Hydrogen Storage Engineering
CENTER OF EXCELLENCE

Systems Engineering of Chemical Hydrogen, Pressure Vessel, and Balance of Plant for On-Board Hydrogen Storage

J. Holladay (P.I.), K. Brooks, K. Simmons, E. Rönnebro, M. Weimar, A. Karkamkar, R. Pires, M. Westman

DOE Fuel Cell Technology Program
Annual Merit Review

Washington, DC
May 14, 2013
Technology Development Managers: Ned Stetson and Jesse Adams

U.S. Department of Energy
Energy Efficiency and Renewable Energy
Bringing you a prosperous future where energy is clean, abundant, reliable, and affordable

Pacific Northwest
NATIONAL LABORATORY

Project ID: ST005

Overview

- Timeline
  - Start: Feb. 2009
  - Project End: Jan. 2014
    - End Phase 1: 2011
    - End Phase 2: 2013
    - End Phase 3: 2014
  - Percent complete: 65%

- Budget
  - $5.8M Total (PNNL) Program
    - DOE direct funded
    - No cost-share required for National Lab
  - FY13: $700k
  - FY12: $895k
  - FY11: $960k

- Barriers
  - A. System Weight and Volume
  - B. System Cost
  - C. Efficiency
  - D. Durability
  - E. Charging / Discharging Rates
  - G. Materials of Construction
  - H. Balance of Plant (BOP) Components
  - J. Thermal Management
  - O. Hydrogen Boil-Off
  - S. By-Product/Spent Material Removal

- Partners

Relevance: Hydrogen Storage

- Impact to FCT Program
  - Demonstrate hydrogen storage system that meets DOE 2017 targets for light duty vehicles using chemical hydrogen storage
  - Apply materials discoveries from the Materials Centers of Excellence
  - Discover/develop engineering solutions to overcome material's deficiencies
  - Identify minimal performance for materials to be applicable in engineered H_2 storage systems for light duty vehicles.
- Hydrogen Storage Community at Large
  - Develop and/or advance modeling and simulation tools for the optimum design and engineering of on-board storage systems
  - Provide functional prototype systems available to OEMs
  - Provide engineering methodologies, analysis tools, and designs applicable to stationary storage and portable power applications
  - Demonstrate on-board storage to advance state of the art.
  - Identify, develop and validate critical components either for performance, mass, volume, or cost.

Approach:

- PNNL's Roles Supporting Engineering Center Structure
  - Technology Area Lead (TAL) for Materials Operating Requirements
  - Coordinate activities as the Technology Team Lead (TTL)
    - Bulk Materials Handling (Transport Phenomena)
    - Pressure Vessels (Enabling Technologies)
    - Manufacturing and Cost Analysis (Performance Analysis)
  - Liaison to VT Program projects and resources
- Technical Objectives of PNNL Scope:

Chemical Hydrogen
  - Design chemical hydrogen H_2 storage system & BOP components
  - Develop system models to predict mass, volume, performance
  - Reduce system volume and mass while optimizing storage capability, fueling and H_2 supply performance

All Systems
  - Mitigate materials incompatibility issues associated with H_2 embrittlement, corrosion and permeability
  - Demonstrate the performance of economical, compact lightweight vessels for hybridized storage
  - Guide design and technology down selection via cost modeling and manufacturing analysis
  - Perform value engineering of BOP to minimize cost, volume and mass
- Phased/ gated progressions aligning with HSECoE go/no-go decisions

FY13 Objectives

- Chemical Hydrogen Storage Design
  - Validate models and concepts via experiments
  - Scale-up slurry production
  - Assess feasibility of liquid-slurry chemical hydrogen storage
  - Assess feasibility of volume-exchange tank
  - Assess feasibility of slurry use with heat exchanger, pump, valves.
- Pressure Vessel for Cryo Adsorbent Hydrogen Storage
  - Exercise "tankinator" model to assess materials and design options for type I, III, and IV vessels
  - Optimize vessel design in terms of cost
  - Assess vessel cost as function of pressure and temperature
- Balance of Plant
  - Maintain BOP library
  - Size components (heat exchangers, valves, pumps,…)
  - Determine material compatibility
  - Identify where improvements can be made
- Cost Modeling

Accomplishments: Milestones FY13

Q2	Task 1	Report on Feasibility of a volume exchange tank operation with AB slurry
Q2	Task 1	Report on ability to identify a system design having mass<97kg, volume <118L, and be able to meet all the drive cycles
Q1	Task 2	Report on settling and flocculation rates for a 45 wt% AB slurry (both fresh and spent)
Q3	Task 2	Report on feasibility to scale-up the slurry production process
Q1	Task 4	Complete the analysis on which tank type to move forward with in Phase III.
Q2	Task 4	Complete the tank design mass and volume models for publication on the HSECoE website.
Q3	Task 4	Complete the materials database from components in the SA designs
4/30	Task 5	Update Cost Analysis for Chemical Hydrogen and Cryo-Sorbents

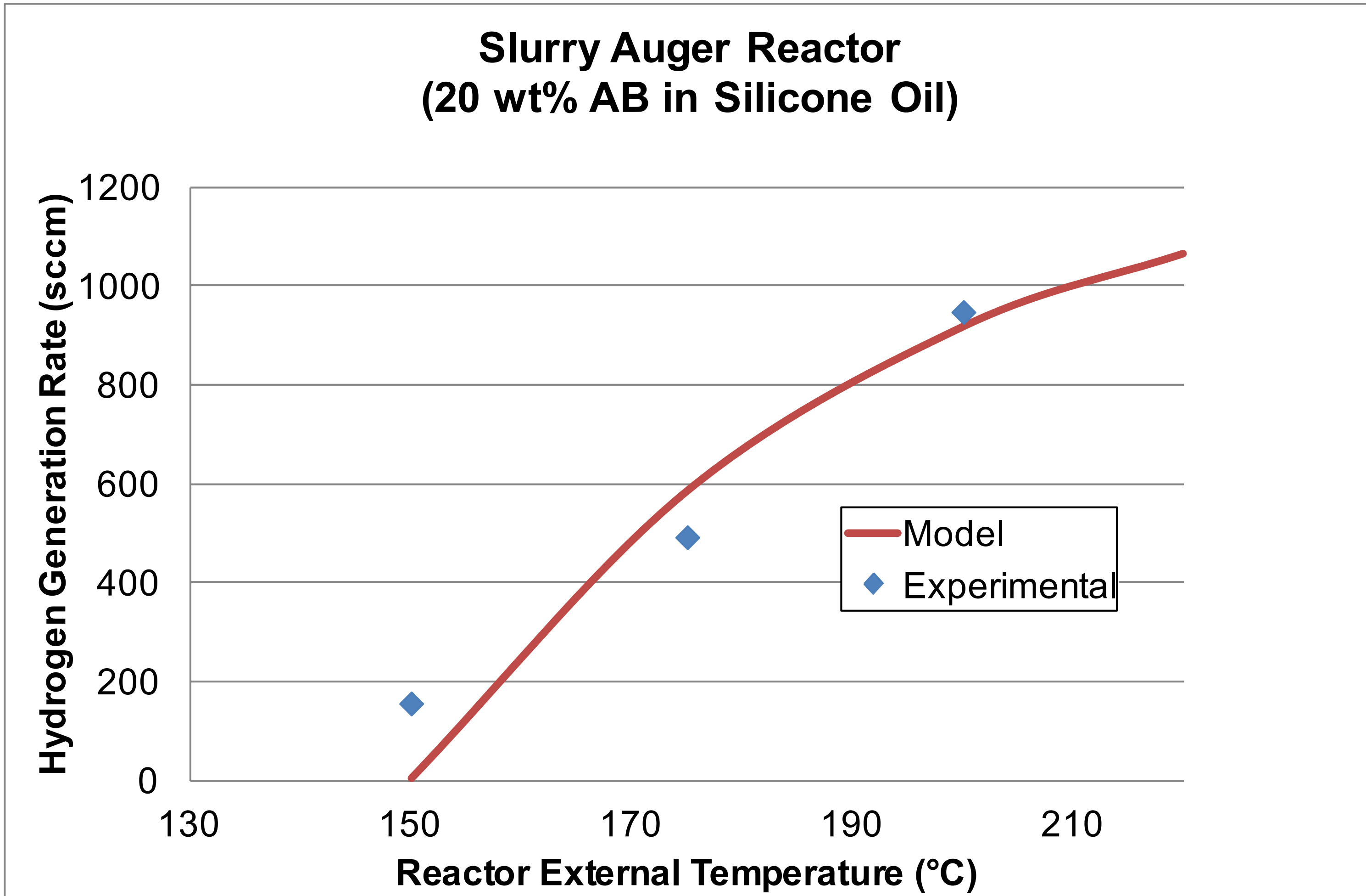
= complete
= on schedule
= at risk
= behind

Pacific Northwest
NATIONAL LABORATORY

Chemical Hydrogen Storage Development

- Modeling and Validation
  - FY12: System Modeling and Operational Envelope
  - FY13: System improvements (mass, volume, cost)
  - FY13 Component Validation
    - Reactor: LANL Model validation: PNNL
    - Gas-Liquid- Separator: UTRC
    - Radiator/Heat Exchanger: PNNL
    - Pump : PNNL
    - Displacement volume tank: PNNL
- Liquid-Slurry development (reviewer section)
  - Endothermic liquid-slurry: Alane surrogate leverage BNL's work
  - Exothermic liquid-slurry: Ammonia borane surrogate
    - 45-55 wt%
    - Flow reactor
    - Scale-up
    - Settling/flocculation rates

