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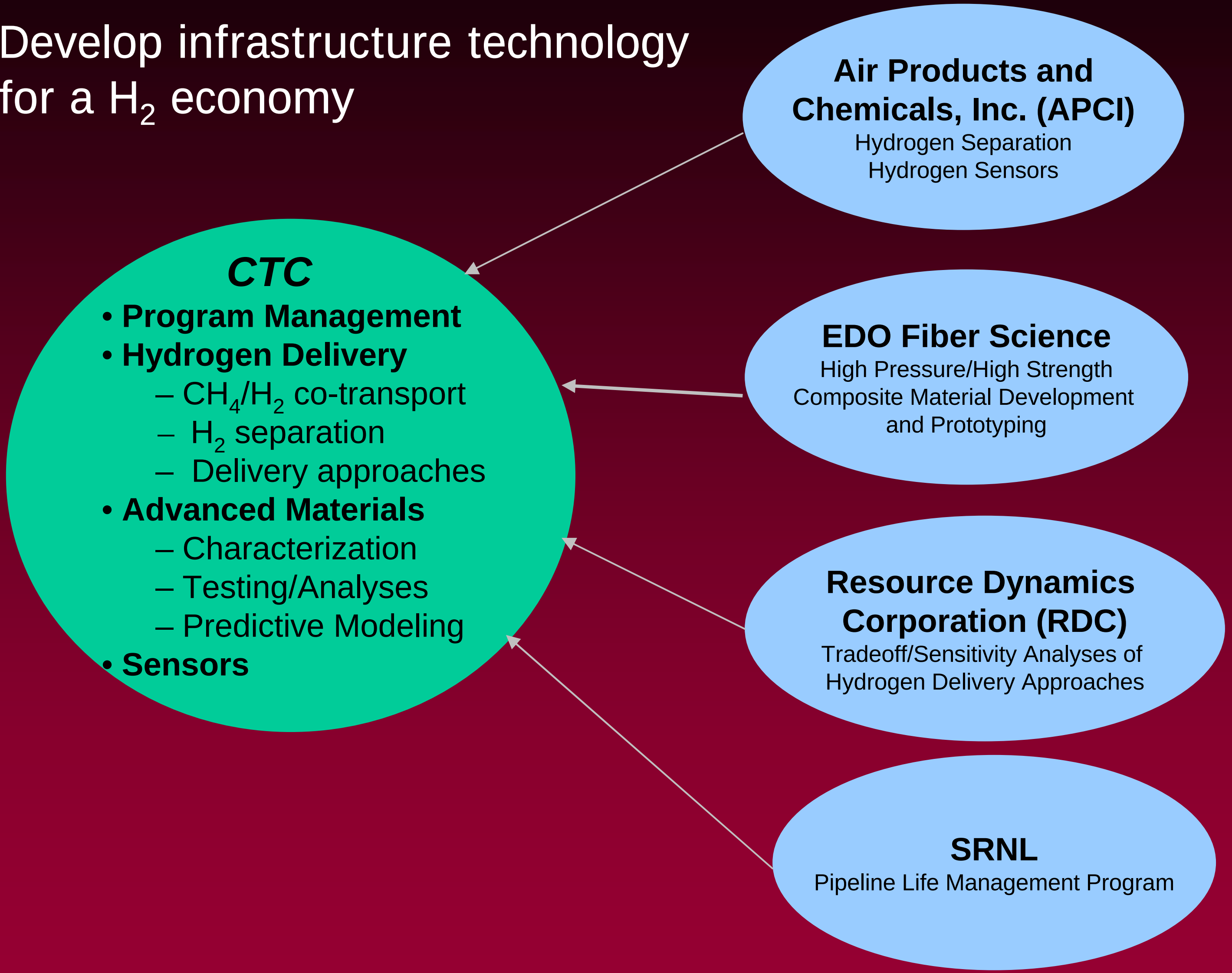
HYDROGEN REGIONAL INFRASTRUCTURE PROGRAM IN PENNSYLVANIA

Melissa Klingenberg, PhD

Hydrogen Program

Develop infrastructure technology for a H_2 economy



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- **Program Management**
- **Hydrogen Delivery**
  - CH_4/H_2 co-transport
  - H_2 separation
  - Delivery approaches
- **Advanced Materials**
  - Characterization
  - Testing/Analyses
  - Predictive Modeling
- **Sensors**

Air Products and Chemicals, Inc. (APCI)
Hydrogen Separation
Hydrogen Sensors

EDO Fiber Science
High Pressure/High Strength Composite Material Development and Prototyping

Resource Dynamics Corporation (RDC)
Tradeoff/Sensitivity Analyses of Hydrogen Delivery Approaches

SRNL
Pipeline Life Management Program

Aims to serve as “go-to” organization to catalyze PA Hydrogen and Fuel Cell Economy development

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Funding and Duration

- FY04 funding
  - DOE: $2,943,232
  - Contractor: $738,965
- Award notification
  - September 1, 2004
- Contract start date
  - November 23, 2004
- Contract end date
  - March 31, 2006

Hydrogen Regional Infrastructure Program in Pennsylvania

- **Objectives**
  - Capture data pertinent to H_2 delivery in PA
  - Identify opportunities for safe/reliable delivery options

- **H_2 Delivery**
  - Co-transportation of H_2 and natural gas in existing pipelines
  - Separation of H_2 from H_2/natural gas blends at the point of use
  - Examine most attractive options for H_2 delivery approach(es) in PA

Hydrogen Regional Infrastructure Program in Pennsylvania

- **New Material Development**
  - Evaluate novel material approaches for pipelines and compressed gas storage tanks

- **Hydrogen Sensor Development**
  - Evaluate the ability of H_2-specific sensors to determine %H_2 in feed gas (including gas blends) and ppm-level H_2 for leaks

H_2 Delivery Approach

- Assess current gas pipeline materials and operational characteristics
  - Identify construction materials used in the US and PA according to:
    - Feed gas composition
    - Pressure Flow Rate
    - Ambient conditions
    - Temperature
- Identify and quantify tradeoffs between alternative H_2 delivery approaches in PA
  - RDC
    - Examine economic, risk, and technology tradeoffs
      - Use data collection, economic analysis and sensitivity analysis
    - Recommend best approaches for delivering hydrogen from production facilities to end users
  - *CTC*
    - Provide inputs to assist with economic model
      - Natural gas demands
      - Co-transport deliver scenarios

