Sulfuric Acid Decomposition with Heat and Mass Recovery Using a Direct Contact Exchanger

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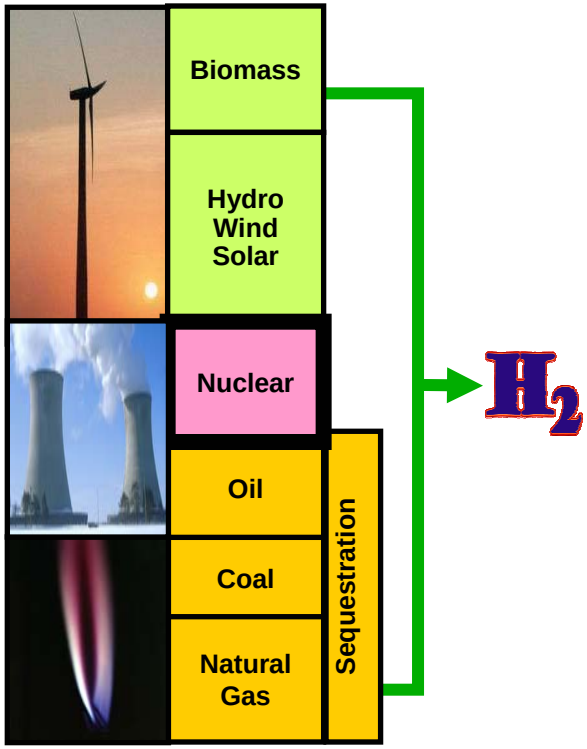
Nuclear Hydrogen Initiative



- The US DOE is investigating H_2 production using all primary energy sources
- Nuclear Hydrogen Initiative (NHI) is focusing on production options using very high temperature gas cooled reactors (VHTR). Research includes:
- *Thermochemical cycles and high temperature electrolysis to produce hydrogen from water*
- *The development of high temperature heat exchanger materials and designs needed for the temperatures and pressures of VHTR*