Accomplishments: Reactor Model Validation

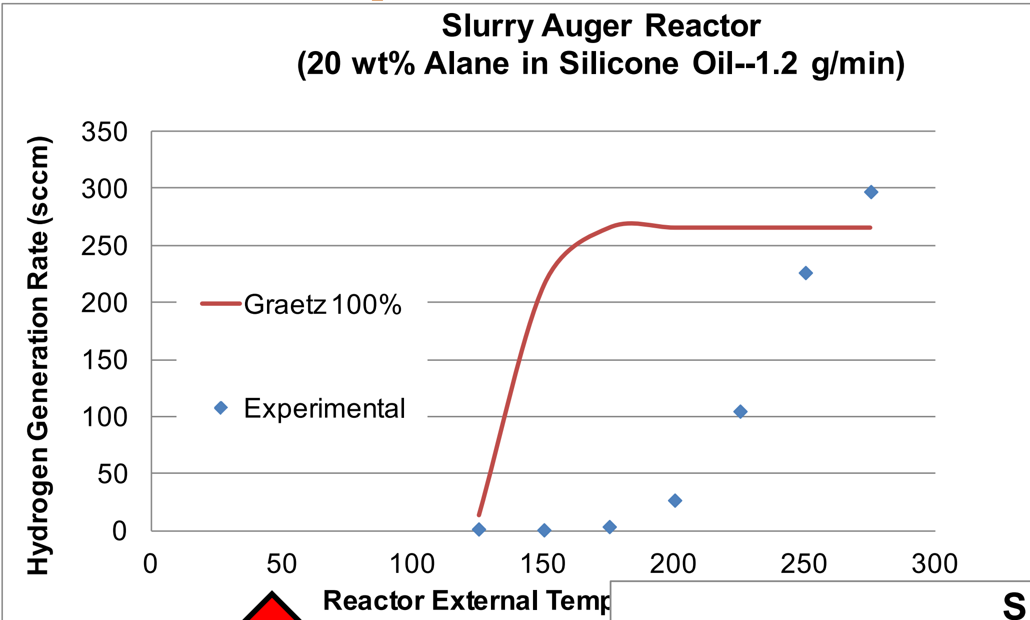


Good fit between experimental and model

Los Alamos NATIONAL LABORATORY Pacific Northwest NATIONAL LABORATORY

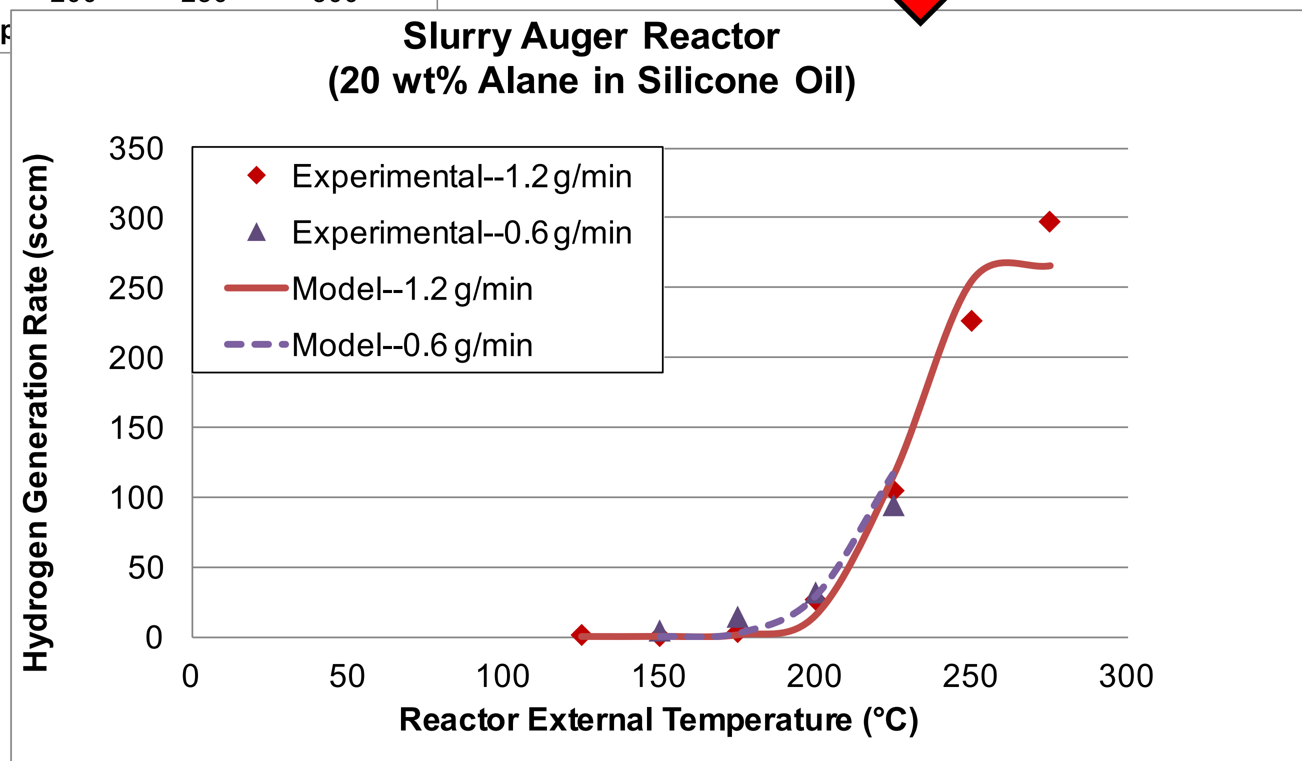
Pacific Northwest NATIONAL LABORATORY

Accomplishments: Reactor Model Validation



Fit model to data at 1.2g/min Checked model against 0.6 g/min flow- good fit!

Graetz kinetics uses "pre-treated" (or activated) alane, LANL's alane was not pre-treated