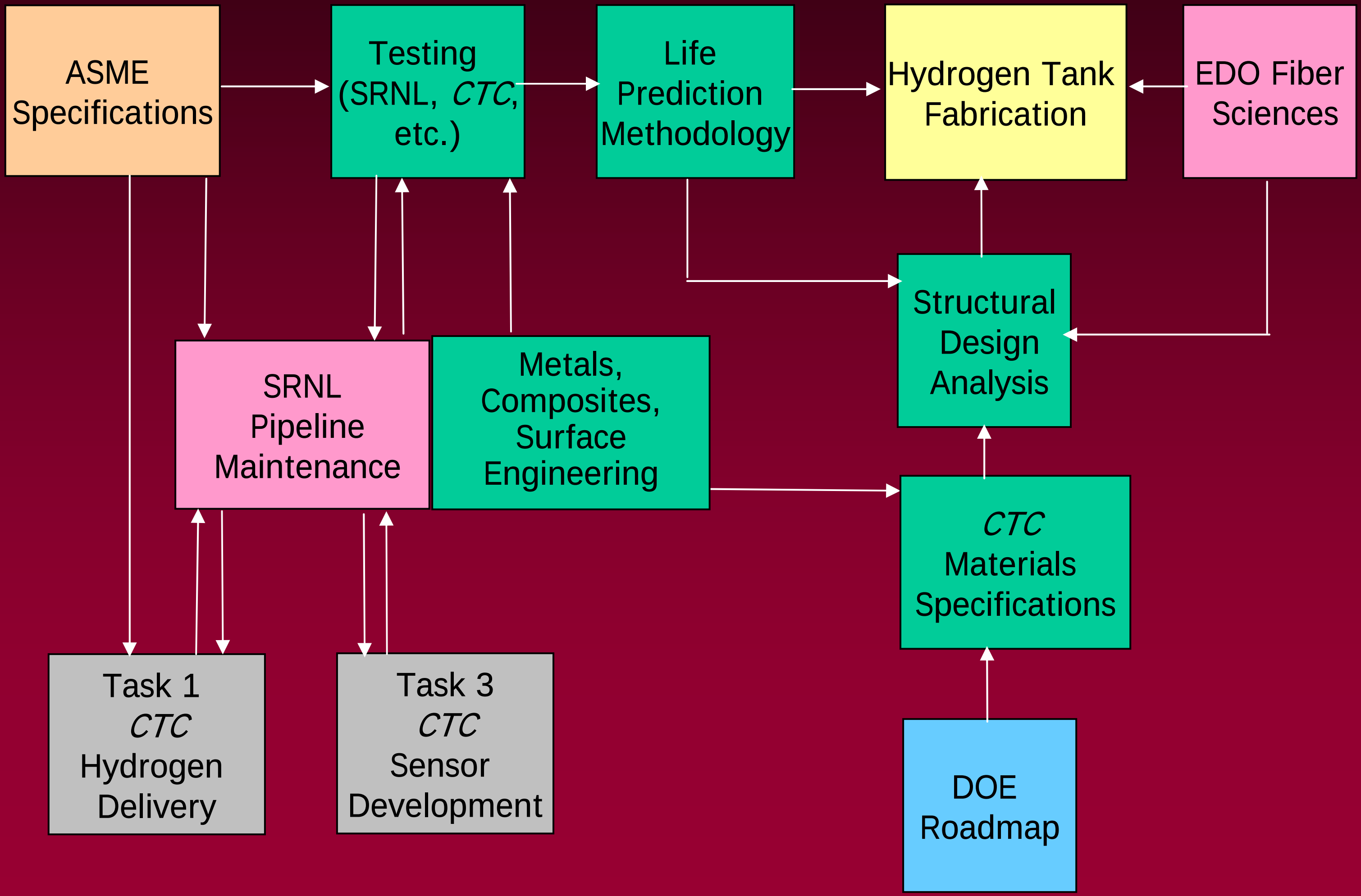
H_2 Delivery Approach

- Investigate separation at point of use
  - Based on co-transport of natural gas and hydrogen
- Examine delivery scenarios and resulting effects on separation technology selection
  - Test and determine suitability of available technologies
- Assess current separation technologies
  - Organic membranes
  - Pressure Swing Absorption (PSA)
  - Vacuum Swing Absorption (VSA)
  - Palladium alloy membranes
  - Cryogenic distillation
  - External field-based approaches (thermal gradient, centrifuge)
  - Ceramic membranes
  - Zeolite membranes

Materials Approach

- Benchmark current or potential material issues
- Develop test protocols and perform materials testing
- Develop lifing and survivability model
  - Identify models and input parameters for lifing/survivability
  - Incorporate test data into lifing/survivability models
  - Investigate existing materials test data
- Simulate pipeline lifetime based on model data
- Investigate composite tanks
- Fabricate and test prototype off-board storage tank

Materials Approach



ASME Specifications

Testing (SRNL, *CTC*, etc.)

Life Prediction Methodology

Hydrogen Tank Fabrication

EDO Fiber Sciences

Structural Design Analysis

SRNL Pipeline Maintenance

Metals, Composites, Surface Engineering

CTC Materials Specifications

Task 1 *CTC* Hydrogen Delivery

Task 3 *CTC* Sensor Development

DOE Roadmap

Sensors Approach

- Define H_2 sensor performance requirements
- Access available sensor technologies
- Create test protocols for testing sensors against performance requirements
- Test priority sensor technologies in H_2 and gas blends
  - Identify effects of:
    - Contaminants
    - Humidity
    - Pressure
    - Temperature
  - Assess calibration and maintenance capability of sensors

Hydrogen Delivery Accomplishments

- Identified H_2 co-transport issues in existing natural gas system
  - Hydrogen production and injection location
  - Hydrogen/natural gas transport ratio as a function of demand
  - End user demands
  - Utility companies and PA Public Utility Commission
  - Gas-blend related issues and current pipeline failure modes
  - Potential effects of pressure drop losses in pipelines for various hydrogen/natural gas blends
- Performed research and demographic studies for PA H_2 demand scenarios
  - Performed sample calculations
    - Estimated required refueling station quantities and capacities
- Completed report on existing natural gas pipeline materials and associated operational characteristics

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Hydrogen Delivery Accomplishments

- Identified transmission and distribution pipeline characteristics for the US and PA
  - Materials
  - Failures (leaks)
    - Significant corrosion issues in PA vs. US
  - Year of Construction
  - Operation parameters
- Identified operation concerns
  - State regulations and tariffs (BTU content)
  - Wobbe Index
  - Hydrogen loss cost to the end user
  - Odorants
  - Thermodynamic properties
  - Piping system layout

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Comparison of US and PA Transmission Pipeline

Category	US	PA
Material	**Percent of Total Miles**	**Percent of Total Miles**
Steel	99.73	98.5
Other	0.27	1.5
Total	**100 (291,704 mi)**	**100 (9,501 mi)**
Decade of Installation	**Percent of Steel Miles**	**Percent of Steel Miles**
Unknown	2.9	0
Installed Pre-1940	5.1	4.5
Installed 1940-1949	8.7	9.3
Installed 1950-1959	24.5	28.7
Installed 1960-1969	24.6	19.5
Installed 1970-1979	10.8	7.8
Installed 1980-1989	9.3	16.6
Installed 1990-1999	10.6	10.2
Installed 2000-Present	3.5	3.4
Leaks	**% Leak Repairs**	**% Leak Repairs**
Corrosion Leaks	**44.7**	**71.8**
Mat'l/Welds Leaks	19.4	18.8
Other/Forces Leaks	35.9	9.4
Based on 2003 Data		