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NHI Thermochemical Cycles

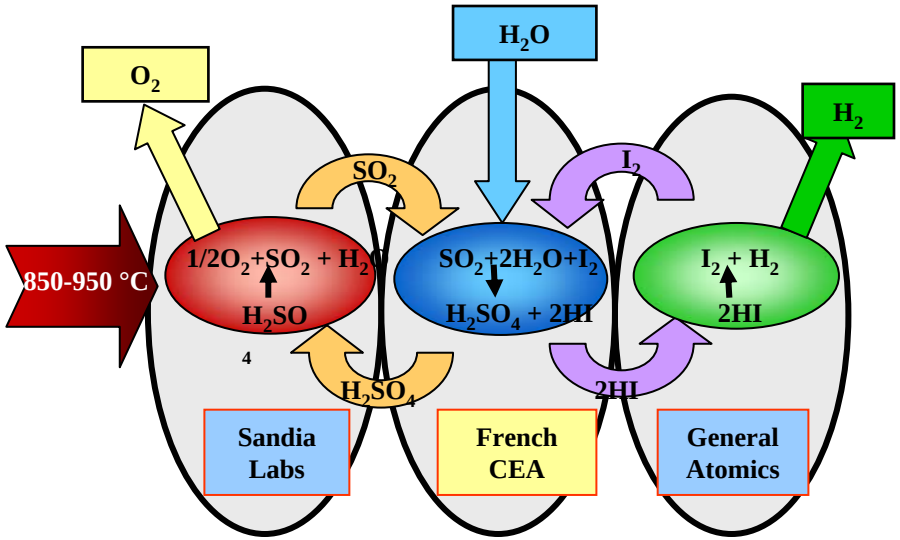
Sulfur Based Thermochemical Cycles

Sulfur Iodine

(1) $H_2SO_4 \rightarrow H_2O + SO_2 + 1/2O_2$

(2) $2HI \rightarrow I_2 + H_2$

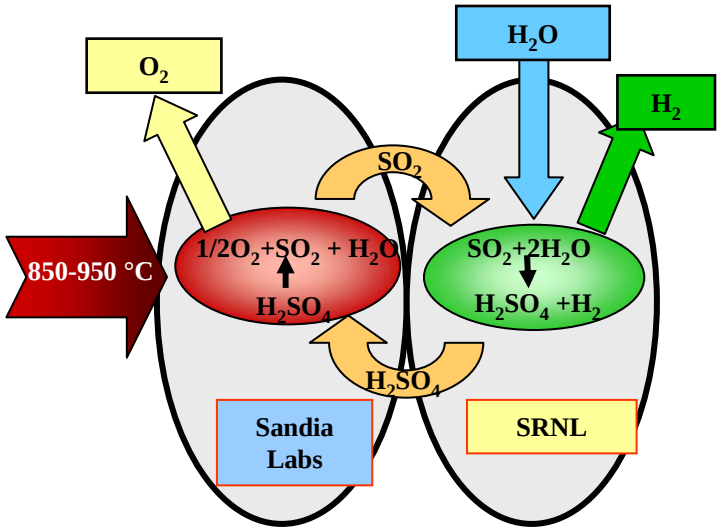
(3) $2H_2O + SO_2 + I_2 \rightarrow H_2SO_4 + 2HI$



Hybrid-Sulfur

(1) $H_2SO_4 \rightarrow H_2O + SO_2 + 1/2O_2$

(2) $2H_2O + SO_2 \rightarrow H_2SO_4 + H_2$



Alternative Thermochemical Cycles

- NH3-CO3-Hg (875-975K)
- Hybrid Cu-Cl (805K)
- Hybrid Cu-SO4 (1100K)
- Hybrid Zn-SO4 (1150K)
- NiMnFe (1075K)
- K-Bi (825K)
- Mg-Cl (875 K)
- Eu-Br (625 K)

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Sandia Programmatic Goals

- Develop and construct a H_2SO_4 decomposition process with a production capacity of 100 – 200 l SO_2/hour (equivalent to 100 – 200 l H_2/hour)
- Integrate the Sandia H_2SO_4 decomposition process with the two other sections of the S-I cycle, being developed by General Atomics Corporation and the French Commissariat a l'Energy Atomique (CEA), into a demonstration scale process
- The full S-I cycle is to be operated at the General Atomics Facility in San Diego in 2007

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Experimental Design

- Construction of glass lined steel, Hastelloy and glass
- Ozturk et al (1995) direct contact heat/mass exchanger
- Gravity feed of acid into acid boiler/superheater/decomposer
- Platinum catalyst
- Operating conditions: acid decomposition 750 to 875ºC and pressures between 6 to 11 bar.