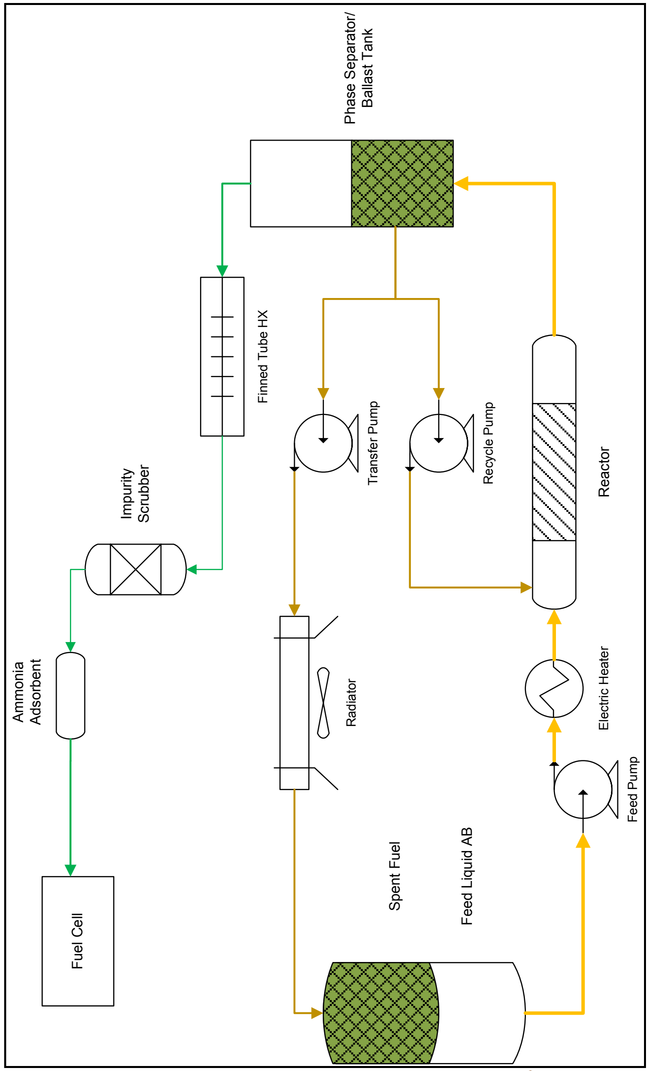


Los Alamos NATIONAL LABORATORY

Pacific Northwest NATIONAL LABORATORY

FY12

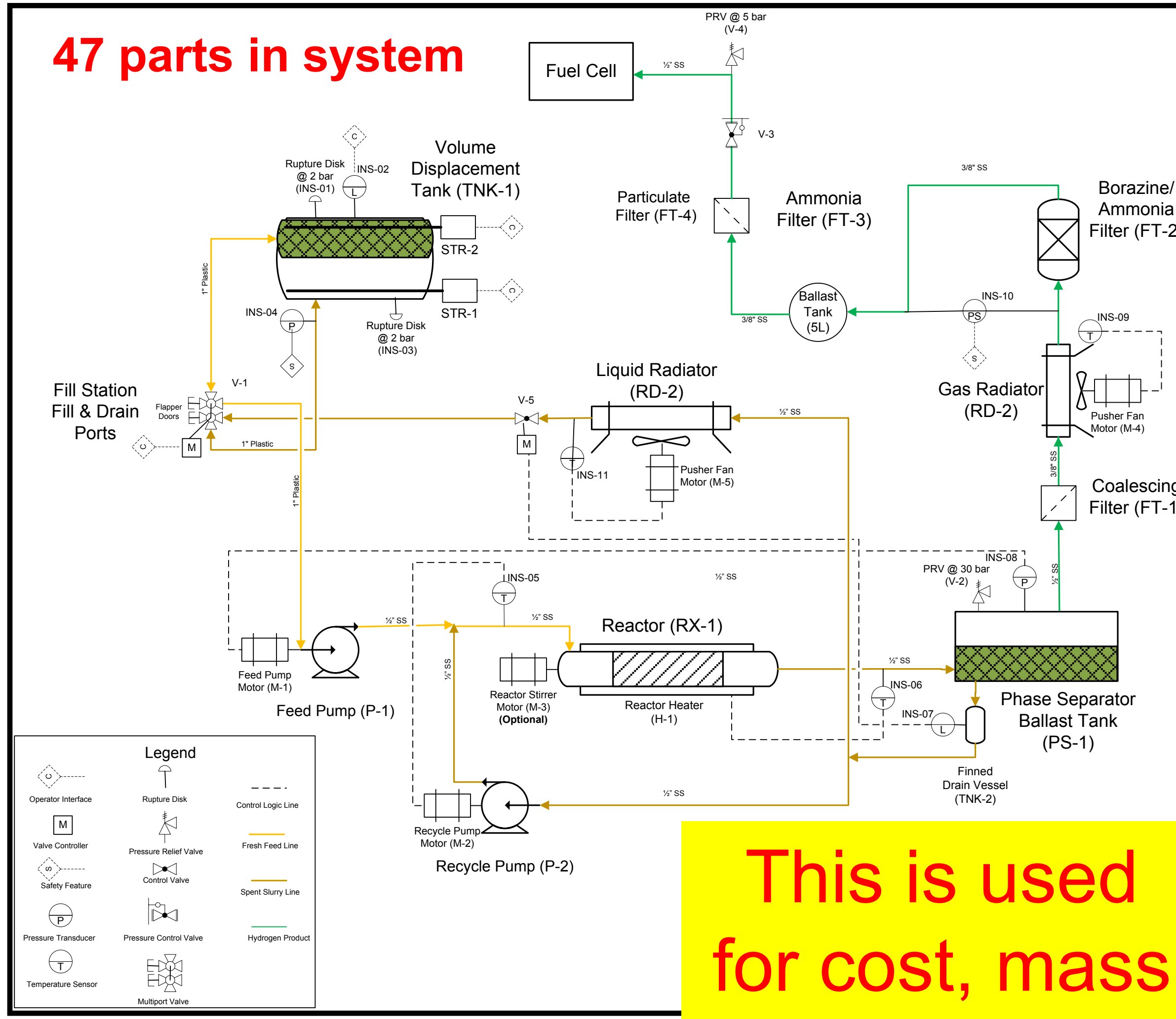
12 parts in system



FY13

Added Instrumentation, Controls, Control Logic, Engineering Improvements

47 parts in system



This is used for cost, mass volume

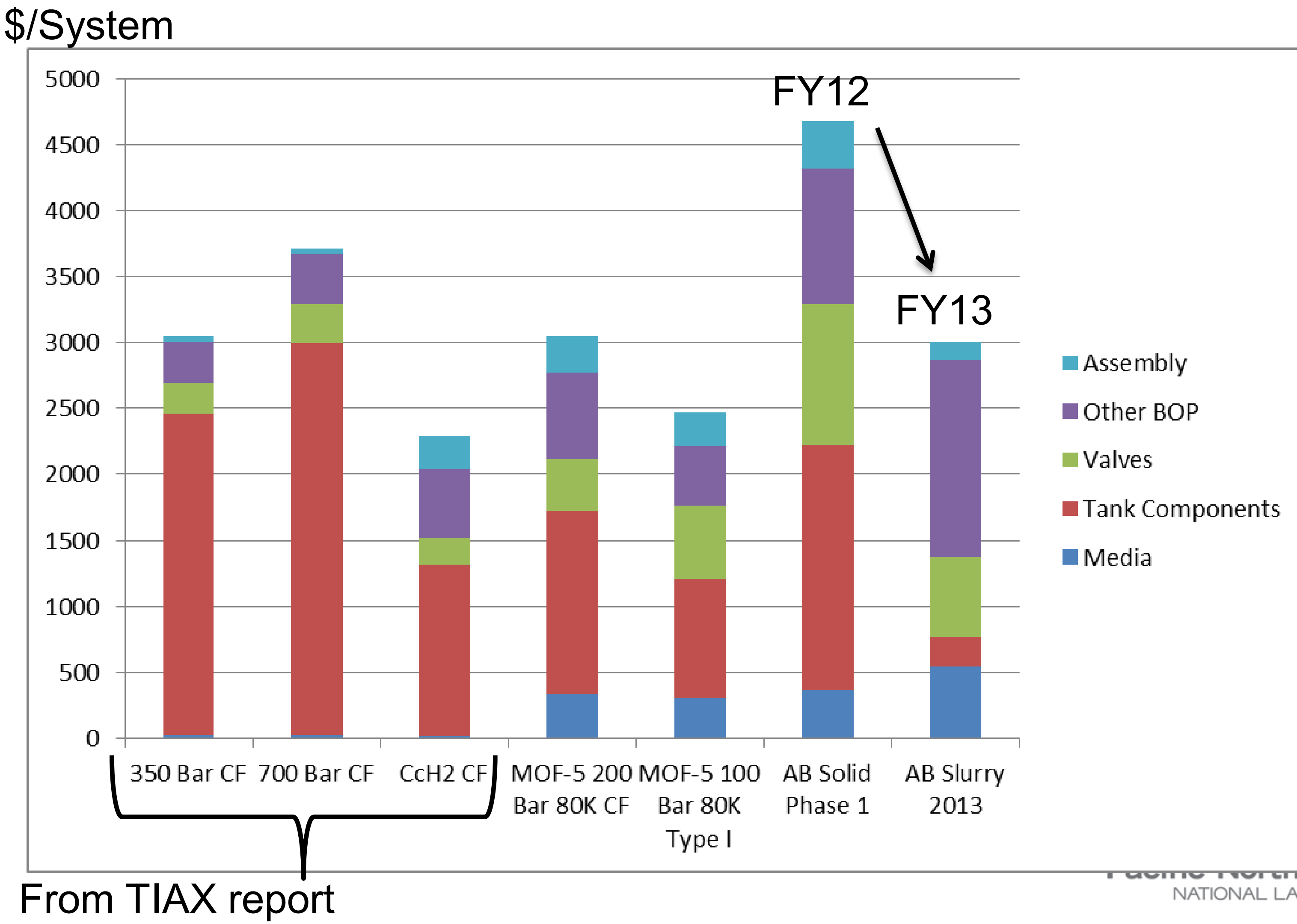
Pacific Northwest NATIONAL LABORATORY

Los Alamos NATIONAL LABORATORY

United Technologies Research Center

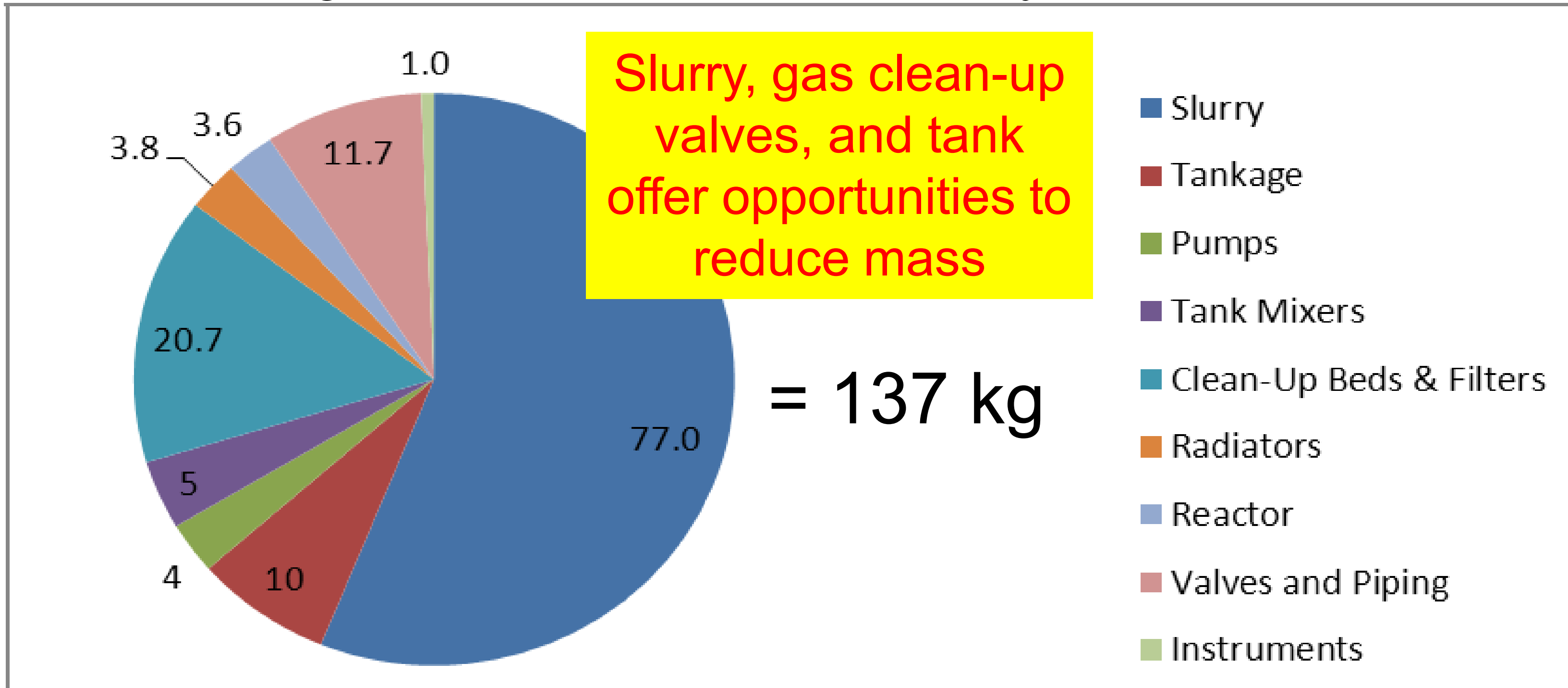
Accomplishment: Chemical Hydrogen Storage Cost

- Tank significantly reduced costs by moving from high pressure carbon fiber tank to low pressure fiberglass tank



Accomplishment: Milestone: System Mass and Volume

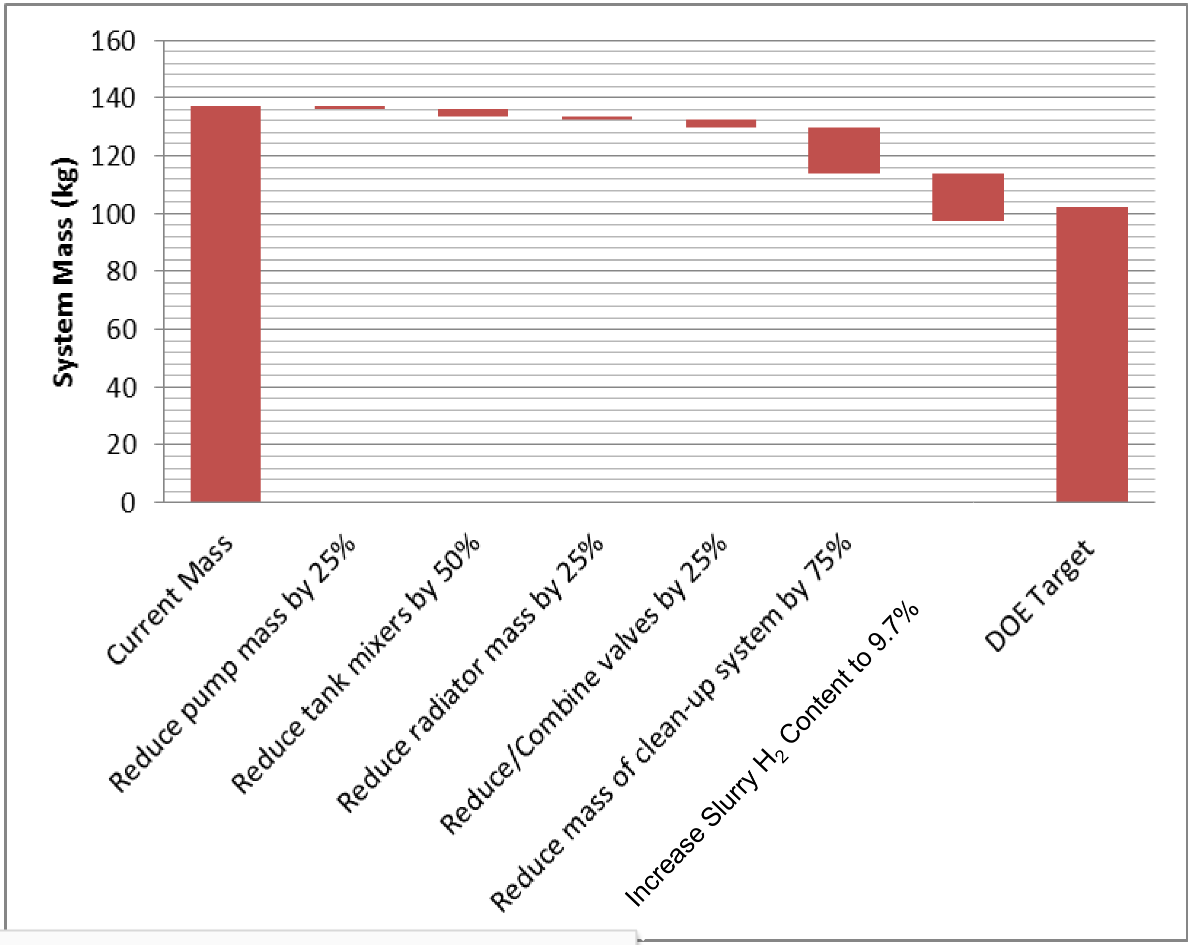
- Purpose
  - Demonstrate SMART Milestone: “Report on ability to identify a system design having . . “
    - mass less than 97 kg
    - volume less than 118 liters
    - meeting the all of the HSECoE drive cycles



Values shown are in kilograms

Smart Milestone: Chemical Hydrogen BoP

Report on ability to identify BoP components (does not include AB slurry) suitable for Chemical Hydrogen system having a mass no more than 41kg and a system volume no more than 57 liters.