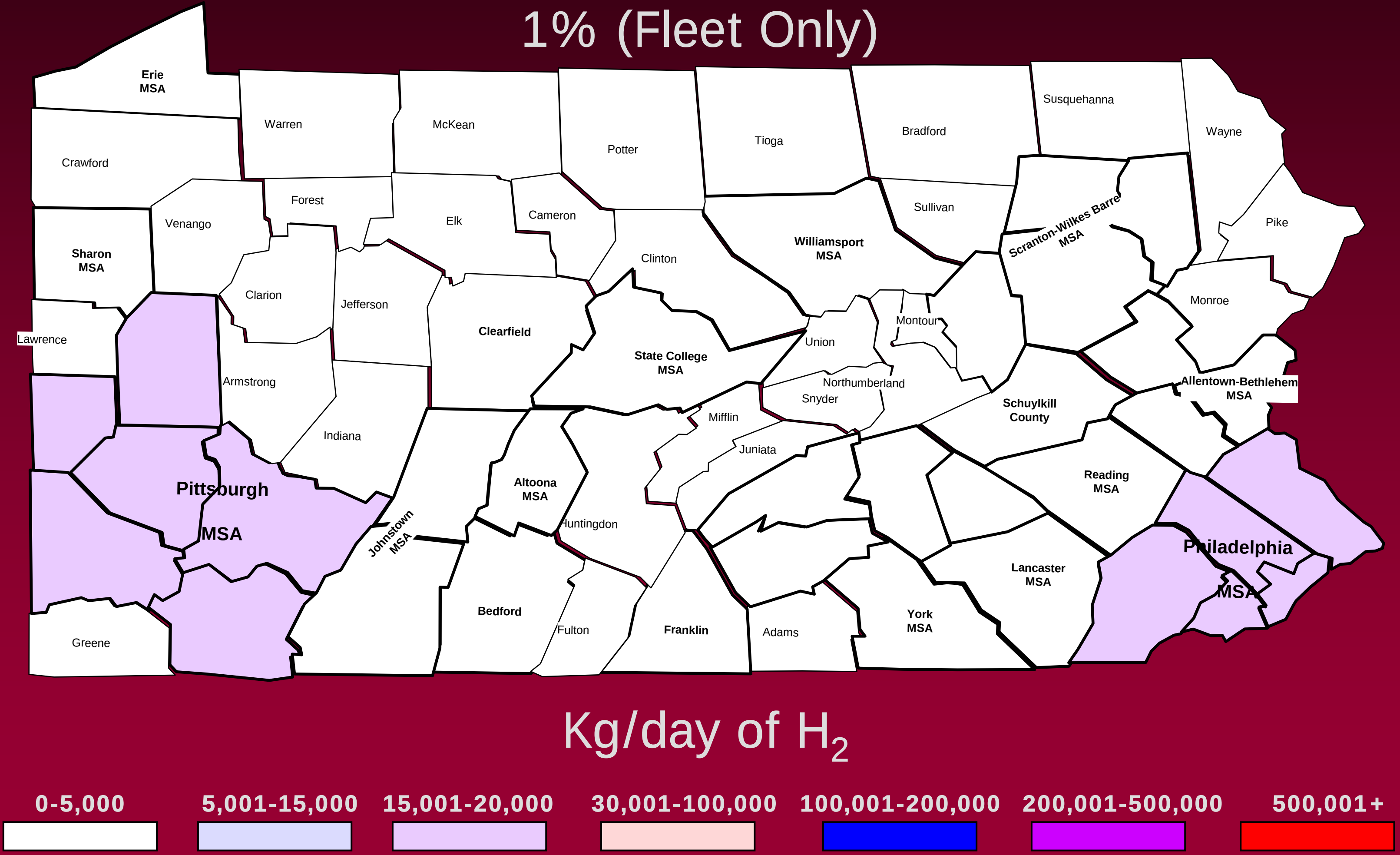
Comparison of US and PA Distribution Pipeline

Category	US	PA
Material	**Percent of Total Miles**	**Percent of Total Miles**
Steel	50.4	55
Plastic	45.7	35
Other	3.9	10
Total	**100 (1,097,994 mi)**	**100 (40,584 mi)**
Leaks	**% Leak Repairs**	**% Leak Repairs**
Corrosion	**35**	**62.8**
Outside Force	8.6	16.8
Third Party	17.9	4.1
Material Defect	6.3	2.4
Construction Defect	3	0.5
Other Causes	29.2	13.4
Based on 2003 Data		

Hydrogen Delivery Accomplishments: H_2 Delivery Options

- Estimated potential feedstocks required and availability
  - PA Electricity, natural gas, biomass, coal, petcoke, gasoline, methanol
- Developed production scenarios
- Developed data on existing infrastructure
  - Roads, pipelines, power plants, refineries, coal mines, biomass sources
- Developed spreadsheets to perform cost analysis
- Discussed H2A model with NREL
- Testing H_2A component model
- Refining spreadsheets to perform cost analysis

Hydrogen Delivery Accomplishments: PA H_2 Demand Scenarios



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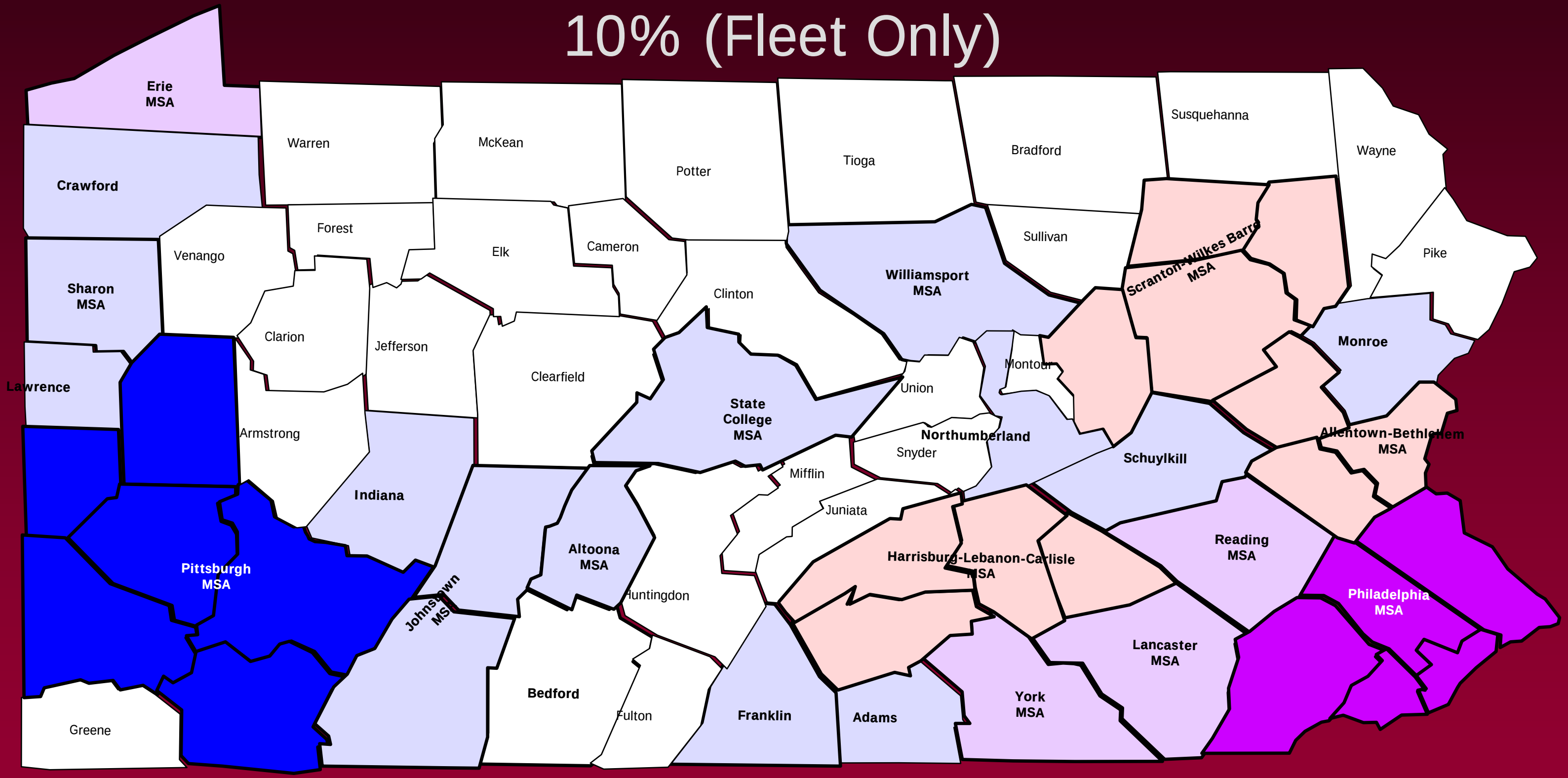
Hydrogen Delivery Accomplishments: PA H_2 Demand Scenarios