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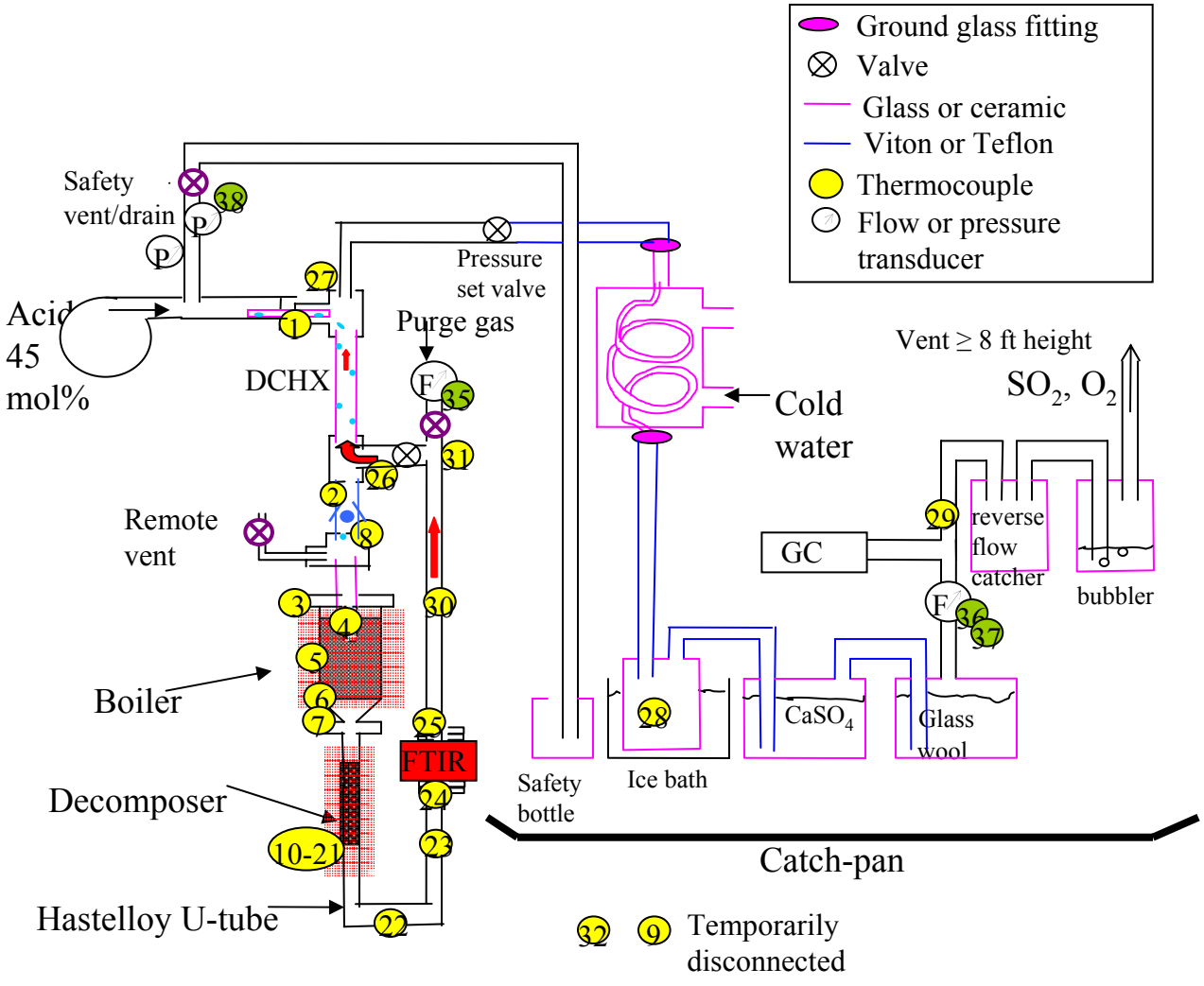
Experimental System



Surrounding chemical sorbent roll around tent perimeter

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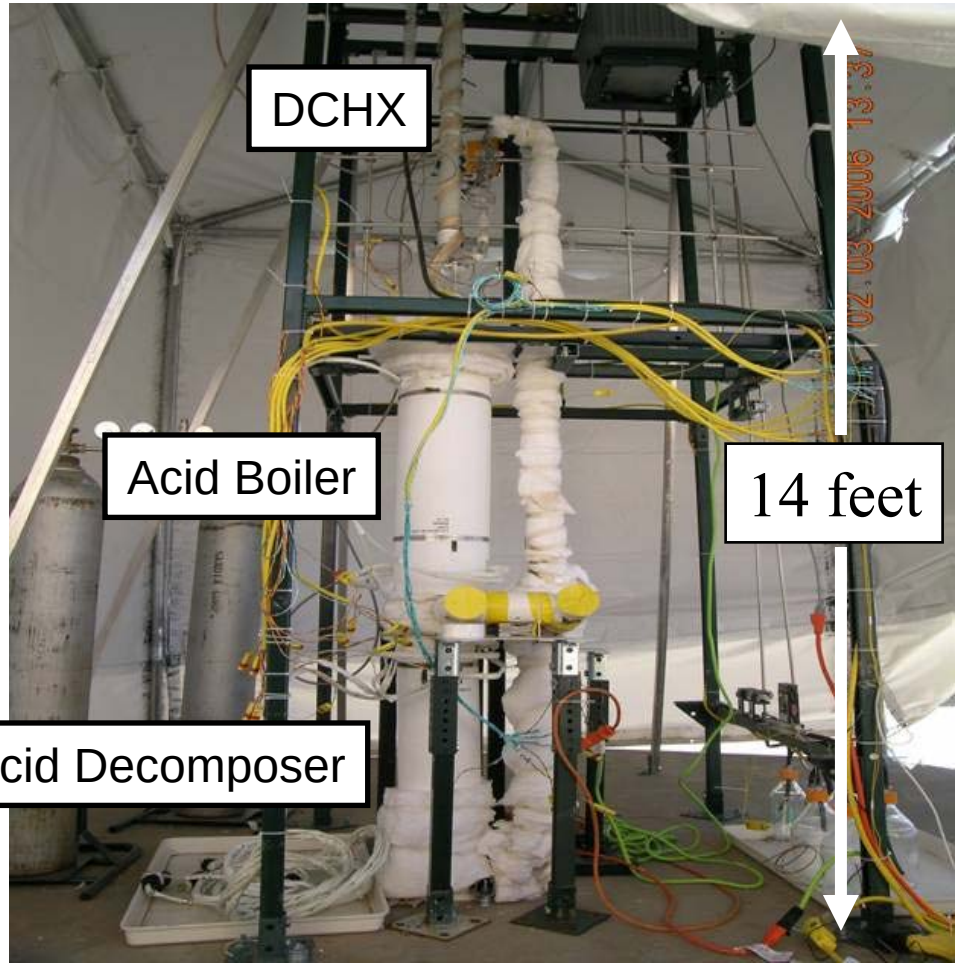
Experimental System

