was supported by the U.S. Department of Energy (DOE) through a subcontract with Martin Marietta Energy Systems, Inc., Oak Ridge, TN. The results of Phase I have been reported separately. This report summarizes the results of Phase I, and details the Phase II program.

The primary objective of the program was to define natural gas concentration levels necessary to insure that internal corrosion of CNG cylinders does not constitute a hazard over the lifetimes of the cylinders. A literature search was performed and companies in the natural gas transmission and distribution industries were contacted:

to identify and determine the composition ranges of contaminants in natural gases; and to obtain information regarding corrosion damage of CNG cylinders and cylinder materials. Metallurgical analyses of nine (eight steel and one aluminum) used CNG cylinders were performed. Corrosion and stress corrosion cracking (SCC) tests were performed on the cylinder materials most widely used in CNG cylinders in the United States (4130X and 15B30 steels and 6061-T6 aluminum alloy). Corrosion and SCC tests were conducted in: natural gases from several producing wells and from an interstate pipeline; and in aqueous solutions saturated with varying concentrations of hydrogen sulfide (H_2S) and carbon dioxide (CO_2), the natural gas contaminants primarily responsible for corrosion.

No environmentally induced cracking or significant corrosion damage was found in any of the cylinders. None of the cylinder materials were susceptible to SCC or to significant corrosive attack in the absence of liquid water. Aluminum alloy 6061-T6 was immune to corrosion and SCC in all aqueous environments tested, regardless of the concentrations of H_2S and CO_2 present. Both 4130X and 15B30 steels were susceptible to SCC and corrosion in aqueous environments containing H_2S and/or CO_2. The degree to which the steels were susceptible to corrosion depends upon: the concentrations of H_2S and CO_2 in the natural gas; the heat-treatment condition of the steel; and the steel hardness.

Conclusions drawn from program results are as follows:

- The principal corrosive contaminants in natural gases in the U.S. are H_2S and other sulfur-containing species, CO_2, oxygen, and water.
- Aluminum alloy 6061-T6 is suitable for use in CNG cylinders, regardless of the natural gas composition. Aluminum alloy 6061-T6 is immune to stess corrosion cracking, embrittlement, and other forms of general and localized corrosion in natural gas environments, including H_2S and CO_2 environments that are capable of inducing cracking, embrittlement, pitting, and general corrosion in steels.

- Corrosion of CNG cylinders made of steel may be prevented by maintaining the water vapor concentration of CNG gas supplies below the dew point for the anticipated range of temperatures and pressures. Steels are not subject to significant corrosion in natural gas environments, regardless of the concentrations of other contaminants, unless liquid water is present.

- Normalized 4130X steels are not suitable for use in CNG cylinders unless the water vapor concentration of the supply gas is sufficiently low to prevent condensation of liquid water. Normalized HRC 21/22 4130 steel specimens cracked in environments containing as little as 0.05 psia H_2S or 7.0 psia CO_2.

- Quenched-and-tempered 4130X steels are suitable for use in CNG cylinders at hardnesses to HRC 25/26 for natural gas supplies in which the H_2S partial pressure is 0.15 psia or less and the CO_2 concentration does not exceed 7 psia. In the absence of CO_2, quenched-and-tempered 4130X steel at a hardness of HRC 29/30 is acceptable.

- Quenched-and-tempered 15830 steels are suitable for use in CNG cylinders at hardnesses to HRC 29/30 for natural gas supplies in which the H_2S partial pressure is 0.50 psia or less and the CO2 concentration does not exceed 7 psia.

The limitation of 7 psia CO2 for quenched-and-tempered 15B30 steels is necessary to prevent general corrosion and pitting in these materials. Higher levels of CO_2 can be tolerated by quenched-and-tempered 4130X steels without significant general corrosion or pitting, but test results indicated a limit of 7 psia CO_2 is appropriate for these steels to minimize the possibility of stress corrosion cracking.

These conclusions indicate that stress corrosion cracking is possible in steel CNG cylinders for certain combinations of steels, heat treatment conditions, hardnesses, and gas compositions. Since current DOT regulations allow normalized steels to be used in CNG cylinders, one of the most significant findings of the program is that normalized 4130 steels with hardnesses of HRC 21/22 can suffer stress corrosion cracking at very low levels of H_2S or CO_2, if liquid water also is present.

Several of the eight used 4130X steel cylinders that were examined in the program had hardnesses in excess of HRC 21/22 and microstructures that were not fully quenched and tempered. The absence of significant corrosion in these cylinders, particularly the absence of crack growth from large fabrication flaws found in several of the cylinders, suggests that CNG supplies currently being used in the U.S. have very low levels of H_2S and CO_2, or the typical water vapor concentration of the gases used in the cylinders examined was very low. Analyses of natural gases obtained from wells, pipelines, and distribution systems are consistent with this observation. With the exception of water, which was very high in a few gases from distribution lines, corrosive contaminants in the gases analyzed were well within limits established by DOT for CNG supplies.

The results of the program were used to develop a gas-quality standard for CNG that is sufficient to prevent internal corrosion of CNG cylinders without being economically impractical. The recommended standard incorporates three options, depending upon the CNG cylinder material used and the manner in which CNG suppliers choose to control gas compositions, as follows:

- Aluminum Cylinders. No restrictions on the concentrations of corrosive contaminants in natural gas are required for CNG cylinders made of aluminum alloy 6061-T6.
- Steel Cylinders. When the dew point of the natural gas entering a steel CNG cylinder is below the lowest anticipated cylinder temperature at the highest anticipated cylinder pressure, no limitations are required on the concentrations of other corrosive contaminants in the gas; or
- Steel Cylinders. When the dew point of the natural gas entering a steel CNG cylinder is not below the lowest anticipated cylinder temperature at the highest anticipated cylinder pressure, the gas-quality in the cylinder shall comply with the following limitations on corrosive contaminants:

- Hydrogen Sulfide (H_2S) and 'Other Soluble Sulfides--0.05 psia partial pressure, maximum.
- Carbon dioxide (CO_2)--7.0 psia partial pressure, maximum.
- Oxygen--0.5 volume percent, maximum.
- Water Vapor--7 lb/MMCF, maximum.

This recommended standard has been adopted by the National Fire Protection Association (NFPA).

As noted earlier, the results of the experimental test program revealed that SCC and embrittlement of normalized 4130X steels at a hardness of HRC 21/22 is possible at very low levels of H_2S and CO_2, and that quenched-and-tempered steels of the same composition are not susceptible to cracking and embrittlement at significantly higher hardnesses and H_2S levels. In view of these results, it is **recommended** that 49 CFR 178.37, and other standards applicable to CNG cylinders, be amended to prohibit the use of normalized steels in new CNG cylinders. Consideration should also be given to requiring that such cylinders be removed from CNG service or to requiring more frequent inspection of normalized steel cylinders.

Section 1

INTRODUCTION

BACKGROUND

Compressed natural gas (CNG) has been used as a vehicular fuel for more than 30 years in Italy, and there are over 300,000 CNG-fueled vehicles operating there now (1).* Canada and New Zealand also are rapidly developing CNG vehicle fleets, and in the United States there are more than 30,000 dual-fuel vehicles which can be operated on either CNG or gasoline (2). In all of these instances CNG has been used safely. There have been no reported cases of CNG fuel cylinder failures anywhere in the world. Further, no evidence of significant corrosion or corrosion-related damage (e.g., stress corrosion cracking (SCC), corrosion fatigue, or hydrogen embrittlement) to fuel cylinders has been reported in the U.S., although small cracks of unknown origin were found in some Italian fuel cylinders.

Natural gas suppliers, natural gas vehicle operators, and various local, state, and federal government agencies are concerned about safe operation of CNG vehicles, in particular with regard to the potential of contaminants in natural gas to cause corrosion damage to internal surfaces of CNG cylinders. In view of the possibility that significant corrosion damage to CNG fuel cylinders could occur, however small that possibility might be, a committee of the National Fire Protection Association (NFPA) attempted in 1984 to define allowable contaminant levels for CNG which prevent significant internal corrosion of CNG fuel cylinders and storage cylinders. After investigating existing data and codes, the NFPA committee concluded that sufficient technical data upon which to base gas-quality standards did not exist.

(*)Underlined numerals in parentheses refer to references given in Section 5.

This report details a portion of a research project conducted at Southwest Research Institute (SwRI) to provide the data needed to develop a gas-quality standard for natural gases to be used as CNG. The project was conducted in two parts. Phase I was jointly sponsored by the New York State Energy Research and Development Authority (NYSERDA), Albany, NY, and the New York Gas Group (NYGAS), New York, NY, an association of gas companies operating in New York State. Phase II work was supported by the U.S. Department of Energy (DOE) through a subcontract with Martin Marietta Energy Systems, Inc., Oak Ridge, TN. The results of Phase I have been reported separately (3,4). This report summarizes the results of Phase I, and details the Phase II program.

OBJECTIVES

The principal objective of the total program was to define natural-gas contaminant concentration limits necessary to insure that internal corrosion of CNG cylinders does not constitute a hazard over the lifetimes of the cylinders. Secondary objectives of the program included definition of the effects cf materials variables, cylinder fabrication procedures, and other CNG system parameters on internal corrosion of CNG cylinders and cylinder materials. An objective of Phase I was to determine if exposure of CNG cylinder materials to untreated natural gases from wells in New York State would cause SCC of those materials in order to establish whether such gases require treatment before use as CNG.

The work performed was successful in accomplishing the program objectives. The limiting concentrations of corrosive contaminants in CNG necessary to prevent internal corrosion of CNG fuel and storage cylinders have been defined. This knowledge will minimize potential hazards of using CNG as a vehicle fuel. It also should lead to reduced costs of CNG used as a vehicle fuel, since it has been shown that reduction of contaminants to the very low levels currently specified by the U.S. Department of Transportation (DOT) and the Canadian Transport Commission (CTC) is not necessary.

SCOPE OF WORK

The work accomplished in the overall program was divided into four tasks. Tasks 1 and 3 and a part of Task 2 constituted the Phase I portion of the program. Phase I results are reported in detail in a separate report (3) and have been reported in the technical literature (4). The Phase I results are summarized herein. Phase II included the balance of Task 2 and Task 4. The Phase II program and the results obtained are detailed in this report. The four tasks are outlined below.

Task 1 -- Industry Contacts and Literature Review

The purposes of Task 1 were to identify contaminants present in natural gas and to determine to what extent they are corrosive to CNG cylinder materials. Technical literature was reviewed and personnel in the natural gas transportation industry and in companies manufacturing CNG cylinders were contacted to:

- Identify and determine the composition range of contaminants present in natural gases used as CNG supplies;
- Determine manufacturing processes and materials of construction used in the production of CNG cylinders in the U.S.; and
- Obtain information regarding corrosion or corrosion-related damage of CNG cylinders and cylinder materials.

The results of Task 1 are summarized in Section 2 of this report.

Task 2 -- Experimental Program

Approximately half of the experimental program was conducted in Phase I, and half, in Phase II. The purpose of this task was to develop corrosion and SCC data needed for a practical and safe CNG gas-quality standard. Phase I tests concentrated on determining effects of three indigenous New York State gases and a representative pipeline gas on corrosion and SCC susceptibility of CNG cylinder materials. Phase II tests concentrated on determining the effects of specific contaminants, heat treatment, and hardness (strength level) on corrosion and SCC susceptibility of two steels commonly used in CNG cylinders manufactured in the U.S. The results of the Phase I portion of Task 2 are summarized in Section 2 of this report. Phase II is described in detail and results are presented in Section 3.

Task 3 -- Metallurgical Evaluation of Used CNG Cylinders

The purpose of Task 3 was to determine the extent and type of service-induced damage or deterioration which has occurred in representative CNG storage and fuel cylinders. Eight steel cylinders and one cylinder made of an aluminum alloy were removed from service and examined to determine their condition. Analyses included identification of liquid residues and scales present in the cylinders and analyses of cylinder materials for conformance with appropriate specifications. Nondestructive inspections of all nine cylinders were performed to locate flaws on internal surfaces, and metallurgical examinations of selected portions of internal surfaces were conducted to determine the nature and extent of internal corrosion.

Results of Task 3 are summarized in Section 2 of this report.

Task 4 -- Analyses

Task 4 consisted of analyses of the results of the other tasks to determine factors responsible for corrosion and SCC of CNG cylinder materials and to define guidelines to minimize corrosion and corrosion-related damage in CNG cylinders. These are presented in Section 4 of this report. A gas-quality standard to minimize internal corrosion in CNG cylinders, based on the results of the research conducted and information in the technical literature, is recommended in Section 4. The recommended gas-quality standard has been adopted by the NFPA (5).

Section 2

SUMMARY OF PHASE I PROGRAM

TASK 1 -- INDUSTRY CONTACTS AND LITERATURE REVIEW

A survey of interstate gas transmission companies was made to determine gas-quality standards used by the industry and the range of contaminants present in natural gases transported in interstate pipelines. The surveyed companies include major companies in the industry which operate in several regions of the U.S. Gas-quality information also was supplied by NYGAS members, gas distribution companies, and companies active in the NFPA. A survey of cylinder manufacturers was conducted to establish CNG cylinder manufacturing procedures, standards, and materials of construction, and a search of the corrosion literature was performed to determine effects of gas contaminants on cylinder materials.

Gas cylinders used in the transportation of natural gases, including CNG cylinders, were found to be under the jurisdiction of DOT. Rigorous limits for gas contaminant concentrations are specified by DOT Specification E 8009. CNG storage cylinders are under the jurisdiction of individual states and municipalities, most of which require compliance with provisions of the ASME Boiler and Pressure Vessel Code, Section VIII, Division 1.