Chemical Hydrogen System BoP

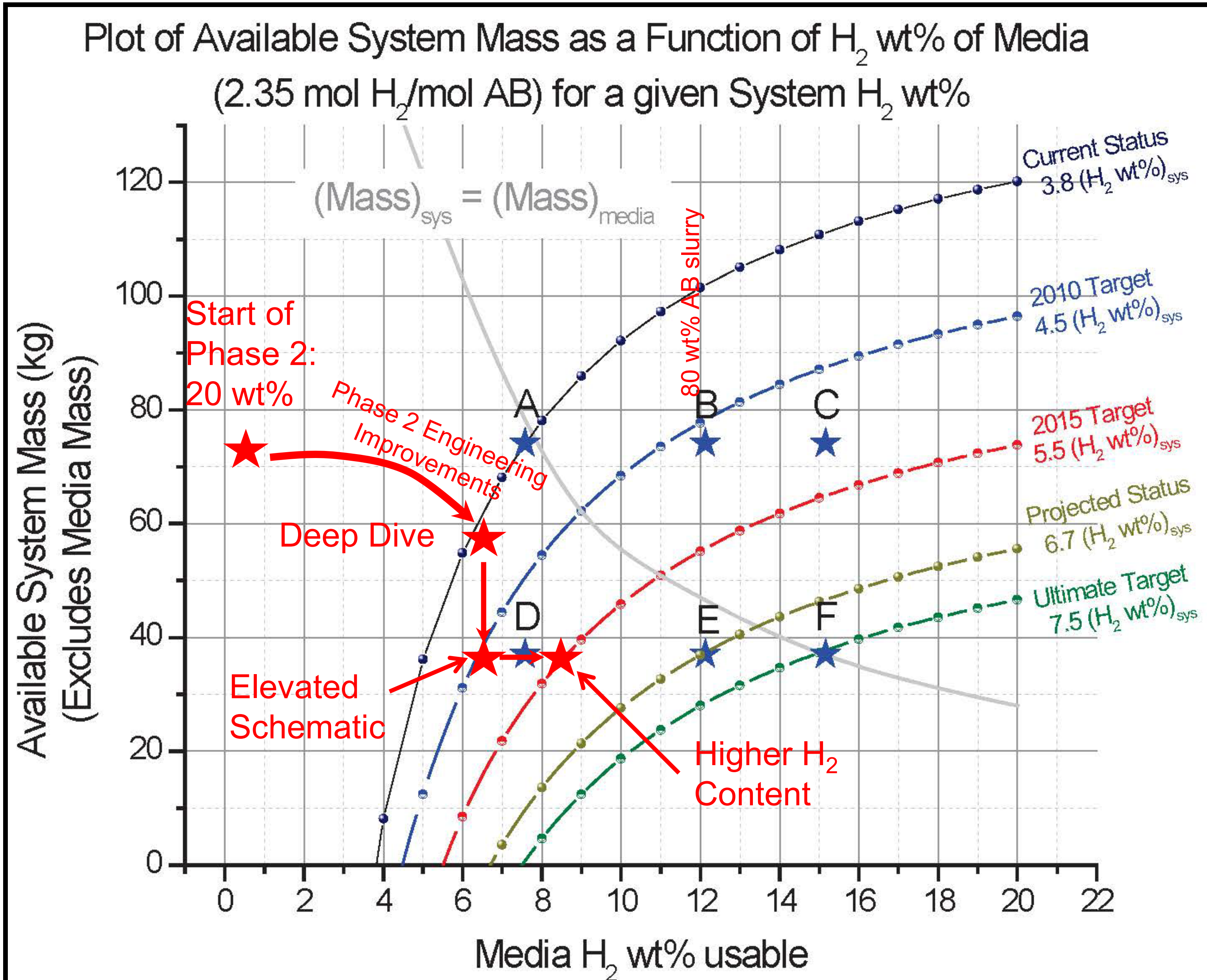
Pathway to meet Milestone Targets Proposed

Current
BOP Mass 53.8 kg
BOP Volume 61.2

Proposed pathway
BOP Mass 38kg
BOP Volume 41L

Pacific Northwest NATIONAL LABORATORY

Accomplishments: Progress in Phase 2



orthwest
AL LABORATORY

Accomplishment: What about Alane?

- Subtractions
  - No clean-up adsorbent beds (-19 kg)
  - No recycle pump (-2 kg)
- Additions
  - Larger volume displacement tank
    - Lower H_2 loading (assuming 50 wt%) (+39 kg)
    - Larger fraction needed for parasitic losses (+10 kg)
  - Larger reactor (+1 kg)
  - Recuperator (+1 kg)
- Net ~ 30 kg heavier for alane
- Other considerations: Easier pumping, easier gas clean-up

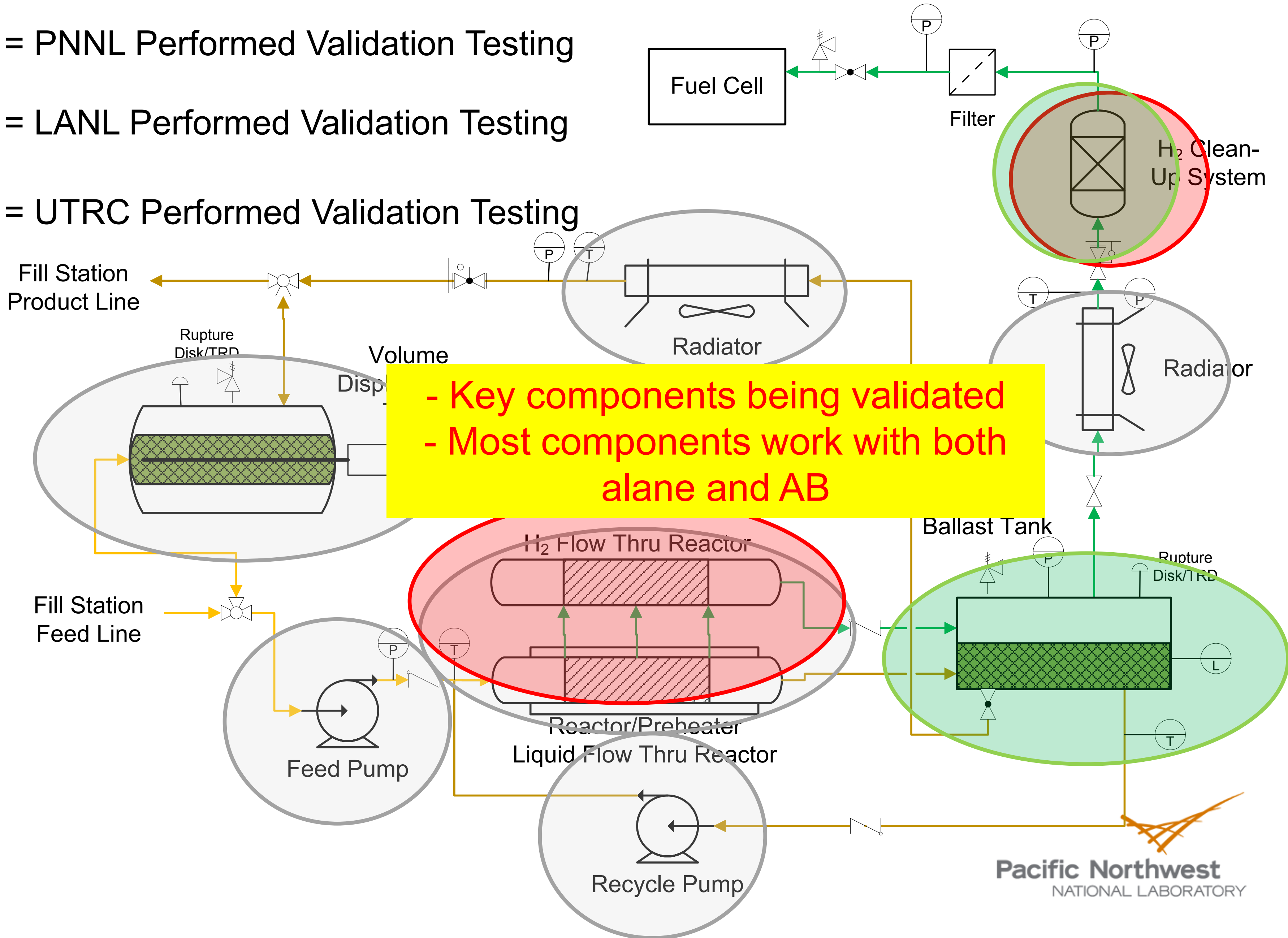
Meeting mass target more difficult with alane

FY13: Component Validation

= PNNL Performed Validation Testing

= LANL Performed Validation Testing

= UTRC Performed Validation Testing

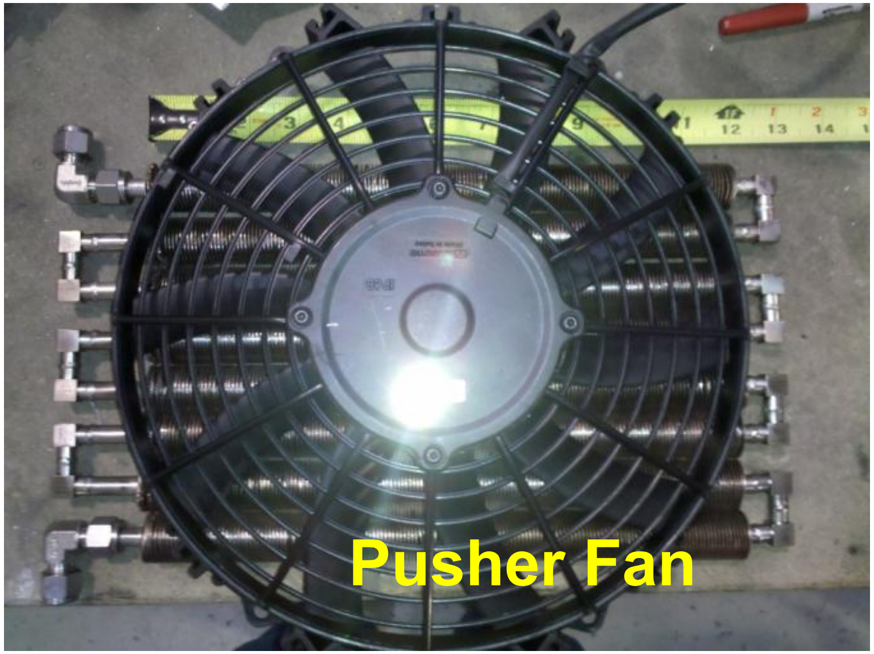


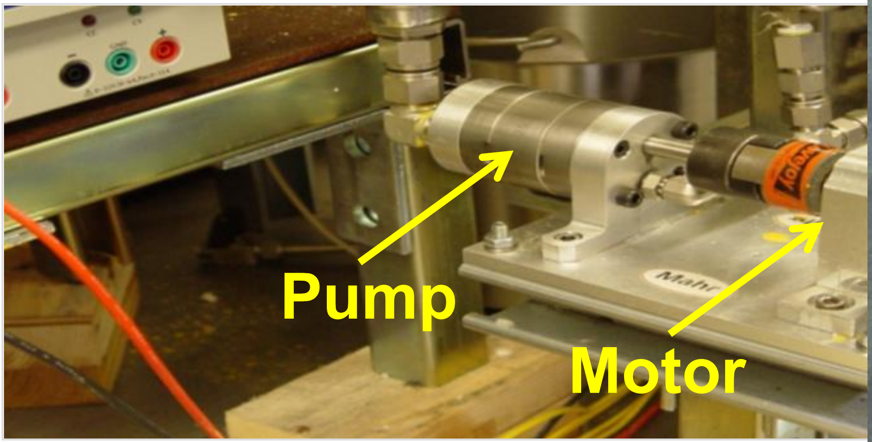
- Key components being validated
- Most components work with both alane and AB