10% (Fleet Only)



Kg/day of H_2

0-5,000

5,001-15,000

15,001-20,000

30,001-100,000

100,001-200,000

200,001-500,000

500,001+

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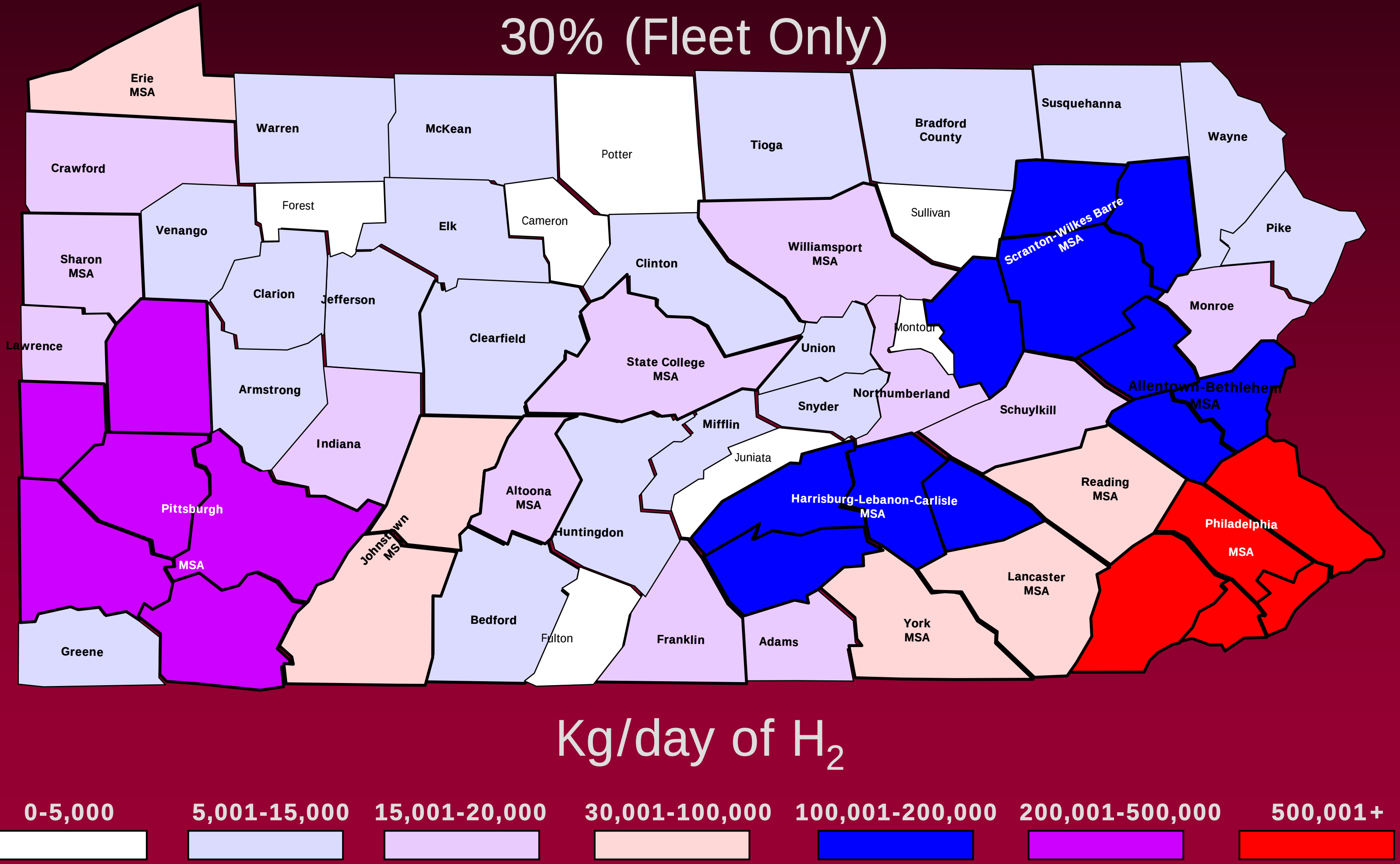
Hydrogen Delivery Accomplishments: PA H_2 Demand Scenarios

30% (Fleet Only)



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Hydrogen Delivery Accomplishments: Separation

- Made assumptions to evaluate technologies
  - Composition: 80% NG / 20% H_2
    - Typical NG composition
    - H_2 feedstock at 50, 100, or 200 psig
  - Hydrogen refueling station conditions
    - Pressure - 6000 psig
    - Demand - 100 kg/day H_2
    - Tolerances –
      - 1 ppm CO
      - 500 ppm inert species
      - <10 ppb H_2S
  - Loss via incomplete recovery in a separation device or to natural gas consumers

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Hydrogen Delivery Accomplishments: Separation

- Identified and reviewed candidate separation technologies
  - PSA
  - VSA
  - Organic membranes
  - Combinations: Organic membranes + temperature swing absorption (TSA), Organic membranes + PSA or VSA
  - Palladium alloy membranes
  - Selectively reacting H_2 with hydride + TSA to regenerate
  - Cryogenic distillation
  - External field-based approaches (thermal gradient, centrifuge)
  - Ceramic and Zeolite membranes
- Modeling PSA recovery
  - Performed modeling for PSA using SIMPAC software
    - Results show good recovery of 85^+% at 99.95^+% purity
    - Suggests that organic membrane addition will not greatly improve recovery/purity
  - Considering modeling palladium membrane (ASPEN?)
    - Interested due to its selectivity to H_2

