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Hybrid Sulfur Process Overview

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Energy Security Directorate

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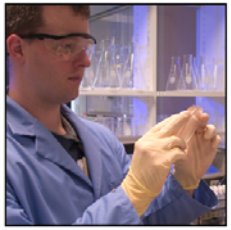
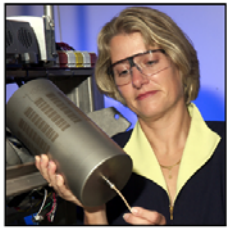
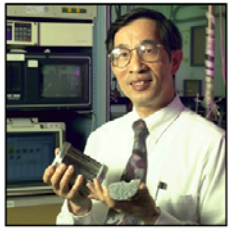

SDE Info Exchange and Workshop, Aiken, SC

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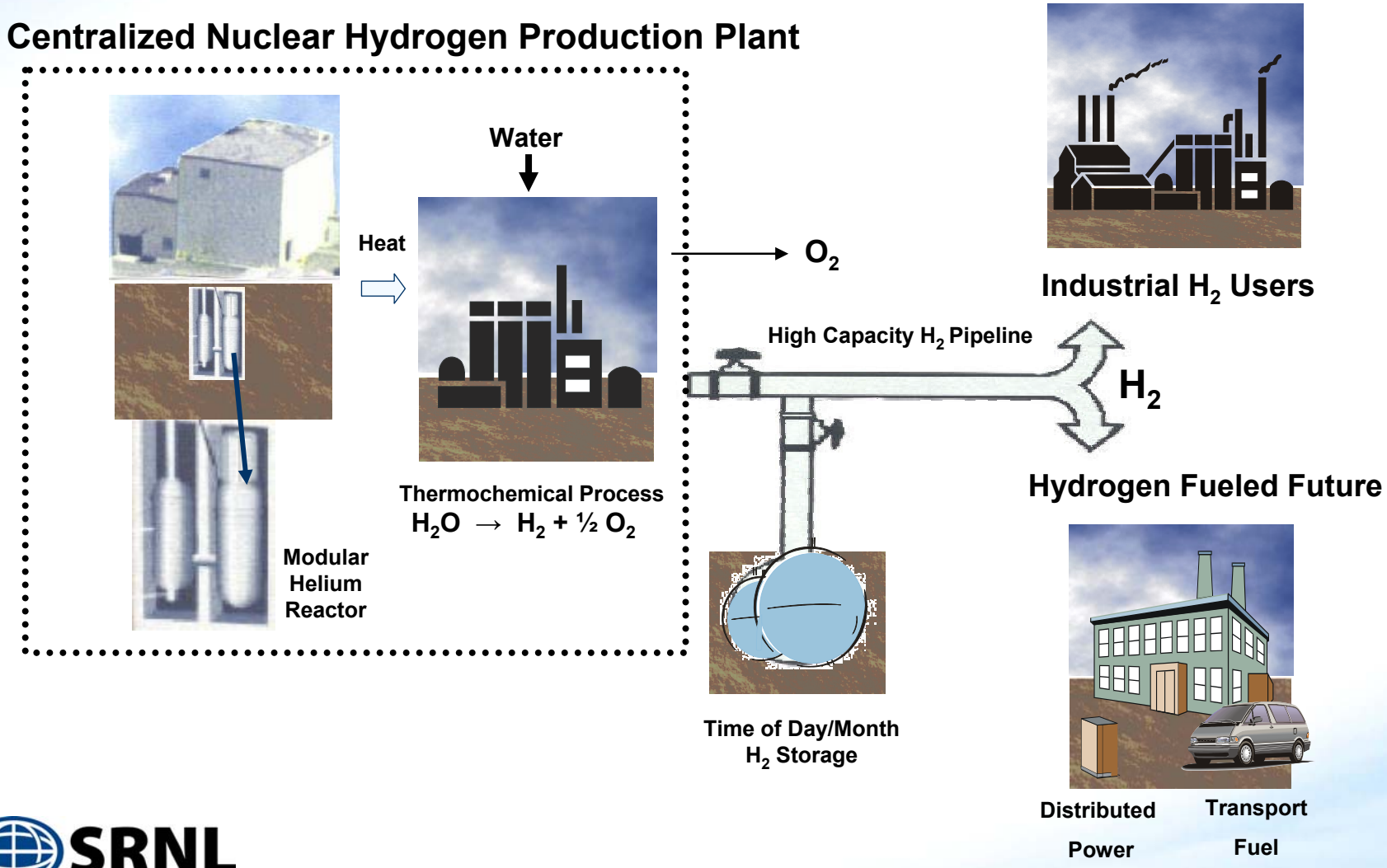
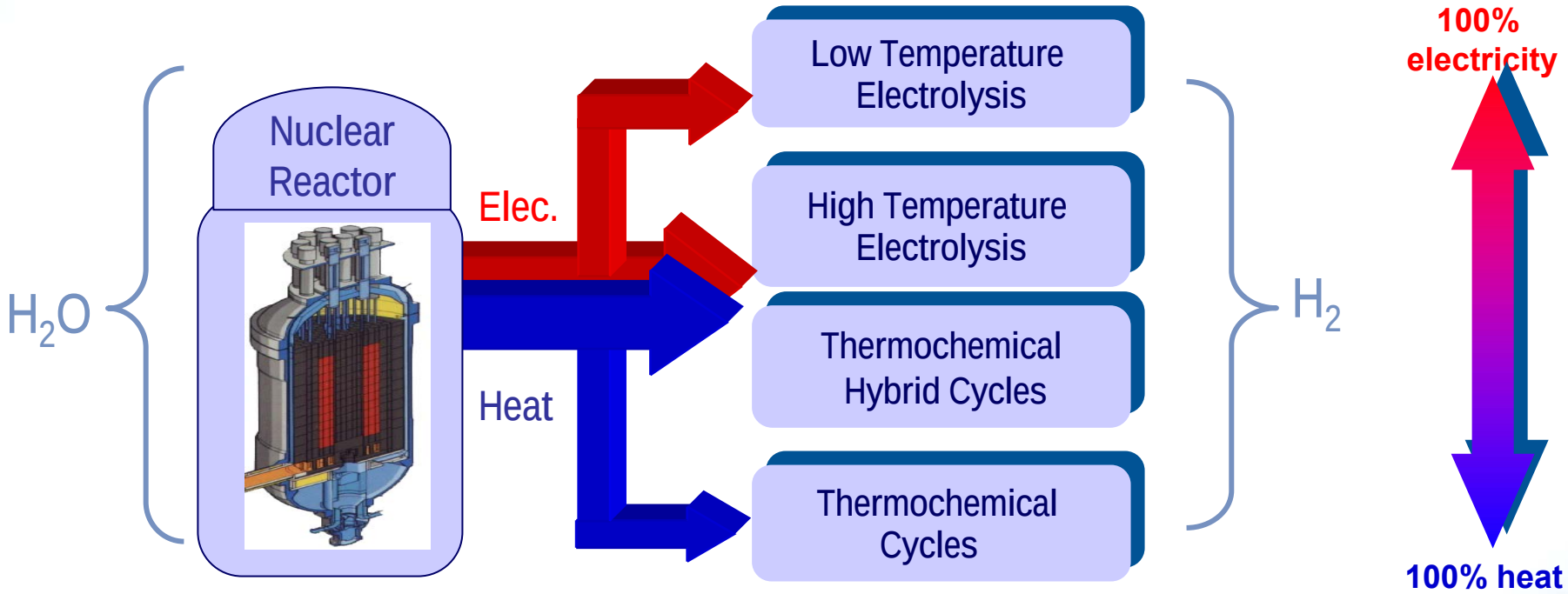
Nuclear Hydrogen Future