Pacific Northwest NATIONAL LABORATORY

Component Photographs

not shown: 3- way valves and PRV





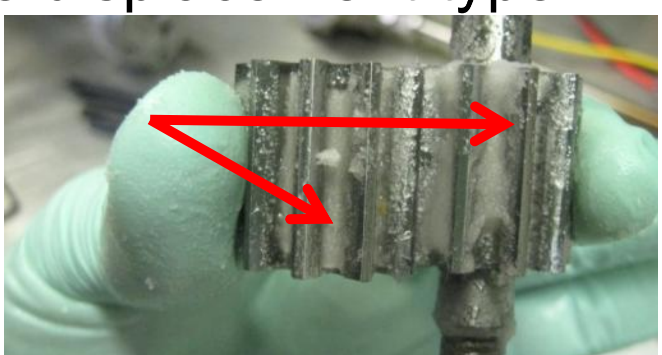
Results of System Flowability Tests

- FY12 FMEA identified as major concern
- Settling Tests
  - Pump had no difficulty pumping any of the simulants after settling
    - Polyimide powder—100 hours settling: Pressure fluctuations associated with slugs of slurry moving through flow restrictions
    - Spent AB—70 hours settling: No increase in start-up load, no pressure fluctuations
  - System disassembly revealed no major slurry issues
    - Some slurry solids deposited in radiator bends with polyethylene slurry after ~14 hours of settling and running: large radius bends recommended
    - Additional tests need to be done
- Cold Start-up Tests
  - Polyethylene simulant flows at -24°C
  - Polyimide flows at -29°C and spent AB at -20°C

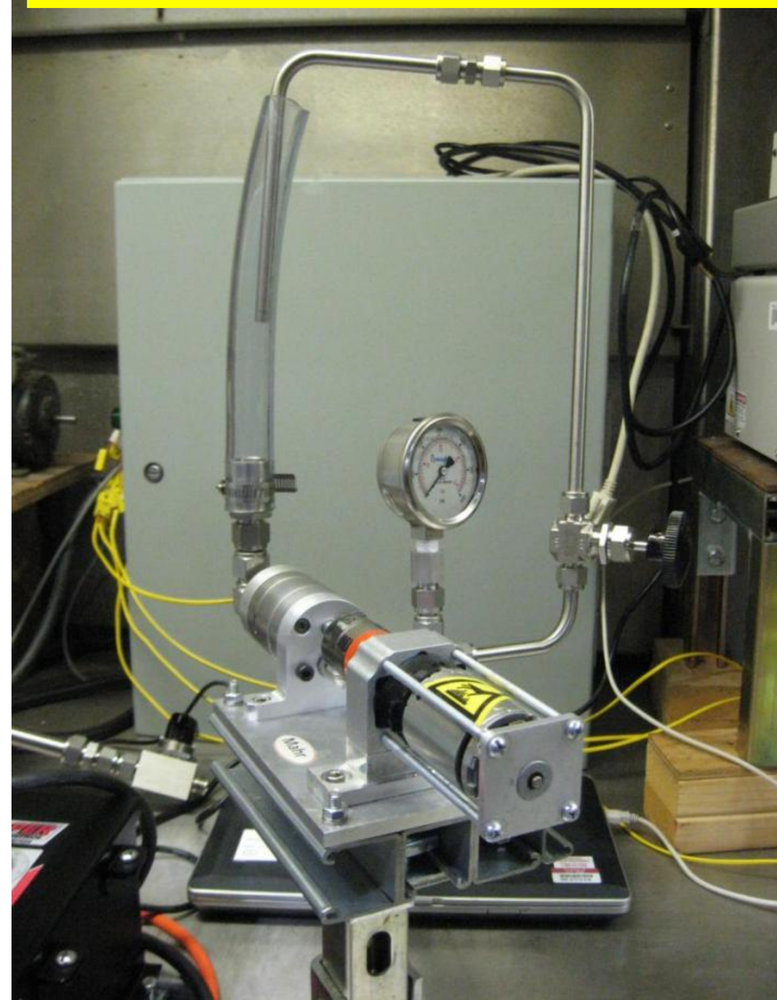
Tests with spent AB and simulants show no immediate show stoppers

Flowability Tests with Fresh AB

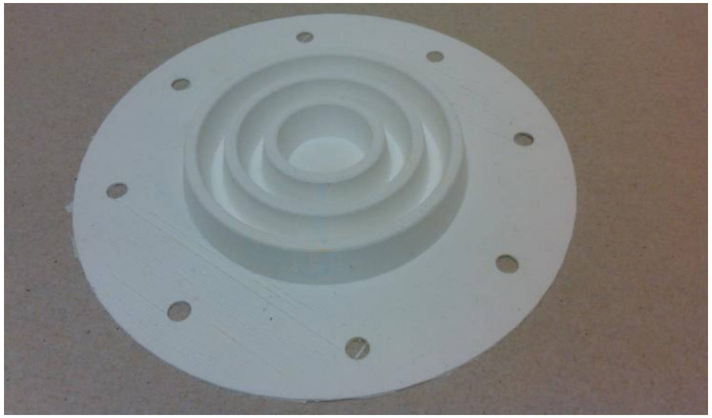
- Approach
  - Tested 50 mL of 20 wt% AB
  - Pumped in a simple loop with 3/8” tubing, pressure gauge and valve
  - Smaller loop required because limited material available
- Results
  - Spent AB- no issues
  - AB formed clogged gears
- Peristaltic pump and syringe
- R&D needed to scale down positive displacement type pumps



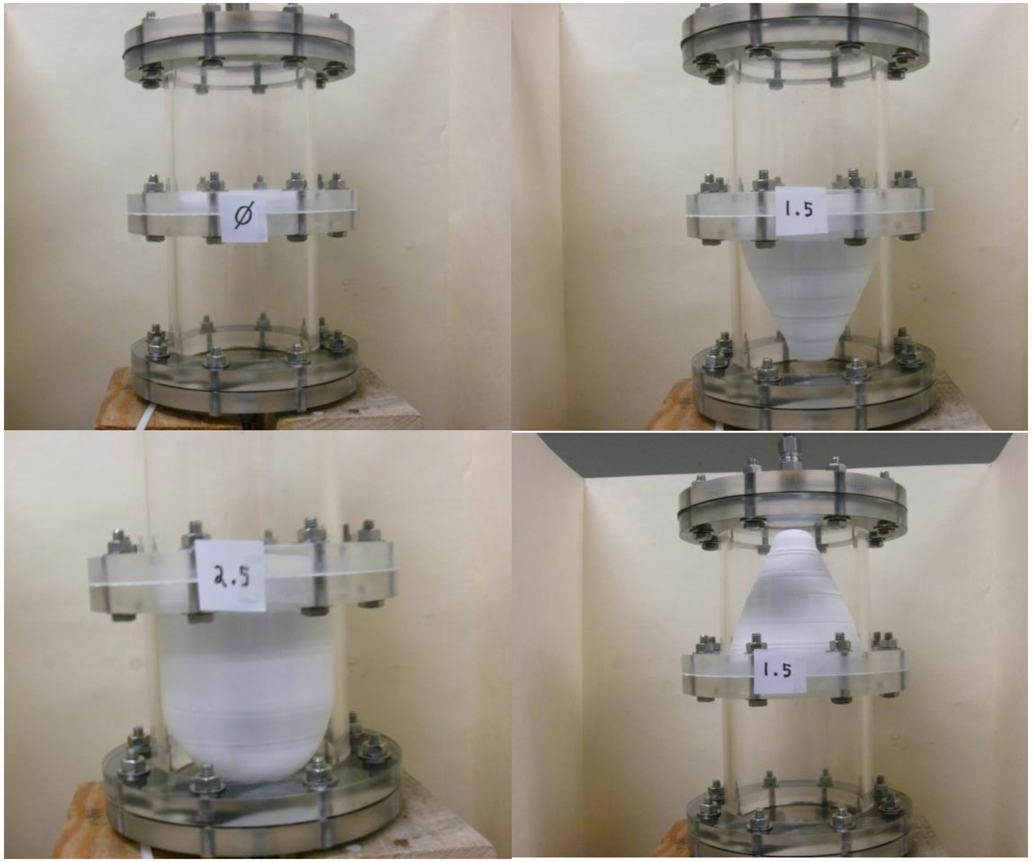
- Peristaltic/ syringe pump okay for Phase III
- Gear pumps clogged
- R&D needed



Accomplishments: Volume Exchange Tank- "Pleated" Membrane

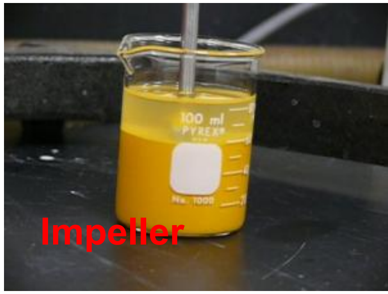


- **Purpose**
  - **Minimize the amount of stretching of the membrane to prolong its life**
  - Allow the use of a wider range of elastomers
  - **Pleated membranes enable conformable tanks**
- **Approach**
  - Fabricated a small scale (4" diameter) membrane with silicone
  - Test with water and air to understand the issues and demonstrate the concept