At the time the survey was conducted (1985), four manufacturers were producing CNG cylinders in the U.S. Two manufacturers produced conventional seamless (unwelded) cylinders from 4130X steels. Such cylinders must comply with the provisions of Title 49, Code of Federal Regulations, Paragraph 178.37 (49 CFR 178.37), and are designated either "DOT-3AA" (cylinders with a capacity of less than 1,000 pounds of water) or "DOT-3AAX" (cylinders with a capacity of more than 1,000 pounds of water). An exception to 49 CFR 178.37, Exemption DOT-E 8963, was granted to a third U.S. manufacturer for the production of seamless, hoop-wrapped, fiber-reinforced CNG cylinders made of 15B30 carbon-boron steel. Cylinders of this type are designated "Type 3HW." A fourth U.S. manufacturer produced seamless, hoop-wrapped, fiber-reinforced Type 3HW CNG cylinders made of aluminum alloy 6061-T6, under the provisions of 49 CFR 178.88 and 49 CFR 178.46. These cylinders are designated "DOT-3AL." No failures of CNG cylinders made by any of the four U.S. manufacturers have been reported.

In general, gases entering the interstate transmission pipeline system are treated to meet gas-quality specifications of individual pipeline companies. No single national specification or standard exists for "pipeline" gas. Specifications obtained from pipeline and distribution companies revealed that the principal corrosive contaminants limited in natural gases are water, carbon dioxide (CO_2), hydrogen sulfide (H_2S), and other soluble sulfides, such as mercaptans. Water is the key contaminant, since none of the other contaminants produces significant corrosion of cylinder materials in the absence of liquid water. On this basis, corrosion of CNG cylinders may be prevented by maintaining the water vapor concentration in natural gas below the saturation concentration (dew point) for temperatures above the freezing point. Most companies limit water vapor to 7.Ø lb/MMCF, a concentration above the dew point under many operating conditions. The more restrictive DOT Specification E 8ØØ9 for CNG limits water vapor to Ø.5 lb/MMCF.

Hydrogen sulfide potentially is the most detrimental of the contaminants commonly found in natural gases. Partial pressures of H_2S greater than Ø.Ø5 psia are capable of inducing SCC in many steels. NACE Standard MR-Ø1-75 states that H_2S-induced SCC of steels may be controlled by maintaining the H_2S partial pressure below Ø.Ø5 psia or by maintaining the hardness of the steel below HRC 22. Pipeline specifications set H_2S limits between Ø.25 and 1.Ø grains/1ØØ ft^3, while DOT E 8ØØ9 limits H_2S to Ø.1 grain/1ØØ ft^3. Total sulfur is limited in pipeline specifications to between 1Ø and 2Ø grains/1ØØ ft^3 and in DOT E 8ØØ9 to a maximum of Ø.2 grains/1ØØ ft^3. Carbon dioxide may produce significant acidic attack of steels, and oxygen may cause steels to rust. Pipeline company specifications and DOT E 8ØØ9 have the same limits for CO_2 and oxygen, 3.Ø volume percent and 1.Ø volume percent, respectively.

References in the technical literature indicated that none of the contaminants found in natural gases is corrosive to aluminum and aluminum alloy 6061-T6 (6,7). Available analyses of natural gases in U.S. transmission and distribution pipelines showed that corrosive contaminants usually are well within limits set by pipeline companies and the DOT specification for CNG. An exception was water vapor which was found to be very high in some distribution systems. However, it was found that transmission and distribution companies do not routinely analyze their products for oxygen, H_2S, other sulfur species, and water.

TASK 2 -- EXPERIMENTAL PROGRAM

Materials and Procedures

Gases. The Phase I experimental program concentrated on determination of general corrosion and SCC susceptibility of CNG cylinder alloys in five gas environments: (1) a typical natural gas from an interstate transmission pipeline; (2) untreated natural gases from three wells in New York State; and (3) high-purity methane, representative of natural gases meeting the specifications of DOT E 8ØØ9. Chemical analyses showed that all five gases met the specifications for pipeline gas as well as the requirements of DOT E 8ØØ9 for H_2S, CO_2, O_2, and other sulfur compounds. Water vapor concentrations were not determined because the volumes of the gases available were too small to permit meaningful analyses. Baseline tests also were conducted in high-purity argon, representative of a benign environment which would not be expected-to cause corrosion or SCC; and in H_2S, representative of an aggressive environment which is known to cause both SCC and corrosion of steels.

Alloys. Representative plates of 413ØX steel, 15B30 steel, and aluminum alloy 6061-T6 were used to make corrosion and stress corrosion test specimens. The chemical compositions of the three alloys and the appropriate DOT chemical-composition limits for each are given in Table 1. The three test materials met all of the chemical composition requirements. The aluminum plate met all mechanical propertles requirements. Mechanical-property requirements for 413ØX and 1583Ø steels are not given in DOT specifications for CNG cylinders. Hardness measurements for the 413ØX steel ranged from 19 to 22 HRC, indicating the ultimate tensile strength of this material was approximately 11Ø ksi. Hardness measurements on the 1583Ø steel ranged from 84 to 87 HRB, indicating an ultimate tensile strength of approximately 8Ø ksi.

The microstructure of the 413ØX steel consisted primarily of bainite, with an equiaxed grain structure, typical of a low-alloy steel that has been normalized. The microstructure of the 15B30 steel consisted of a banded mixture of ferrite and lamellar pearlite, typical of a hot-rolled steel. The microstructure of the 6061-T6 aluminum alloy consisted of elongated grains of aluminum solid solution containing blocky precipitates; such a microstructure is typical for the alloy in the T6 (solution heat treated and artificially aged) heat treatment condition.

Test Methods. SCC tests were conducted using the slow-strain-rate test method. Cylindrical test specimens with nominal cross-sectional diameters of Ø.25 in. and gauge lengths of 1 in. were used. Specimens were exposed in two multi-specimen test systems. Each system consists of a 1-gallon stainless steel autoclave mounted in a screw-driven tensile test machine. Six tensile specimens--two of each of the three test materials--were exposed simultaneously in each environment evaluated. Specimens were galvanically isolated from one another and from a loading frame mounted inside the autoclave by the use of nonmetallic materials. Loading was applied to each specimen through six pull rods which penetrate the autoclave head.

Visual inspection and metallographic examination for evidence of cracking were the primary methods used to interpret test results. However, cracking susceptibility also was evaluated by comparing ductility parameters (percent elongation and percent reduction in area) of specimens tested in the natural-gas environments to the same parameters obtained from tests in high-purity methane and high-purity argon.

General corrosion rates were determined from the weight change of duplicate coupons of each of the three CNG cylinder alloys exposed in each environment evaluated. General-corrosion test coupons were exposed with the SCC specimens in the multi-specimen system autoclave. Specimens were prepared and evaluated in accordance with procedures given in ASTM Standard G1, "Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens." Specimens were cleaned after exposure using the electrochemical procedure contained in ASTM G1.

Test Conditions. The inside surface of a CNG cylinder may be in contact with three potentially corrosive environments: (1) a gas phase with a water vapor concentration less than the saturation concentration; (2) a gas phase saturated with water vapor; and (3) condensed liquid water saturated with the various contaminants present in the gas phase. Initially, these three conditions were simulated for each of the five primary test gases. Environments with water vapor concentrations below saturation consisted of the as-received gases. Water-saturated gases were produced by placing several ounces of deaerated, deionized water in the bottom of the autoclave, such that test specimens were exposed only to the gas phase above the water. Condensed water saturated with gas contaminants was simulated by first covering the gauge lengths of the SCC test specimens with deaerated, deionized water and then introducing the test gases to the test pressure. In the latter case, general corrosion test specimens also were immersed in the liquid phase.

All three conditions were evaluated with the pipeline gas, high-purity methane, and one of the three natural gases from New York. Water-saturated tests were not conducted with the two other New York gases because results indicated no significant differences between specimens tested in water-saturated and as-received gases.

All tests were conducted at a temperature of 140°F, a temperature selected to represent a typical temperature expected in a vehicular fuel cylinder during the summer months. A strain rate of 2 x 10^{-7} sec^{-1} was used for the SCC tests, after preliminary tests at differing rates indicated that this strain rate produced the most severe cracking in a known cracking environment (deionized water saturated with H_2S at a pressure of 50 psig). A load equal to 75 percent of the yield strength of the lowest-strength material (6061-T6 aluminum alloy) was applied to all six SCC test specimens and was maintained for 24 hours before straining was initiated. This was done to increase the time for hydrogen (produced by reaction of specimen materials with environmental constituents) to enter the test specimens. Slow-straining was initiated at the end of the 24-hour holding period and was continued until all six specimens had fractured. Tests were conducted at a total pressure of 3,000 psig to simulate maximum anticipated CNG cylinder pressures in the U.S. Actual CNG cylinder pressures in the the U.S. currently are limited to approximately 2,400 psig.

Test Results. Detailed presentations of SCC and general corrosion test data are contained in References 3 and 4. The results of the tests conducted are summarized here.

Stress Corrosion Cracking. The three CNG cylinder alloys were not susceptible to SCC in any gaseous or liquid environment containing the three natural gases from New York State wells or the pipeline gas. The 4130X and 15B30 steels were susceptible to severe SCC in liquid water saturated with H_2S. Aluminum alloy 6061-T6 was not susceptible to SCC in any of three H_2S-saturated liquid water environments, all of which caused severe SCC of the steels.

While SCC did not occur, in any of the environments containing the four natural gases, significant differences in ductility parameters were observed. Reduction-in-area values are plotted in Figures 1 and 2 for the 4130X steel and aluminum alloy 6061-T6, respectively; results for the 15830 steel were essentially the same as for the 4130X steel. Ductilities of 4130X specimens exposed in as-received and water-saturated gases were not significantly different. However, for both steels, the ductilities of specimens exposed in liquid water were 15 to 30 percent lower than those of specimens exposed in the gaseous environments. This observation was true for tests in which the liquid was saturated with high-purity argon and high-purity methane, as well as the four natural gases. The cause of this embrittlement of the two steels in water was not determined. In contrast, the measured ductilities of 6061-T6 aluminum alloy specimens (Figure 3) were independent of the test environment, including H_2S- and water-containing environments.

General Corrosion. General corrosion rates for aluminum alloy 6061-T6 were insignificantly small in all test environments. The corrosion rates for the two steels were less than 0.001 in./yr (1 mpy) in all five environments: the three H_2S-containing liquid environments; water saturated with pipeline gas; and water saturated with natural gas from one of the New York wells. In these environments, the average steel corrosion rates ranged between 5 and 50 mpy. Such rates are to be expected for liquid solutions saturated with H_2S. The relatively high rates observed in water saturated with

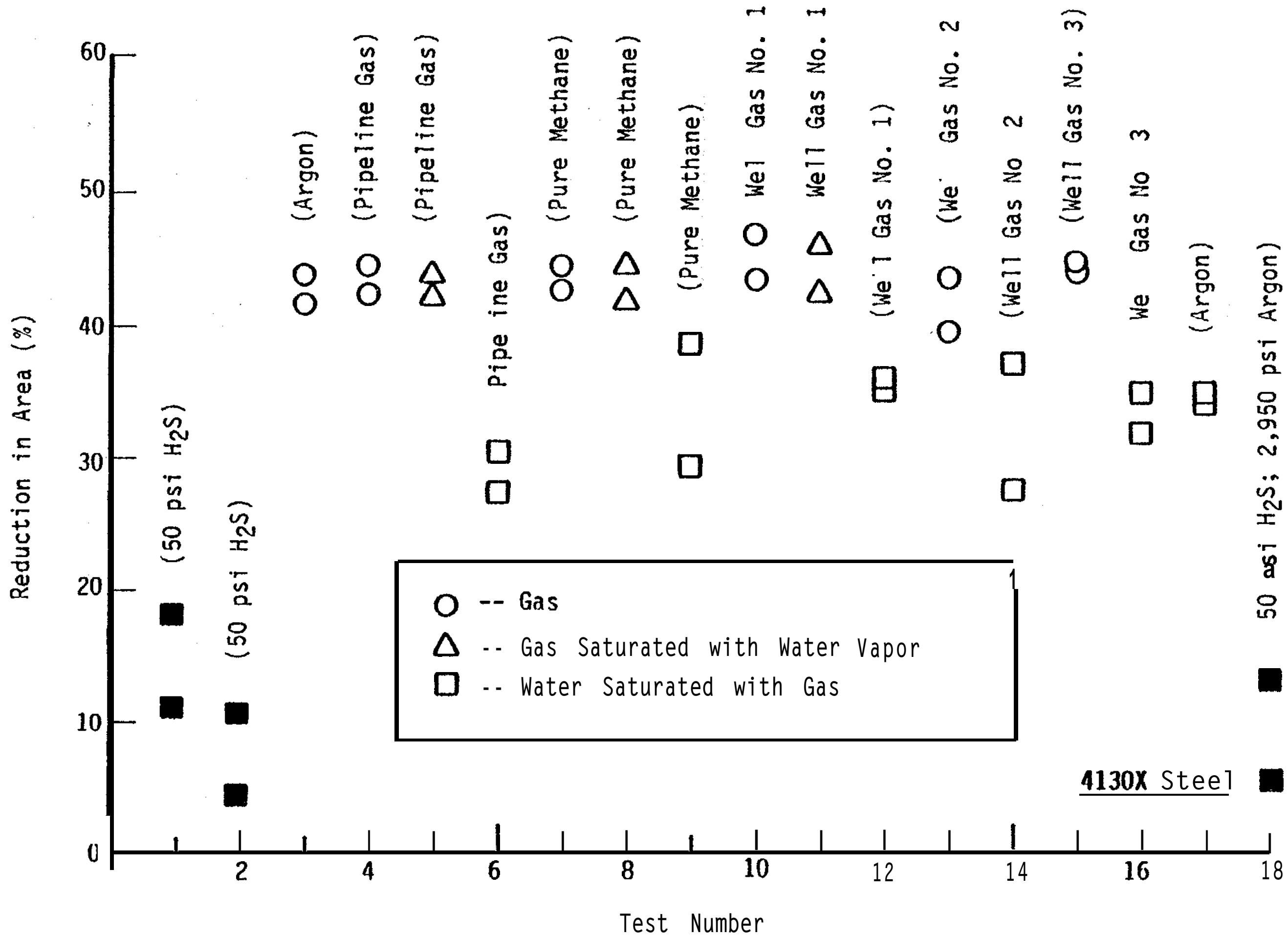


FIGURE 1, VARIATION OF REDUCTION IN AREA WITH TEST ENVIRONMENTS FOR 4130X STEEL SLOW-STRAIN-RATE SPECIMENS EXPOSED IN PHASE I EXPERIMENTAL PROGRAM. Solid points indicate cracking; open points indicate no cracking. Tests were conducted at a temperature of 140°F and a total pres ure of 3,000 psi except as indicated. The strain rate for Test No. 1 was 1×10^{-6} sec^{-4}; the strain rate in all other tests was 2×10^{-7} sec^{-1}.

