Materials Solutions for Hydrogen Delivery in Pipelines

Dr. Subodh K. Das
SECAT Inc.

This presentation does not contain any proprietary or confidential information
**Overview**

**Timeline**
- Project start date: 05/2005
- Project end date: 09/2008
- Percent complete: 14%

**Barriers and Targets**

**Barriers addressed**
- High capital cost and Hydrogen Embrittlement of Pipelines

**Technical Targets (2015):**
- Capital cost ($0.8 Million/Mile)
- Cost of delivery of hydrogen <$1.00/gge
- High Reliability of operation with metrics to be determined

**Budget**
- Total project funding
  - $1650K
  - $1110K (contractor share)
- Funding received in FY04: None
- Funding for FY05:
  - Requested: $550K
  - Actual: $200K

**Partners**

**SECAT CONSORTIUM**
- Advanced Technology Corporation
- ASME Standards and Technologies, LLC
- Chemical Composite Coatings Intl
- Columbia Gas
- Hatch Moss MacDonald
- Oregon Steel Mills
- Schott North America
- DGS Metallurgical Solutions, Inc.

**Oak Ridge National Laboratory**

**University of Illinois**
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

• The overall objectives of the project are:
  – 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
Key Technical Barriers

• Extent of hydrogen embrittlement of base material, and welds in pipeline steels and other common steels on exposure to high pressure $H_2$ is not known

• Only a limited understanding of the mechanisms of hydrogen embrittlement along with the effect of metallurgical variables such as alloying element additions, and microstructure of steels is available at the present time; hence the path to remediation and control is not well defined

• Although it is known that barrier coatings are effective in reducing hydrogen embrittlement, detailed knowledge of the effectiveness of various metallic and non-metallic coatings in minimizing the deleterious effect of $H_2$ under high pressures is not known

• Very little information is available on the potential avenues for reducing the cost of construction of pipelines for transport of hydrogen and the cost of technologies to remediate the effect of hydrogen embrittlement
Approach

Our approach consists of the following major tasks:

Task 1: Evaluate hydrogen embrittlement characteristics of existing commercial pipeline steels under high-pressure hydrogen

Task 2: Develop and/or identify alternate alloys and evaluate hydrogen embrittlement

Task 3: Develop coatings to minimize dissolution and penetration of hydrogen

Task 4: Evaluate the hydrogen embrittlement in alloys coated with selected coatings

Task 5: Perform financial analyses and incorporate knowledge into codes and standards
Schematic of Overall Approach

1. Down-select promising steel compositions
2. Evaluate hydrogen embrittlement in selected alloys
3. Understand composition-structure-hydrogen embrittlement relationship
4. Refine existing compositions and/or develop new compositions
5. Evaluate Effectiveness of Coatings in decreasing Embrittlement
6. Evaluate cost of fabrication of pipelines
7. Develop coatings compositions and processes

Thermodynamic/Kinetic Modeling, Mechanical Testing
Breakdown of Major Activities by Year

YEAR 1
- Evaluation and down-selection of alloys for further study
- Development of coatings and processes
- Initial evaluation of pipeline costs and development of cost models

YEAR 2
- Modeling and microstructural characterization of alloys
- Evaluation of mechanical properties of uncoated alloys in high H₂ pressures
- Characterization of structure and chemistry of coatings
- Down-selection of best coatings and coating of alloys
- Evaluation of costs of new technologies

YEAR 3
- Microstructural characterization of alloys
- Evaluation of mechanical properties of coated alloys in high H₂ pressures
- Optimization of structure, chemistry of coatings and coating processes
- Incorporation of cost of new technologies into pipeline models
- Incorporation of findings into ASME codes and standards
Roles of Project Partners

IMPROVED MATERIALS TO ENABLE HIGH-PRESSURE DELIVERY OF HYDROGEN

U. S. Pipeline Company
Oregon Steel Mills

Fundamental Studies- University of Illinois
University Project: Hydrogen Embrittlement of Pipeline Steels: Causes and Remediation
• H₂ embrittlement and failure mechanisms
• Microstructure effect on hydrogen embrittlement
• First principles study of alloying element additions
• Surface chemistry and physics