Accomplishments: Mixing in Volume Displacement Tank

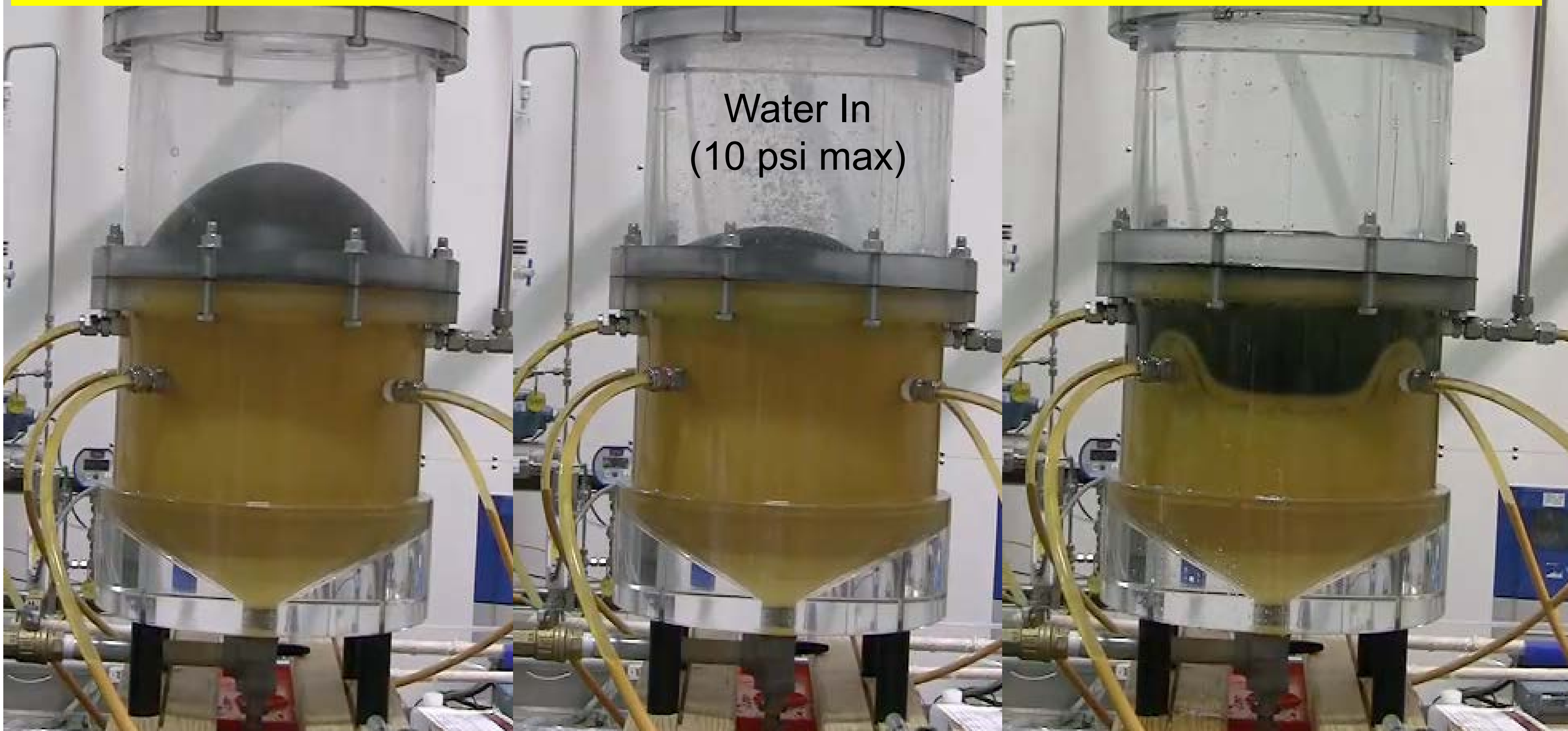
- Scoping Tests Performed
  - Fresh AB/Fresh AB simulant (polyethylene in water/glycerin)
    - Poor Mixing: Ultrasound Testing, vibration
    - **Good Mixing: Mixing with impeller**
    - **Good Mixing: Tea Press Mixing**
  - Spent AB/Spent AB simulant (polyimide in silicone oil)
    - Poor mixing: Ultrasound Testing, vibration, whoopee cushion test
    - Mixed, but had other issues: mixing with impeller, extrusion
    - **Good Mixing: Tea Press Mixing**
    - **Good Mixing: Jet Mixing**



Jet Mixing and Tea Press moved forward to larger scale testing

Accomplishment: Volume Exchange Tank Spent Chemical Hydride Tea Press Test

1.7 minutes to fluidize settled solids and remove 10.9 kg of simulant from tank meeting exchange tank milestone



t = 0

Tea Press
8 strokes
7 kg max force

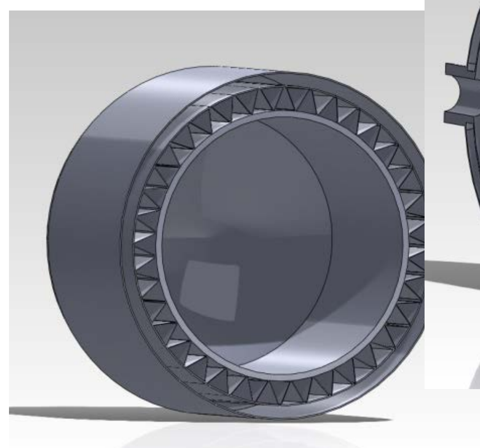
t = 30 sec

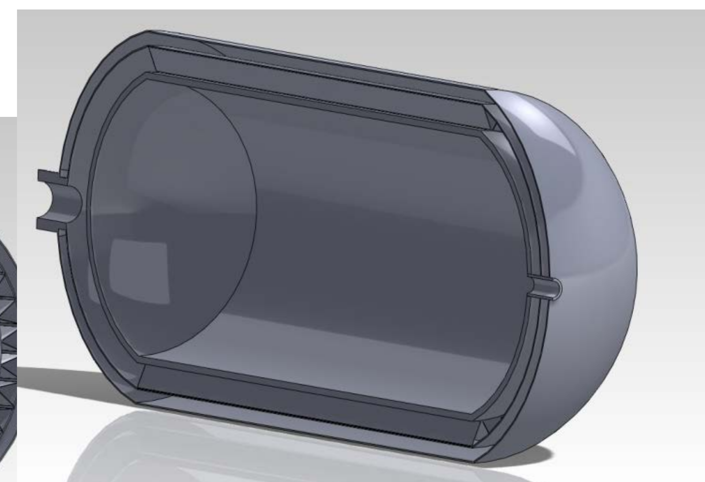
Drain
10.9 kg simulant
35 wt%

t = 100 sec
0.32 kg remaining

Cryo-Adsorbent Hydrogen Storage

- FY12:
  - Exercise “tankinator” model to assess materials and designs
  - Optimize vessel design in terms of cost
  - Assess chemical compatibility of polymer liners for type IV
- FY13
  - Sent tankinator model to SRNL for posting
  - Integrate tankinator model into SRNL model (SRNL complete)
  - Examined tank pressure and types to understand costs
  - Costed135 vessels as function of pressure and temperature (with Hexagon Lincoln and SRNL)
  - Identified welding techniques for use with adsorbents
  - Out selected type IV
  - BoP assessment
  - Thermos bottle design
    - Test in Phase III





Smart Milestone: Cryo-Adsorbent Type IV Vessel Liner

Type IV Cryogenic Pressure Vessel Manufacturing

HEXAGON LINCOLN

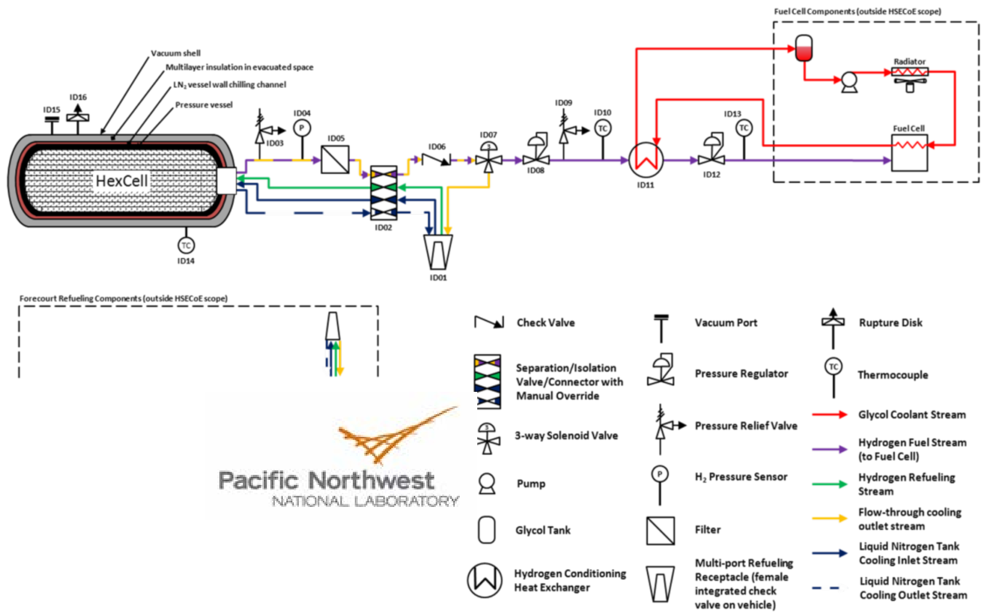
- Report on ability to identify Type IV tank liner materials suitable for 40K operation having a mass less than 8 kg and a volume less than 3 liters (2.55 mm thickness).

Metric not feasible

Evaluated 8 different materials.
2.55 mm liner separates from shell at pressure<35bar
Recommended type I or III vessel

Smart Milestone: Cryo-Adsorbent Balance of Plant

- Report on ability to identify BoP materials (excluding internal HX, external HX, and combustor) suitable for 60 bar cryogenic adsorbent system having mass less than 17 kg and a volume less than 18.5 liters.



100 Bar System

Exceeded Milestone Targets

Total System Mass 159 kg

BoP Components 9.4 kg

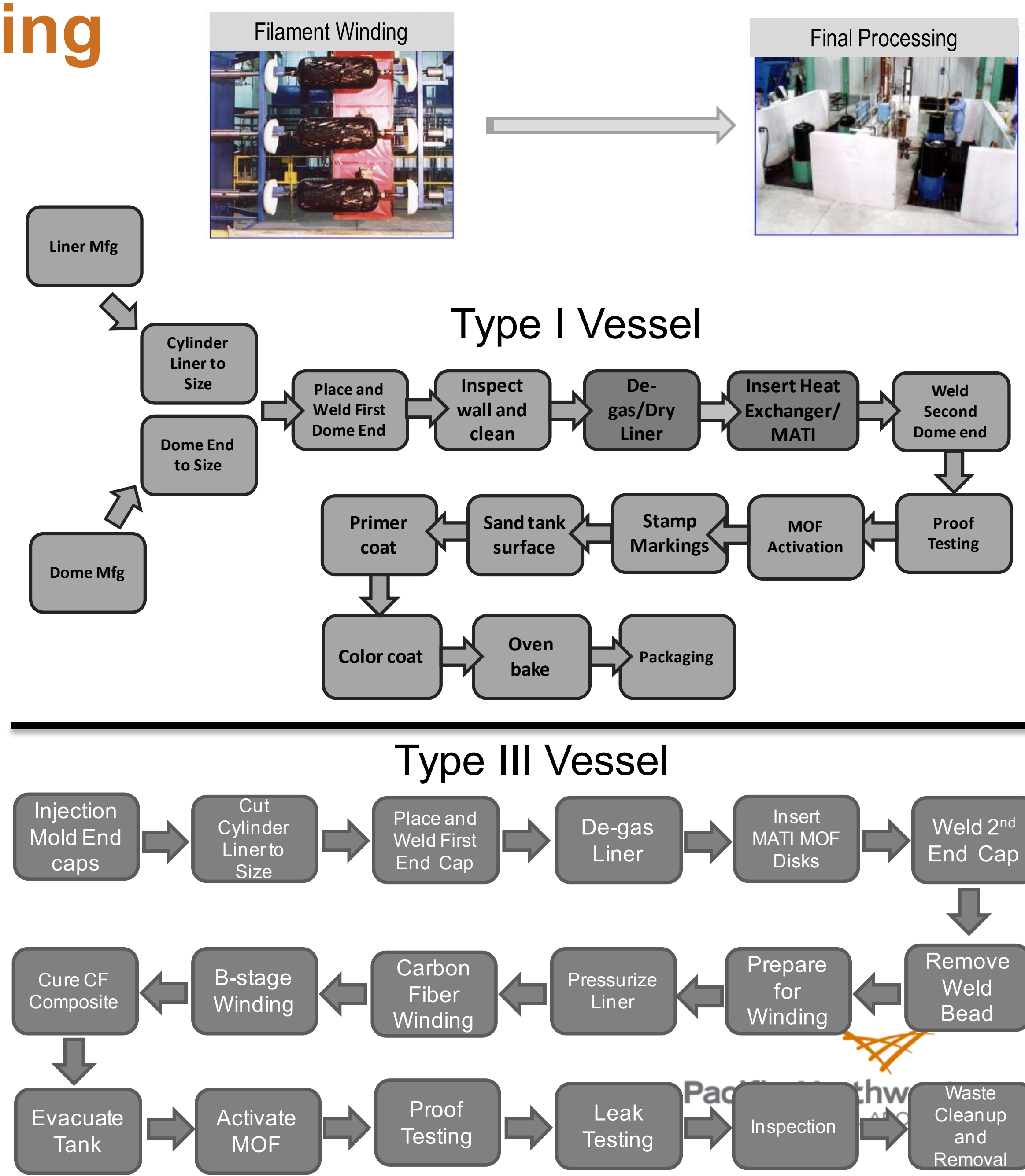
Total System Volume 320 L

BoP Components 11.6 L

Pacific Northwest
NATIONAL LABORATORY

Accomplishments – Cryo-Adsorbent Pressure Vessel Manufacturing

- Developed a Type I & III manufacturing approach
  - Processing conditions
  - Developed manufacturing approach for MATI or heat exchanger insertion
  - Tradeoff study in manufacturing and joining techniques
  - Identified friction stir welding as best technique to minimize temperature effects on MOF and heat treated material