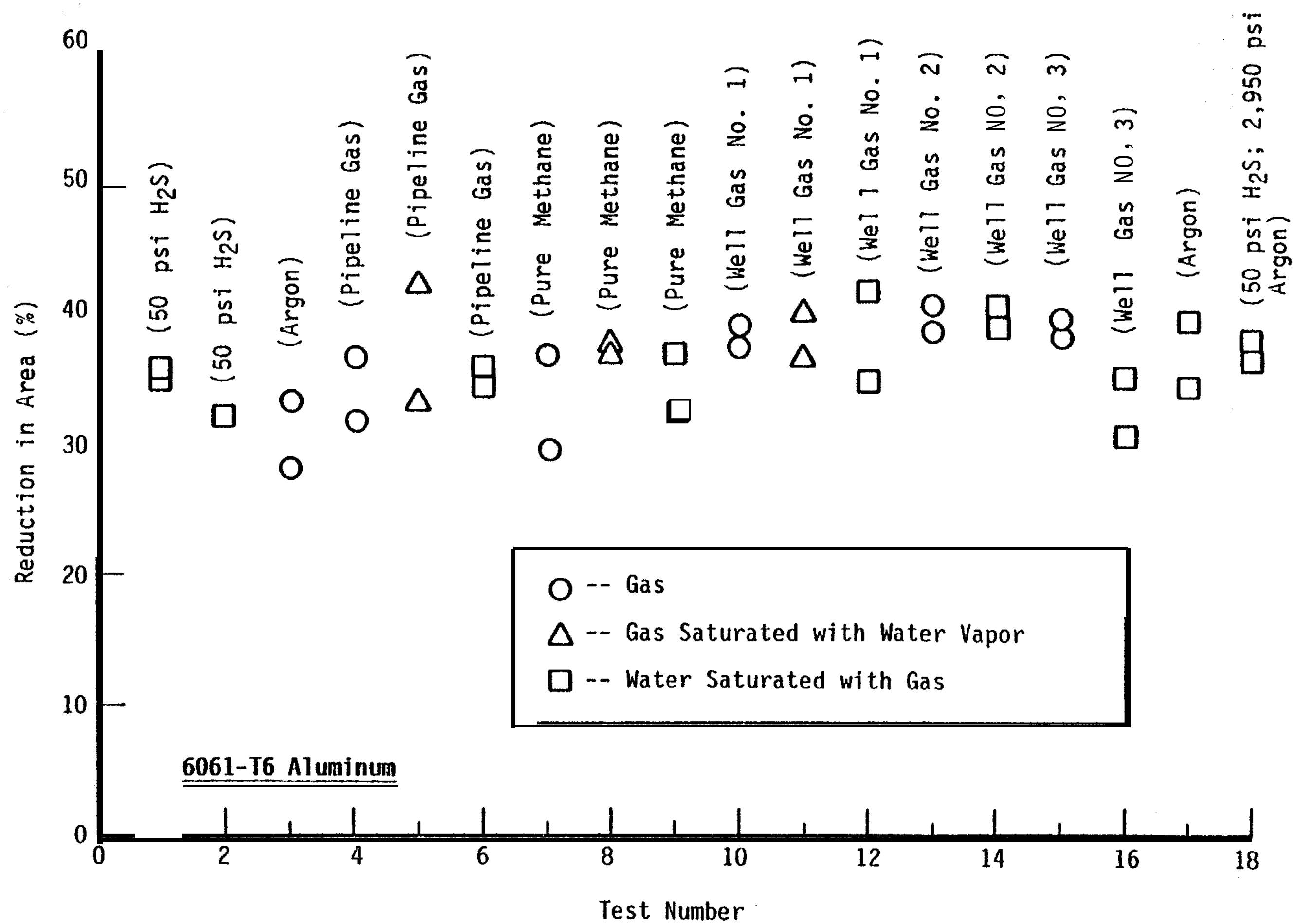
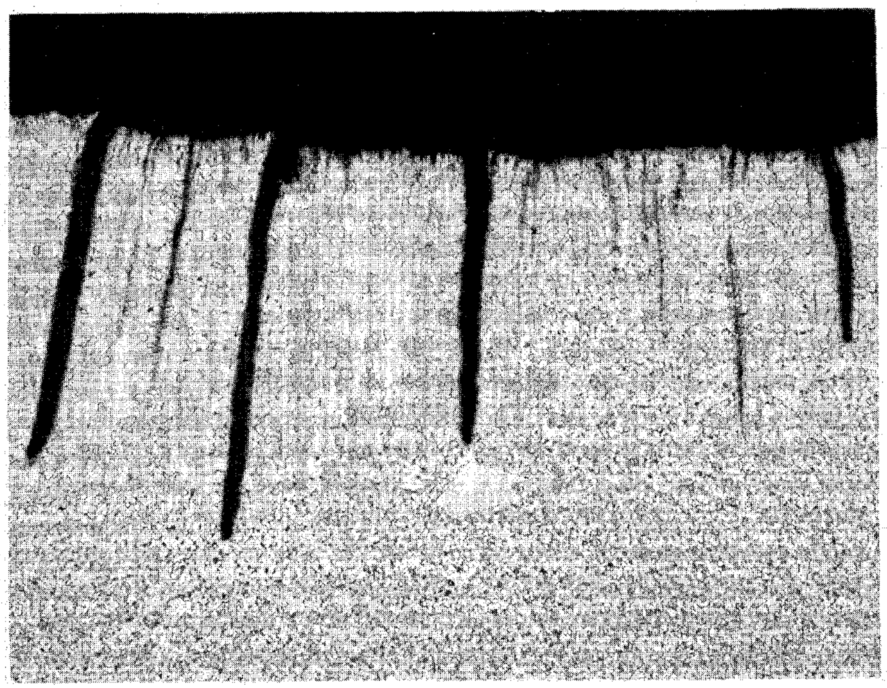


FIGURE 2. **VARIATION OF REDUCTION IN AREA WITH TEST ENVIRONMENTS FOR 6061-T6 ALUMINUM ALLOY SLOW-STRAIN-RATE SPECIMENS EXPOSED IN PHASE I EXPERIMENTAL PROGRAM.** Solid points indicate cracking; open points indicate no cracking. All tests conducted at a temperature of 140°F and a total pressure of 3,000 psi except as indicated. The strain for Test No. 1 was $1 \times 10^{-6} sec^{-1}$; the strain rate in all other tests was $2 \times 10^{-7} sec^{-1}$.



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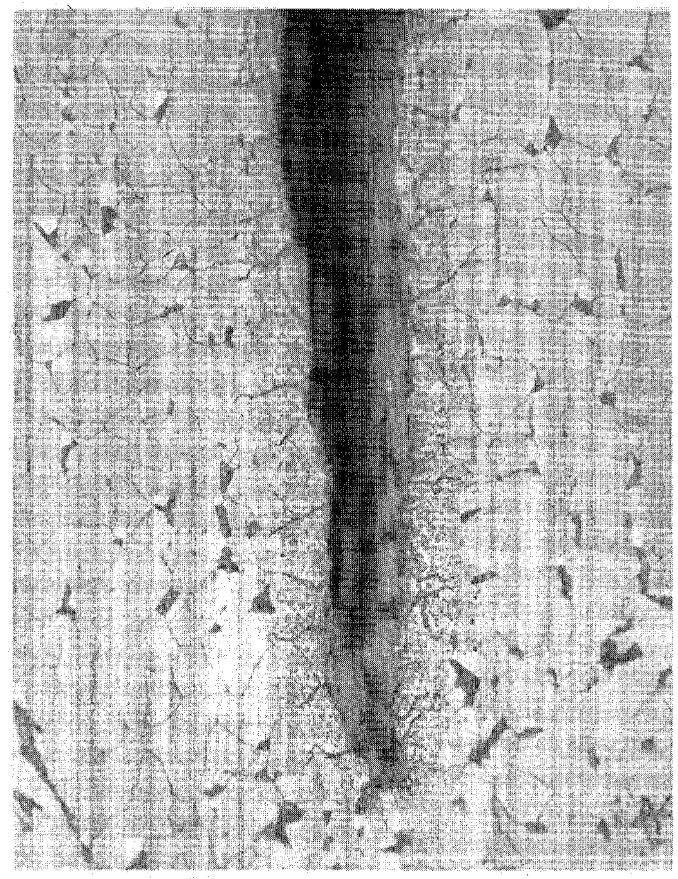

(b) Tip of fissure at arrow

FIGURE 3. PHOTOMICROGRAPHS OF TYPICAL FISSURES FOUND IN DOME-SHAPED HEADS OF SOME 4130X STEEL CNG CYLINDERS EXAMINED IN PHASE I.

the pipeline gas (6.5 and 4.2 mpy for 1583Ø and 413ØX steels, respectively) are attributed to the presence of Ø.49 volume percent of CO_2 in the pipeline gas. As a general rule, liquid water saturated with CO_2 at a partial pressure of approximately 7 psi or more is corrosive to steels (8). The partial pressure of CO_2 in the test with the pipeline gas was 14.7 psi.

The test in water saturated with one of the New York natural gases produced corrosion rates of 18.1 and 14.5 mpy for 15B30 and 4130X, respectively. In this case, the oxygen concentration of the gas was Ø.391 volume percent, which was about 2Ø times greater than the oxygen concentration of other natural gas used in the program. It is believed that the general corrosion experienced by the steels in the test is the result of the high oxygen level.

There was a definite pattern to the corrosion rates of the steels with respect to the test conditions used. Corrosion rates were lowest in the as-received gases, were higher in gases saturated with water vapor, and were highest in liquid water saturated with the test gases. However, it should be noted that no significant corrosion occurred in any of the gaseous environments, including those saturated with water vapor. The test results clearly show that liquid water was necessary for severe corrosion to occur. Also, in all cases the corrosion rate of the 15B30 steel was greater than that of the 413ØX steel, indicating that 15B30 steel is inherently more susceptible to corrosion than is 413ØX steel.

TASK 3 -- EVALUATION OF USED CNG CYLINDERS

An in-depth evaluation of selected CNG cylinders which had been removed from service was performed to establish the overall condition of the cylinders and to identify any service-induced damage or deterioration. Eight DOT 3AA steel cylinders of different sizes and service histories and one hoop-wrapped, fiber-reinforced DOT 3AL aluminum cylinder were evaluated. The cylinders had been in service for from two to thirteen years. Some had been used in vehicles, some had been used as storage cylinders in vehicle refueling stations, and some had been used in both types of service.

All of the steel cylinders were made of 4130X steels. The aluminum cylinder was made from alloy 6061-T6. Six of the steel cylinders had been made and used in the U.S. These six cylinders had hardnesses ranging from 96 HRB to 25 HRC. Microstructures ranged from normalized in some cylinders to fully quenched-and-tempered in others. Considerable variation in microstructure occurred within the same cylinder in several cases, indicating that the heat treatments those cylinders received had not been uniform. The other two steel cylinders were made in Italy. One was typical of higher-strength CNG cylinders used in Italy, with a hardness of HRC 30-32 and a microstructure consisting entirely of tempered martensite. The eighth cylinder had been produced for use in Canada. It had a slightly lower hardness (HRC 25-27) and a microstructure consisting of ferrite, tempered bainite, and martensite.

Nondestructive ultrasonic inspections of each cylinder were performed and the cylinders were drained of any liquid residues. They then were sectioned by saw-cutting, and a 100 percent magnetic particle inspection was performed on the inside surfaces of each cylinder. Metallographic examinations and bulk chemical analyses were performed to characterize the materials and to identify the nature of any defect indications. Residual liquids removed from some of the cylinders and inside surface deposits also were analyzed.

The inside surface of the aluminum cylinder was smooth and silver-white in color, except for a few isolated white and brown spots. No evidence of corrosion of any kind or of cracking was found in the aluminum cylinder.

Blue-black and/or red-brown scales were present on the inside surfaces of the steel cylinders. All of the scales contained oxides, and several contained sulfides, indicating that the cylinders had contained gases with corrosive sulfur species. Shallow pits ranging from 0.002 to 0.004 inch deep were found in several of the cylinders. Pitting of this depth is essentially a surface phenomenon, representing loss of less than one percent of the wall thickness and presenting no danger to the structural integrity of the cylinders.

Fifteen small mid-wall lamellar defects were found in the higher strength Italian cylinder. These defects are believed to be casting flaws which were elongated and flattened during cylinder fabrication. Since they were isolated at the mid-plane of the cylinder wall, they did not result from in-service degradation. These defects were too small to be detrimental to the service life of the cylinder.

Several of the steel cylinders contained deep, narrow, crack-like, fissures near valve openings in the hemispherically shaped, formed ends of cylinders. Photomicrographs of typical fissures are shown in Figure 3. Wall thicknesses at these locations were considerably greater than typical thicknesses in the walls of cylinder bodies. The fissures were blunt and filled with oxide. Also, progressive internal oxidation and decarburization was evident along the sides of fissures. These features are evidence that the fissures were developed at an elevated temperature and, therefore, they are related to the manufacturing operation and not to service. It is believed that the fissures are folds produced during cylinder closure operations. There was no evidence of crack propagation from the ends of the folds.

Liquid residues found in three of the steel cylinders consisted of water, solvent, and hydrocarbons, predominantly oils from compressors used to fill the cylinders.

FINDINGS OF THE PHASE I PROGRAM

The most significant findings of the Phase I program are summarized below.

