

Research at NIST on the Compatibility of Hydrogen and Carbon Steels*

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ABSTRACT

The demand for gaseous hydrogen fuel is expected to necessitate a continuous supply of hydrogen that can be delivered only through networks of existing and new pipelines and storage units. The focus of the Hydrogen Project at the National Institute of Standards and Technology (NIST), of the Materials Reliability Division, in Boulder, CO is to characterize the mechanical behavior of pipeline and pressure-vessel materials exposed to highly pressurized hydrogen gas. The material properties will be used to generate databases and develop codes and standards essential to the safe and reliable transportation of gaseous pipelines.

Keywords: gaseous hydrogen, materials, pipeline, pressure-vessels

1 INTRODUCTION

Recent fluctuations in oil prices have spurred serious consideration of alternative fuel sources and a drive toward energy independence. While increased domestic oil production and ethanol-based fuels offer short-term solutions, the major thrust in long-term energy sustainability has revolved around hydrogen as a fuel source. There is currently significant on-going research and development on fuel cells for conversion of hydrogen to usable electrical energy. There has been much less attention, however, to the means by which the hydrogen fuel can be transported and distributed throughout the US. If a hydrogen economy is indeed to become a viable path to energy independence, the logistics of a nationwide distribution system for this new fuel will need to be developed.

The cheapest and most efficient method for transporting large volumes of liquid and gaseous fuels is generally through pipeline distribution systems. Gas pipeline failures have the potential for serious safety problems and can result in extremely hazardous conditions. Hydrogen is odorless and highly flammable in concentrations above 4 % in air and, unlike natural gas, it burns with a colorless flame, making hydrogen fires difficult to see and control. There are currently approximately 2.4 million kilometers of natural gas transmission and distribution pipelines in the US, while the length of pipelines repurposed for hydrogen gas transport is only about 1,127 kilometers [1]. Large economic benefits

could be realized if the existing natural gas pipeline network could eventually be used to transport hydrogen gas over long distances.

The conversion of existing natural gas pipelines to hydrogen gas pipelines is not a straight forward task, however. There are several key issues that must be addressed before hydrogen can be transported in large volumes through pipelines, but the two major concerns are required increased pressures and hydrogen embrittlement. The pressures required to transport hydrogen gas are expected to be higher than those used for natural gas. The hydrogen gas pressures in existing carbon-steel pipelines are generally less than 14 MPa [2], but should a hydrogen economy come about, it will be desirable to transport the gas at higher pressures. The desire for increasing the pressure results mainly from the anticipated demand. Should hydrogen use become a widespread source of fuel for both transportation and power generation, the demand will likely be higher than for natural gas, and increasing gas pressures through pipelines is one way of economically increasing the on-demand supply.

While pressure poses a potential problem associated with hydrogen gas transportation, a more critical obstacle to the use of existing natural gas pipelines is connected to the embrittling effects of hydrogen in steels of the type from which these pipelines are constructed. The effects of hydrogen on metals, specifically ferrous alloys, have been studied extensively over the past several decades [3-6]. It is generally accepted that the mechanical properties of carbon steels are degraded when exposed to atomic hydrogen. Also, as the strength of the steel increases, the effects of hydrogen generally become more pronounced [6]. In a recent study, the ductility of current pipeline materials was found to decrease by approximately 60 % when charged with hydrogen [3]. Potentially, of more concern for pipelines, the fatigue crack growth rate of even low strength pipeline materials has been shown to increase by a factor of 100 when exposed to relatively low pressure (7 MPa) hydrogen gas [4]. Determining the full effects of gaseous hydrogen on the mechanical behavior of pipeline steels is necessary before full-capacity hydrogen gas transportation can occur safely.

A new facility capable of performing mechanical property tests on materials exposed to high-pressure hydrogen gas is currently under development at NIST, Boulder, CO. This facility will be dedicated to the testing of materials for hydrogen transportation, storage and

distribution. The capabilities of the new test facility, as well as future plans for its operation, are described in this paper.

2 TEST FACILITY

Once operational, the NIST gaseous hydrogen test facility will be one of only a few in the country capable of determining the mechanical behavior of materials exposed to highly pressurized hydrogen gas. The hazardous conditions associated with hydrogen gas have already been mentioned. To minimize the risks of hydrogen fires or explosions during testing programs, several safety mechanisms have to be in place. The NIST facility consists of two buildings, one where hydrogen will be present (Building A) and the other for remotely controlling the tests (Building B), as indicated in Figure 1.



Figure 1: View of NIST hydrogen test facility

Building A was built into a pre-existing blast wall on one side of the building and faces one of Boulder's foothills on the other. This configuration will limit the consequences of a potential leak and ignition. Also, there are several levels of safety in place where hydrogen gas will be used. Tests will be controlled remotely from Building B, and no one will be permitted in Building A during the purging operation. All materials used for pressurizing, transporting and storing of hydrogen in the facility will be constructed of either 316 stainless steel or A286 steel, since these materials are virtually immune to hydrogen embrittlement. The plumbing will initially be checked for leaks after filling the system with helium gas and the pressures will be remotely monitored during testing. Hydrogen sensors will be strategically placed throughout Building A and will provide information on the level of hydrogen within the building, should a leak occur. If the concentration of hydrogen reaches half of the flammability limit (2 % in air), then the supply gas valve will automatically close and the venting valves will be opened. The final level of security lies within building A's electrical system. Electrical devices rated explosion-proof in

hydrogen environments and conductive flooring are installed within Building A, eliminating any potential source of spark.