- **Constructed of highly corrosion resistant metals, glass, and ceramics**
- **Sections of the process were bolted or compression fit together**
- **Although no observed corrosion, high-temperature connections continue to be a problem.**



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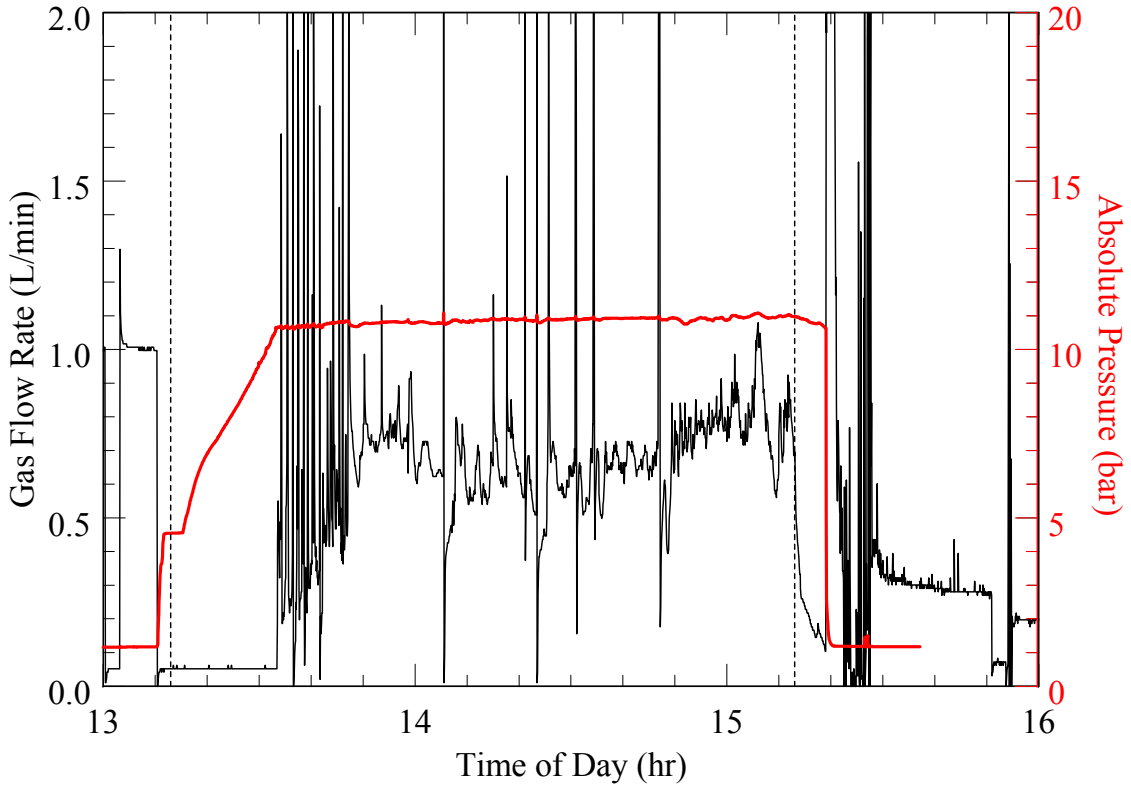
Experimental Results