DOE Nuclear Hydrogen Initiative

Large quantities of hydrogen can be produced by splitting water through reliable clean power sources, e.g., heat and electricity, generated from nuclear energy systems.

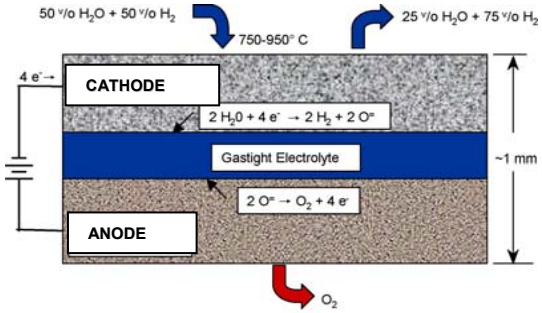


The hydrogen production technologies may also be compatible with centralized solar thermal energy systems

Nuclear Hydrogen Initiative R&D Approach

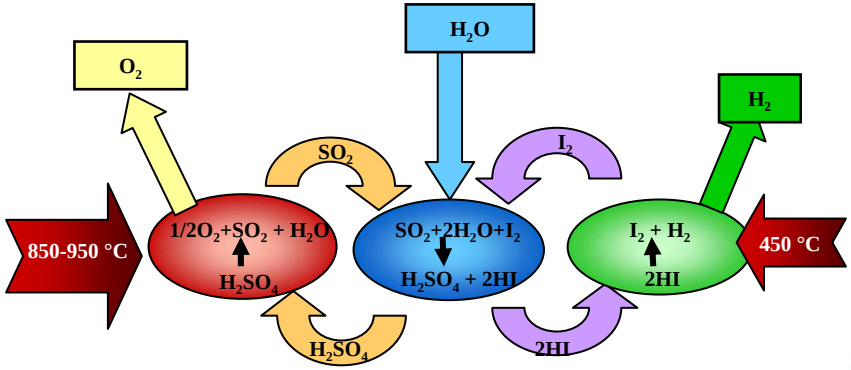
1. High Temperature Electrolysis

- Single, multi-cell stack development and experiments
- Integrated Laboratory-Scale Experiment (ILS) ~15 kW
- Pilot Scale Exp. ~200 kW



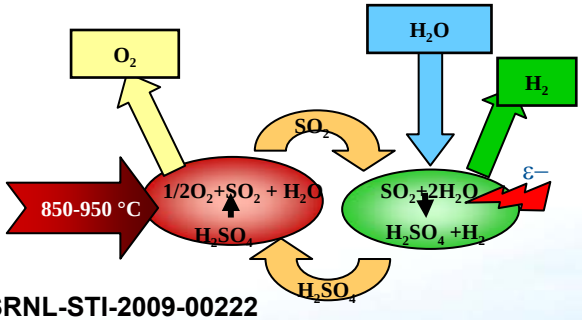
2. Thermochemical Cycles

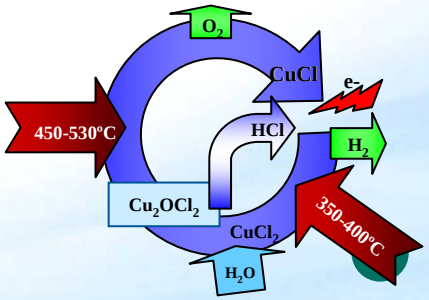
- Validate thermochemical cycles performance potentials and resolve engineering issues
- ILS Experiments ~5-10 kW
- Pilot Scale Exp. ~ 0.5 - 1 MW



3. Supporting & Alternatives Activities

- Enabling technologies development (membranes, catalysts)
- Low temp Cu-Cl cycle





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Thermochemical water-splitting

- Series of coupled chemical reactions – lowers temp needed to thermally dissociate water
- Water consumption only; all intermediates regenerated
- Thermal input only (pure cycles) or thermal plus one or more electrochemical steps (hybrid cycles)
- Extensively studied in 1970s
- Over 3000 potential cycles have been suggested with 115 cycles reported in literature
- Thermodynamics typically dictate high temperature (>800°C)
- Potential for high plant thermal efficiency maximizing conversion of nuclear or solar energy into hydrogen