- The principal corrosive contaminants in U.S. natural gases are CO_2, H_2S, other sulfur species, oxygen, and water.
- Natural gas transmission and distribution companies in the U.S. do not routinely analyze their products for H_2S, other sulfur species, and water. Results of general corrosion tests showed that water is the key contaminant, since none of the other contaminants produced significant corrosion of cylinder materials in the absence of liquid water.
- Available analyses of U.S. natural gases from transmission pipelines and distribution systems indicate that corrosive contaminants in natural gases generally are well within limits set by transmission companies for natural gases entering transmission pipelines and by the U.S. Department of Transportation for natural gases to be used in CNG service. An exception was water vapor which was very high in some distribution lines.
- Both 4130X and 15830 steels were susceptible to SCC in liquid water environments saturated with H_2S.
- The 15B30 steel was more susceptible to general corrosion than was the 4130X steel, i.e., in corrosive environments the general corrosion rates of the 15B30 steel were greater than the general corrosion rates of the 4130X steel.
- None of the CNG cylinder alloys was susceptible to SCC in environments containing a typical pipeline gas or three untreated natural gases from wells in New York State.
- Aluminum alloy 6061-T6 was not susceptible to SCC or general corrosion in any environment tested, including H_2S-containing environments which induced severe cracking in the 4130X and 15830 steels.
- No environmentally induced cracking or significant corrosion damage of any kind was found in extensive visual, ultrasonic, magnetic particle, spectrographic, and metallographic analyses of nine CNG cylinders which had been in CNG service for periods ranging from two to thirteen years. These cylinders included eight 4130X steel cylinders made by three U.S. manufacturers and one Italian

> manufacturer, and one hoop-wrapped, fiber-reinforced aluminum alloy 6061-T6 cylinder made in the U.S. The eight steel cylinders were of various sizes and wall thicknesses, and the hardnesses of the 4130X steels used varied from HRB 96 to HRC 32. These hardness levels correspond to a variation in ultimate tensile strength from a minimum of about 103 ksi to a maximum of about 144 ksi.

The most significant finding of the work performed in the Phase I program was the condition of the nine used CNG cylinders. Analyses indicated that the cylinders had been exposed to corrosive environments, and several of the cylinders contained manufacturing defects of sufficient size to act as crack starters. However, no evidence of environmentally induced crack growth or crack initiation and only minor general corrosion and pitting were found in the cylinders. No environmentally induced damage of any kind was found in the examination of the aluminum cylinder. These results, while limited to nine CNG cylinders, suggest that significant internal corrosion damage to CNG cylinders containing typical U.S. natural gases is not likely.

The observed immunity of aluminum alloy 6061-T6 to corrosion and SCC in H_2S-containing environments which caused SCC and corrosion of the steels and the excellent condition of the used aluminum CNG cylinder also are significant. These results indicate that 6061-T6 aluminum CNG cylinders may be expected to provide superior corrosion resistance in high-H_2S environments that are capable of inducing SCC and significant general corrosion in steels.

Section 3

PHASE II PROGRAM

OBJECTIVES

The results of the Phase I program established: (1) the immunity of aluminum alloy 6061-T6 in typical and highly-contaminated natural gases; (2) that typical steels used in CNG cylinders (4130X and 15B30) were not susceptible to SCC or to significant corrosion damage in environments containing four typical natural gases; and (3) that the primary contaminants in natural gases that are corrosive to steels used in CNG cylinders are H_2S and other sulfur compounds, CO_2, water vapor, and oxygen. The thrust of the Phase II program was to accomplish the remaining objectives of the overall program:

- to define the concentration limits for corrosive contaminants in natural gases that are necessary to insure that internal corrosion of steel CNG cylinders does not constitute a hazard to the structural integrity of cylinders over their lifetimes, and recommend a gas-quality standard; and

- to define the effects of materials variables such as strength (hardness) and microstructure on corrosion and SCC susceptibility of steels used in CNG cylinders.

These objectives were accomplished through the conduct of additional corrosion and SCC tests and analysis of the overall program results. The experimental program conducted in Phase II and the results obtained are presented and discussed below. Recommendations based on the results of the overall program and a gas-quality standard developed from analysis of the results are presented in Section 4.

CORROSION TEST PROGRAM

Background

The technical literature reviewed in Phase I, and, to some extent, the results of the Phase I test program, indicated that H_2S is the natural gas contaminant of most concern with respect to the structural integrity of steel CNG cylinders because of the ability of H_2S to induce sulfide stress corrosion cracking (SSC) in carbon and low-alloy steels. The problem of selecting metallic materials for the containment and handling of H_2S-containing gases has been dealt with by the National Association of Corrosion Engineers (NACE). NACE Standard MR-Ø1-75, "Sulfide Stress Cracking Resistant Material for Oil Field Equipment," (9) details limitations on gas quality and mechanical properties of metals necessary to prevent failure of metals by SSC. (It should be noted that MR-Ø1-75 does not apply to other forms of corrosion damage; it is applicable only to SSC). Paragraph 1.3 of MR-Ø1-75 indicates the parameters governing SSC resistance are as follows:

> Fluids containing water as a liquid and hydrogen sulfide are considered sour environments and may cause SSC of susceptible materials. This phenomenon is affected by complex interactions of parameters including: (1) metal chemical composition, strength, heat treatment, and microstructure; (2) pH; (3) hydrogen sulfide concentration and total pressure; (4) total tensile stress; (5) temperature; and (6) time.

For sour gas environments, MR-Ø1-75 requires that:

> Materials shall be selected to be resistant to SSC or the environment should be controlled if the gas being handled is at a total pressure of 65 psia or greater and if the partial pressure of H_2S in the gas is greater than Ø.Ø5 psia.

In the case of steels and other ferrous materials, MR-01-75 states:

> Most ferrous metals, hardenable by heat treatment and/or cold work can be made susceptible to SSC. Conversely, many ferrous metals may be heat treated to provide acceptable resistance to SSC.

In general, carbon and low-alloy steels are acceptable under MR-Ø1-75 at a maximum hardness of HRC 22 in all normal heat-treatment conditions (as rolled, annealed, normalized, normalized and tempered, and quenched and tempered), provided they contain less than one percent nickel. Restrictions may be more rigorous or less rigorous for specific steels. For example, CrMo steels, of which 413ØX is one, are acceptable under MR-Ø1-75 at a maximum hardness of HRC 26, if they are in the quenched-and-tempered heat treatment condition.

MR-Ø1-75 also deals with other materials than steels. Importantly with regard to CNG cylinders, all aluminum-base alloys are acceptable for use in sour gas environments.

However, it should be noted that MR-Ø1-75 covers all steels, and as a result of this "universal applicability" approach, MR-01-75 may be too restrictive for specific steels. Higher H_2S partial pressures, higher hardnesses, or both may be acceptable for specific steels and environments. Recent work has shown that CrMo oil-field steels are not susceptible to SSC in sour environments at hardness levels between HRC 25 and 29 for H_2S partial pressures ranging from Ø.15 to 1.5 psia, with the exact acceptable H_2S limit for a given steel depending upon steel composition, heat treatment, and hardness (1Ø).

Test Materials, Conditions, and Procedures

Both MR-Ø1-75 and the Phase I program results indicated that aluminum alloy 6061-T6 is immune to corrosive attack in natural gas environments, including aqueous environments highly contaminated with H_2S. The major portion of the Phase II test program therefore was directed toward defining acceptable H_2S and hardness limits for 4130X and 15830 steels, the materials which have been most widely used in the manufacture of CNG cylinders. Further, since Phase I test results showed that these steels were not susceptible to significant corrosion or SCC in the absence of liquid water, all tests in Phase II were conducted in liquid water. Five H_2S partial pressures--0.05, 0.15, 0.50, 1.50, and 5.00 psia--were used in the test program. These pressures were selected to range from the maximum H_2S partial pressure allowed under MR-01-75 without hardness control to an H_2S partial pressure greater than the largest partial pressure used in the experimental study mentioned previously (10). The complete range of H_2S partial pressures was studied for the more widely used 4130X steel. Tests on the less common 15B30 steel were limited to H_2S partial pressures of 0.05, 0.50, and 5.00 psia.

All tests were conducted at a total pressure of 3,000 psig, with the balance of the pressure supplied by high-purity methane. Specimens in all tests were submerged in deaerated, deionized water which was saturated with the gases of interest. Baseline tests in water saturated with high-purity methane also were conducted. Test equipment and procedures were the same as in the Phase I test program, with the exception of the procedure followed to establish H_2S partial pressures. The autoclaves containing test specimens were flushed with argon and deaerated, deionized water was then introduced. The autoclave was alternately flushed with argon and then evacuated several times to remove any remaining air. Hydrogen sulfide was then slowly bubbled through the aqueous phase until the required partial pressure was established in the gas phase above the water. A manometer system accurate to 0.01 psia was used to measure partial pressures less than one atmosphere.

The hardness levels investigated were selected to be representative of CNG cylinders used in the U.S. and other countries. Three hardness levels--HRC 21/22, HRC 25/26, and HRC 29/30--were used. Information obtained in Phase I indicated that CNG cylinders used in Italy and Canada can have hardnesses as high as HRC 32 and HRC 26, respectively; the two higher hardness values were selected to be representative of steel conditions in CNG cylinders used in these countries. There currently are no hardness limits for CNG cylinders used in the U.S. Cylinders examined in Phase I which had been used in the U.S. ranged in hardness from HRB 96 to HRC 25. However, the MR-01-75 criteria for handling H_2S-containing gases are widely accepted and have been incorporated into or referenced in laws in several states. Therefore, it was considered important to evaluate the applicability of the HRC 22 hardness limit to CNG cylinders, and HRC 22 was selected as the third hardness value used in the Phase II test program.

Test specimens were made from the same steel plates used in the Phase I program. The compositions of the two steels are given in Table 1. The majority of steel cylinders in CNG service in the U.S. are in the quenched-and-tempered heat treatment condition, although 49 CFR 178.37 also allows the use of normalized cylinders. Correspondingly, the Phase II program was designed to compare corrosion and SCC susceptibility of steels in the quenched-and-tempered and normalized conditions. The plates were quenched and tempered at Southwest Research Institute to produce the three desired hardnesses using heat treatment procedures which were developed experimentally. The heat treatment conditions used to produce the three hardness levels for the 4130X and 15B30 steels are given in Table 2.

The technical literature examined in Phase I suggested that after H_2S, CO_2 was the natural gas contaminant with the greatest potential for significant internal corrosion damage to CNG cylinders. Gas company gas-quality standards and DOT Specification E 8009 for CNG both allow a maximum of 3 volume percent CO_2. Therefore, the CO_2 partial pressure in a CNG cylinder operated at a total pressure of 3,000 psi could be as high as 90 psia and still be within the CO_2 limits of the existing specifications. However, oil-and-gas industry experience

TABLE 1

CHEMICAL COMPOSITIONS OF TEST MATERIALS

Alloy or Specification	Elemental Composition (Weight Percent)													
	C	Mn	P	S	Si	Cr	Mo	B	Fe	Cu	Mg	Zn	Ti	Al
DOT 3AA -- 4130X Steel Specification	0.25-0.35	0.40-0.90	0.04 max	0.05 max	0.15-0.35	0.80-1.10	0.15-0.25	--	Bal.	--	--	--	--	--
4130X Test Steel[a]	0.33	0.54	0.007	0.019	0.23	1.07	0.19	--	Bal.	--	--	--	--	--
DOT 3AA -- Carbon-Boron Steel	0.27-0.37	0.80-1.40	0.035 max	0.045 max	0.3 max	--	--	0.0005-0.003	Bal.	--	--	--	--	--
15B30 Test Steel[a]	0.32	1.18	0.012	0.008	0.17	--	--	0.0022	Bal.	--	--	--	--	--
DOT 3AL -- 6061 Alloy Specification	--	0.15 max	--	--	0.40-0.8	0.04-0.35	--	--	0.7 max	0.15-0.40	0.8-1.2	0.25 max	0.15 max	Bal.
6061-T6 Test Alloy[b]	--	0.12	--	--	0.71	0.18	--	0.0001	0.40	0.29	0.96	0.11	0.020	Bal.

(a) Obtained in the form of 1/2-in. thick plate from Pressed Steel Tank Company, Milwaukee, Wisconsin.
(b) Obtained in the form of 1/2-in. thick plate from Metal Samples, Inc., Munford, Alabama.

TABLE 2

HEAT TREATMENT CONDITIONS FOR STEELS TESTED(*

Steel	Hardness	Annealing Conditions Temp. (°F)	Annealing Conditions Time (Mins)	Tempering Conditions Temp. (°F)	Tempering Conditions Time (Hrs)
4130X	HRC 21/22	1575	30	1312	2
	HRC 25/26	1575	30	1250	2
	HRC 29/30	1575	30	1205	2
15B30	HRC 21/22	1600	40	1120	1.5
	HRC 25/26	1600	40	1030	1.5
	HRC 29/30	1600	40	940	1.5

(*) Steels were quenched from the annealing temperature to room temperature in UCON-A, a proprietary quench medium. After tempering, specimens were air cooled to room temperature.

indicates that if liquid water is present, CO_2 partial pressures greater than 7 psia can cause significant corrosion of steels, and that significant corrosion damage is probable for CO_2 partial pressures greater than about 15 psia (8). These findings suggested that current CO_2 partial pressure limits for natural gas may be too high for CNG if liquid water can be formed within the cylinders. The effects of CO_2 on quenched-and-tempered 15B30 and 413ØX steels were studied at CO_2 partial pressures of 7, 3Ø, and 9Ø psia. These values are the oil-and-gas industry "rule of thumb," and the CO2 concentrations corresponding to 1 percent CO_2 and 3 percent CO2 in a CNG cylinder at a total pressure of 3,ØØØ psig. Tests also were conducted in environments containing both H_2S and CO_2 in the gas phase. The purpose of these tests was to determine if the two contaminants together produced more severe corrosion damage than when only H_2S or only CO_2 was present.