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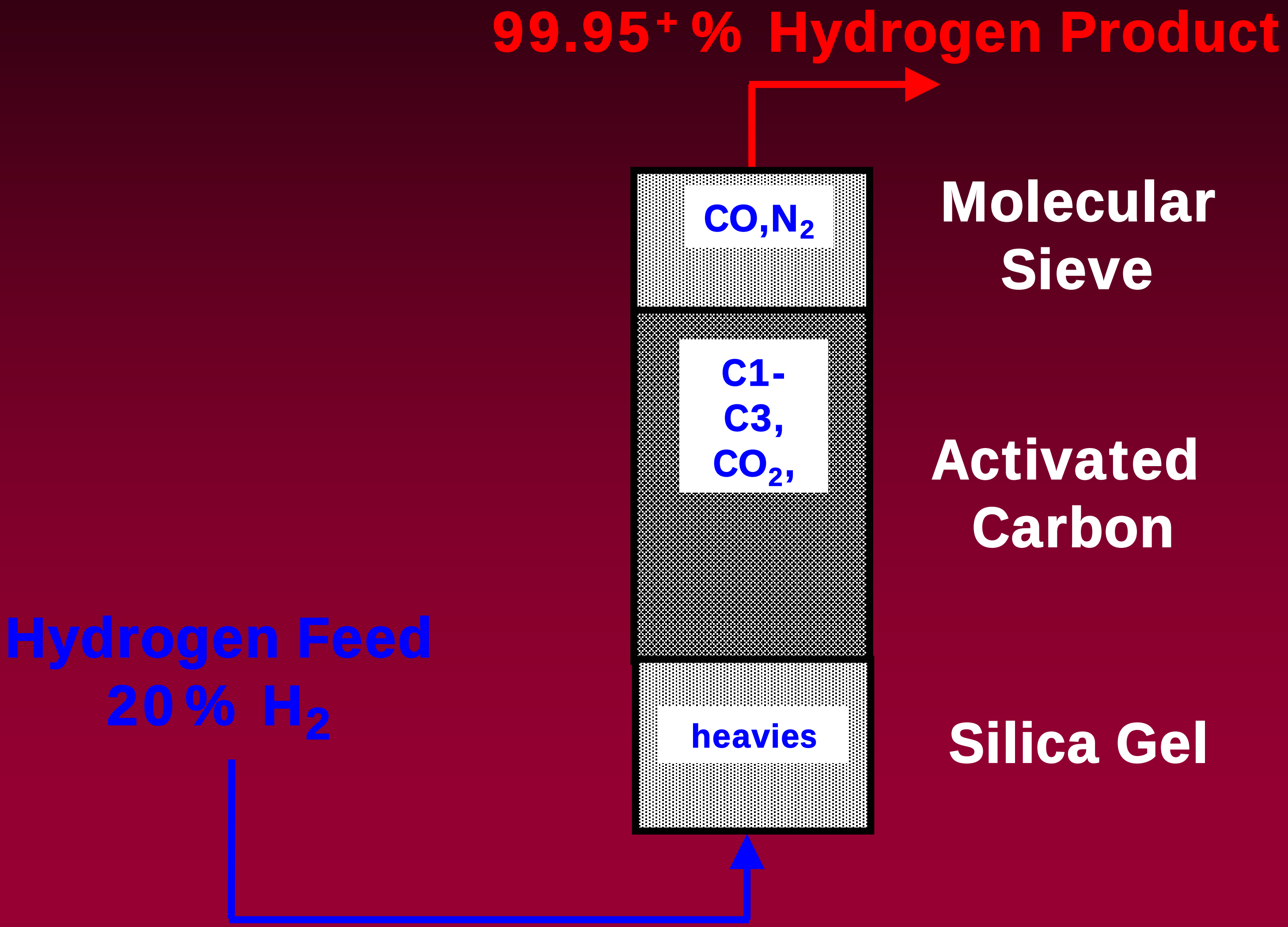
Hydrogen Delivery Accomplishments: Separation - PSA



99.95^{+} % Hydrogen Product

CO, N_2

Molecular Sieve

C1-C3, CO_2,

Activated Carbon

heavies

Silica Gel

Hydrogen Feed

20% H_2

Materials Accomplishments

- Performed baseline assessments related to hydrogen delivery materials
  - Evaluated material issues based on
    - Failures
    - Pressures
    - Blends
    - Prevalence in infrastructure
- Assessed currently available high pressure composite tanks
  - Investigating where manufacturing costs can be reduced
    - Builds on 15+ years experience with Navy materials work

Materials Accomplishments

Materials	**Metals**		**Composites**		**Plastics**	
	High Strength Low Alloy	**Low Carbon Steels**	**Metal Liner**	**Plastic Liner**	**PE**	**PVC/Other**
Prevalence in Infrastructure	Future high pressure applications	Existing NG Pipeline Distribution 50.4% Transmission >99%	Future Applications (pipe, tank, miscellaneous hardware)		Existing NG Pipeline Distribution 45.7% Transmission <1%	
Pressure (psi)	0 - 10,000	0-1,200	6,600**	10,000**	<100*	<100*
Possibility of Distortion under cyclic conditions	N/A		Possibile		Possible for higher pressures than currently used	
Potential or Existing Failures	H_2 embrittlement, fatigue, and corrosion		H_2 embrittlement, fatigue, and corrosion	H_2 permeation, embrittlement, and fatigue	H_2 permeation, embrittlement, and fatigue	
Issues related to use	Joining/welding		Joints and thermal expansion/fatigue at interface in hybrid structures		Joints	
* Typical pressures, although up to 125 psi have been documented, **Pressures related to composite tanks currently available						

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Materials Accomplishments: Composites

Company Manufacturer	Operational Pressure Burst Test Pressure	Structural Material	Liner Material	Service Life
Dynetek Industries Ltd.	3,000-6,500psi/ 6,600-14,300psi	wound layer of carbon fiber reinforced composite material	seamless aluminum liner	15 years
Quantum Technologies	5,000-10,000psi 15,000-23,500psi	multiple layers of carbon fiber/epoxy laminate and a proprietary external protective layer for impact resistance	seamless, one piece, permeation resistant, cross-linked ultra-high molecular weight polymer liner	15 years
Lincoln Composites	7,000-10,000psi 11,750-23,000psi	high strength carbon fiber blended with tough glass filaments placed on the liner. Then an energy absorbing material followed by a fiberglass outer layer	plastic high density polyethylene (HDPE) liner that is permeation and embrittlement resistant	20 years