Technology is still in early stages

High chemical-to-hydrogen weight ratios lead to large recycle flows and equipment sizes

Major design challenges due to corrosive chemicals, impurities, reactant separation, high temperature heat exchange, and high capital costs

Must be scalable to very large capacities (>1000 MW)

Plant must be designed for 40+ years of operation

Currently in lab-scale development stage

Candidate Thermochemical Cycles for Nuclear Reactors

Peak Temperature = 700 – 900 °C

Two processes are current baselines

- **Sulfur-Iodine Cycle (SI)**
- **Hybrid Sulfur Process (HyS)**

Other less-mature cycles under development

- **Calcium Bromine (former Japanese UT-3 cycle)**
- **Copper Chloride (lower temperature)**
- **Various less developed alternative cycles**

Hybrid Sulfur Process (HyS)

The only 2-step, all-fluids thermochemical cycle – based on sulfur oxidation and reduction; only S-H-O compounds

$$SO_2 + 2\,H_2O \rightarrow H_2SO_4 + H_2 \qquad (1)$$

(electrochemical; 80-120 °C)

$$H_2SO_4 \leftrightarrow H_2O + SO_2 + \tfrac{1}{2}\,O_2 \qquad (2)$$

(thermochemical; 800-900 °C)

Net Reaction: $H_2O \rightarrow H_2 + \tfrac{1}{2}\,O_2$ (3)

HyS Process History

Patent for "Sulfur Cycle" issued to Westinghouse Electric Corporation	1975
Two-compartment Diaphragm Cell Built	1977
Closed-loop Process Demonstration by (W)	1978
Solar-driven Process Design Completed by (W)	1983
Development "Hiatus"	1984-2003
New Process Design work by (W)	2004
Updated Conceptual Design of HyS by SRNL	2005
Proof-of-Concept for PEM-based SDE*	2005
Pressurized, Elevated Temperature SDE Testing	2006
Continuous 100-hour Longevity Test	2007
Testing of 100 lph H_2 Multi-cell Stack	2008

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* SO2-Depolarized Electrolyzer