As-received (normalized) 413ØX specimens, with a hardness of HRC 21/22, and quenched-and-tempered specimens of the same hardness were tested to evaluate the effects of the different heat treatments separately from the effects of hardness.

Two types of corrosion tests were conducted: SCC and general corrosion. The same equipment and procedures used in Phase I (see Section 2) were used in the Phase II SCC tests. Duplicate tensile specimens for each alloy-heat treatment condition evaluated were used. Normalized (as-received) 414ØX steel at a hardness of HRC 21/22, and quenched-and tempered specimens at hardnesses of HRC 25/26 and HRC 29/30, were exposed in 11 tests. The HRC 21/22 normalized specimens were used to evaluate the effects of heat treatments. Samples of the 413ØX steel at a hardness of HRC 22 in quenched-and-tempered and in normalized heat-treatment conditions were exposed in two tests to separate effects of hardness and heat treatment. Quenched-and-tempered specimens of 1583Ø steel at the three hardness levels were exposed in seven tests.

A slow strain rate of 2 x 10^{-7} sec^{-1} was used in all SCC tests, as in Phase I. However, Phase II SCC tests were conducted at a temperature of 77°F (25°C), rather than the 140°F test temperature used in Phase I, because most steels display maximum susceptibility to H_2S-induced stress cracking near this temperature.

General corrosion test specimens consisted of coupons with nominal dimensions of 1 inch x 1 inch x 1/8 inch. Duplicate specimens of each steel were exposed for each heat-treatment condition. Corrosion rates were determined from weight-change measurements, and selected specimens were examined metallographically. General corrosion tests in the Phase II program were limited to CO_2-containing solutions. Tests-durations of 1,000 hours were used.

Tests were conducted at CO_2 partial pressures of 30 psia and 90 psia to simulate and evaluate the effects of 1 volume percent and 3 volume percent CO_2 in CNG. Tests were conducted on the 4130X steel in the normalized (as-received) condition at a hardness of HRC 22 and in the quenched-and-tempered condition at hardnesses of HRC 21/22, HRC 25/26, and HRC 29/30 to define the effects of hardness and heat treatment on general corrosion. Similarly, 15830 steel specimens were tested in the as-rolled (as-received) condition at a hardness of HRB 84/87 and in the quenched-and-tempered condition at hardnesses of HRC 21/22, HRC 25/26, and HRC 29/30.

Stress Corrosion Cracking Test Results

4130X Steel. Stress corrosion cracking test conditions and results for the 4130X steel are given in Table 3. Test specimens with hardnesses of HRC 25/26 and HRC 29/30 were in the quenched-and-tempered heat treatment condition. Test specimens with hardnesses of HRC 21/22 were in the normalized (as-received) condition, except in Test No. 19. In Test No. 19, one HRC 21/22 specimen (Specimen B) was

TABLE 3

STRESS CORROSION CRACKING TEST RESULTS FOR 4130X STEEL[a]

			Material Condition											
			HRC = 21/22[d]				HRC = 25/26[e]				HRC = 29/30[e]			
Test No.	Environment	Specimen No.	RA (%)	EL (%)	UTS (ksi)	Secondary Cracking	RA (%)	EL (%)	UTS (ksi)	Secondary Cracking	RA (%)	EL (%)	UTS (ksi)	Secondary Cracking
1	Water saturated with pure CH_4	1	36.0	11.1	ND[b]	No	61.5	18.2	ND	No			ND	No
		2	42.5	12.3	ND	No	60.7	18.2	ND	No	56.4	17.0	Nd	No
		Avg.	39.2	11.7			61.1	18.2			59.3	17.0		
2	Water saturated with CH_4 + 0.05 psia H_2S	3	43.9	12.6	120.1	Yes	63.7	18.8	121.9	No	60.2	18.0	133.6	No
		4	31.9	10.3	121.0	Yes	[illegible]	64218.2	124.9	No	56.0	17.9	142.2	No
		Avg.	37.9	11.4	120.6		74.0	18.5	123.4		58.1	18.0	137.9	
3	Water saturated with CH_4 + 0.15 psia H_2S	5	43.7	12.5	120.8	No	63.5	18.6	124.1	No	61.1	17.2	140.1	No
		6	37.8	12.4	120.3	No	63.8	17.9	122.7	No	60.8	16.9	141.6	No
		Avg.	40.8	12.4	120.6		63.6	18.2	123.4		60.9	17.0	140.8	
4	Water saturated with CH_4 + 0.50 psia H_2S	7	45.9	12.9	125.4	Yes	63.3	17.6	124.3	No	60.4	16.4	143.6	No
		8	45.0	17.6	123.0	Yes	63.2	18.2	124.0	No	62.2	—	137.0	No
		Avg.	45.4	15.2	124.2		63.2	17.9	124.2		61.3	17.2	140.3	
5	Water saturated with CH_4 + 1.50 psia H_2S	9	23.7	10.2	ND	Yes	49.8	17.8	ND	Yes			ND	Yes
		10	17.6	8.3	ND	Yes	61.1	18.4	ND	No	55.9	16.2	ND	Yes
		Avg.	20.6	9.2			60.4	18.1			57.4	16.6		
6	Water saturated with CH_4 + 5.00 psia H_2S	11	0.4	1.4	107.1	Yes	36.1	15.8	132.4	Yes	21.5	9.6	140.0	Yes
		12	2.4	3.4	121.0	Yes	49.0	18.0	127.0	Yes	14.7	9.0	136.6	Yes
		Avg.	1.4	2.4	114.0		42.6	16.9	129.7		18.1	9.3	138.4	
8	Water + 0.5 psia H_2S[c]	15	51.7	15.8	122.8	No	61.2	17.9	127.5	No	61.0	17.3	140.9	No
		16	51.1	16.4	121.7	No	64.2	18.8	123.7	No	61.3	17.4	137.4	No
		Avg.	51.4	16.1	122.2		62.7	18.4	125.6		61.2	17.4	139.2	

(a) Total pressure is 3,000 psig unless otherwise noted.
(b) ND -- not determined due to equipment malfunction.
(c) Total pressure was 0.5 psia.
(d) As-received hardness, unless otherwise noted.
(e) Austenitized, quenched, and tempered to indicated hardness at SwRI.

TABLE 3

STRESS CORROSION CRACKING TEST RESULTS FOR 4130X **STEEL**[a]
(Continued)

			Material Condition											
			HRC = 21/22[d]				HRC = 25/26[e]				HRC = 29/30[e]			
Test No.	Environment	Specimen No.	ELRA (%(%)	(ksi)	UTS	Secondary Cracking	RA (%)	EL (%)	UTS (ksi)	Secondary Cracking	RA (%)	EL (%)	UTS (ksi)	Secondary Cracking
7	Water saturated with	13	28.2	12.2	123.3	No	62.6	18.4	122.9	No	55.1	16.4	140.4	No
	CH_4 + 90 psia CO_2	14	19.8	9.0	123.6	No	63.0	18.8	121.8	No				No
			Avg. 24.0	10.6	123.4		Avg. 62.8	18.6	122.4		Avg. 60.8	17.5	138.4	
9	Water saturated with	17	23.7	11.2	125.2	No	62.5	18.4	122.7	No	60.2	18.0	138.4	No
	CH_4 + 30 psia CO_2	18	28.2	12.0	125.3	No	64.0	18.7	124.6	No	60.9	17.4	138.1	No
			Avg. 26.0	11.6	125.2		Avg. 63.2	18.6	123.6		Avg. 60.6	17.7	138.2	
10	Water saturated with	19	29.9	10.1	120.4	Yes	64.2	18.2	125.0	No	62.2	19.0	135.7	No
	CH_4 + 7 psia CO_2	20	25.2	8.1	121.0	Yes	65.4	19.6	120.6	No	58.5	17.1	141.5	No
			Avg. 27.6	9.1	120.7		Avg. 64.8	18.9	122.8		Avg. 60.4	18.0	138.6	
19	Water saturated with	A	24.0[e]	10.1	112.6	No	55.9	16.6	118.4	No	55.4	17.4	131.3	Yes
	CH_4 + 0.05 psia H_2S	B	62.9[e]	19.0	107.0	No	60.8	17.4	118.4	No	55.4	16.0	131.8	Yes
	+ 7 psia CO_2						Avg. 58.4	17.0	118.4		Avg. 55.4	16.7	131.6	

(a) Total pressure is 3,000 psig unless otherwise noted.
(b) ND -- not determined due to equipment malfunction.
(c) Total pressure was 0.5 psia.
(d) As-received hardness, unless otherwise noted.
(e) Austenitized, quenched, and tempered to indicated hardness at SwRI.

tested in the quenched-and-tempered condition to provide a direct comparison with the normalized specimen (Specimen A) used in the same test. Results of additional tests to compare susceptibilities of normalized and quenched-and-tempered 4130X specimens are given in Table 4.

Figure 4 is a graphical presentation of results from SCC tests on 4130X steel specimens in H_2S-containing environments. Figure 5 is a similar presentation of results from tests on 4130X steel specimens in CO_2-containing environments. Percent-reduction-in-area values are plotted versus H_2S and CO2 partial pressures, respectively.

Baseline Test. Baseline data for 4130X steel specimens were obtained in water saturated with pure methane (Test No. 1). The normalized HRC 21/22 steel specimens were inherently more brittle than the higher-hardness, quenched-and-tempered 4130X specimens. The ductility parameters of the normalized HRC 21/22 specimens were about 30 percent less than those of the quenched-and-tempered HRC 25/26 and HRC 29/30 specimens.

H_2S Effects. H_2S was the only gaseous contaminant in Test Nos. 2 through 6 and Test No. 8. The normalized HRC 21/22 material was susceptible to cracking at H_2S partial pressures of 0.50 psia or higher and at 0.05 psia. It is not clear why the normalized specimens did not crack at the intermediate pressure of 0.15 psia H_2S. However, this was not the only ambiguity in results from the normalized material. Test No. 8, a repetition of Test No. 4 in which both specimens cracked, did not produce cracking, and both normalized specimens had good ductility in Test No. 8.

Results from the HRC 25/26 and HRC 29/30 specimens were more uniform. One of the HRC 25/26 specimens was not susceptible to cracking at an H_2S partial pressure of 1.50 psia, while the second specimen was susceptible (Test No. 5); both of the HRC 29/30 specimens

TABLE 4

STRESS CORROSION CRACKING TESTS ON 413ØX STEEL IN DIFFERENT HEAT-TREATMENT CONDITIONS

			As Received (HRC/21/22)					Quenched and Tempered (HRC 21/22)			
lest No.	Environment		E RA (%(%)		UTS (ksi)	Secondary Cracking		RA ((%)		UTS (ksi)	Secondary Cracking
17	Water saturated with CH_4 + 1.50 psia H_2S		33.4	9.2	113.0	Yes		63.3	20.1	103.8	No
			25.7	10.2	112.8	Yes		61.6	19.4	103.8	No
		Avg.	29.6		112.9		Avg.	62.4	19.8	103.8	
18	Water saturated with CH_4 + 7 psia CO_2		28.9	11.9	119.9	No		52.3	20.2	110.8	No
			25.0	10.0	119.6	No		61.4	18.5	112.8	No
		Avg.	27.0	11.0	119.8		Avg.	56.8	19.4	111.8	

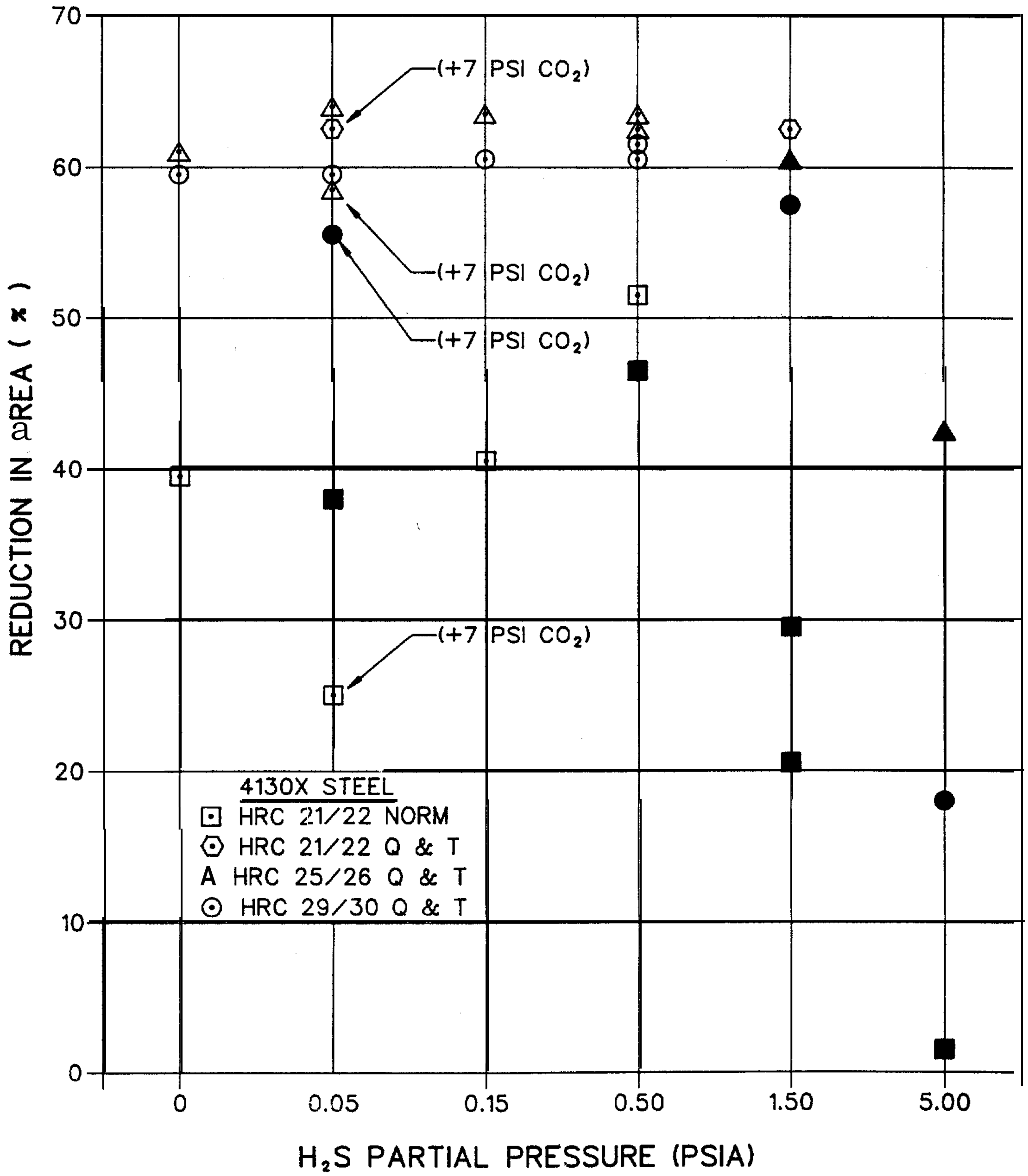

FIGURE 4. SUMMARY OF STRESS CORROSION CRACKING TEST RESULTS FOR 4130X STEEL EXPOSED IN H_2S-CONTAINING SOLUTIONS. Solid points indicate cracking; open points indicate no cracking.

