III.E.2 Materials Solutions for Hydrogen Delivery in Pipelines

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Subcontractors:

- Oregon Steel Mills (OSM), Portland, OR
- Schott North America, Duryea, PA
- Chemical Composite Coatings Int'l, LLC, Alpharetta, GA
- Advanced Technology Corporation (ATC), Oak Ridge, TN
- Columbia Gas of Kentucky, Lexington, KY
- ASME Standards and Technologies LLC, New York, NY
- DGS Metallurgical Solutions, Inc, Vancouver, WA
- Hatch Mott MacDonald, Monroe, LA

Start Date: May 2005
Projected End Date: September 2009

Objectives

Overall goal of the project is to develop materials technologies that would enable minimizing the problem of hydrogen embrittlement associated with the high-pressure transport of hydrogen.

- To identify steel compositions and associated welding filler wires and processes that would be suitable for construction of new pipeline infrastructure.
- To develop barrier coatings for minimizing hydrogen permeation in pipelines and to develop *in situ* deposition processes suitable for these coatings.
- To understand the cost factors related to the construction of new pipelines and modification of existing pipelines and to identify the path to cost reduction.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(D) High Capital Cost and Hydrogen Embrittlement of Pipelines

(K) Safety, Codes and Standards, Permitting

Technical Targets

The objective of the project is to develop materials technologies that would enable minimizing the problem of hydrogen embrittlement associated with the high-pressure transport of hydrogen through pipelines. Such materials technologies in combination with cost-effective excavation and fabrication technologies will facilitate reducing the capital cost of pipelines. Insights gained from these studies will be applied toward the design and construction of hydrogen delivery systems that meet the following hydrogen delivery pipeline transmission targets:

- By 2017, achieve levels of reliability (relative to H_2 embrittlement concerns and integrity) acceptable for hydrogen as a major energy carrier:
  - Evaluate hydrogen embrittlement characteristics of existing commercial pipeline steels under high-pressure hydrogen.
  - Develop alternate alloys and evaluate hydrogen embrittlement.
  - Develop coatings to minimize dissolution and penetration of hydrogen.
  - Evaluate the hydrogen embrittlement in alloys coated with selected coatings.
- Pipeline transmission total capital cost; by 2012, achieve a target of $600K/mile for a 16" pipeline.
  - Financial analysis and incorporation into codes and standards.

Accomplishments

Work has been delayed in FY 2007 due to delays in receipt of funding. Accomplishments to date are as follows:

- ATC completed work on a 2,000 psi hydrogen pressure chamber for *in situ* stress strain microprobe (SSM) testing of uncoated and coated pipeline steel samples.

- ATC tested uncoated samples of Alloy "A–X70", "D"–X52/X60" along with pipeline grades B and X80 during exposure to H_2 at 2,000 psi up to a total exposure time of 200 hours.
- National Association of Corrosion Engineers (NACE) Hydrogen-Induced Cracking (HIC) Solution A testing completed on four pipeline alloys "A", "B", "C", and "D" at OSM.
- ORNL has successfully applied glass coatings to specimens of steel composition C and sent them to the University of Illinois for low pressure H_2 permeation testing.
- Actual construction costs of a pipeline project supplied by Columbia Gas of Kentucky reviewed by the project team.
- Task list revamped to reflect FY 2007 funding delays.

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Introduction

Pipeline transmission is the most economical method for hydrogen delivery in large quantities from the point-of-generation to point-of-use. As transmission pressures are increased, steel pipelines that could be used for the transport of hydrogen at low pressures are prone to hydrogen embrittlement at the welds, the heat-affected-zone and/or the base metal regions in the pipeline. Literature to date clearly shows that hydrogen embrittlement of pipeline steels is one of the limiting factors in the cost-effective, high-pressure transport of hydrogen. The work in this project represents an integrated approach to developing and testing new materials solutions to enable pipeline delivery of hydrogen at high pressures. The scope of the project includes (1) development of barrier thin film coatings that would minimize the hydrogen permeation in the current natural gas pipelines, (2) identification of steel compositions and associated welding filler wires and processes that would be suitable for new pipeline infrastructure for transport of hydrogen at requisite high pressures, and (3) understanding the cost factors related to the construction of new pipelines and modification of existing pipelines, and to identify the path to cost reduction.