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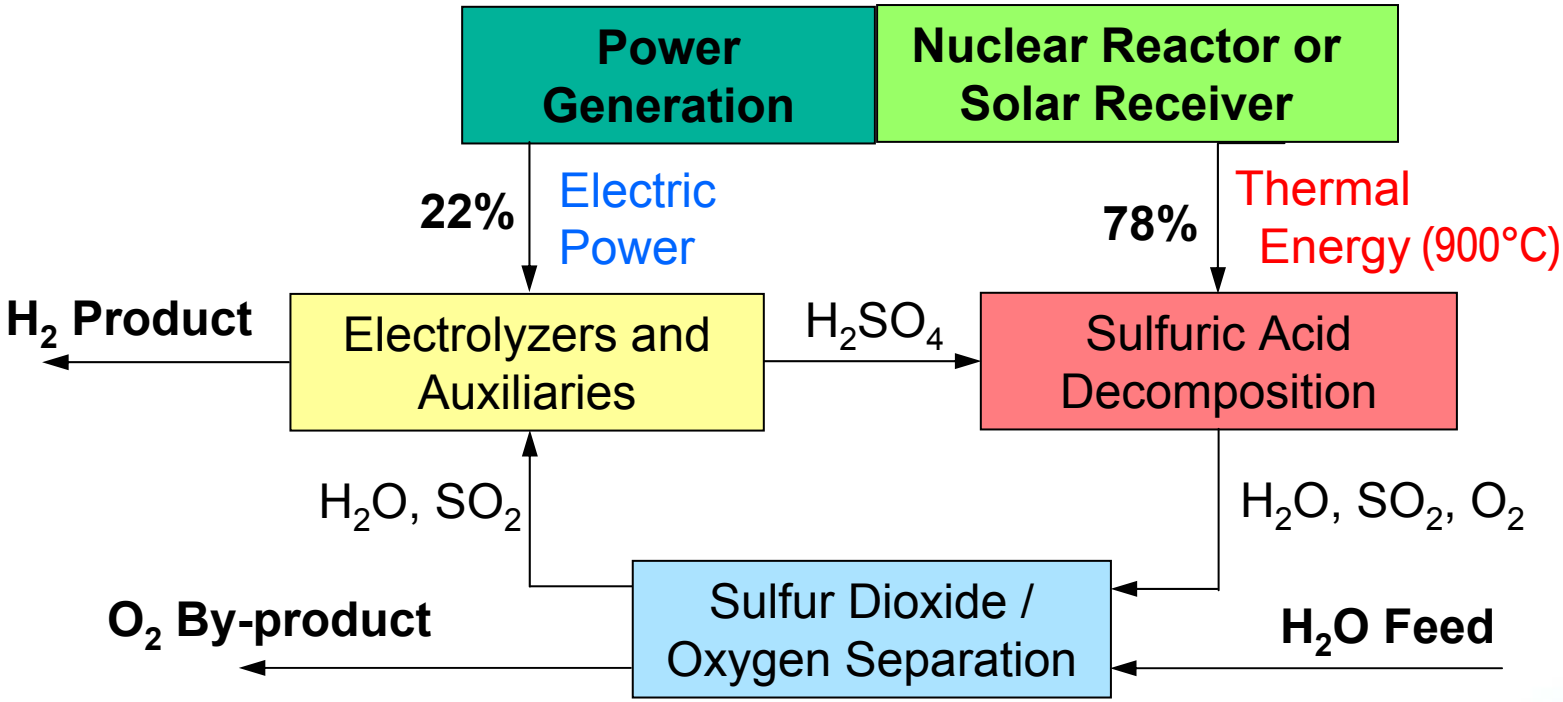
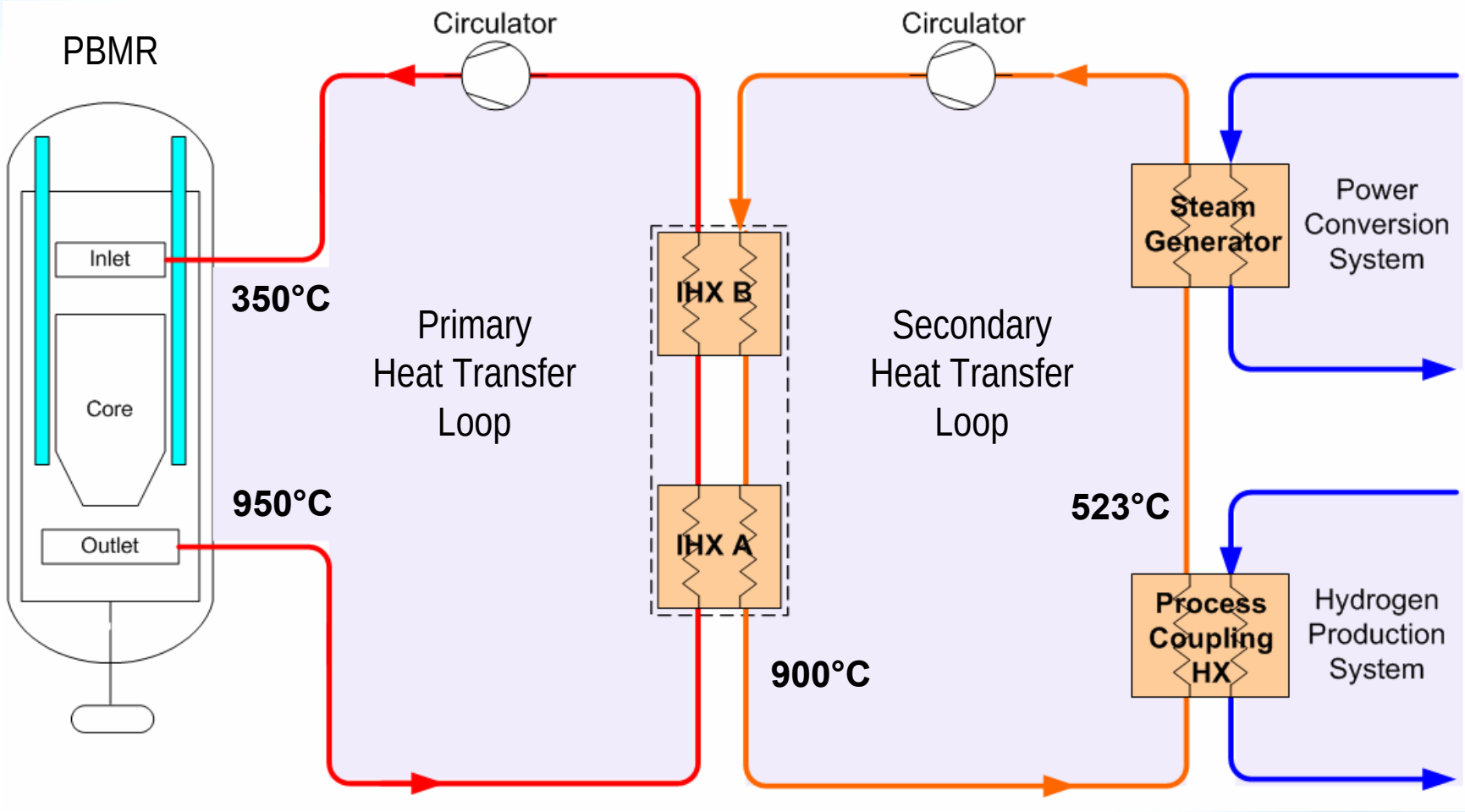
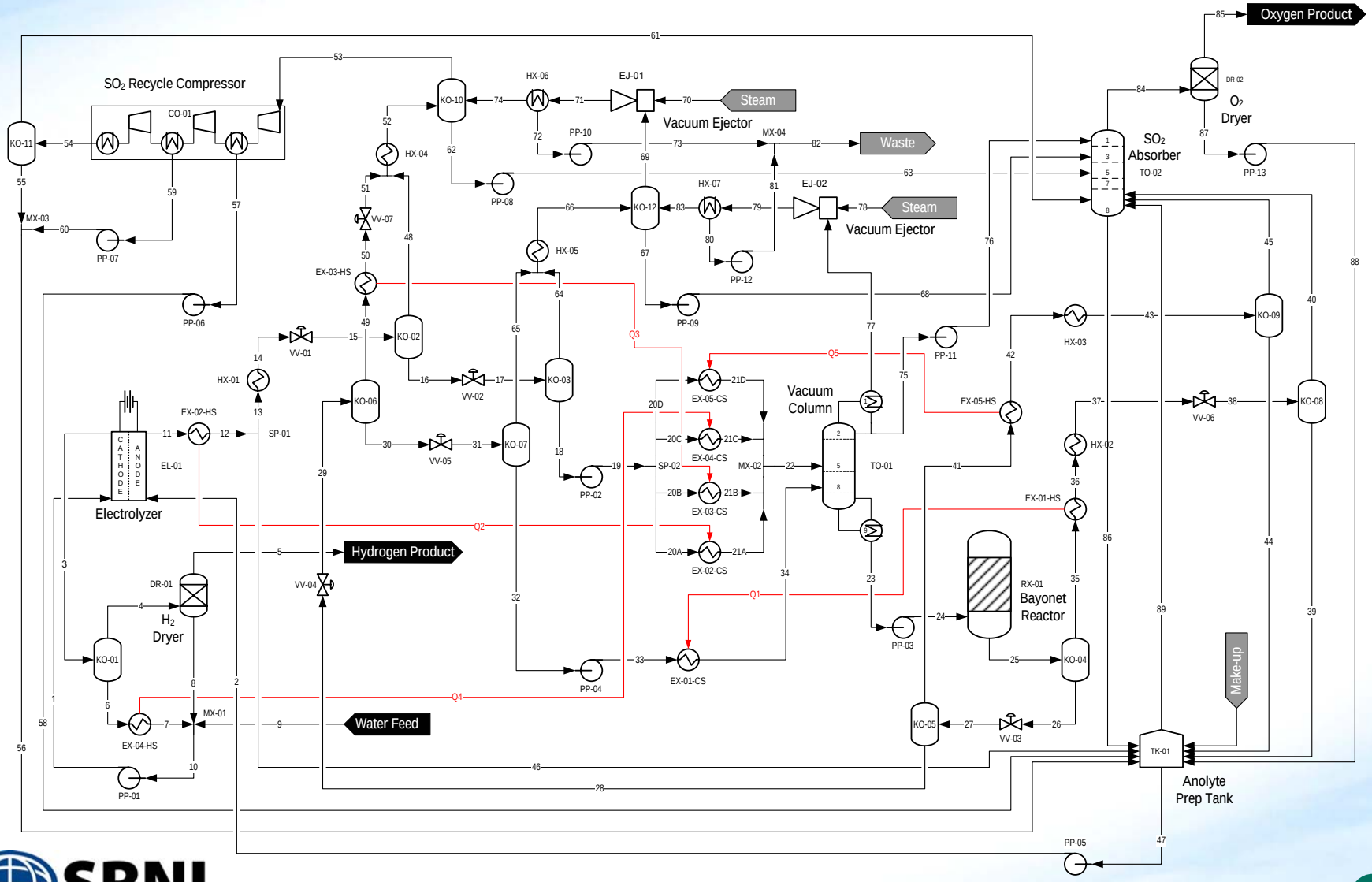
HyS Process Simplified Flowsheet



