Hydrogen Production from Hydrogen Sulfide in IGCC Plants

University of South Florida

Clean Energy Research Center

University Coal Research Contractors Review Meeting

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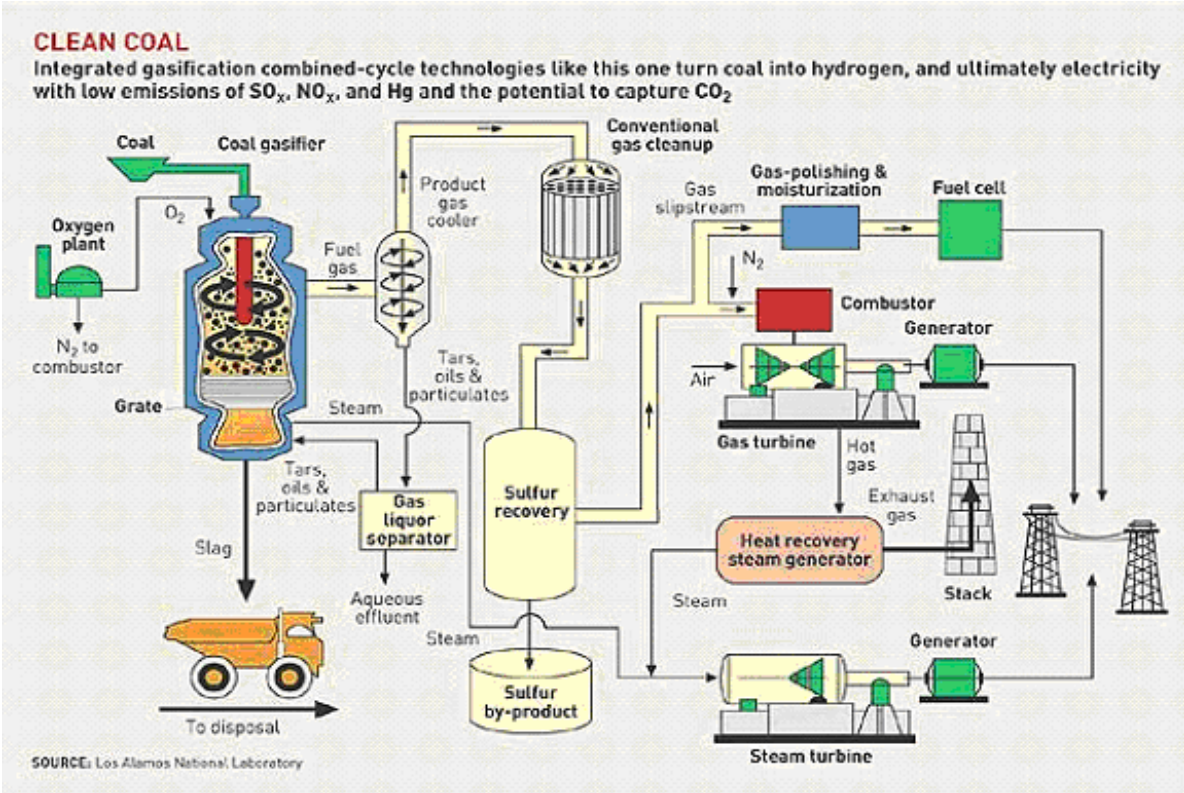
Objectives

- Produce hydrogen by clean technologies using plentiful U.S. Coal supplies or using process/waste streams particularly H_2S.
- Provide a technique to reduce costs to help remove economic barriers to clean IGCC power production.

Overview

- IGCC System Description and Benefits
- Analytical Sulfur Extraction System Comparison
  - Energy Benefit
  - Economic Benefit
- Laboratory Experiments
- Status