Total gas flow rate of effluent and system pressure for pressurized acid test at 11 bars. The vertical broken lines on the left and right correspond to the times at which the acid pump was turned on and off, respectively.

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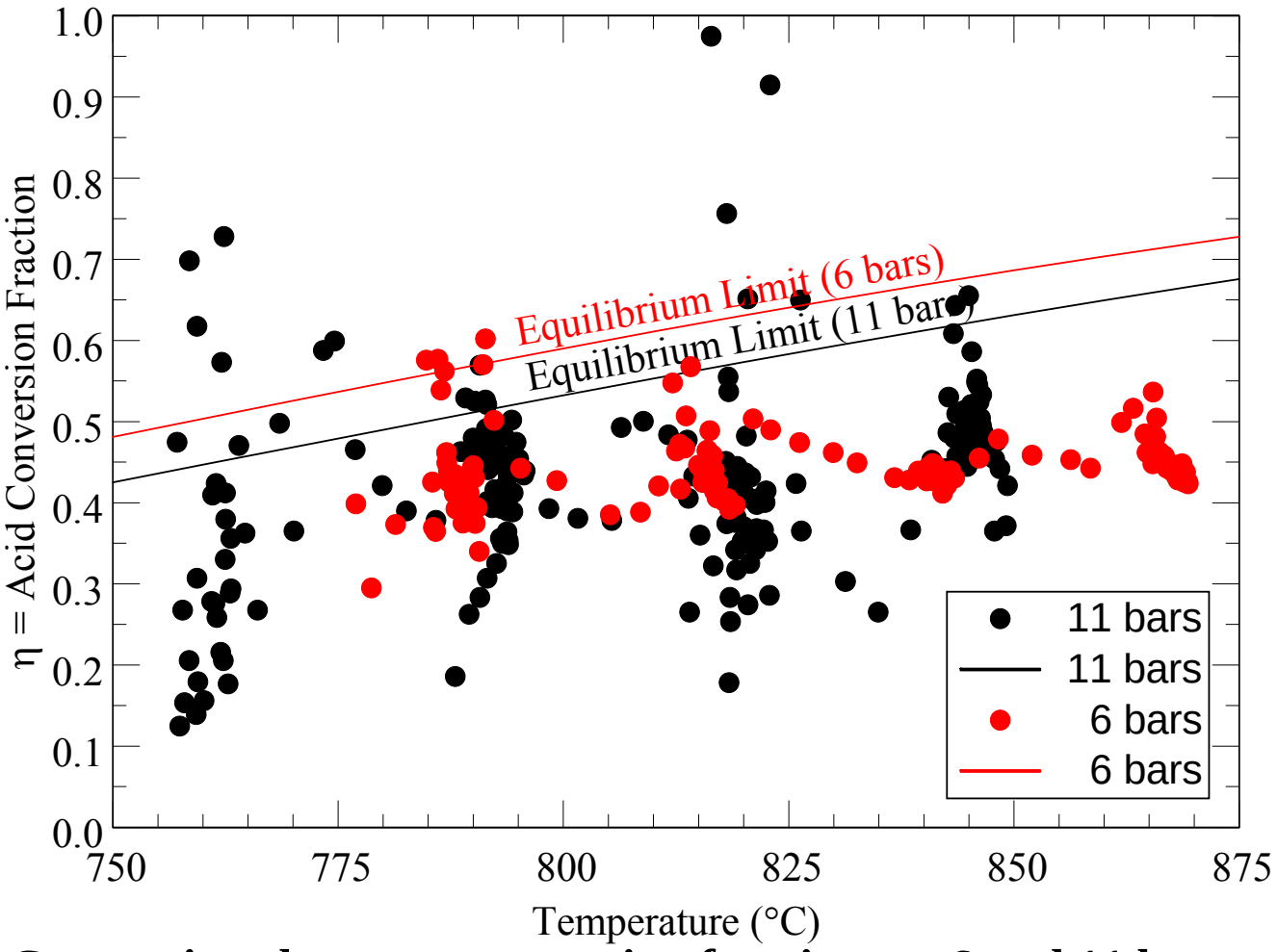
Experimental Results