Integration of HyS with a Nuclear Heat Source



Detailed Flowsheets and Process Analyses have been developed



Nuclear Hydrogen Plant Design and Cost Study

Key design improvements:

Optimized heat integration between reactor, hydrogen plant and bottoming cycle

Improved thermal efficiency for HyS thru pinch analysis

Increased hydrogen production per PBMR by over 150%

Overall process efficiency = 37% (over 40% more H2 than conventional reactor+elect.)

Capital costs and cost of hydrogen estimated w/H2A; Baseline = $5.34/kg with range of $4.15 - $7.10/kg

HyS Process can also be coupled with solar reciever

Central Receiver Test Facility at Sandia National Lab

Test Facility Capabilities at SNL Test Facility

- 5 MW total thermal power
- Peak flux to 260 w/cm^2
- Illumination of target areas to 2,800 m^2
- Successfully demonstrated falling particle receiver operation
- Could be used for HyS demonstration plant

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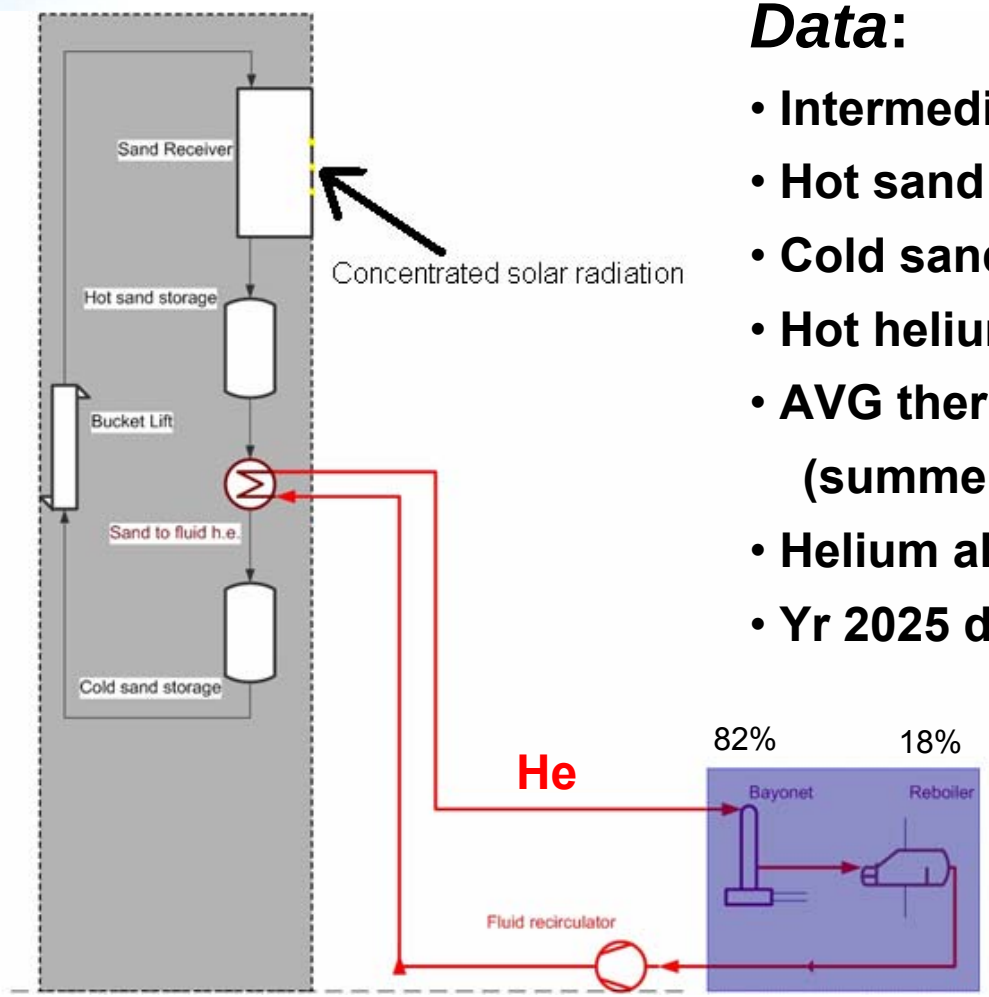
Solar tower matching



***Data*:**

- **Intermediate fluid** **He**
- **Hot sand storage** **~1000 C**
- **Cold sand storage** **~600 C**
- **Hot helium** **950 C**
- **AVG thermal power** **329 MW**
  (summer solstice)
- **Helium also provides reboiler heat**
- **Yr 2025 design eliminates He loop**