The facility will have a 100 kN servo-hydraulic test frame and a one-liter hydrogen pressure-vessel rated to 200 MPa. This will allow for both tensile and compression tests, where slow strain-rate tensile tests, cyclic fatigue tests and monotonic loading tests can be carried out. Two hydrogen compressors, capable of increasing the hydrogen gas pressures from 1 MPa to 130 MPa will be used to control the pressure during testing. A second, 1,000 kN test frame will hold a larger pressure-vessel, with pressure capabilities up to 35 MPa. This system will be used to perform tests on actual pipe sections.

High-purity (99.9999 %) hydrogen and helium gas will be used in the early stages of testing, but the facility will be capable of purging other gas species for studies on gas inhibitors for preventing hydrogen embrittlement. A glove box in Building A will be used to avoid adsorption of contaminant gases as specimens are prepared for testing. Also, thermoelectric sensors will be used to measure the hydrogen concentrations in specimens during testing [7]. The same sensors will be used to measure permeation of materials under various hydrogen pressures.

3 MATERIALS CHARACTERIZATION

The facility will mainly be dedicated to mechanical testing of current and potential hydrogen-pipeline and storage-vessel materials. Pipeline materials are generally steel and are designated according to yield strength, *i.e.*, X80 is a pipeline steel with yield strength of 522 MPa (80 ksi). Traditional natural gas pipeline steels have yield strengths less than 483 MPa (70 ksi), but materials for next-generation pipelines have higher yield strengths (X100 or X120), where either higher operating pressures or thinner pipe wall thicknesses can be utilized. Since the effects of hydrogen on steels are more pronounced in higher strength steels, it is likely that repurposing of natural gas pipelines for hydrogen gas will begin with alloys of lower strength.

A review of previous work has outlined several key mechanical properties of materials that are affected by exposure to pressurized hydrogen gas [8]. Results from notched and unnotched tensile specimens have shown that specimen ductility and notched ultimate strengths can be greatly reduced in carbon-steel specimens exposed to gaseous hydrogen. Also, fatigue crack growth rates in pipeline materials are generally much higher when tests are conducted in pressurized hydrogen gas. This is of great concern for pipeline designers, since designers typically use defect-tolerant design principles for these types of structures. Fatigue crack growth measurements, as well as fatigue crack initiation and fatigue crack growth threshold stresses, all need to be quantified for many pipeline and pressure-vessel steels before their use can be greatly expanded for hydrogen transport.

The mechanical-property measurements and materials to be tested in the new facility will be selected on the basis of national need for code and standards development for materials used in hydrogen systems. In August of 2007, NIST hosted a workshop on Materials Test Procedures for Hydrogen Pipelines [9]. Attendees at the meeting represented both industry and government agencies active or invested in high-pressure hydrogen gas systems. The purpose of the workshop was to develop a prioritized list of research needs on materials for hydrogen pipelines. The workshop attendees agreed that it would be most beneficial to begin by testing natural gas pipe materials currently in use, with yield strengths lower than 480 MPa (70 ksi). Mainly metallic materials were identified, but nonmetallic pipe materials were also mentioned, in which both permeation and mechanical properties will need to be determined. The effect of microstructure on resistance to hydrogen damage was identified as an important and not fully understood component in the development of codes and standards for hydrogen pipelines. Also, the effects of gas pressure on mechanical properties will need to be determined before the pressures can be increased to meet the anticipated demands. In addition to the effects of gas pressure, studies have shown that inhibitor gases may limit the effects of hydrogen on fatigue crack growth [10], and therefore one area of study at NIST may be the evaluation of inhibitor gases for improved resistance to hydrogen embrittlement and hydrogen-induced crack growth.

The first phase of testing will involve completing the NIST-Boulder portion of a round-robin to assist in standardizing the tensile testing procedure used at three national labs active in high-pressure gaseous hydrogen testing. For this experiment, smooth tensile specimens of X52 and X100 pipeline steel will be tested at 14 MPa, and the resulting tensile properties among the labs will be compared. High-purity (99.9999 %) hydrogen will be used as the gas supply for these tests, and gas specimens will be taken during tensile testing to determine whether gas contamination occurs from outside sources. Mechanical testing of materials under high-pressure hydrogen can be quite time consuming, therefore, once the round robin experiment is complete, the national laboratories involved will be able to coordinate testing plans to meet the vast measurement needs to design safe and reliable hydrogen pipelines.

The round robin tests are expected to be completed in the summer of 2009. Following this experiment, research will begin on characterizing the mechanical behavior of pipeline and pressure-vessel steels under exposure to highly pressurized hydrogen gas. Several research areas have been identified, including fatigue behavior, role of microstructure in hydrogen embrittlement, and gas inhibitor effects on mechanical properties. More specifically, the fatigue crack growth rates of specimens exposed to pressurized hydrogen gas will need to be determined. Optimized microstructures for resistance to hydrogen embrittlement need to be identified. Finally, the adsorption of hydrogen gas on steel

surfaces should be studied further, since both inhibitor gases and metal impurities could largely affect the rate of adsorption.

4 SUMMARY

As the nation transitions from traditional carbon-based fuel sources to alternative energies, such as hydrogen fuel, a safe and reliable infrastructure must be in place to transport and deliver the hydrogen to end users. A new NIST facility, in Boulder, CO, dedicated to the testing of materials in high-pressure hydrogen gas atmospheres is currently being completed. The test program will mainly involve potential hydrogen-pipeline and pressure-vessel materials, so that codes and standards for transportation of hydrogen gas can be developed. The first phases of testing in this facility will commence in May of this year.

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