Approach

Understanding the mechanisms of hydrogen embrittlement of commercially available transmission pipeline steels will involve characterization of the mechanical properties and microstructures in both the absence and presence of high pressure hydrogen gas. The study of vintage pipeline steels along with current pipeline steel technology and potential alternative alloy designs will help determine the optimum mechanical properties and microstructure required to operate in a high pressure hydrogen gas environment (see Table 1). Both *in situ* and ex-situ methods will be used to study the effect of hydrogen gas under pressure on microstructural and mechanical properties. Thermokinetic modeling and microstructural characterizations will be used in the analysis of the effect of microstructure on embrittlement characteristics. In addition, the work will explore the use of glass and oxide coatings to impede the permeation of hydrogen. Mechanical properties of the coated steels will be studied in the presence of high pressure hydrogen gas and compared to those of uncoated specimens. Successful coatings will be tested for resistance to damage related to required pipeline operational non-destructive testing techniques. Factors related to materials and construction costs are incorporated into the project. This understanding will allow for recommendations for optimum material selections and fabrication of transmission pipeline systems suitable for high pressure hydrogen gas transport.

TABLE 1. Vintage, Commercial, and Alternative Grade Pipeline Steels for Evaluation

Grade	Code	C	Source	Comment
Vintage	?	0.30	ORNL 2	Rep. Older Line
Vintage	?	0.18	ORNL 2	Rep. Older Line
X70 Std	A	0.08	OSM	Current Std
X70/X80	B	0.05	OSM	Potential
X70/X80	C	0.04	OSM	Potential
X52/X60 HIC	D	0.03	OSM	Consider Best
Bainitic/Mart	E	0.10	OSM	Optional Micro
Martensite	F	0.14	OSM	Optional Micro

Results

Four commercially available pipeline steels have been down-selected for initial study of their hydrogen embrittlement under high pressure hydrogen. Steel A represents chemistry used in pipelines in the past 10-15 years, B and C represent chemistries used recently in pipelines while Steel D represents a sour service grade. It is anticipated that a study of these steels would be representative of advanced steels and would point to additional compositions that need to be studied in order to develop an appropriate relationship between compositions, structure, and hydrogen embrittlement characteristics.

Mechanical properties of these alloys received from our industrial partner OSM have been characterized through mechanical testing at Oak Ridge National Laboratory (ORNL) along with the Automated Ball

Indentation (ABI) testing method. Thermokinetic modeling and microstructural characterization of three of the steels were completed and reported last year. In addition, Sandia National Laboratories did a preliminary study of embrittlement of selected alloys using ex-situ high-pressure (20,000 psi) hydrogen charging and tensile testing also reported last year.

Microstructural volume fraction and grain size characterization have been completed on the four pipeline alloys. Alloy A shows a ferrite/pearlite microstructure. The pearlite was banded and varied from 4% at the surface layer to 6 to 8% towards the center by volume. Alloy B shows a ferrite/acicular ferrite microstructure with no significant change in the grain size from surface to center. Alloy C shows a ferrite/acicular ferrite microstructure with no significant change in the grain size from surface to center. Alloy D shows a ferrite/acicular ferrite microstructure with the grain size increasing from the surface to center. Future work of alloys B, C, and D will include characterization of the volume fraction of the acicular ferrite present.