Financial Analysis, Codes and Standards
• Financial analysis: “FLOW” (SECAT, ORNL)
• Codes and Standards (ASME Standards and Technologies)
• Implementation (SECAT, Columbia Gas)

Coatings Development
• Rare earth oxide:C3
• Glass Coatings: SCHOTT

Materials Characterization
• Mech testing in hi-press H₂ (ORNL)
• In-Situ Automated Ball Indentation (ABI) tensile and FT testing in hi-pressure H₂ (ATC)
• Microstructural studies (SECAT, ORNL)

Alloy and Weld Filler Development
• Thermodynamic and kinetic modeling
• Experimental alloy preparation (ORNL)

Pipeline lifetime prediction model
University of Illinois

Pipeline lifetime prediction model
U. S. Pipeline Company
Oregon Steel Mills

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• Surface chemistry and physics

OAK RIDGE NATIONAL LABORATORY
U.S. DEPARTMENT OF ENERGY
Technical Accomplishments/Progress/Results

• Project Kick-off meeting conducted March 15-16 at Lexington, KY
  – Near-term activities were outlined
  – Internal milestones for individual project team-members were defined
  – Contract details and agreement for intellectual properties were discussed
Task 1: Evaluate hydrogen embrittlement characteristics of existing commercial pipeline steels under high-pressure hydrogen

- Very little data is available on the effect of high pressure hydrogen on the mechanical properties and hydrogen embrittlement of pipeline steels
- Typical pipeline steel compositions will be down-selected
- Mechanical properties of these steels will be measured in-situ in high pressures of H₂ (up to 5000 psi) as a function of metallurgical variables such as heat treatments, grain size, and processing such as welding
- Automated Ball Indentation (ABI), a novel test method, will be used to characterize the effects of various times of exposure to high pressure hydrogen on the fracture toughness and tensile properties of base metal and welds of several pipeline steels
- Failed specimens will be characterized to understand the failure mode and compare with existing knowledge of failure modes
- Thermodynamic and kinetic modeling will be combined with microstructural characterization to understand the relationship between hydrogen embrittlement, alloy composition, and microstructure
- Best compositions will be down-selected for further work with barrier coatings
Proposed Work For FY 2005/2006

Steels

- Survey compositions of pipeline steels and other steel compositions for applicability in pipeline construction
- Identify a screening test to rapidly evaluate hydrogen embrittlement characteristics of steels of interest
- With the use of screening tests and industrial input, down-select four steel compositions for further detailed study of hydrogen embrittlement characteristics under high pressure H₂ (FY 2005 milestone)
- Initiate microstructural characterization, thermodynamic, and kinetic modeling
- Initiate permeability testing of selected steel compositions in high pressure hydrogen atmosphere
- Start assembly of equipment for in-situ mechanical testing of materials under high hydrogen pressures along with setting up associated safety measures and controls at ORNL
- Prepare preliminary chamber design to perform in-situ high pressure H₂ Automated Ball Indentation (ABI) mechanical testing (tensile/fracture toughness) at ATC
Steels and Their Compositions

- Four steels have been down-selected for initial study
- A: Represents chemistry used in pipelines in the past 10-15 years
- B, C: Represents chemistry used recently in pipelines
- D: Represents a sour service grade

<table>
<thead>
<tr>
<th>API Grade</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Cu</th>
<th>Ni</th>
<th>V</th>
<th>Nb</th>
<th>Al</th>
<th>Cr</th>
<th>Ti</th>
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<tr>
<td>A X70</td>
<td>0.08</td>
<td>1.53</td>
<td>0.28</td>
<td>0.01</td>
<td>0.00</td>
<td>0.050</td>
<td>0.061</td>
<td>0.031</td>
<td>0.01</td>
<td>0.014</td>
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<td>B X70/ X80</td>
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<td>0.12</td>
<td>0.23</td>
<td>0.14</td>
<td>0.001</td>
<td>0.092</td>
<td>0.036</td>
<td>0.25</td>
<td>0.012</td>
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<td>1.61</td>
<td>0.14</td>
<td>0.22</td>
<td>0.12</td>
<td>0.000</td>
<td>0.096</td>
<td>0.037</td>
<td>0.42</td>
<td>0.015</td>
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<tr>
<td>D X52/ X60</td>
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<td>1.14</td>
<td>0.18</td>
<td>0.24</td>
<td>0.14</td>
<td>0.001</td>
<td>0.084</td>
<td>0.034</td>
<td>0.16</td>
<td>0.014</td>
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</table>
Continuous Cooling Transformation Diagrams Have Been Calculated for Three Alloys