Comparison between conversion fractions at 6 and 11 bars over the temperature range 750 °C to 875 °C. Values in red and black are for 6 and 11 bars, respectively.

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Problems Encountered

- Failure of components due to mismatch in thermal expansion
- Corrosion
  - Glass and/or ceramics required for hot liquids to avoid corrosion
- Failure of Connections at High Temperature
  - Metal-to-glass and metal-to-metal connections required several resealing and adjustments due to metal warping.

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Conclusions

- The apparatus for sulfuric acid decomposition was successfully operated at 750 to 875ºC at pressures between 6 to 11 bar.
- Total gas flow rates, SO_2 and O_2, averages approximately 0.7L/min (42 L/hour) with conversion fractions ranging from 0.4 to 0.5 at 6 bar and 0.3 to 0.55 at 11 bar.
- Problems with metal corrosion by hot liquid acid, but no observable corrosion of Hastelloy by acid vapors. No observable corrosion of glass or silicon carbide components with liquid or gaseous acid.

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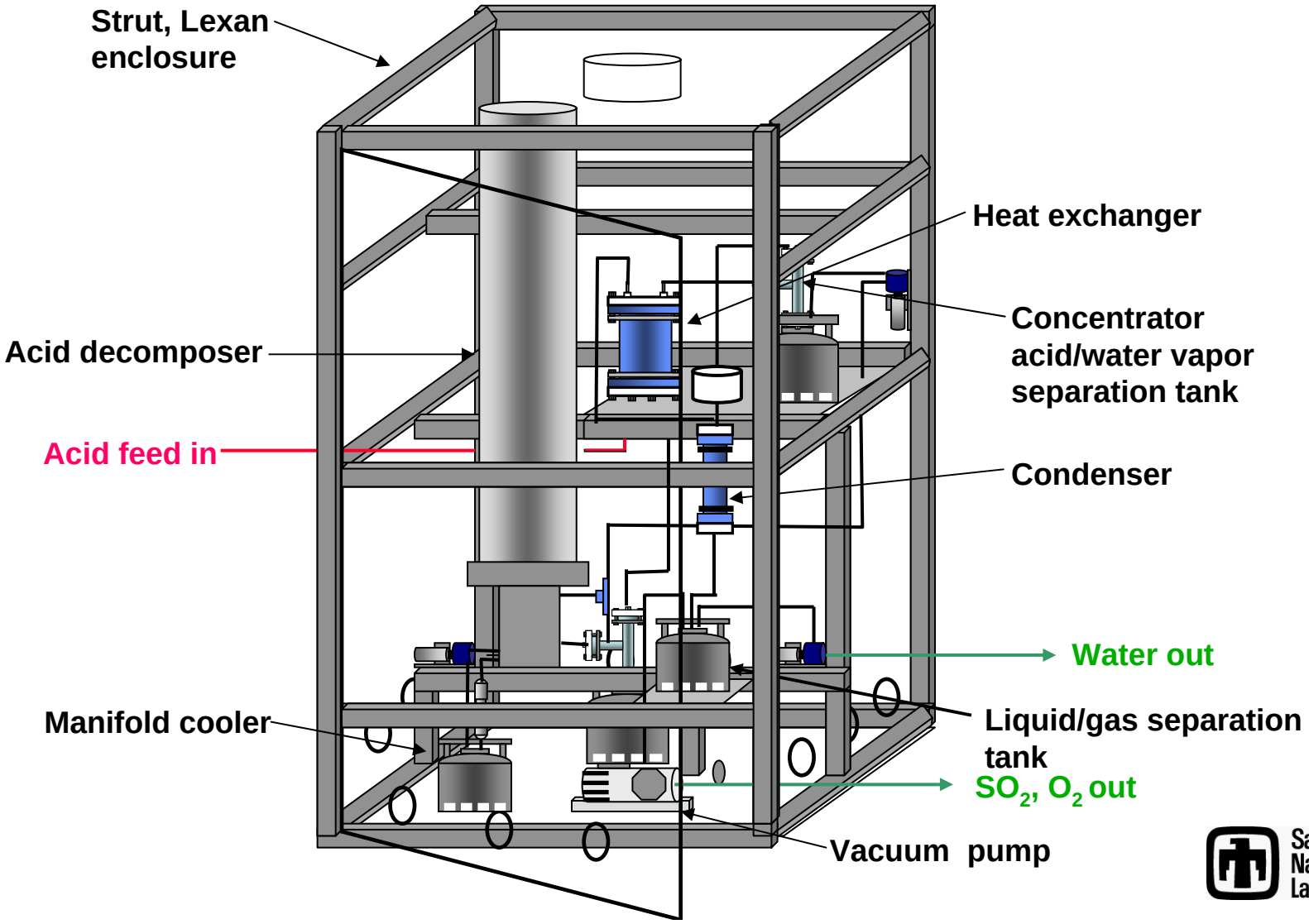
Future Work: Sulfuric Acid Process Skid Configuration