SO_2-Depolarized Electrolysis (SDE)

- Uses sulfur dioxide to depolarize the anode of a water electrolyzer and lower cell voltage (Standard Cell Potential reduced from 1.23 V to 0.158 V)
- Produces sulfuric acid rather than oxygen at the anode; requires high temperature acid decomposition step to regenerate the SO_2 and release oxygen
- At practical conditions, electricity required per unit of hydrogen is reduced by up to 70% vs. water electrolysis
- Economical design requires <u>low cell voltage</u> and <u>high current density</u>; goal set at 600 mV at 500 mA per cm2
- Offer potential to leverage large investments and technical advances for proton-exchange-membrane (PEM) fuel cells

SO_2-Depolarized Electrolyzer Cell Potential

SDE half-cell reactions:

Anode: $2\ H_2O(l) + SO_2(aq) \rightarrow H_2SO_4(aq) + 2\ H^+ + 2\ e^-$

Cathode: $2\ H^+ + 2\ e^- \rightarrow H_2(g)$

Overall: $2\ H_2O(l) + SO_2(aq) \rightarrow H_2SO_4(aq) + H_2(g)$

Standard cell potential: $E° = -0.158$ V at 25°C

= -0.173 V in 30% H_2SO_4
= -0.262 V in 50% H_2SO_4

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Electrolyzer Development Approach

- Select electrolyzer design approach meeting goals and performance targets (**PEM-type cell selected**)
- Conduct **Component Development** tasks to identify membrane, electrocatalysts and other key cell features, including materials and operating conditions. Verify in small-scale electrolyzer.
- Build and operate **test facilities at prototypical T&P**
- Use versatile **single cell electrolyzer** (60-cm^2 active area) for proof-of-concept tests leading to long-term lifetime tests
- Scale-up to **multi-cell stacks** and larger cell sizes
- Work with partners on **alternative approaches** (e.g. gap cell)
- Demonstrate **Integrated Lab-Scale Experiment** with Bayonet Acid Decomposer (developed by SNL for S-I project)

Reduction of Sulfur Deposition is a Key Technical Objective

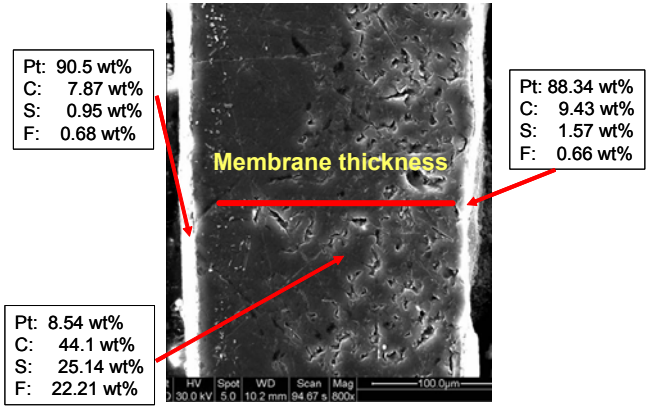
SO_2 can diffuse thru PEM

Reduction at cathode can result in S deposits

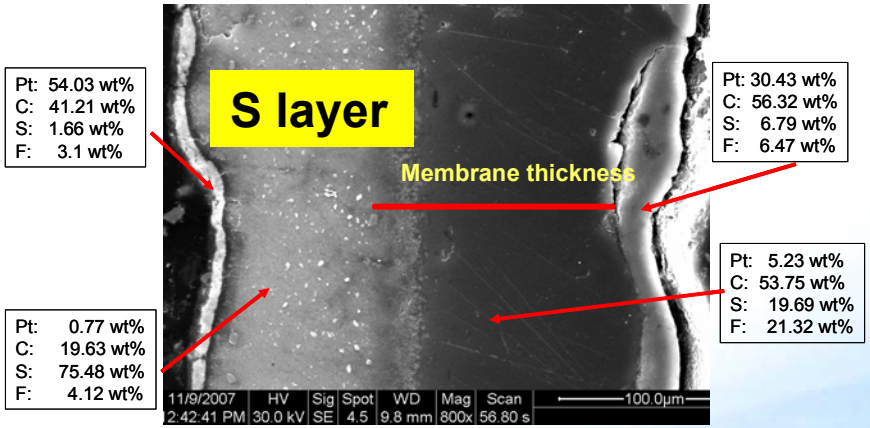
Certain designs and operating conditions avoid deposits

Multiple approaches

- **Modify membrane & catalyst**
- **Modify operating conditions**
- **Alternative cell design**



MEA 9, N117 with Pt black catalyst



MEA 20, N115 with Pt/C catalyst

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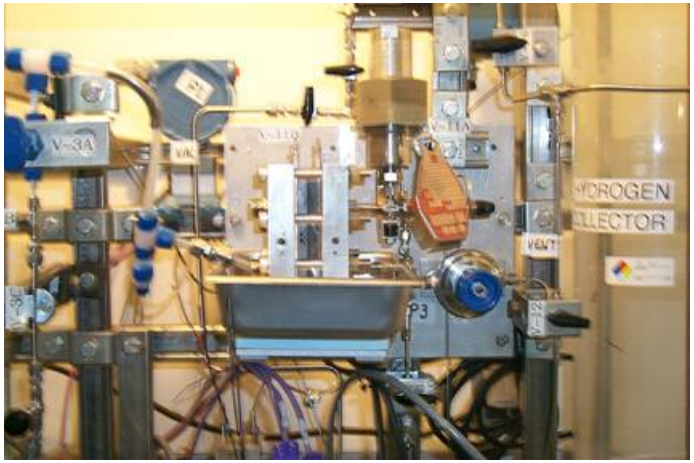
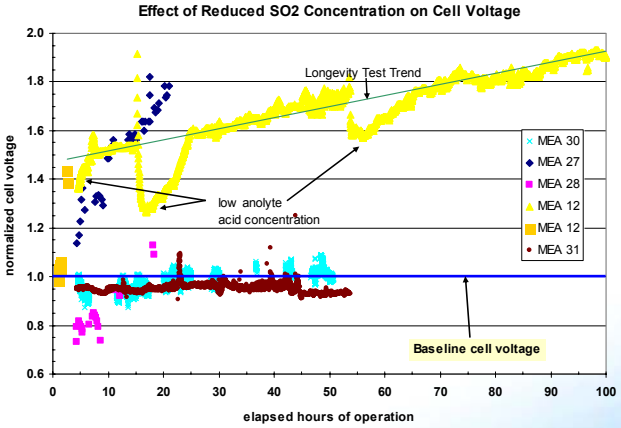
Recent progress on preventing sulfur crossover