Current Technology



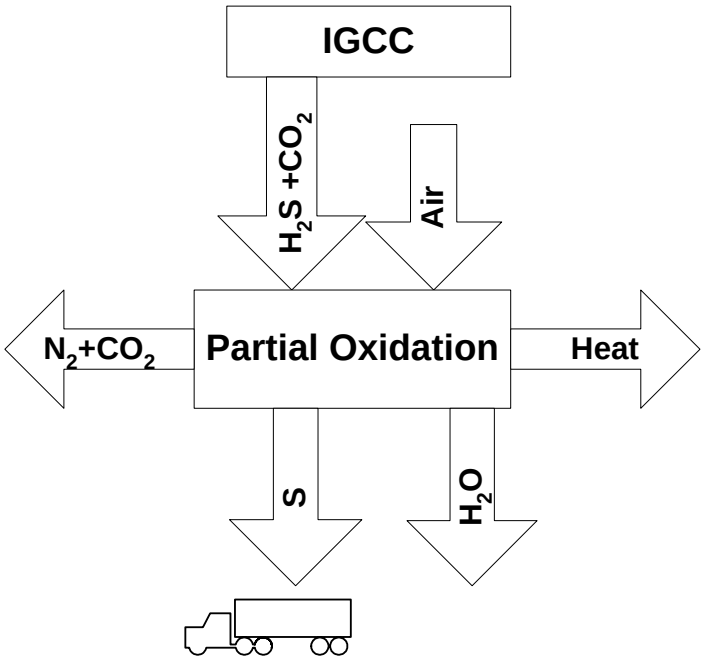
➢IGCC Power Plant Schematic

Benefits of IGCC

- Reduced Emissions
  - SO_2
- Potentially Reduced Emissions
  - CO_2
  - Mercury
- Byproduct Production
  - Sulfur or Sulfuric Acid
  - Possibly H_2
- Higher Efficiency