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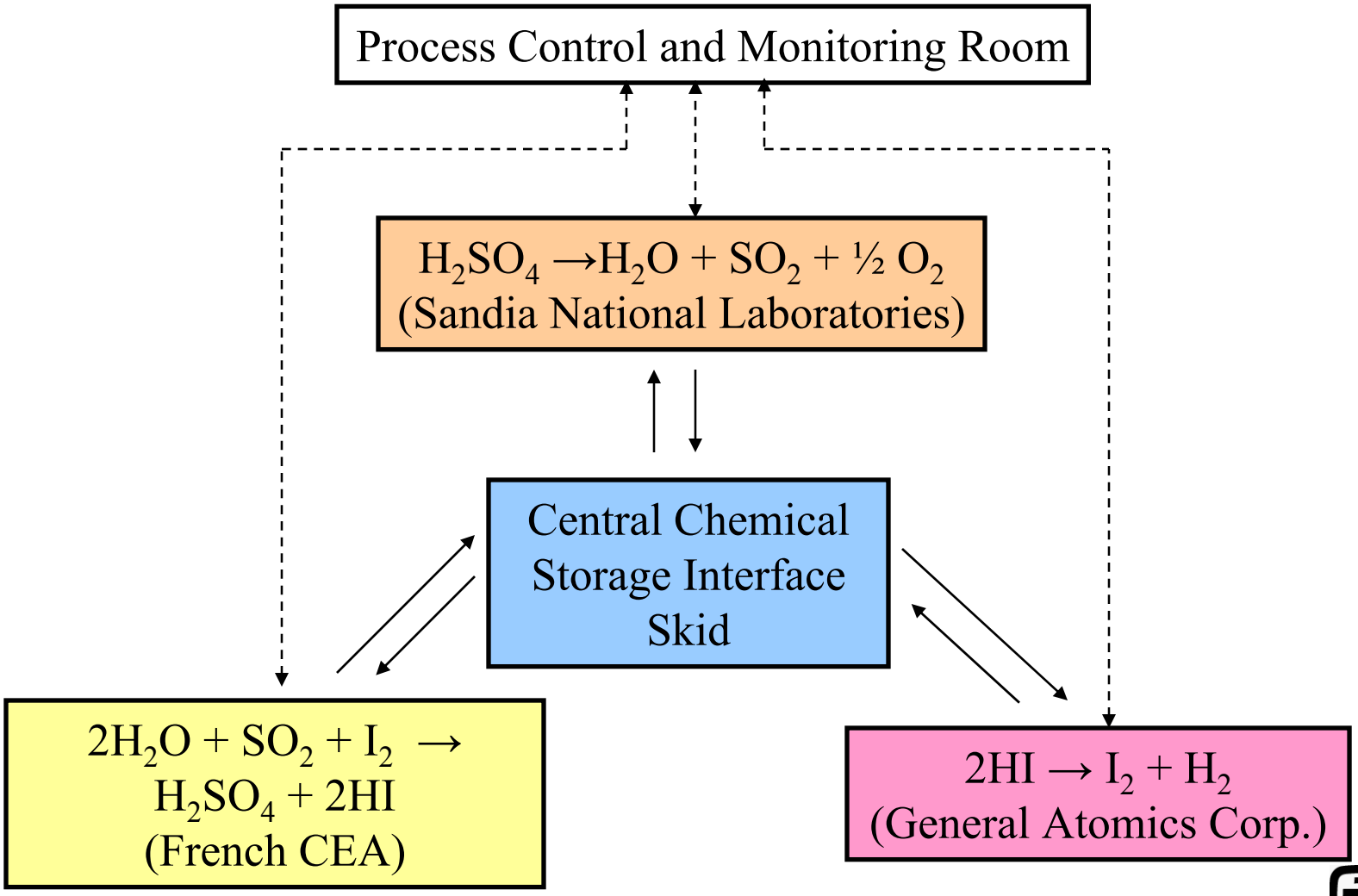
Future Work: Integrated S-I Cycle Testing