Pearlite start line shifts to the right (time increases) from A to C
Comparison Between CCT Diagram and Observed Microstructure of Alloy A

Transverse Section

Microstructure of Alloy A shows presence of both ferrite and pearlite
Comparison Between CCT Diagram and Observed Microstructure of Alloy B

Microstructure of Alloy B shows very little pearlite mixed with ferrite and acicular ferrite
Comparison Between CCT Diagram and Observed Microstructure of Alloy C

Microstructure of Alloy B shows very little pearlite mixed with ferrite and acicular ferrite.
Specimens Have Been Prepared for Evaluation of Hydrogen Embrittlement with ex-situ Tests

- Tensile specimens conforming to ASTM-E8 have been machined from three alloys, A, B, and C
- Tensile tests have been conducted at ORNL
- Samples have been sent to Dr. Brian Somerday at Sandia National Laboratory, Livermore for study of embrittlement using
  - Ex-situ high-pressure hydrogen charging, and
  - Tensile testing

1.972”
Tensile Tests Are Being Performed in Transverse-Oriented Samples at ORNL
Mechanical Properties Determined at ATC using the Automated Ball Indentation (ABI) test of the SSM System

ATC’s Patented SSM system is used to determine the following key mechanical properties from each single ABI test:

- True-Stress/True-Plastic-Strain
- Yield Strength
- Work-Hardening Exponent and Strength Coefficient
- Estimated Engineering Ultimate Tensile Strength
- Uniform Ductility
- ABI-Hardness
- Fracture Toughness and Reference Temperature
Baseline Tensile and Automated Ball Indentation (ABI) Tests Have Been Completed at ATC

Comparisons were made between the non-destructive physical testing utilizing the ABI method vs. traditional destructive physical testing.

ABI indents made using a 0.030-in (0.76-mm) Tungsten Carbide indenter
Example Comparison Between True-Stress/True-Strain Data Using Miniature Tensile Testing and ABI Testing of Steel Sample C
Baseline Tensile Tests of Four Selected Steels Have Been Completed by ATC
Summary of ABI Measured Mechanical Properties of Four Selected Steels

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>YS (ksi)</th>
<th>Calc. Eng. UTS (ksi)</th>
<th>Calc. Unif. Ductility (%)</th>
<th>YS/UTS Ratio</th>
<th>Hardness ABI-H</th>
<th>Fracture Toughness (ksi*in^0.5)</th>
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<tbody>
<tr>
<td>All API Plate Samples</td>
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<tr>
<td>API X70, A-1</td>
<td>82.8</td>
<td>102.3</td>
<td>7.9</td>
<td>0.81</td>
<td>242</td>
<td>217.8</td>
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<td>API X70, A-2</td>
<td>82.3</td>
<td>101.3</td>
<td>7.8</td>
<td>0.81</td>
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<td>216.2</td>
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<td>API X70, A-3</td>
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<td>100.9</td>
<td>8.0</td>
<td>0.81</td>
<td>239</td>
<td>214.4</td>
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<td>93.4</td>
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<td>8.3</td>
<td>0.79</td>
<td>221</td>
<td>210.4</td>
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<td>API X80, B-3</td>
<td>77.4</td>
<td>94.3</td>
<td>7.6</td>
<td>0.82</td>
<td>225</td>
<td>208.5</td>
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<td>API X80, C-1</td>
<td>86.4</td>
<td>104.8</td>
<td>7.5</td>
<td>0.82</td>
<td>252</td>
<td>219.4</td>
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<tr>
<td>API X80, C-2</td>
<td>84.8</td>
<td>104.5</td>
<td>7.9</td>
<td>0.81</td>
<td>248</td>
<td>216.3</td>
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<tr>
<td>API X80, C-3</td>
<td>86.2</td>
<td>105.9</td>
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<td>0.81</td>
<td>252</td>
<td>218.9</td>
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<td>API X60, D-1</td>
<td>64.6</td>
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<tr>
<td>API X60, D-2</td>
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<td>7.5</td>
<td>0.82</td>
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<td>190.7</td>
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<tr>
<td>API X60, D-3</td>
<td>63.8</td>
<td>78.4</td>
<td>8.1</td>
<td>0.81</td>
<td>189</td>
<td>194.5</td>
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</tbody>
</table>
Future work