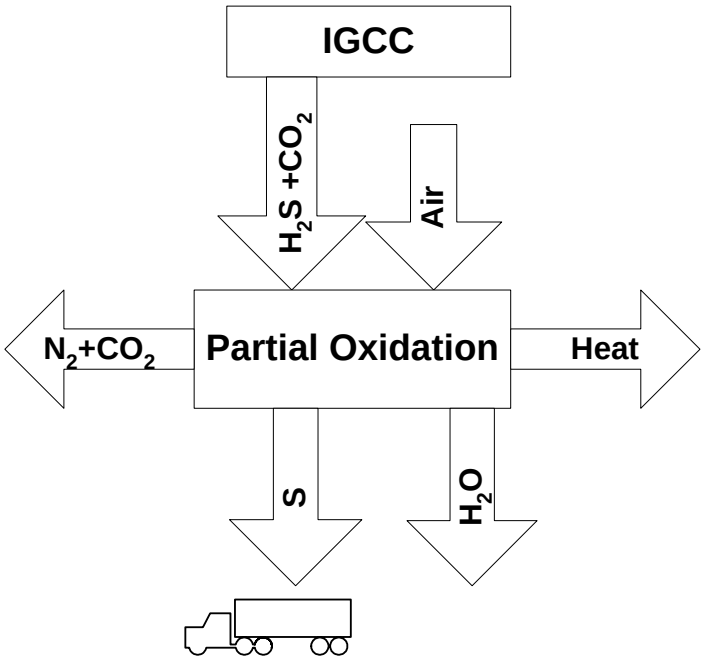
Process Block Diagrams

Claus Process

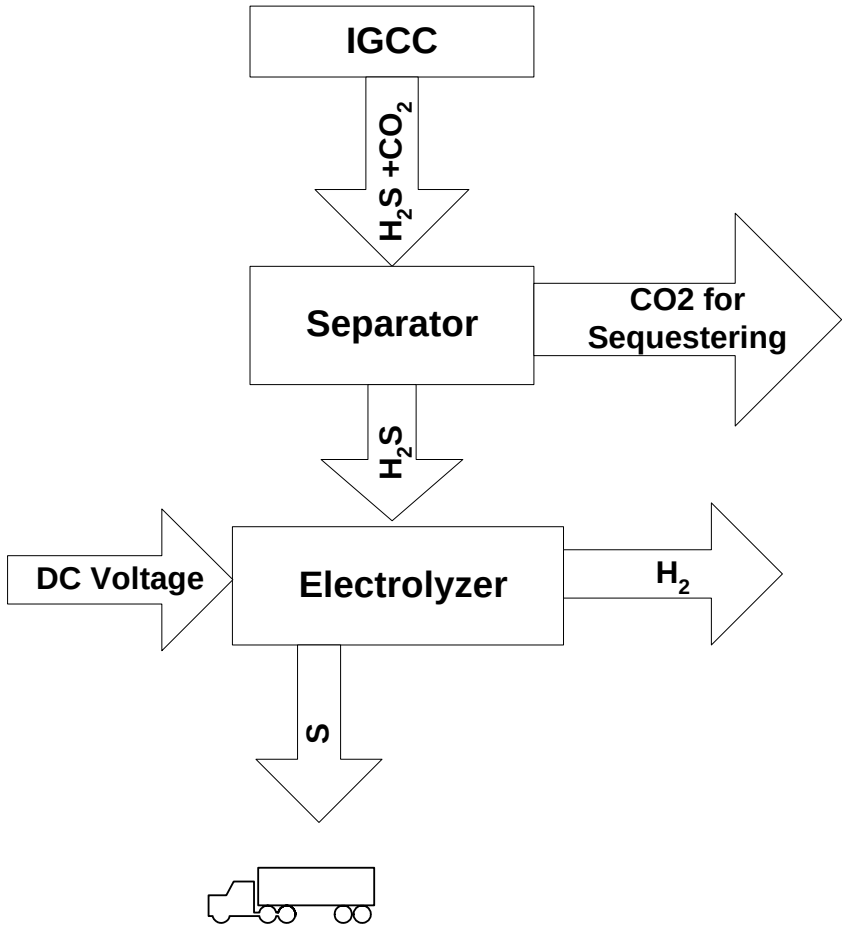


Process Block Diagrams

Claus Process



Electrolytic Process



Energy Benefit

$H_2S(g) \rightarrow S(l) + H_2(g) - 2$ Faradays @ 0.19V (1)

$\Delta G^o = 8.9$ kcal/mole @ 400K

$H_2O(l) \rightarrow H_2(g) + \frac{1}{2} O_2(g) - 2$ Faradays @ 1.2V (2)

$\Delta G^o = 56$ kcal/mole

Parameters

- Scale: 250 MW (net) IGCC Power Plant
- 335 days/year availability
- 2.01 million MWh/yr electric energy produced
- 2500 tons-coal/day
- 2.5% coal sulfur content
- 3.04 tons/hr acid gas carbon
- 30 year plant life
- Straight Line Depreciation
- 15% Cost of Capital
- Near term H_2 and electricity prices
- Electrolyzer prices based on water electrolyzers.[1,2,3]

(1) Board on Energy and Environmental Systems. "The Hydrogen Economy: Opportunities, Costs, Barrier, and R&D Needs". The National Academies Press. 2004. National Academy of Engineers. 29 June 2005. <http://www.nap.edu/openbook/0309091632/html/221.html>.

(2) Braun, Harry. "The California Phoenix Project Plan". Phoenix Project Foundation. 08 Nov 2003. Phoenix Porject Foundation. 29 June 2005. <http://www.phoenixprojectfoundation.us/user/California%20PPP.pdf>.

(3) Office of Nuclear Energy, Science and Technology. "Nuclear Hydrogen R&D Plan". US Department of Energy Hydrogen Program. March 2004. Department of Energy. 29 June005.<http://www.hydrogen.energy.gov/pdf/nuclear energy h2 plan.pdf>.

Production Costs

ELECTROLYSIS PLANT INVESTMENTS	
Carbon Dioxide Separator	$586,849
Electrolyzer	$4,560,000
Balance of Plant	$6,213,151
Total Electrolysis Plant Investments	$11,360,000
ANNUAL CAPITAL AND O&M COSTS	
Annualized Capital Costs	$1,730,000
Labor	$516,000
Catalysts, water and other operating costs	$632,417
Electricity	$2,500,000
Total Annual Capital and O&M Costs	$5,378,417

Hydrogen Value

UNIT COSTS	
Costs to Produce 1 Ton of S + 125lb. of H2	$245
Avoided Cost of Claus Process/Ton of S	$137
Net Production Cost of 125 lb. of H2	$108
Net Production Cost of 1 lb. of H2 Gas	$0.86
Hydrogen Liquefaction Cost ($/lb.)	$0.55
Net Production Cost of 1 lb. of Liquid H2	$1.41
MARKET PRICE OF LIQUID H2 ($/LB.)	$2.00
GROSS PROFIT ON LIQUID H2 ($/LB.)	$0.59
SAVINGS ($/MWh)	$0.63

Market Hydrogen: ($/lb Cryogenic Liquid Delivered) **$2.22 – 3.45/lb** ($/lb High Pressure Delivered) **$3.27 – 4.99/lb**