- **Developed new method of operating cell in SO_2-limited condition to prevent S crossover**
- **Completed 50 hour test run with no indication of sulfur**
- **Other qualitative measures also indicated reduced sulfur at cathode**
- **Test facility being modified for unattended operation to permit long-term testing**
- **Major step in SDE development**



Single Cell Electrolyzer (60 cm^2 active area)



SO_2-limited Cell Operation

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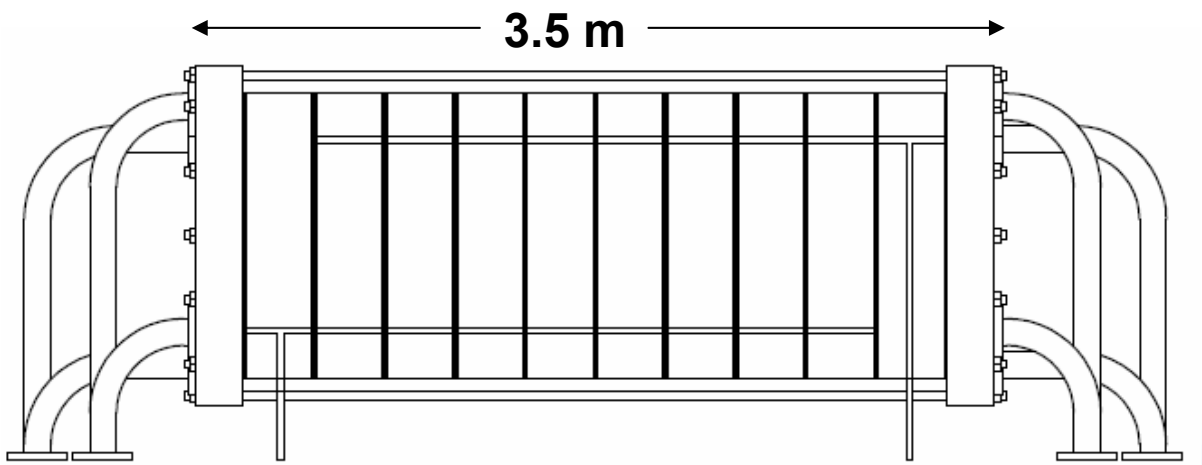
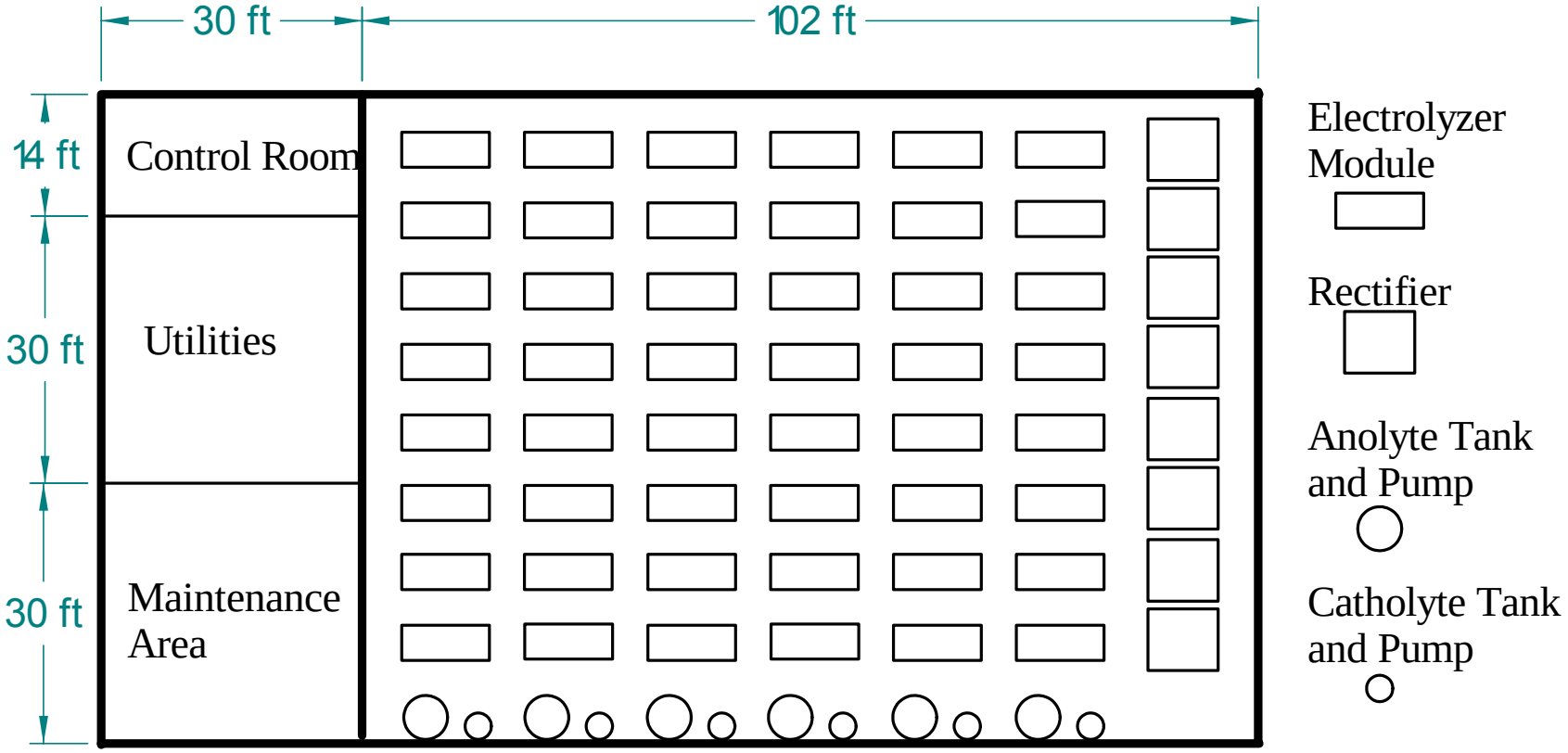
Commercial Scale HyS Electrolyzer Concept