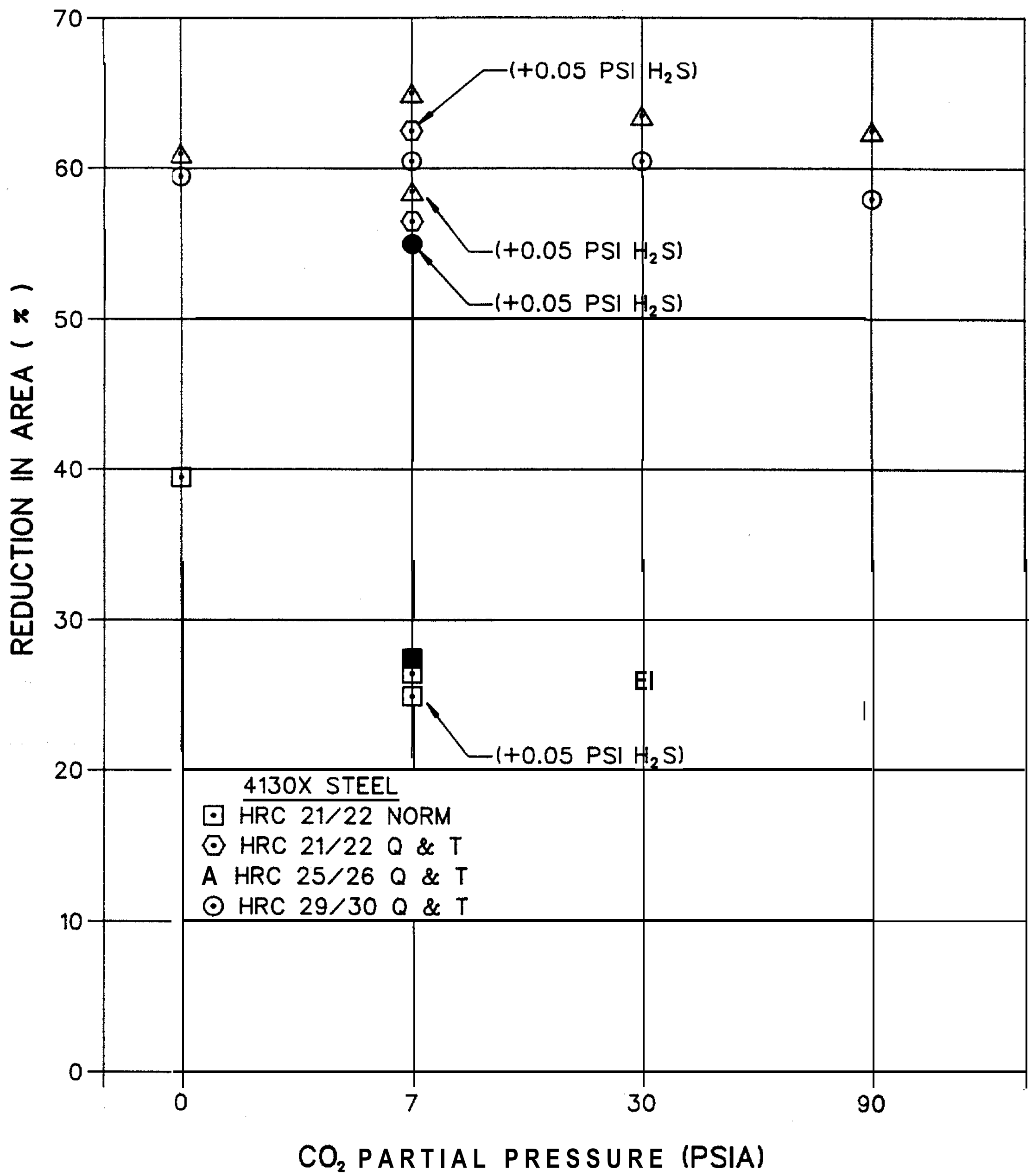

FIGURE 5. SUMMARY OF STRESS CORROSION CRACKING TEST RESULTS FOR 4130X STEEL EXPOSED IN CO_2-CONTAINING SOLUTIONS. Solid points indicate cracking; open points indicate no cracking.

were susceptible at this pressure. All of the HRC 25/26 and HRC 29/30 specimens were susceptible to cracking at H_2S partial pressures of 5.00 psia. While the 4130X steel was susceptible to cracking in all three heat treatment conditions at an H_2S partial pressure of 5.00 psia, the normalized HRC 21/22 specimens were significantly more brittle (i.e., ductility parameters were smaller) than any of the quenched-and-tempered specimens. In general, at the same H_2S partial pressures the HRC 29/30 specimens were embrittled more than the HRC 25/26 specimens.

Test No. 17 (Table 4) was conducted to compare the behavior of normalized and quenched-and-tempered specimens at the same hardness under conditions previously shown to cause cracking and embrittlement of the normalized material. The hardness of all the specimens was HRC 21/22. An H_2S partial pressure of 1.50 psia was used. Both normalized specimens cracked and were severely embrittled. The quenched-and-tempered specimens were not susceptible to cracking or to embrittlement.

CO_2 Effects. Test Nos. 7, 9, and 10 (Table 3) were conducted in water saturated with 90, 30, and 7 psia of CO_2, respectively. None of the quenched-and-tempered HRC 25/26 and HRC 29/30 specimens were susceptible to cracking or to embrittlement in any of the tests containing CO_2. The normalized HRC 21/22 specimens were not susceptible to cracking at CO_2 partial pressures of 90 and 30 psia (Test Nos. 7 and 9), although all of the normalized specimens exposed in these two tests suffered some embrittlement. Both normalized specimens were susceptible to cracking and embrittlement in Test No. 10 at a CO_2 partial pressure of 7 psia.

Test No. 18 (Table 4) was conducted to compare the behavior of normalized and quenched-and-tempered specimens at the same hardness. The hardness used was HRC 21/22, and the CO_2 partial pressure used was 7 psia. Unlike Test No. 10 in which the normalized specimens cracked at a CO_2 partial pressure of 7 psia, neither normalized specimen cracked in Test No. 18, although both specimens displayed some loss of ductility. Neither of the quenched-and-tempered specimens was susceptible to cracking, and both displayed good ductility.

Combined H_2S and CO_2 Effects. A single test (Test No. 19, Table 3) was conducted with Ø.Ø5 psia H_2S and 7 psia CO_2 present in the gas phase. One quenched-and-tempered HRC 21/22 specimen and one normalized HRC 21/22 specimen were exposed. All of the HRC 25/26 and HRC 29/30 specimens were in the quenched-and-tempered condition. Neither of the HRC 21/22 specimens developed cracks. However, the normalized specimen (Specimen A) was severely embrittled. The ductility parameters of the quenched-and-tempered HRC 21/22 specimen were similar to those of the quenched-and-tempered HRC 21/22 specimens in Test No. 18 (Table 4). Neither of the quenched-and-tempered HRC 25/26 specimens was susceptible to cracking in the combined H_2S-CO_2 environment, but both displayed lower ductility values than in the test with Ø.Ø5 psia H_2S only (Test No. 2) or in the test with 7 psia CO_2 only (Test No. 1Ø). Both quenched-and-tempered HRC 29/30 specimens were susceptible to cracking in the combined H_2S-CO_2 environment, whereas specimens of this hardness were not susceptible in the pure H_2S environment (Test No. 2) or in the test with 7 psia CO_2 only (Test No. 1Ø).

The results of Test No. 19 show that the combined H_2S-CO_2 environment was more severe than environments containing only H_2S at a partial pressure of Ø.Ø5 psia or only CO_2 at a partial pressure of 7 psia. It is believed that the embrittlement and cracking of 413ØX steel specimens in the combined environment were caused by hydrogen. The pH of the combined H_2S-CO_2 environment was not measured, but it would have been/lower than either the H_2S environment in Test No. 2 or the CO2 environment in Test No. 1Ø. As a result, in the combined H_2S-CO_2 environment more hydrogen ions would have been available to be reduced to hydrogen atoms, and the amount of atomic hydrogen available to enter the steels and cause hydrogen embrittlement and cracking would have been correspondingly greater. A hydrogen mechanism is consistent with the fact that cracking occurred in the highest strength (highest hardness) specimens, since susceptibility of steels to hydrogen-induced cracking increases as the yield strength of a steel is increased.

__15B30 Steel.__ Results of stress corrosion cracking tests conducted on 15B30 steel specimens are tabulated in Table 5 and are shown graphically in Figure 6 for H_2S-containing environments, and in Figure 7 for CO_2-containing environments. All 15B30 specimens tested were in the quenched-and-tempered condition. As with the 4130X steel, specimens of the 15830 steel were tested at hardnesses of HRC 21/22, HRC 25/26, and HRC 29/30.

__H_2S Effects.__ Test Nos. 11, 12, and 13 (Table 5) were conducted in water saturated with H_2S at partial pressures of 0.05 psia, 0.15 psia, and 5.00 psia, respectively. No specimens were susceptible to cracking at H_2S partial pressures of 0.05 psia and 0.15 psia. One specimen at each of the three hardness levels cracked in Test No. 13 at an H_2S partial pressure of 5.00 psia. Ductility parameters were not significantly affected at pressures of 0.05 and 0.15 psia H_2S, but all of the specimens tested at 5.00 psia H_2S were severely embrittled. Embrittlement was hardness dependent, i.e., the HRC 29/30 specimens were more severely embrittled than the HRC 25/26 specimens, which were more severely embrittled than the HRC 21/22 specimens.

__CO_2 Effects.__ Test Nos. 14, 15, and 16 (Table 5) were conducted in water saturated with 90, 30, and 7 psia of CO2, respectively. None of the 15830 specimens was susceptible to cracking in any of the three tests. The ductilities of the HRC 25/26 and HRC 29/30 specimens at CO_2 partial pressures of 90 and 30 psia (Test Nos. 14 and 15) were substantially reduced. The HRC 29/30 specimens also were embrittled in the test at a CO_2 partial pressure of 7 psia (Test No. 16), but the

TABLE 5

STRESS CORROSION CRACKING TEST RESULTS FOR 15B30 STEEL[a]

			Material Condition											
			HRC = 21/22[d]				HRC = 25/26[d]				HRC = 29/30[d]			
Test No.	Environment	Specimen No.	RA (%)	EL (%)	UTS (ksi)	Secondary Cracking	RA (%)	EL (%)	UTS (ksi)	Secondary Cracking	RA (%)	EL (%)	UTS (ksi)	Secondary Cracking
11	Water saturated with 0.05 psia H_2S[b]	1	59.6	19.1	109.5	No	56.3	18.2	120.2	No	57.5	16.4	136.5	No
		2	56.4	18.3	110.7	No	53.6	16.9	121.1	No	[illegible]	[illegible]	138.4	No
		Avg.	58.0	18.7	101.0		55.0	17.6	120.6		56.8	16.2	137.4	
12	Water saturated with 0.50 psia H_2S[b]	3	57.5	18.6	110.8	No	55.6	17.2	120.4	No	48.8	14.5	137.9	No
		4	56.9	19.0	111.4	No	55.4	17.6	121.6	No	55.5	16.2	137.7	No
		Avg.	57.2	18.8	111.1		55.5	17.4	121.0		52.2	15.4	137.8	
13	Water saturated with 5.00 psia H_2S[b]	5	14.3	10.1	113.7	No	7.9	2.8	114.9	Yes	4.8	2.3	87.6	No
		6	13.9	9.3	113.0	Yes					7.5	2.9	119.8	Yes
		Avg.	14.1	9.7	113.4		9.6	4.1	117.6		6.2	2.6	103.7	
14	Water saturated with CH_4 + 90 psia CO_2	7	56.3	17.8	79.8	No	46.1	17.8	80.8	No	35.4	12.2	82.0	No
		8	56.1	18.0	79.4	No	53.6	16.9	79.4	No	29.4	10.2	79.3	No
		Avg.	46.2	17.9	79.6		49.8	17.4	80.1		32.4	11.2	80.6	
15	Water saturated with CH_4 + 30 psia CO_2	9	56.0	18.6	NI[c]	No	53.0	17.2	ND	No	41.6	5.0	ND	No
		10	55.1	18.3	ND	No	47.4	23.7	ND	No	[illegible]	[illegible]	ND	No
		Avg.	55.6	18.4			50.2	20.4			34.8	7.1		
16	Water saturated with CH_4 + 7 psia CO_2	11	59.0	18.6	110.2	No	55.3	19.1	120.4	No	41.0	12.9	37.0	No
		12	56.8	18.2	111.6	No	53.6	16.4	120.0	No	31.1	11.5	136.0	No
		Avg.	57.9	18.4	110.9		54.4	17.8	120.2		36.0	12.2	136.5	
20	Water saturated with CH_4 + 0.05 psia H_2S + 7 psia CO_2	13	61.2	18.7	108.3	No	53.3	16.1	112.5	No	43.0	14.2	131.1	No
		14	60.9	19.0	108.7	No	54.5	16.8	112.1	No	50.2	15.0	128.9	
		Avg.	61.0	18.8	108.5		53.9	16.4	112.3		46.6	14.6	130.0	

(a) Total is 3,000 psig unless otherwise indicated.
(b) Total pressure is the H_2S pressure
(c) ND -- not determined due to equipment malfunction.
(d) Austenitized, quenched, and tempered to indicated hardness at SwRI.