• Complete assembly of equipment for *in-situ* mechanical testing of materials in high hydrogen pressures along with setting up associated safety measures and controls at ORNL

• Complete fabrication and installation of high pressure hydrogen chamber to perform *in-situ* Automated Ball Indentation (ABI) mechanical testing for various hydrogen exposure times at ATC

• Complete measurement of mechanical properties and hydrogen embrittlement characteristics of at-least two down-selected steels at ORNL and ATC

• Complete thermodynamic, and kinetic modeling of initial down-selected steel compositions

• Complete microstructural characterization of tested steels before and after exposure to hydrogen to understand the effect of microstructure on embrittlement
Details of Approach-Task 3

- Task 3: Develop coatings to minimize dissolution and penetration of hydrogen

  - Laboratory studies have shown that surface barrier coatings (both metallic and non-metallic) including stainless steel liner materials are effective in reducing hydrogen embrittlement due to an external source of hydrogen
  - This work will evaluate the effectiveness of coatings from two industrial partners: multi-component oxides with rare earths from C³, and glass coatings from Schott North America
  - Coating chemistries and processes to deposit coatings on steel substrates (including techniques appropriate for *in-situ* deposition in the field) will be developed
  - Quality, integrity of coatings, adhesion to the substrate, microstructure of coatings and that of substrates, wear characteristics, and barrier properties of coatings will be characterized
  - Chemistries of coatings, and deposition processes will be modified to optimize required properties and two best coating compositions will be down-selected for Task 4
Proposed work for FY 2005

• Identify processing needs for deposition of coatings on steel substrates (thermal expansion coefficients, temperature and time of curing, wetting characteristics etc) and deposit coatings

• Characterize coatings with particular reference to their adhesion with the substrate, integrity (free from pinholes, cracks etc), and the substrate for structural changes due to the deposition process
Status of Coatings Work at Schott NA

- **Steel Characterization**
  - Measured thermal expansion of two selected steel compositions

- **Glass Development**
  - Selected two glass compositions, and adjusted composition to match the thermal expansion of said steel compositions
  - Manufactured 0.5l of each glass for coating tests

- **Coating**
  - Based on glass properties, selected coating approach for samples and started to optimize technique

- **Next Steps**
  - Supply coated steel samples to ORNL to measure \( H_2 \) permeation
Thermal Expansion of Steel A

Steel A Rod B
Each Run had a 1 Hour Hold at $T_{\text{MAX}}$

![Graph showing thermal expansion of Steel A Rod B with data points and error estimate.](image)

- Run 1 to 200°C
- Run 2 to 300°C
- Run 3 to 300°C
- Run 4 to 700°C
- Run 5 to 700°C
- Error Estimate
Thermal Expansion of Steel D

Steel D Rod B
Each Run had a 1 Hour Hold at $T_{\text{MAX}}$

[Graph showing the expansion of Steel D Rod B with temperature from 0 to 800°C, with data points for runs 1 to 200°C, 2 to 300°C, 3 to 300°C, 4 to 700°C, and 5 to 700°C, and an error estimate line.]
Comparison of the Thermal Expansion of the Two Steels

**Steel A**

All CTE values below are in ppm/K

<table>
<thead>
<tr>
<th>Run#</th>
<th>CTE20..200</th>
<th>CTE20..300</th>
<th>CTE20..416</th>
<th>CTE20..460</th>
<th>CTE20..520</th>
<th>CTE20..700</th>
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<td>2</td>
<td>12.51</td>
<td>13.33</td>
<td></td>
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<tr>
<td>3</td>
<td>12.54</td>
<td>13.28</td>
<td></td>
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<td></td>
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</tbody>
</table>

Ice pack was not used on Run#1. Result is hook at start of data and a lower CTE value than expected.