- Bipolar cell arrangement
- Active cell area = 1 m2
- No. cells = 200
- Avg. cell voltage = 600 mV
- Current density = 500 mA/cm2
- Module current = 5000 amps
- Module voltage = 120 VDC
- DC power input = 600 kW
- H2 output = 37.6 kg/h
- H2 energy = 1.5 MW_t (HHV)



200-Cell Electrolyzer Module

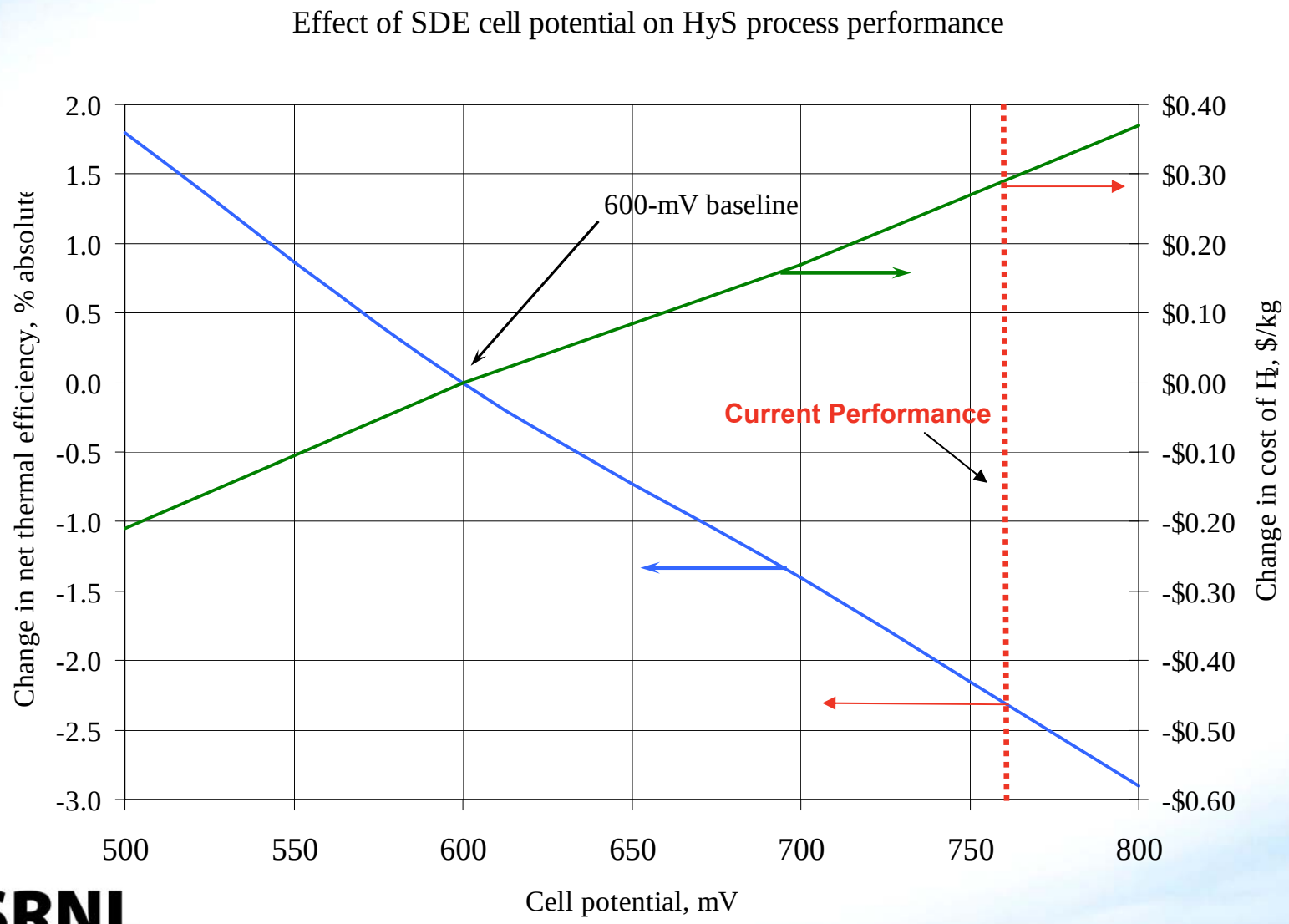
Commercial Cell Room Arrangement



Electrolyzer Array 1 of 4

48-module Cell Room Arrangement (4 req'd). H2 Output = 40 TPD each

Cell voltage is important, but very low voltage (<600 mV) may not be necessary or optimum



Future Work

- Continue electrolyzer development; identify optimum membrane and electrocatalyst; extend operation to more severe conditions; scale-up to larger capacities
- Modify test facility for unattended operation and conduct long-term tests to demonstrate operation without sulfur accumulation
- Upgrade test facilities for higher T&P operation (120°C, 10 atm) using advanced high-temperature membranes
- Design and build an Integrated Lab-Scale (ILS) Experiment of HyS, including high temperature acid decomposition and SO_2/O_2 separation (not funded at this time)
- Design and build a 1-MWth Pilot Plant