Source: **Chemical Market Reporter**, 2/24/03

NASA Hydrogen Price ($/ lb Cryogenic Liquid Delivered) **$2. 00/ lb**

Source: Addison Bain, FSEC- CR-1359- 02

CO_2 Sequestration Value

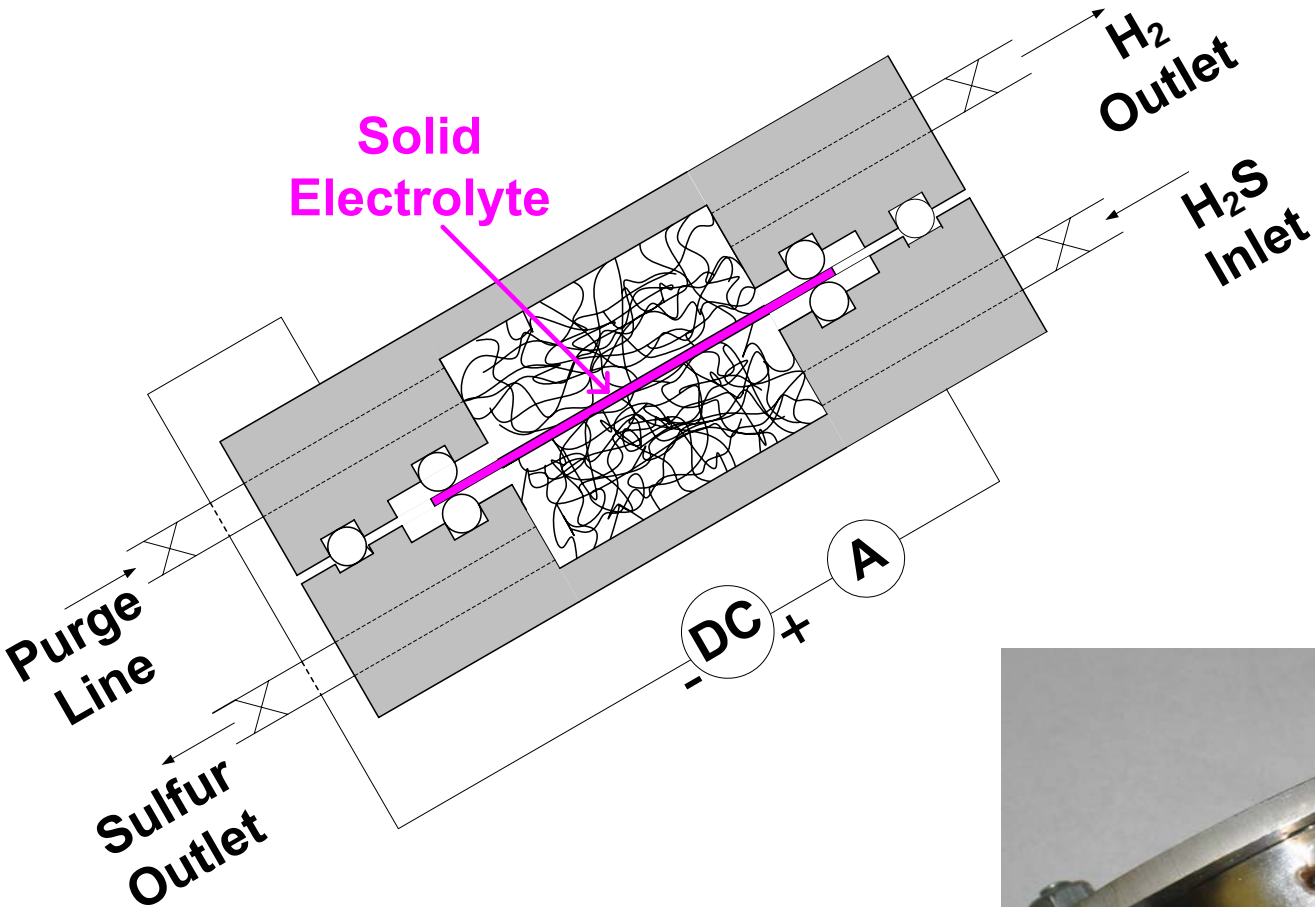
Sequestration Process Costs[1] ($/ton C)	Current	Proposed
Carbon Capture	150	0
Storage, Transportation and Sequestration	50	50
Carbon Value		
CO2 Trading Price ($/ton CO2)[2]	38.01	38.01
CO2 Trading Price ($/ton C)	139.38	139.38
Profits or Losses		
Revenue From Collection, Storage, Transportation and Sequestration ($/ton C)	-60.62	89.38
Revenue From Collection, Storage, Transportation and Sequestration ($/MWh)	-0.58	0.86