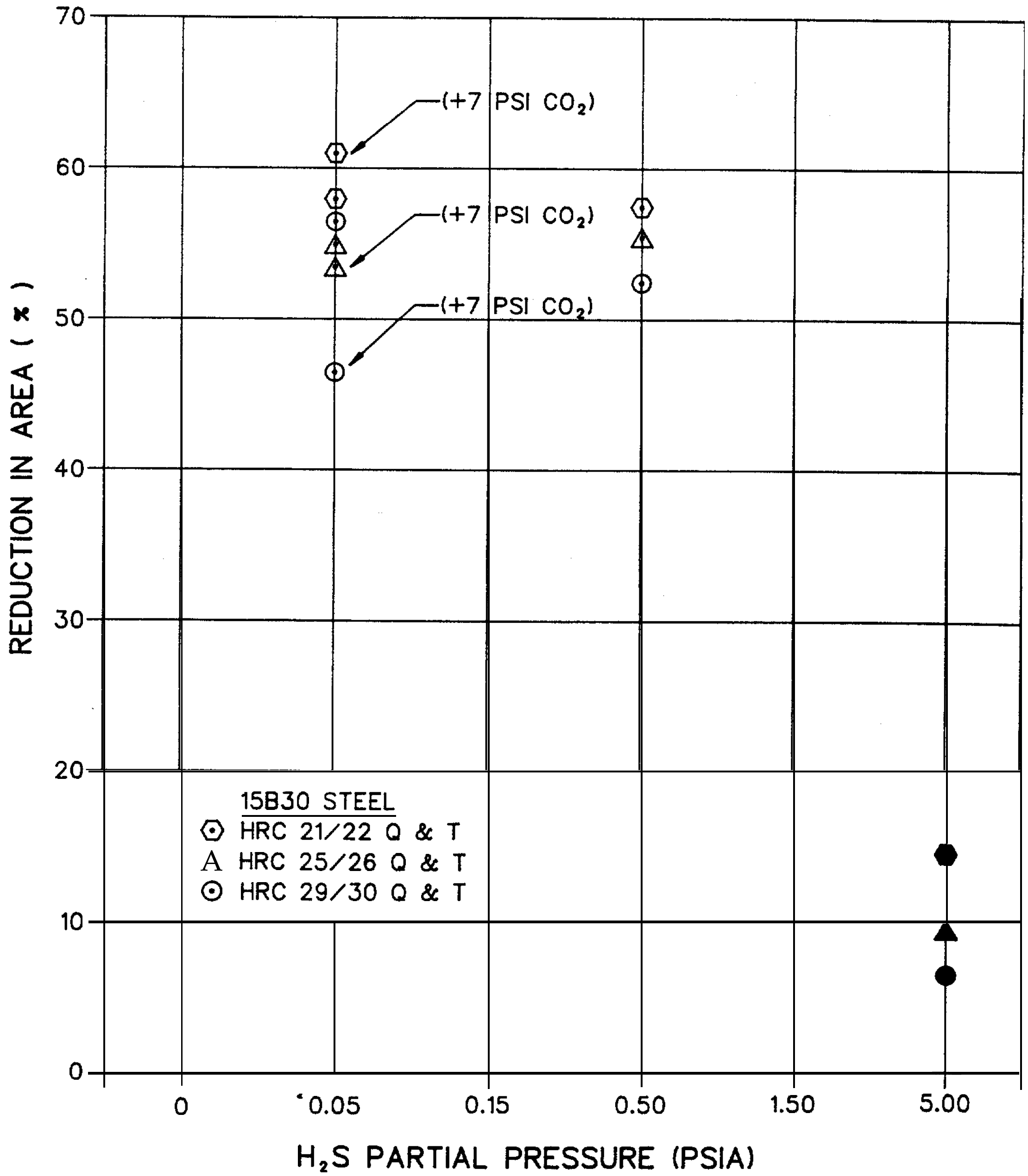

FIGURE 6. SUMMARY OF STRESS CORROSION CRACKING TEST RESULTS FOR 15B30 STEEL EXPOSED IN H_2S-CONTAINING SOLUTIONS. Solid points indicate cracking; open points indicate no cracking.

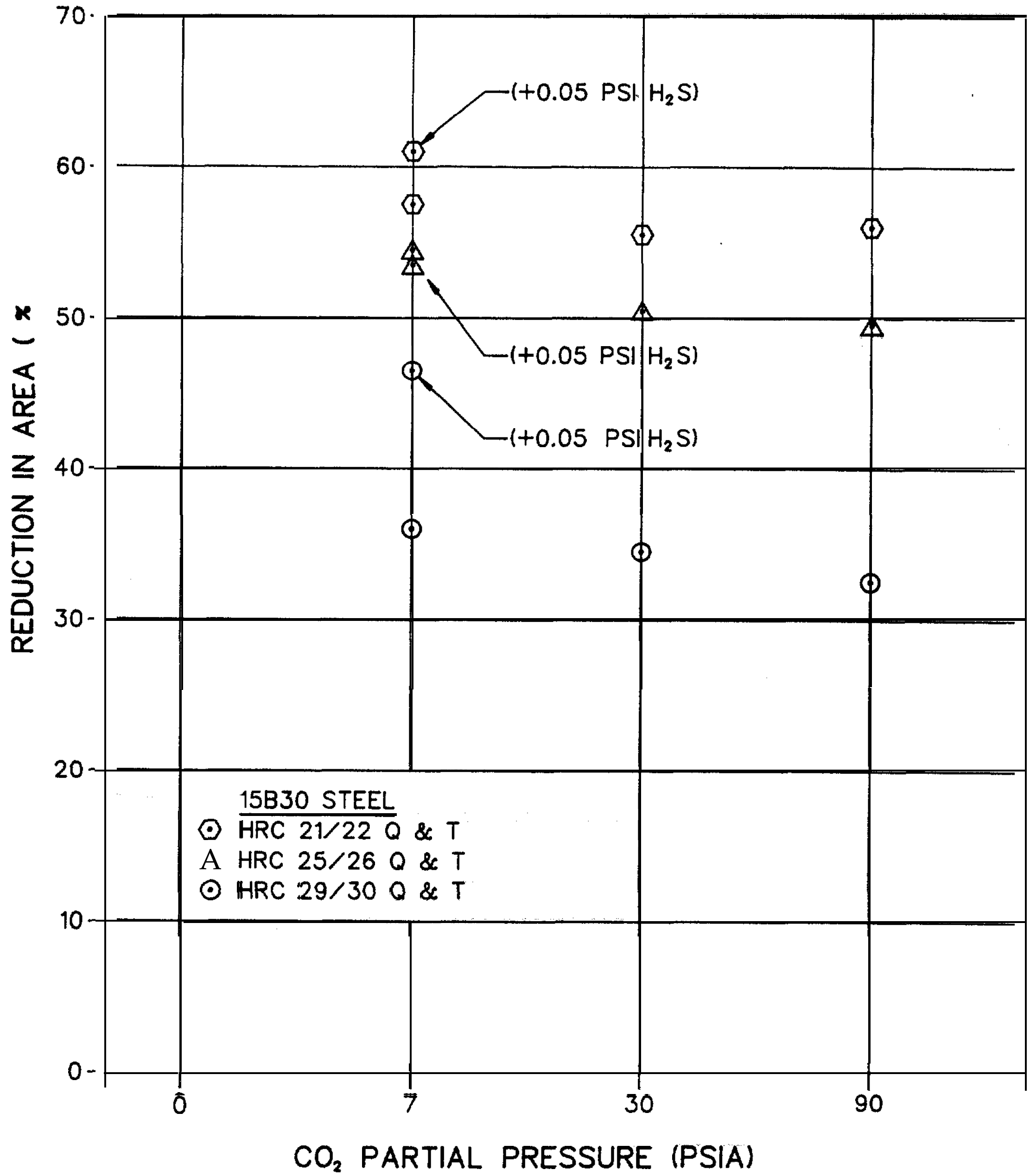

FIGURE 7. SUMMARY OF STRESS CORROSION CRACKING TEST RESULTS FOR 15B30 STEEL EXPOSED IN CO_2-CONTAINING SOLUTIONS. Solid points indicate cracking; open points indicate no cracking.

ductility parameters of the HRC 25/26 specimens were not affected. HRC 21/22 specimens were not subject to embrittlement in any of the CO_2-containing environments.

Combined H_2S and CO_2 Effects. A single test (Test No. 2Ø, Table 5) was conducted with Ø.Ø5 psia H_2S and 7 psia CO_2 present in the gas phase. The 15B30 steel was not susceptible to cracking at any of the three hardness levels. The HRC 29/30 specimens suffered some loss in ductility. The degree of embrittlement was greater than when the environment contained only H_2S at a partial pressure of Ø.Ø5 psia (Test No. 11) and was less than when the environment contained only CO_2 at a partial pressure of 7 psia (Test No. 16). Results for the HRC 25/26 and HRC 21/22 specimens in the combined H_2S-CO_2 environment were not significantly different than when only H_2S or only CO_2 were present.

General Corrosion Tests

Two general corrosion test exposures were conducted to determine corrosion rates of 413ØX and 15B30 steels in CO_2-containing solutions. Coupons were exposed for 1,ØØØ hours at 77°F (25°C). Duplicate specimens of as-received (normalized) 413ØX steel, duplicate specimens of as-received (as-rolled) 15B30 steel, and duplicate specimens of both steels quenched and tempered to three hardness levels (HRC 21/22, HRC 25/26, and HRC 29/30) were tested in each environment. The environments in the two tests consisted of deaerated, deionized water saturated with CO2 at partial pressures of 3Ø psi and 9Ø psi, respectively.

Test results from 413ØX and 1583Ø steel coupons are given in Tables 6 and 7, respectively. The presence and severity of pitting corrosion also are indicated in the tables. "Minor" pitting indicates the presence of shallow pits that were less than about 0.002-inch deep, corresponding to a pitting rate of less than about Ø.Ø2Ø in./yr

TABLE 6

1,000-HR CORROSION TESTS ON 4130X STEEL IN CO_2-SATURATED WATER

Heat Treatment Condition	Hardness		Corrosion Rate (mils/year) — CO_2 Pressure: 30 psi	(Notes)*		90 psi	(Notes)*
Normalized	HRC 21/22		15.5	A		30.4	A
			12.6	A		29.7	A
		Avg.	14.0		Avg.	30.0	
Quenched & Tempered	HRC 21/22		4.8	B		7.9	A
			5.9	A		8.2	B
		Avg.	5.4		Avg.	8.0	
Quenched & Tempered	HRC 25/26		5.7	A		8.1	A
			6.8	A		8.0	A
		Avg.	6.2		Avg.	8.0	
Quenched & Tempered	HRC 29/30		6.3	C		8.3	B
			7.6	B		9.1	C
		Avg.	6.9		Avg.	8.7	

*Notes: A -- no pitting; B -- minor pitting; C -- moderate pitting.

TABLE 7

1,000-HR CORROSION TESTS ON 15830 STEEL IN CO_2-SATURATED WATER

Heat Treatment Condition	Hardness		Corrosion Rate (mils/year), CO_2 Pressure: 30 psi	(Notes)*		90 psi	(Notes)*
As Rolled	HRB 84/87		18.7	D		32.1	D
			20.2	D		33.2	A
		Avg.	19.4		Avg.	32.6	
				C			
Quenched & Tempered	HRC 21/22		13.8	C		24.3	A
			12.6			22.9	A
		Avg.	13.2		Avg.	23.6	
Quenched & Tempered	HRC 25/26		18.7	B		41.1	A
			17.7	B		38.5	A
		Avg.	18.2		Avg.	39.8	
Quenched & Tempered	HRC 29/30		17.2	C		40.0	A
			17.Ø	B		43.1	A
		Avg.	17.1		Avg.	41.6	

*Notes: A -- no pitting; B -- minor pitting; C -- moderate pitting.

(mpy). "Moderate" pitting indicates the presence of pits with depths between about 0.002 and about 0.006 inch, corresponding to a pitting rate of about 20 to 50 mpy. And, "severe" pitting indicates the presence of pits deeper than about 0.006 inch, corresponding to a pitting rate greater than 50 mpy.

4130X Steel. The results of the tests on the 4130X steel indicate a significant dependence of general corrosion rate on the heat treatment condition of the material. For both partial pressures of CO_2, the general corrosion rates of the normalized HRC 21/22 specimens were about three times greater than the corrosion rates of the quenched-and-tempered HRC 21/22 specimens and at least twice the corrosion rates of any of the quenched-and-tempered HRC 25/26 and HRC 29/30 specimens. General corrosion rates of the quenched-and-tempered specimens were independent of hardness in both test solutions. For all heat treatment conditions, general corrosion rates were higher in the 90-psi CO2 solution than in the 30-psi CO_2 solution. The 4130X steel specimens suffered minor to moderate pitting, and pitting was essentially independent of CO_2 partial pressure and heat treatment condition.

15B30 Steel. The 15830 steel (Table 7) was significantly more susceptible than the 4130X steel to both general corrosion and pitting. General corrosion rates of the 15B30 steel specimens in the 90-psi CO_2 solution were approximately twice the rates obtained in the 30-psi CO_2 solution. Within a single test solution, general corrosion rates were independent of both heat treatment condition and hardness. Pitting corrosion of the 15B30 steel in the 30-psi CO_2 solution was generally more severe than in the 90-psi CO_2 solution.

FINDINGS OF PHASE II CORROSION TEST RESULTS

The findings of the Phase II corrosion test program are summarized below.