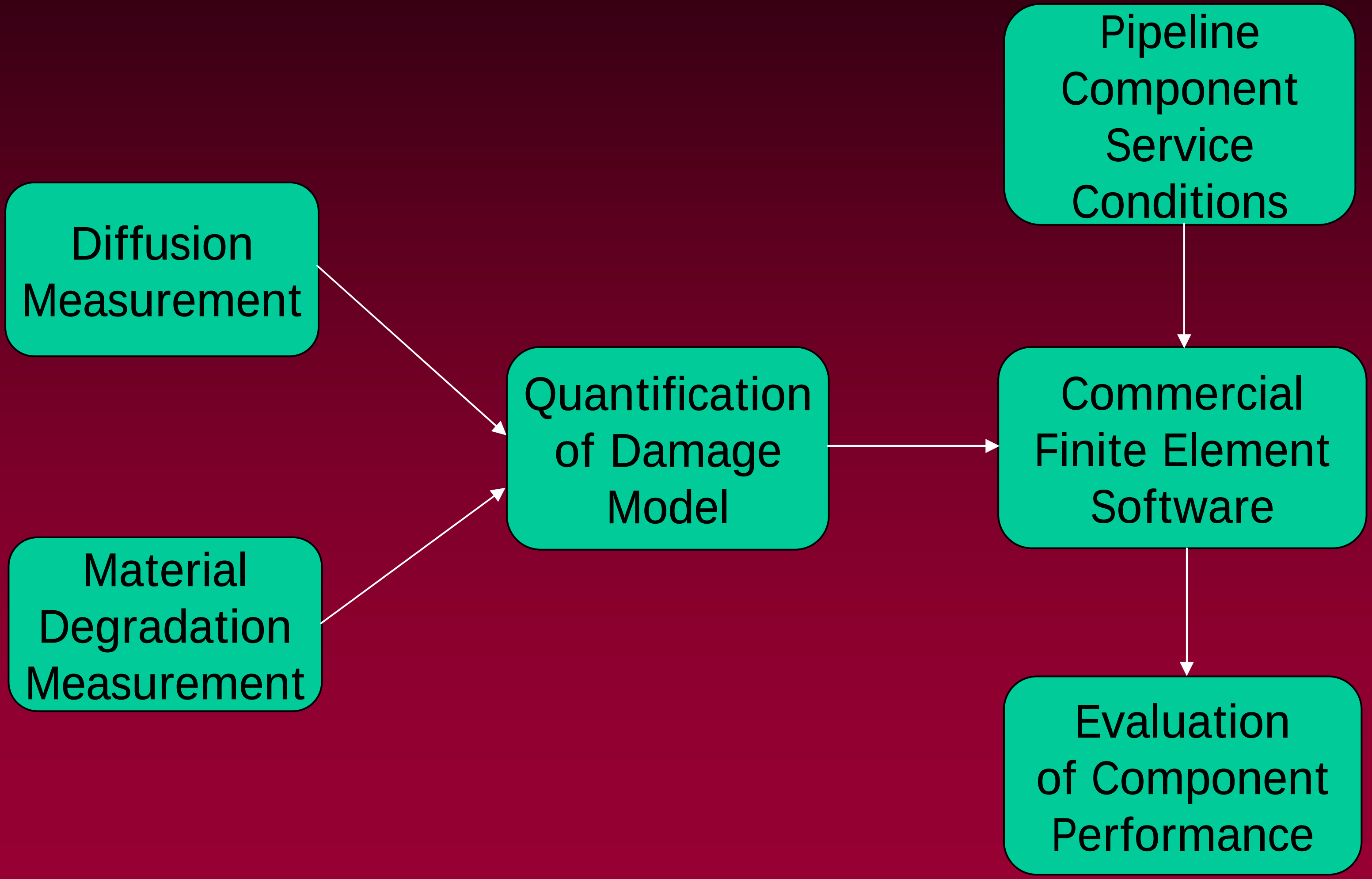
Materials Accomplishments: Lifing and Survivability Model

- Identified material models and supporting material database needs
  - Hydrogen permeation evaluation
  - Identification material properties degradation
- Identified hydrogen embrittlement model voids
  - Finite element programs available
    - Focus on a pre-existing crack and its progression
    - Provide in-depth understanding of the failure process
  - Hydrogen embrittlement analysis packages not available
- Enumerated modeling needs
  - Engineering model to analyze hydrogen embrittlement
  - Numerical scheme to implement the engineering model and evaluate the material

Materials Accomplishments: Lifing and Survivability Model

- Pursuing statistical analysis of hydrogen embrittlement
  - Identified a purely empirical approach (Yokobori)
  - Reviewed prior experiments and analysis (Davies)
  - Identified statistical analysis needs
    - Weibull distribution for tensile failure, fatigue failure, distribution for different materials
- Taking damage mechanics approach for material evaluation
  - Bypassing details in microscopic scale
    - Focusing on overall material performance or material merits
  - Introducing damage parameters to quantify material degradation
  - Used to study the failure of materials with complex structures
    - Includes composite materials and large engineering structures
  - Not previously adopted in the modeling of hydrogen embrittlement

Materials Accomplishments: Lifing and Survivability



Diffusion Measurement

Material Degradation Measurement

Quantification of Damage Model

Pipeline Component Service Conditions

Commercial Finite Element Software

Evaluation of Component Performance

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Initial Tests Needed for Models

Material	Test Type	Prior Exposure	Test Environment	Testing Source
A42	Tensile	None, H2 – 7 MPa,1 hr	Air, 1 atm, RT; H_2, 7 MPa, RT	SRNL
A42 & weld, HAZ	Tensile	None	Air, 1 atm, RT	SRNL
A42	Creep Rupture	None, H2 – 7 MPa,1 hr	Air, 1 atm, RT; H_2, 7 MPa, RT	TBD
Weld, HAZ	Creep Rupture	None, H2 – 7 MPa,1 hr	Air, 1 atm, RT; H_2, 7 MPa, RT	TBD
A42	Fatigue, R=0.7, 0	None, H2 – 7 MPa,1 hr	Air, 1 atm, RT; H_2, 7 MPa, RT	TBD
Weld, HAZ	Fatigue, R=0.7, 0	None, H2 – 7 MPa,1 hr	Air, 1 atm, RT; H_2, 7 MPa, RT	TBD
A42 – Tube	Cyclic, 0 to 1000 psig	None	H_2, RT	TBD
A42 – Tube	Burst	None	H_2, RT	TBD

Sensor Accomplishments

- Created performance requirements for sensors to be evaluated
- Conducted technology assessment of sensors
- Identified and purchased two COTS and one pre-commercial sensor(s)
  - COTS
    - H2 Scan portable hydrogen leak detector
    - Nanomix Sensation Technology wireless hydrogen sensor
- Created test protocols for testing sensors