**Steel D**

All CTE values below are in ppm/K

<table>
<thead>
<tr>
<th>Run#</th>
<th>CTE20..200</th>
<th>CTE20..300</th>
<th>CTE20..416</th>
<th>CTE20..460</th>
<th>CTE20..520</th>
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<td>2</td>
<td>12.37</td>
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<tr>
<td>3</td>
<td>12.62</td>
<td>13.20</td>
<td></td>
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<tr>
<td>4</td>
<td>12.91</td>
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<tr>
<td>5</td>
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<td>13.10</td>
<td>13.72</td>
<td>13.92</td>
<td>14.16</td>
<td>14.70</td>
</tr>
</tbody>
</table>
Future work on Coatings

• **Coatings:**
  – Barrier properties of the coatings will be characterized using permeability testing
  – Coating compositions and/or depositions processes will be modified based on the results of physical, mechanical, and barrier property testing
  – Coatings with new compositions will be deposited and tested
Details of Approach-Task 5

• Task 5: Perform financial analyses and assist in the incorporation of knowledge into codes and standards:

  – The cost of a typical pipeline installation includes many components such as that of materials, construction, inspection, engineering survey, right of way permits, and overhead costs; cost of ownership also includes the cost of maintenance over the lifetime of the pipeline
  – As part of this project, with the help of industrial partners and an ORNL developed financial analysis model-FLOW, we will analyze the current cost components of pipeline construction and maintenance, analyze potential savings that could be feasible, and methods to achieve cost reductions
  – Cost analysis will be updated as the additional cost of newly developed technologies become available and the different possible scenarios for reduction in costs of construction and maintenance will be reevaluated
  – Work will be coordinated with the H2A analysis being carried out as part of the DOE hydrogen program
  – The results of this analysis will be used to re-focus the project if and as appropriate vs. the goal, objectives, and targets for the DOE hydrogen Delivery Multi-Year R&D Plan
Steps in Financial Analysis

Model Development

SECAT
ASME
Hatch Moss McDonald

Construction Cost
Installation Cost
Maintenance Cost
Operation Cost

Model Incorporation into FLOW

Columbia Gas Co.
Oregon Steel Mills

Parameters

Scenarios

FLOW Simulation

Life Cycle Cost
Savings
Meeting Targets
Feed Back Information to Materials Research
RAM Analysis
Compare Scenarios

• New Steels
• Barriers
• New Process

• New Piping
• Existing Piping System

Oregon Steel Mills

ASME

SECAT
Proposed Work for FY 2005

- Obtain from industrial partners, data on the magnitude of the individual components of costs related to pipeline construction and maintenance
- Develop a preliminary model for the pipeline cost function using FLOW for evaluating sensitivity, and uncertainty
- Coordinate information collection and model development with the H2A effort
Progress on Task 5

- H2A model has been analyzed and extracted equations required for cost analyses
- Model will tailored for the current project
- Questionnaire has been prepared to collect information from the industry on various relevant cost factors specific to the ongoing work
Next Steps

Send Questionnaires to Members

Receive comments from Members

Changes?

No

Yes

Make modification to models

Make modified models available for H2A

Models are suitable for current project
Future Work on Financial Analyses

• Finalize cost model for steel pipelines
• Analyze various scenarios using FLOW software and evaluate sensitivities to various parameters in the cost function
• Derive potential avenues for achieving cost savings from the analyses of various scenarios
• Identify research priorities based on analyses of potential cost savings
• Update cost functions as new information on developed technologies become available and reevaluate scenarios