Stress Corrosion Cracking Tests

4130X Steel

- Normalized 4130X steel specimens at a hardness of HRC 21/22 were significantly more susceptible to embrittlement and stress corrosion cracking in water environments containing H_2S or CO_2 than were quenched-and-tempered 4130X steel specimens at hardnesses of HRC 21/22, HRC 25/26, and HRC 29/30.

- Normalized HRC 21/22 specimens were susceptible to embrittlement and cracking at an H_2S partial pressure of 0.05 psia.

- Quenched-and-tempered HRC 21/22 specimens were not susceptible to cracking at an H_2S partial pressure of 1.50 psia. Quenched-and-tempered HRC 25/26 and HRC 29/30 specimens were susceptible at an H_2S partial pressure of 1.50 psia, but they were not susceptible at the lower H_2S partial pressures evaluated in the program.

- Normalized HRC 21/22 specimens were susceptible to SCC at a CO_2 partial pressure of 7 psia, but not at higher CO_2 partial pressures.

- Quenched-and-tempered HRC 21/22 specimens were not susceptible to cracking at a CO_2 partial pressure of 7 psia, the only pressure at which HRC 21/22 specimens were tested, and quenched-and-tempered HRC 25/26 and HRC 29/30 specimens were not susceptible at any of the CO_2 partial pressures studied.

- The 4130X steel generally was more susceptible to embrittlement and/or stress corrosion cracking in a combined H_2S-CO_2 (0.05 psia H_2S-7 psia CO_2) environment than in environments containing only H_2S (0.05 psia) or CO_2 (7 psia).

15B30 Steel

- Quenched-and-tempered 15830 steel specimens at hardnesses of HRC 21/22, HRC 25/26, and HRC 29/30 were not susceptible to stress corrosion cracking in H_2S-containing solutions when the H_2S partial pressure in the gas phase was 0.50 psia or less. 15830 specimens of all three hardnesses were susceptible to cracking and embrittlement at an H_2S partial pressure of 5.00 psia.

- Quenched-and-tempered 15B30 steel specimens were not susceptible to stress corrosion cracking in any of the CO_2 environments evaluated. HRC 21/22 and HRC 25/26 specimens were not susceptible to embrittlement in any of the CO2 environments, but the HRC 29/30 specimens were susceptible to embrittlement at all three CO_2 partial pressures studied.

- The behavior of 15830 steel specimens exposed in an H_2S-CO_2 (0.05 psia H_2S-7 psia CO_2) environment was similar to results obtained in an environment containing only CO_2 (7 psia). The HRC 29/30 specimens were moderately embrittled, but did not crack. Lower-hardness specimens were not susceptible to embrittlement or cracking.

General Corrosion

- General corrosion rates of quenched-and-tempered 4130X steels were low and were essentially independent of hardness in environments saturated with CO_2 at partial pressures of 30 psia and 90 psia. However, the susceptibility of the quenched-and-tempered 4130X steels to pitting generally increased with hardness.

- Normalized 4130X steels displayed high general corrosion rates in environments saturated with CO_2 at partial pressures of 30 psia and 90 psia.

- Quenched-and-tempered 15B30 steel specimens of all three hardness levels displayed high general corrosion rates in environments saturated with CO_2 at partial pressures of 30 psia and 90 psia.

- 15B30 steel was more susceptible to pitting in CO_2-containing solutions than was the 4130X steel.

Section 4

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

The primary conclusions of the overall program are as follows:

- The principal corrosive contaminants in natural gases in the U.S. are H_2S and other sulfur-containing species, CO_2, oxygen, and water.

- Aluminum alloy 6061-T6 is suitable for use in CNG cylinders, regardless of the natural gas composition. Aluminum alloy 6061-T6 is immune to stress corrosion cracking, embrittlement, and other forms of general and localized corrosion in natural gas environments, including H_2S and CO_2 environments that are capable of inducing cracking, embrittlement, pitting, and general corrosion in steels.

- Corrosion of CNG cylinders made of steel may be prevented by maintaining the water vapor concentration of CNG gas supplies below the dew point for the anticipated range of temperatures and pressures. Steels are not subject to significant corrosion in natural gas environments, regardless of the concentrations of other contaminants, unless liquid water is present.

- Normalized 4130X steels are not suitable for use in CNG cylinders unless the water vapor concentration of the supply gas is sufficiently low to prevent condensation of liquid water. Normalized HRC 21/22 4130 steel specimens cracked in environments containing as little as 0.05 psia H_2S or 7.0 psia CO_2.

- Quenched-and-tempered 4130X steels are suitable for use in CNG cylinders at hardnesses to HRC 25/26 for natural gas supplies in which the H_2S partial pressure is 0.15 psia or less and the CO_2 partial pressure does not exceed 7 psia. In the absence of CO_2, quenched-and-tempered 4130X steel at a hardness of HRC 29/30 is acceptable.

- Quenched-and-tempered 15B30 steels are suitable for use in CNG cylinders at hardnesses to HRC 29/30 for natural gas supplies in which the H_2S partial pressure is 0.50 psia or less and the CO_2 partial pressure does not exceed 7 psia.

The limitation of 7 psia CO_2 for quenched-and-tempered 15B30 steels is necessary to prevent general corrosion and pitting in these materials. Higher levels of CO_2 can be tolerated by quenched-and-tempered 4130X steels without significant general corrosion or pitting, but test results indicated a limit of 7 psia CO_2 is appropriate for these steels to minimize the possibility of stress corrosion cracking.

The above conclusions indicate that stress corrosion cracking is possible in steel CNG cylinders for certain combinations of steels, heat treatment conditions, hardnesses, and gas compositions. Since current DOT regulations allow normalized steels to be used in CNG cylinders, one of the most significant findings of the program is that normalized 4130 steels with hardnesses of HRC 21/22 can suffer stress corrosion cracking at very low levels of H_2S or CO2 if liquid water also is present.

Several of the eight used 4130X steel cylinders that were examined in' the program had hardnesses in excess of HRC 21/22 and microstructures that were not fully quenched and tempered. The absence of significant corrosion in these cylinders, particularly the absence of crack growth from large fabrication flaws found in several of the cylinders, suggests that CNG supplies currently being used in the U.S. have very low levels of H_2S and CO_2, or the typical water vapor concentration of the gases used in the cylinders examined was very low. The gas analyses reported in Phase I are consistent with this observation. With the exception of water, which was very high in a few gases from distribution lines, corrosive contaminants in the gases analyzed were well within limits established by DOT for CNG supplies.

RECOMMENDATIONS

Gas-Quality Standard

The primary objective of this research program was to develop a CNG gas-quality standard for corrosive contaminants in natural gases that is sufficient to insure that internal corrosion does not constitute a hazard over the lifetimes of the cylinders. A gas-quality standard for CNG is recommended which accomplishes this objective without being economically impractical. It is based upon the results of this program, and it draws upon existing standards (in particular, NACE MR-01-75), practices, and experience in the gas production and transmission industries and upon data available in the technical literature.

The recommended gas-quality standard incorporates three options, depending upon the CNG cylinder material used and the manner in which CNG suppliers choose to control gas compositions, as follows:

- **Aluminum Cylinders.** No restrictions on the concentrations of corrosive contaminants in natural gas are required for CNG cylinders made of aluminum alloy 6061-T6.

- **Steel Cylinders.** When the dew point of the natural gas entering a steel CNG cylinder is below the lowest anticipated cylinder temperature at the highest anticipated cylinder pressure, no limitations are required on the concentrations of other corrosive contaminants in the gas; or

- **Steel Cylinders.** When the dew point of the natural gas entering a steel CNG cylinder is not below the lowest anticipated cylinder temperature at the highest anticipated cylinder pressure, the gas-quality in the cylinder shall comply with the following limitations on corrosive contaminants:

- **Hydrogen Sulfide (H_2S) and Other Soluble Sulfides -- 0.05** psia partial pressure, maximum.

- **Carbon Dioxide (CO_2)** -- 7.Ø psia partial pressure, maximum.

- **Oxygen** - Ø.5 volume percent, maximum.
- **Water Vapor** -- 7 lb/MMCF, maximum.

The first and second options reflect the findings of the test program that aluminum alloy 6060-T6 is not susceptible to corrosion damage in natural gas environments, and that steels are not susceptible to corrosion damage in the absence of liquid water.

The limitation on H_2S and other soluble sulfides in the third option results from the findings of the experimental test program, the provisions of NACE MR-Ø1-75, and the knowledge-that CNG cylinders currently in use are made of steels that were subjected to a number of different heat treatments and, consequently, have a variety of microstructures and hardnesses.

The results of the test program indicate that quenched-and-tempered steels are not susceptible to SCC at H_2S partial pressures as high as Ø.15 psia and hardnesses as high as HRC 25/26. But, the existing DOT regulations governing CNG cylinders permit the use of normalizing heat treatments, and the test results showed that normalized HRC 21/22 steel specimens were susceptible 'to SCC in some, although not all, tests at an H_2S partial pressure of Ø.Ø5 psia. MR-Ø1-75, which is based on many years of practical experience in the oil and gas industries, does not restrict hardness and heat treatment procedures for steels, if the H_2S partial pressure in the gas being contained or processed is maintained below Ø.Ø5 psia.

The presence of small cracks in normalized HRC 21/22 specimens of 413ØX steel tested at Ø.Ø5 psia H_2S indicates some risk is involved in incorporating the MR-Ø1-75 H_2S limit of Ø.Ø5 psia into the recommended CNG gas-quality standard. However, it is believed that a limit of Ø.Ø5 psia H_2S without restriction on metal hardness or heat treatment is justified in view of the favorable experience obtained under MR-01-75 and the fact that cracks formed at Ø.Ø5 psia H_2S were very small.

Little data are available concerning the effects of sulfur-containing species other than H_2S. However, gas analyses indicate that concentrations of other soluble sulfur species, primarily mercaptans, in natural gases are small in comparison to H_2S concentrations, and may be expected to behave similarly to H_2S. Further, non-soluble sulfur species generally are non-corrosive. Consequently, the lack of data concerning effects of other sulfur species was accounted for by assuming that other soluble sulfur species would behave as if they were H_2S, and the combined partial pressure of H_2S and other soluble sulfur species was limited to Ø.Ø5 psia.

The 7 psia limit placed on CO_2 partial pressure in the third option reflects an industry "rule of thumb" and findings of the research program that normalized 413ØX steels and quenched-and-tempered 15B30 steels are subject to high general corrosion rates at CO2 partial pressures corresponding to 1 volume percent and 3 volume percent in a natural gas pressurized to a total pressure of 3,ØØØ psi. Such CO2 concentrations are permissible under both DOT Specification E 8ØØ9 for CNG and individual pipeline company specifications for natural gas. The CO2 partial pressure limitation is the most significant difference between the recommended gas-quality standard and existing natural gas and CNG specifications.

Since the effects of oxygen were not studied in the experimental program, the oxygen limit in the third option was based on existing standards and experience. The recommended oxygen concentration limit of Ø.5 volume percent corresponds to an oxygen partial pressure of 15 psia for CNG at a pressure of 3,ØØØ psi. This limit was selected because available data indicate that an acceptable corrosion rate may be obtained in water saturated with oxygen at a partial pressure of 15 psia (11).

The limit of 7.0 lb/MMCF placed on water vapor in the third option corresponds to the water vapor limit imposed by U.S. gas transmission companies on natural gases transmitted through their pipelines. The dew point for CNG containing this amount of water vapor is between about 45 and 55°F for total gas pressures between 2,000 and 5,000 psi (12). Therefore, the recommended water vapor limit will permit liquid water to be formed at relatively low temperatures, and corrosion is possible if other corrosive contaminants are present. It is for this reason that limits are imposed on the partial pressures of H_2S and CO_2 in the third option.

The alternative, presented as the second option in the recommended gas-quality standard, is to limit the water vapor concentration to a level at which liquid water cannot form in CNG cylinders, i.e., to maintain the water vapor content of of the gas below the dew point at the maximum anticipated gas pressure and the minimum anticipated temperature.

Other Recommendations

Use of Normalized Steels in CNG Cylinders. The results of the test program revealed that stress corrosion cracking and embrittlement of normalized 4130X steels at a hardness of HRC 21/22 is possible at very low levels of H_2S and CO_2, and that quenched-and-tempered steels of the same composition are not susceptible to cracking and embrittlement at significantly higher hardnesses and H_2S levels.

In view of this result, it is recommended that 49 CFR 178.37, and other standards applicable to CNG cylinders, be amended to prohibit the use of normalized steels in new CNG cylinders. Consideration should also be given to requiring normalized steel CNG cylinders to be inspected more frequently or to requiring that such cylinders be removed from CNG service.

Additional Research

Corrosion Fatigue. The work described in this report has been limited to studies of the corrosion and stress corrosion cracking resistance of 4130X and 15B30 steels and aluminum alloy 6061-T6 in natural gas environments. However, CNG cylinders undergo a fatigue cycle each time they are loaded and used, which in some cases may be as often as three or four times daily. Studies of fatigue crack initiation from smooth surfaces and of fatigue crack growth from pre-existing flaws (such as those found in the Phase I portion of this study) in 4130X and 15B30 steels and in aluminum alloy 6061-T6 are recommended. Tests should be conducted under loading and environmental conditions simulating CNG service.

Corrosion and Stress Corrosion Cracking. The corrosion and SCC tests conducted in this study were limited in number and were performed on single heats of the steels studied. Further, evaluation of the effects of all corrosive contaminants in natural gas and of interactions among the various contaminants was not possible within the scope of the program.

It is recommended that additional corrosion and stress corrosion cracking tests be conducted to evaluate effects of:

- Other sulfur-containing species inherently present in natural gas and in odorants that are added to natural gases in distribution systems.
- Interaction between contaminants over composition ranges that are possible under gas company standards, DOT E 8009, and the gas-quality standard recommended in this report.
- Temperature variation.
- Variation in steel composition. Several heats of 4130X steel should be studied, since this is the most widely used CNG cylinder material. Heats studied should include materials from various suppliers, domestic and foreign.

Section 5

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