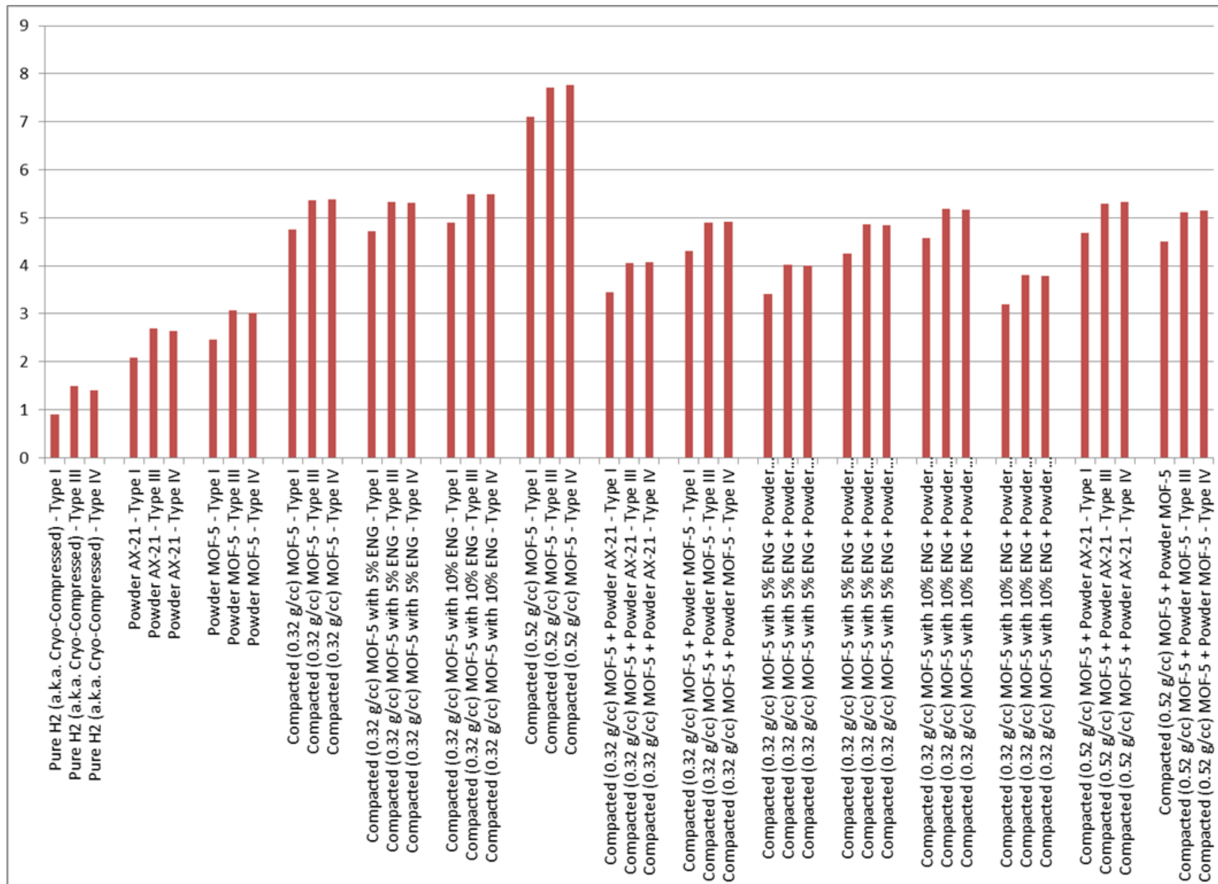


Accomplishments: Costed 135 Cryo-Adsorbent Tank Configurations

- Series of tank evaluations at 60, 80, 100 Bar with appropriate BOP
  - Type I, Type III & Type IV with different media
  - Type III weighs 61% of Type I, but 14% more costly
  - Cost for MOF-5 systems still decreasing at 100 Bar

- **Lowest cost is Type I**
- **Powdered AX-21 - lowest**
- **Powdered MOF-5 next**
- **Significant volume tradeoff**

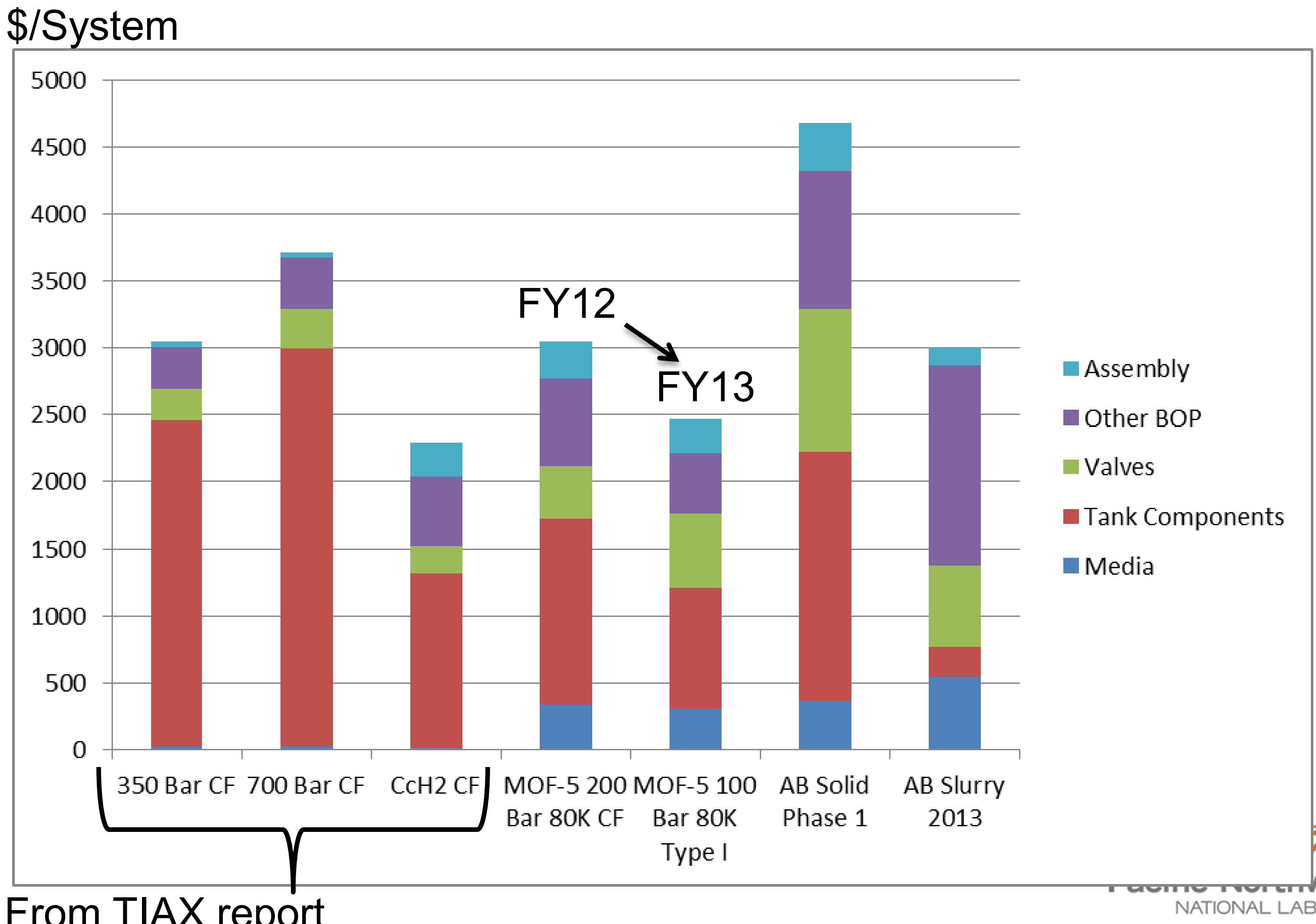
Tradeoff analysis led to choosing 100 Bar Type I MOF-5 system



Pacific Northwest NATIONAL LABORATORY

Accomplishment: Cyro-Adsorbent Hydrogen Storage Cost

- More expensive than CcH2 CF
- Less than previous estimates at 200 Bar



Collaborative Activities

Hydrogen Storage Engineering Center of Excellence	• Hexagon Lincoln - study of CF cost and pressure vessel design modeling • GM - design of structured media bed for MH • Ford – characterization of absorbent materials • UQTR - design and materials characterization of carbon absorbent • OSU - microarchetecture device concept development and thermodynamic analysis • UTRC - develop solutions for H_2 impurities filtering • LANL - AB system design and measure H_2 impurities • NREL - input for tank to wheels analysis and system cost models • SRNL - study AB reactivity and kinetics model development
SSAWG	• Participate in group discussions and analysis
Materials 'Reactivity' Program	• Khalil (UTRC) and Anton (SRNL) - understand reactivity properties of AB • Van Hassel (UTRC) - study impurities in H_2
Independent Analysis	• SA - provide design details for AB refueling cost and feasibility assessment, plus share cost parameters for system cost modeling

Future Work

- Design sub-scale prototype (joint with partners)
  - Exothermic slurry (AB), Exothermic liquid, Endothermic slurry (Alane) to be tested
  - Cryo-adsorbent system design
- Chemical hydrogen
  - AB Slurry production
  - Alane slurry characterization
  - Model verification
    - Compare model to prototype system results
    - Refine model if necessary
  - Materials requirements
- Demonstrate advanced pressure vessel system for dormancy etc. (w/Hexagon Lincoln)
- Elevated design concepts
  - Sorbent: reduce part count by 30%
  - Chemical: reduce part count by 25%
- Refine cost model
  - Update BOP
  - Improve manufacturing estimates

Summary

- **Relevance:**

  Addressing most of the engineering challenges for materials based hydrogen storage for endothermic and exothermic chemical hydrogen and cryo-adsorbents. Providing feedback and recommendations on materials requirements

- **Approach:**

  Developed system models, experimental validation of the models, component validation, sub-scale prototype demonstration, refine models, cost estimates to guide selections.