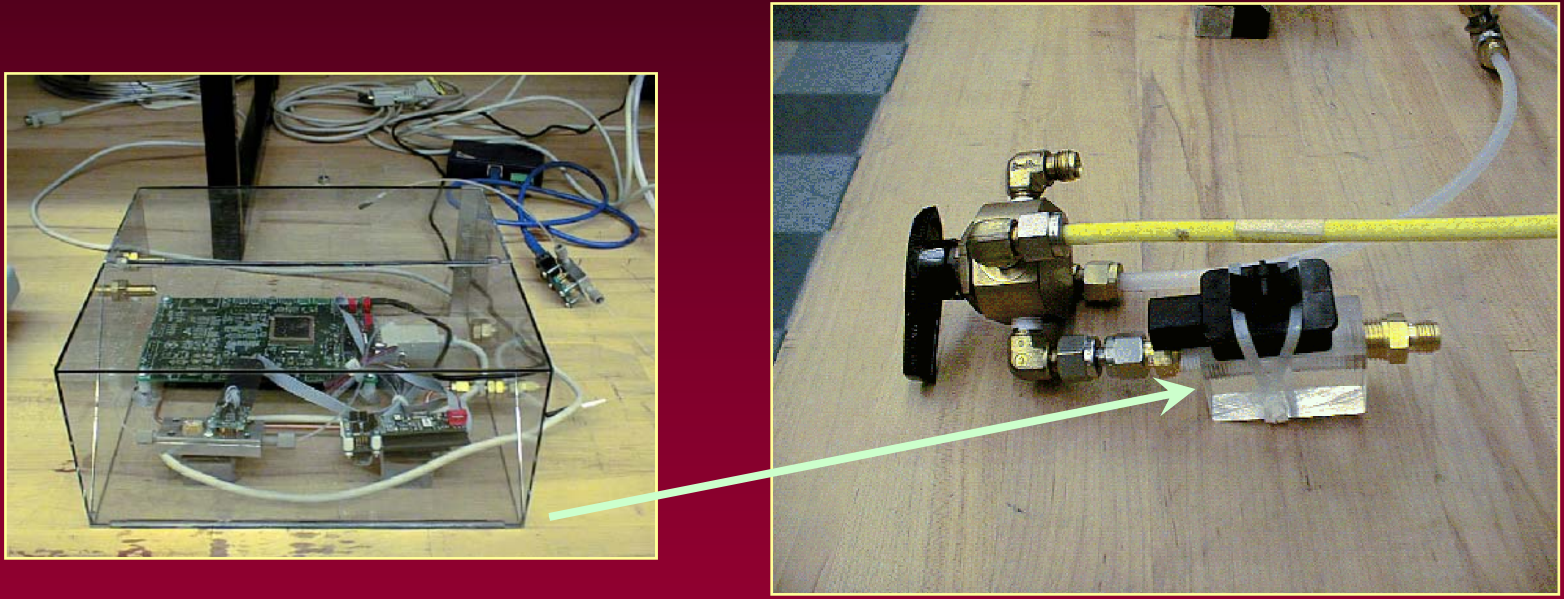
Sensor Performance Requirements

Parameter	Range	Units
Component specificity	H_2	-
Oxygen requirement	not required	-
Operating range	0.01 – 5	%
Chemical interference		
CO	>0.5	ppmv
H_2S	>0.01	ppmv
Humidity	5% - dewpoint	-
VOC (diesel exhaust)	>10 ppmv	-
Precision	+/- 5	%
Calibration drift (short)	< 2.5 (24 hrs)	%
Calibration drift (long)	<10 (3 months)	%
Electrical	noise < 100	ppmv
Response time (> 10 % change)	< 2	sec
Full range (0.1-5%)-time-constant	< 5	sec
Ambient temperature range	-200	° F
Ambient pressure range	0.8 – 1.2	atm
Calibration/validation requirement	One point NIST-Ref	-
Sensor size (w/electronics)	2x2x1	inches
Alarm levels (if process required)		
Level 1	10,000	ppmv
Level 2	20,000	ppmv
Level 3	30,000	ppmv
Level 4	40,000	ppmv
Level 5	50,000	ppmv
Sensor-to-electronics distance	< 6	feet

Sensor Test Parameters/Protocol

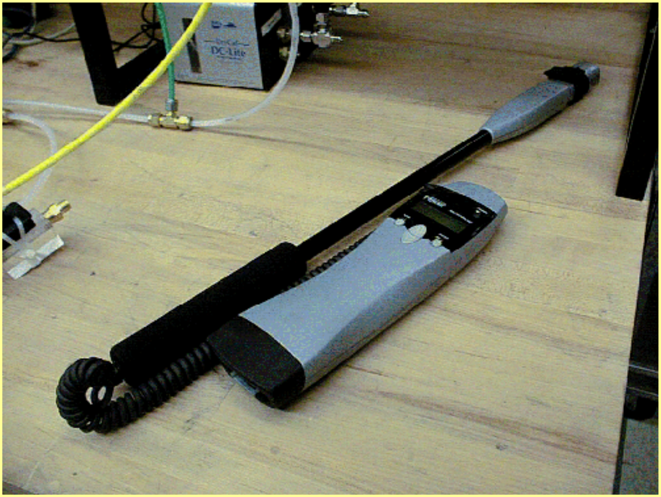
	What	How	Details	Eval. Criteria
A	**Qualification:**			
1	**O_2 effect**	Cycled between N_2 and air (1% H_2)	Flowing challenges	+/- 5% of LEL
			30 minute challenges or until plateau is achieved	< 5% drift over 1 hr
2	**Linearity** from 0.01 to 4% H_2	H_2 challenges in air at 10 points from 0.01% to 4% H_2	Flowing challenge; Random sequence	Std dev < 5% of LEL
			30 minute challenges	
3	**Hysteresis**	H_2 challenges in air at 5 points from 0.01% to 4% H_2	Flowing challenge	< 10 %
			Sequenced from low to high; soak at high for 1 hr and reverse sequence; 30 minute challenges	
4	Statistical **repeatability**	Repeat linearity testing (#4) every other day over 6 days	Statistical regression analysis	+/- 10 %
5	**Inter-sensor variability** of responses between sensors	Repeat linearity testing (#4) on 4 sensors	Statistical regression analysis	+/- 10 %
6	**Effect of ambient temperature** variation on the sensor response	Repeat linearity testing (#4) while module is at constant temperature and changed from -30 °C to 60°C	Sensor can be in a sealed box immersed in a constant temperature liquid or in a heated/cooled oven	< 10 % within +/- 30° C range of room temperature
				TBD outside range
7	**Effects of natural gas constituents** as interferences to H_2 sensing	H_2 challenges in natural gas at 5 points from 0.01% to 4% H_2	Followed by retesting with stds in air.	< 10 %
8	**Effects of controlled ambient air contaminants** as interferences to H_2 sensing	4% H_2 in air diluted 50% with 20% CO in N_2, 100% CO_2,	Each contaminant is followed by retesting with stds in air.	< 10%
B	**Functional Behavior**			
1	**Effects of controlled ambient air contaminants** as interferences to H_2 sensing	4% H_2 in air diluted 50% with N_2 passed through 100% motor car exhaust, N_2 passed through motor oil (devoid of aerosol), N_2 passed through anti-freeze, N_2 passed through food products	Each contaminant is followed by retesting with stds in air.	TBD
2	**Effects of uncontrolled ambient air contaminants** as interferences to H_2 sensing	Operation of unit exposed to ambient air near a farm or factory for 6 days	Followed by retesting with stds in air.	TBD

Purchased Sensors (Applied Sensors)

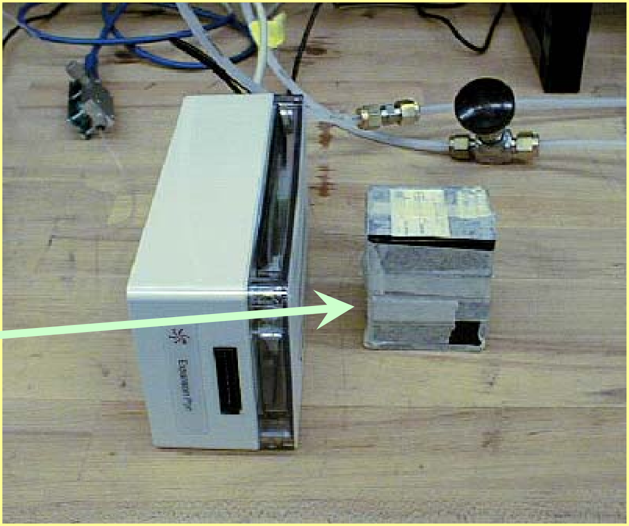


Early version → Current testing system

Purchased Sensors
(H_2 Scan & NanoMix)