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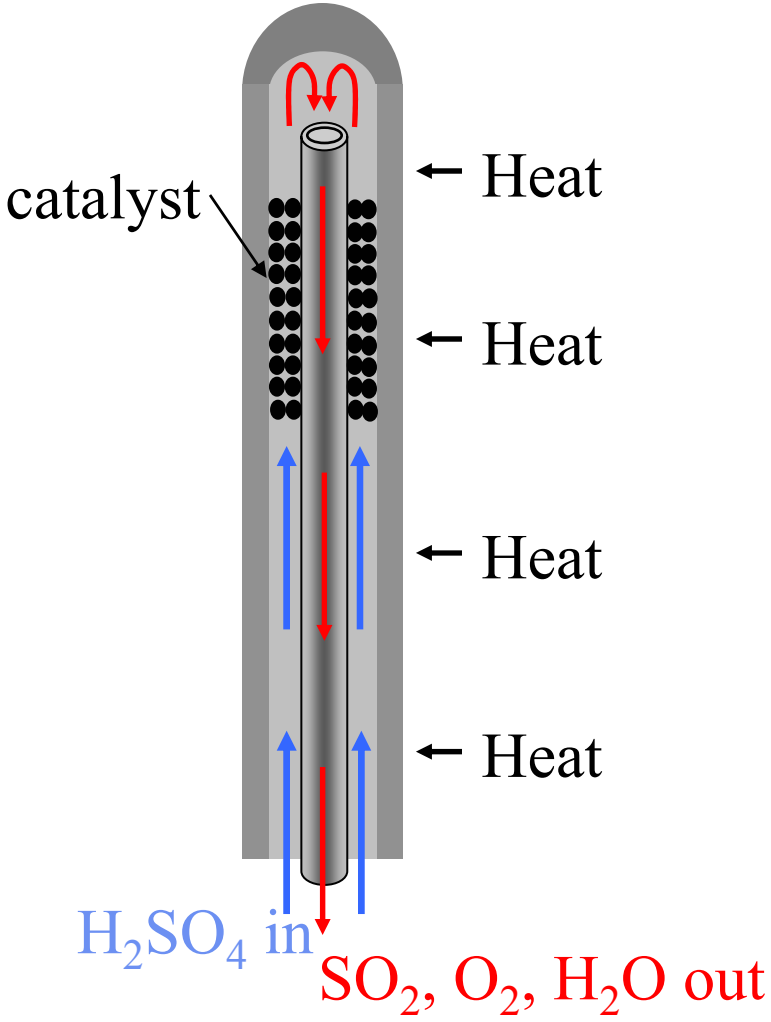
Future Work: Integrated Sulfuric Acid Boiler/decomposer

- **New design based on a dual-tube bayonet type heat exchanger**
- **Silicon carbide construction**
- **Heat recuperation throughout process**
- **No high temperature connections**



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