Two of the selected alloys (Alloy A and D) along with two other additional alloys supplied by our industrial collaborators (ERW API Gr B and Seamless API Grade X80) were tested for their tendency for hydrogen embrittlement in the presence of high pressure hydrogen gas at ATC using the ABI testing methodology. All alloys were exposed to H_2 at a test pressure of 2,000 psi for a period of 200 hours. After 200 hours exposure, it was noted that the fracture toughness of the X80 steel decreased by 30%. This result is consistent with observations obtained from traditional mechanical testing in a hydrogen atmosphere. The other steel grades tested showed no significant degradation during similar exposure to hydrogen atmosphere. It should be noted that the X80 steel tested using ABI tests had a significantly higher carbon content than that in alloys A and D. Figure 1 shows the ABI measured degradation of fracture toughness as a function of time.

In addition to ABI testing, testing of the four selected alloys in a corrosive environment in the presence of hydrogen as described by NACE TM0284, a commonly used test for characterizing hydrogen induced cracking in a sour gas environment, was carried out by OSM. Test Solution A (low pH) was used to characterize the influence of different microstructures on the resistance to cracking in the presence of hydrogen. Alloy A with the highest volume fraction of pearlite in the microstructure showed the highest percentage of cracking. Alloy B showed a very small percentage of cracking with the cracking being associated with undesirable inclusions. Alloys C and D performed without cracking. Literature and other research suggested that microstructures designed to withstand hydrogen embrittlement/cracking in a NACE TM0284 environment would be suitable for use in the presence of high pressure hydrogen gas. Table 2 shows the percentage cracking by alloy in the NACE testing. Further work is needed to understand the influence of variations in steel compositions and microstructures in steels that may have similar mechanical properties but show differences in hydrogen embrittlement characteristics as characterized by the ABI, and NACE tests.

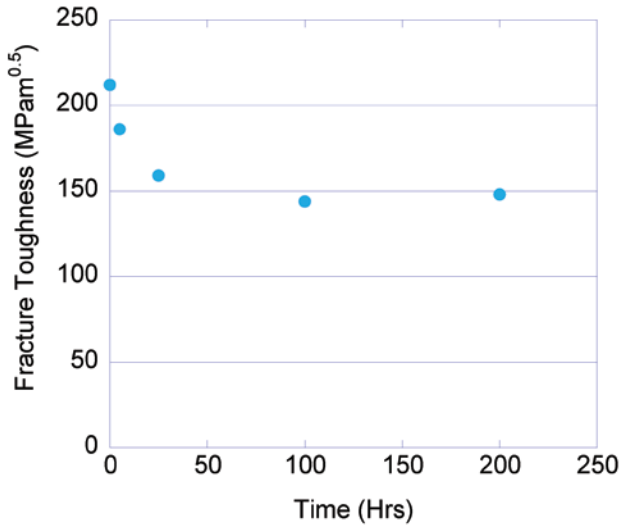

FIGURE 1. Effect of Hydrogen Exposure on Fracture Toughness of X80 Steel as Calculated from ABI Measurements

TABLE 2. NACE TM0284 HIC Test Results of Four Selected Pipeline Alloys

Alloy	NACE Crack Length Ratio (%)	NACE Crack Sensitivity Ratio (%)	NACE Crack Thickness Ratio (%)
A	11.8	0	0.1
B	0.4	0	0
C	0	0	0
D	0	0	0

Significant progress has been made in application of development and application of glass coatings. ORNL has used an infrared furnace to process glassy coatings on one Alloy C with good adhesion to the substrate. Permeability measurements will be carried out to study the effect of the glass coating on hydrogen permeation through steels.

Actual costs to construct a natural gas pipeline were supplied by Columbia Gas of Kentucky. These costs were reviewed and discussed with the project team to assist in identifying major components of pipeline construction costs. In this project material costs constituted approximately 17% of the total cost of construction. Table 3 shows actual costs of construction of a natural gas pipeline as supplied by Columbia Gas of Kentucky.