H2 Scan Hand held
w/extended tip



Nanotube
w/wireless

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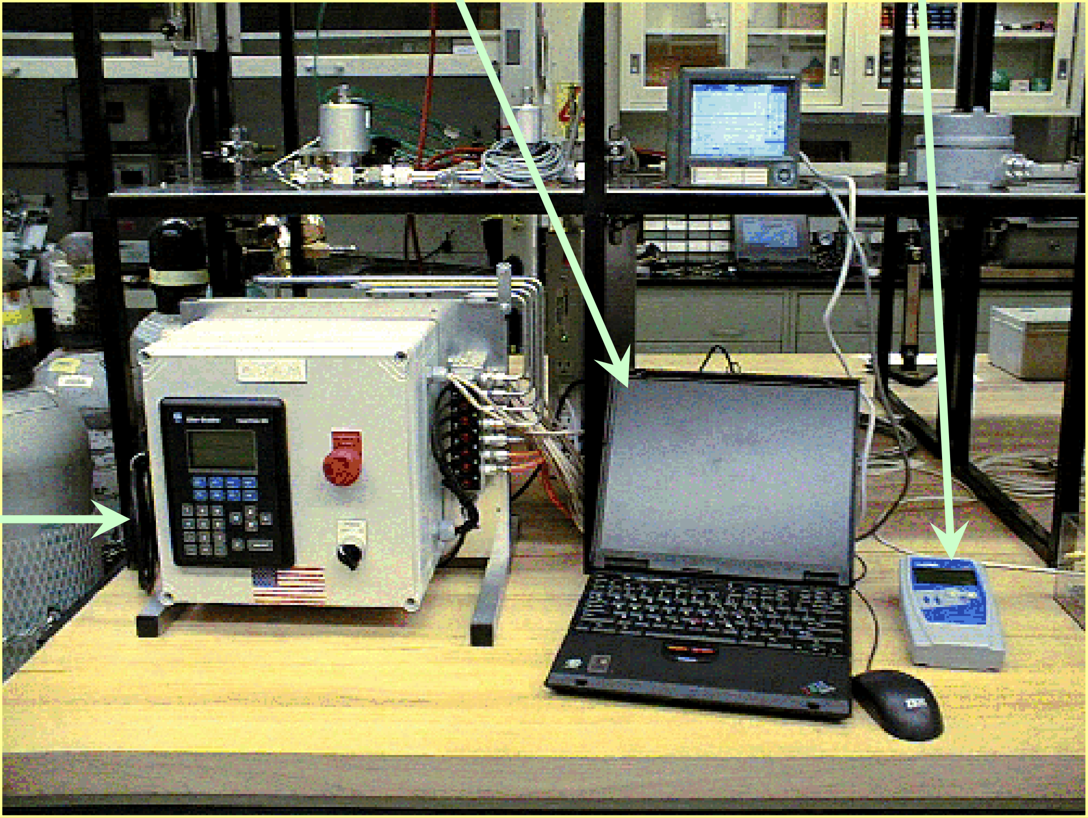
Test Platform / Equipment

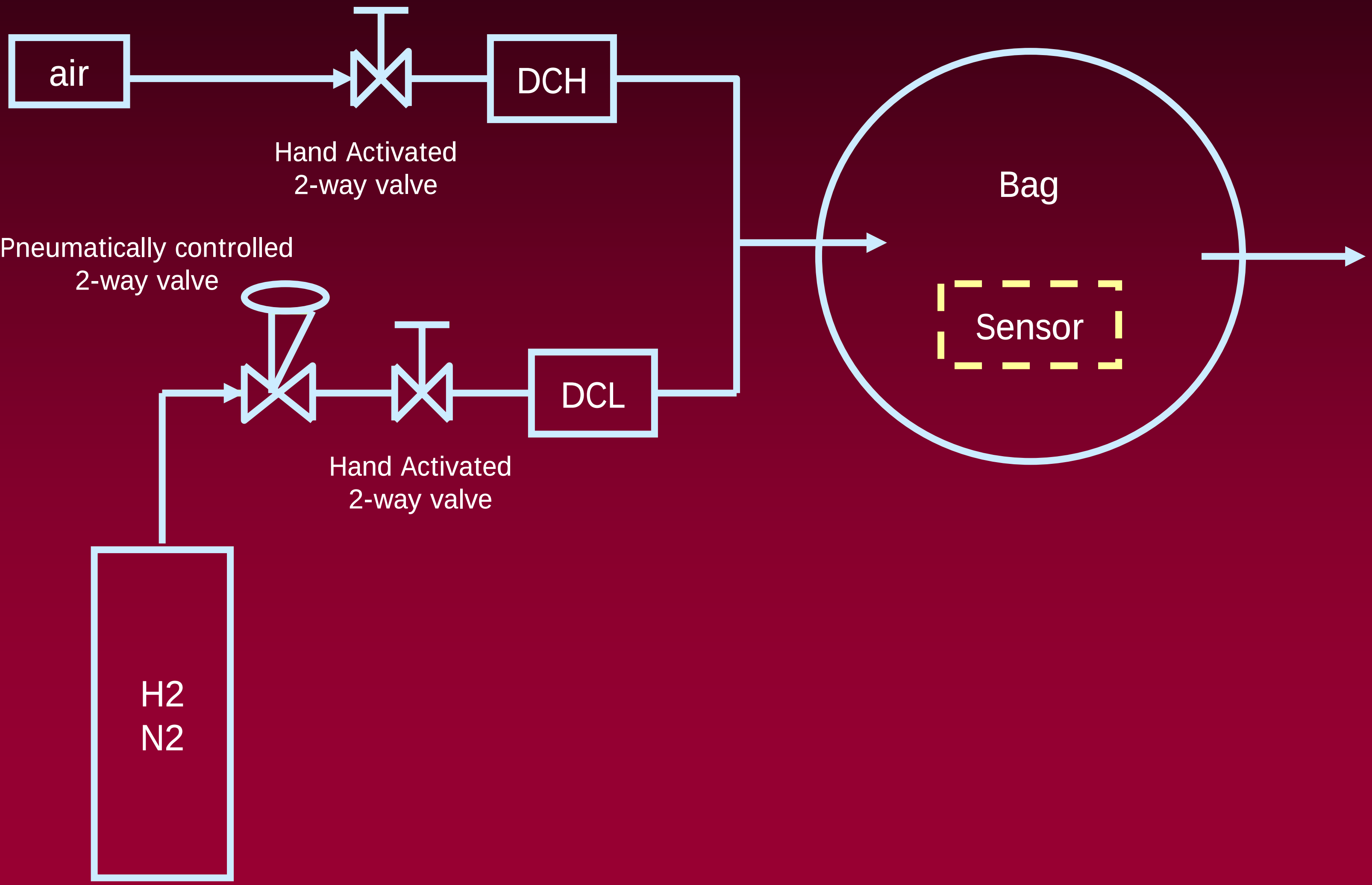


Computer Interface

8-channel Datalogger

Automatic Sequencer

Testing Setup



air

Hand Activated
2-way valve

DCH

Bag

Sensor

Pneumatically controlled
2-way valve

DCL

Hand Activated
2-way valve

H2
N2

Plans

- Evaluate production needs given different demand scenarios
- Evaluate transportation/delivery options
- Complete evaluation of separation technologies
- Determine effects of H_2 on infrastructure materials
- Identify key test data gaps
- Perform lifetime simulation on common pipeline material
  - Input test data into a Lifing and Survivability model
  - Input existing test data into Lifing and Survivability model
- Construct and test prototype tank
- Evaluate COTS H_2 sensors for implementation in transportation and delivery applications
- Complete laboratory test evaluation of 3 sensors
  - Per established test plan/protocol
- Perform limited field testing

Questions