- **Technical Accomplishments:**

  Developed 45+ wt% slurry, tested major components, demonstrated flow reactor, developed pathway to achieve mass/volume targets for chemical hydrogen, achieved mass/volume targets for adsorbent system, down selected vessel type for adsorbent, cost models

- **Collaborations:**

  Extensive collaboration with all of our partners

- **Proposed future work:**

  Demonstrate sub-scale prototype, reduce part count of proposed full scale systems, validate models, cost analysis.

Technical Back-up Slides

Accomplishments: Chemical Hydrogen Settling/flocculation Observations

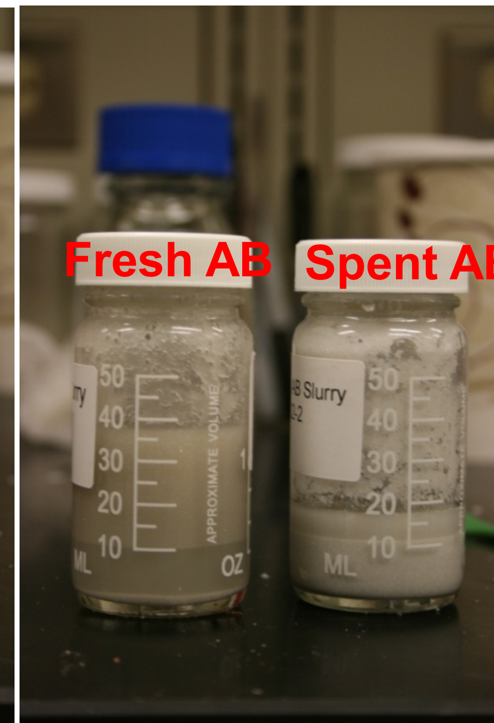
- 45wt% Fresh AB and Spent AB
  - Settling during 3 hours; need to stir to reform slurry

Time	Fresh AB Flocculation	Spent AB Settling
0 min	-	-
5 min	10.4%	21.1%
10 min	21.1.%	26.3%
1h	21.1%	26.3%
2 h	26.3%	36.8%
3 h	26.3%	36.8%
24 h	26.3%	36.8%

Note: % is based on volume change/total volume

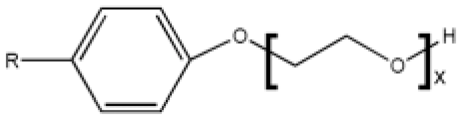
At time zero

After 3 hours



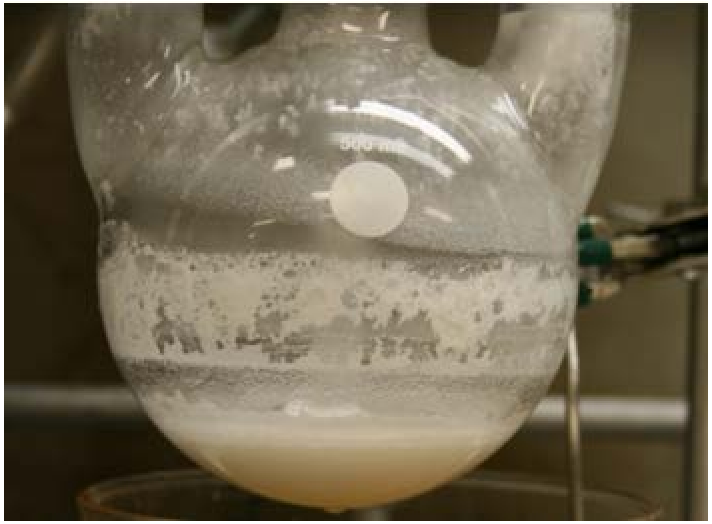
Accomplishments: Chemical Hydrogen Slurry: Additive Screening Dow Triton® Products

- 1-3wt% loading in 35wt% Weylchem AB slurries
- X-15 significantly reduced foaming
  - Kept slurry stable throughout rxn, i.e. no solidification
- X-35 reduced foaming
  - Not as significant as X-15
- X-45 no effect



R = octyl (C8)
x = 1.5 (avg)

Selected Triton® X-15



Slurry AB spent fuel

Pacific Northwest
NATIONAL LABORATORY

SMART Milestone

- Report on ability to develop/identify a radiator/HX capable of cooling the effluent from 525K to 360K (252°C to 87°C) having a mass less than 1.15 kg and a volume less than 10.9 liters.
- Heat Exchanger—1.44 kg and 1.5 liters
- Meet Milestone:
  - Reduce fins from 14/inch to 11/inch—no significant decrease in overall heat transfer (mostly interior limited)

Milestone Can Be Met

Pacific Northwest
NATIONAL LABORATORY

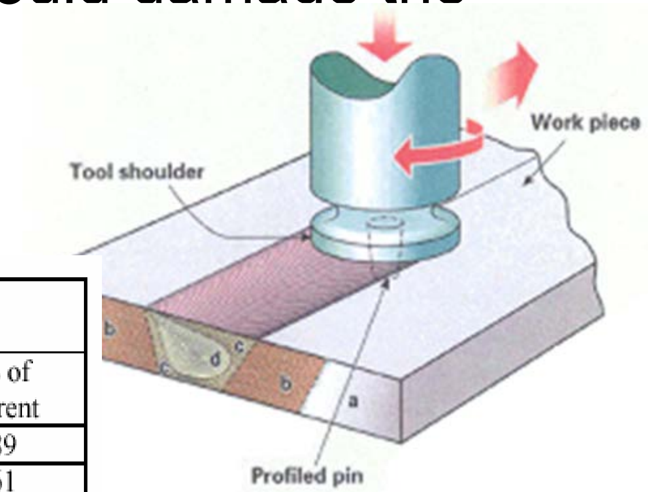
FY13: Validation of the Volume Exchange Tank

- **Milestone:** Report on the feasibility of using a volume exchange tank that provides 5.6 kg of equivalent hydrogen to the process as a homogeneous feed slurry and can be refueled within the DOE target time.
  - Feed shall be on-loaded and product off-loaded in 2.9 minutes (2017 goal for 5.6 kg H_2 equivalent)
  - Volume exchange tank is required to meet DOE gravimetric and volumetric density
  - Develop and demonstrate a robust membrane for the volume exchange tank
  - Demonstrate mixing

Milestone Can Be Met

Cryo-Adsorbent Vessel Manufacturing

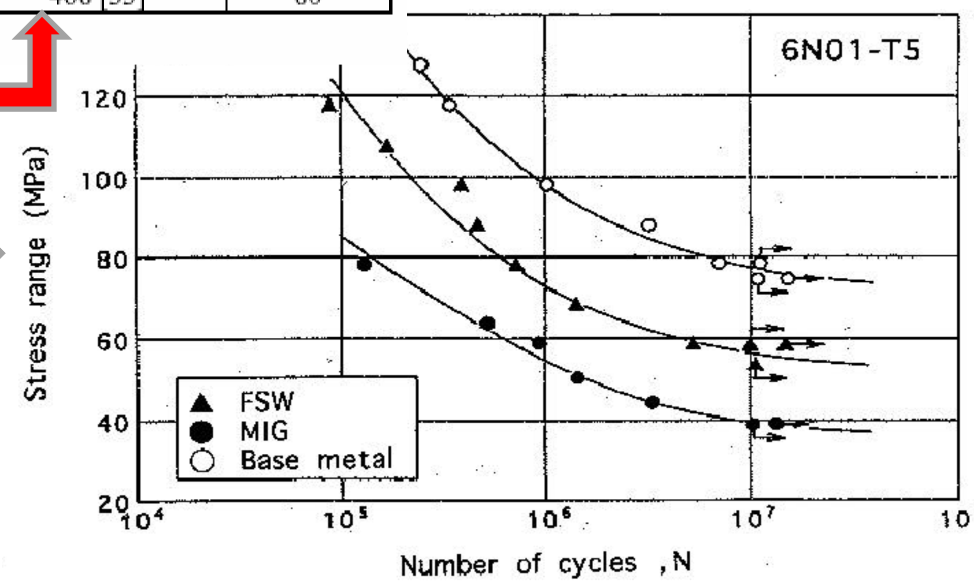
- Challenge: Traditional welding requires heat treatment to release stress. The heat treatment would damage the adsorbent
- Solution: Friction Stir Welding
  - Low temperature



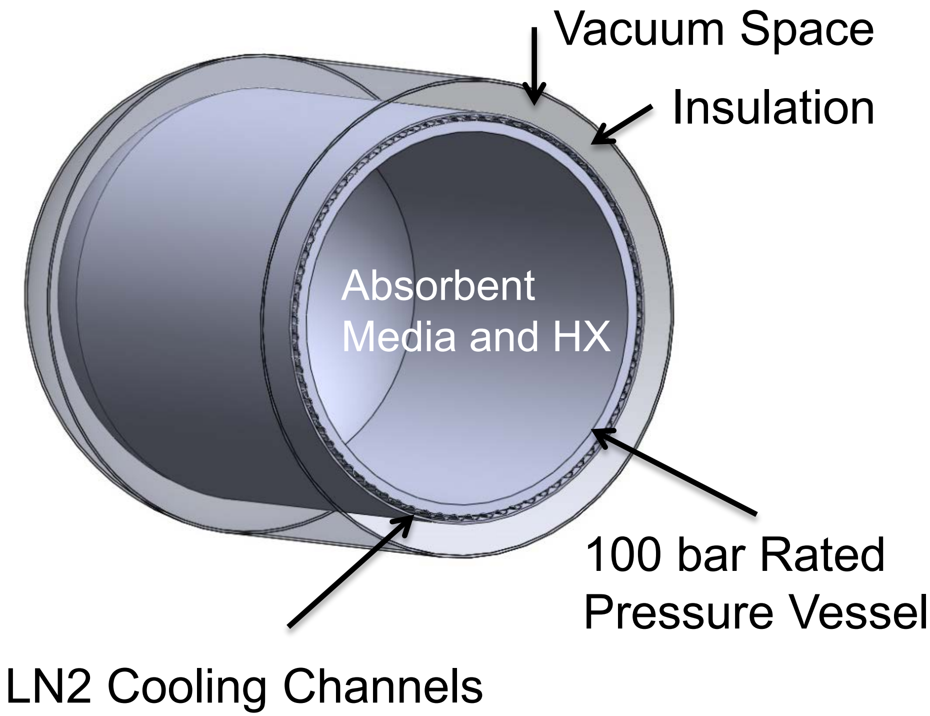
Base Alloy and Temper	Parent Material [30]	Gas-Shielded Arc Welded Butt Joint		Friction Stir Welding	
	Tensile strength (MPa)	Tensile strength (MPa)	% of Parent	Tensile strength (MPa)	% of Parent
2024-T3	485	Non-weldable	-	432 [32]	89
6061-T6	415	207 [35]	50	252 [34]	61
6N01-T5	260	165 [31]	63	200 [31]	77
7075-T6	585	Non-weldable	-	468 [33]	80

High Strength

Good fatigue resistance



Future Plans – Balance of Plant / Cost



- PNNL and Hexagon Lincoln to design and fabricate thermos bottle concept
  - Improved cooling over current designs
  - Uses liquid nitrogen for cooling not cryohydrogen
  - Decreased heat loss for improved dormancy
- Experimental validate pressure vessel cooling
- Experimental validate heat loss with tank design

Pacific Northwest NATIONAL LABORATORY