TABLE 3. Actual Construction Costs for Natural Gas Pipeline Built by Columbia Gas of Kentucky

Exemplar Pipeline Project	
Install 38,200 feet of 12" ERW 0.203 Wall Steel Pipeline	
Designed for Class 4 Location to Operate Less than 40% SMYS	
720 psig Maximum Allowable Operating Pressure (in $)	
Material	1,182,074
Construction Contract	3,561,594
Survey and Land Acquisition Labor	276,497
Contract Engineering	3,731
Outside Legal Fees	450
Company Labor	112,963
Labor Overhead	43,575
Service Line Installations	6,696
Consideration: Easement Acquisition	441,036
Leakage Inspection	1,625
Traffic Control Signage	567
Travel and Expenses	88
Overtime Meals	974
Vehicle Expense	26,007
General Tool Cost	48
Misc.	22
Construction Overheads	1,222,193
Allowance for Funds Used During Construction	200,629
Total Cost	**7,080,767**
Cost Per Foot of 12" Pipe	185
Cost Per Linear Foot of Right-of-Way	12
Cost Per Survey Foot	7

Remaining work for FY 2007 includes (subject to level, availability and timing of funding):

- Begin measurement of mechanical properties and hydrogen embrittlement characteristics of down-selected steels using traditional mechanical testing at ORNL.
- Begin permeation testing of samples of Alloys A, B, C, and D in uncoated and coated conditions.
- Initiate testing and characterization of samples of commercial-grade long seam pipeline welds that have been recently secured.
- Coat samples of steels A, B, C, and D for high pressure hydrogen testing at ORNL.
- Evaluate use and implementation of actual cost numbers as supplied by corporate partners.

Conclusions and Future Directions

Due to delayed FY 2007 funding, major work on this project has begun in the second half of the fiscal year. Preliminary testing in FY 2006 showed that high pressure hydrogen may have an effect on mechanical properties depending on microstructures of the steels. Additional limited testing at ATC showed that mechanical properties, especially fracture toughness of the steels, could be affected in the presence of high pressure hydrogen. NACE testing demonstrated that microstructures; especially those containing pearlite are susceptible to cracking in the presence of hydrogen. These observations support the inference that microstructure is a critical factor affecting resistance to hydrogen embrittlement and its effect needs to be fully understood. Actual material costs on a recently completed natural gas pipeline projects was noted to be 17% of the total construction cost. Initial glass coatings have been selected and specimens of one down-selected steel composition have been successfully coated to enable the University of Illinois to measure the effectiveness of the glass coatings to inhibit hydrogen permeation. The ORNL high pressure hydrogen testing unit should be fully functional in FY 2007.

Pending future funding in FY 2008, the following represents additional work:

- Complete measurement of mechanical properties and hydrogen embrittlement characteristics of down-selected steels using traditional mechanical testing and ABI tests.
- Complete microstructural characterization of down-selected steels before and after exposure to hydrogen to understand the effect of microstructure on embrittlement.
- Start testing and evaluation of other selected alloys E and F in presence of hydrogen.
- Pipeline weld sample microstructural analysis and embrittlement as a function of hydrogen pressure and time of exposure will be included.
- Enhancements to glass coatings and testing of oxide coatings will be explored.
- Continued analysis into cost factors will be continued to evaluate options for lowering material and construction costs.

Results from the testing will be used to help identify optimum alloy/microstructure designs required to safely transport high pressure hydrogen gas through steel pipelines.

FY 2007 Publications/Presentations

1. 4th quarter project report prepared February 9, 2007.

2. A poster presentation regarding the overall project status was given at the DOE Annual Merit Review Meeting (May 2007).

3. Panel participation Second Panel Forum Hydrogen Pipeline Transmission: Updates and Opportunities, ASME

6th International Pipeline Conference, Calgary, Canada, September 2006.

4. Technical publication ASME 6th International Pipeline Conference, Calgary, Canada, September 2006, "The Role of Continuous Cooling Transformation Diagrams in Material Design for High Strength Oil and Gas Transmission Pipeline Steels."

References

1. "Materials Solutions for Hydrogen Delivery" in Pipelines 2007 Poster Presentation from the DOE Annual Merit Review Meeting (May 2006).

2. "Materials Solutions for Hydrogen Delivery" 4th Quarter Project Report.