1)<http://www.fossil.energy.gov/programs/sequestration/capture/index.html>.
2)<http://www.theipe.com/historical/eod.asp?sp=eod_ecxcfif>. 27 Jun, 2005

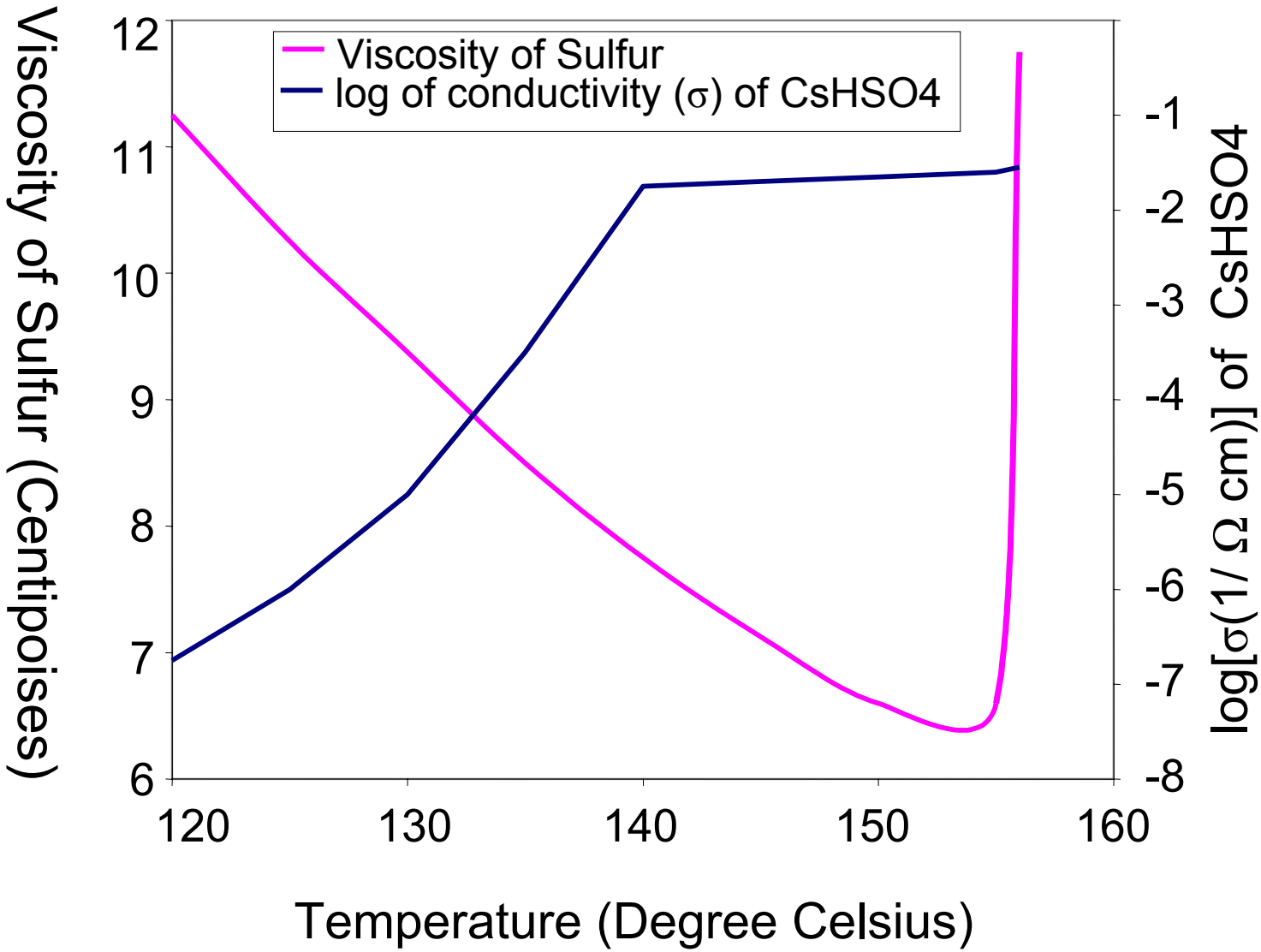
Benefits of H_2 Production and CO_2 Sequestration

Savings from H2 production	$0.63/MWh
Savings from CO2 Sequestration	$0.86/MWh
Total Savings	**$1.49/MWh**

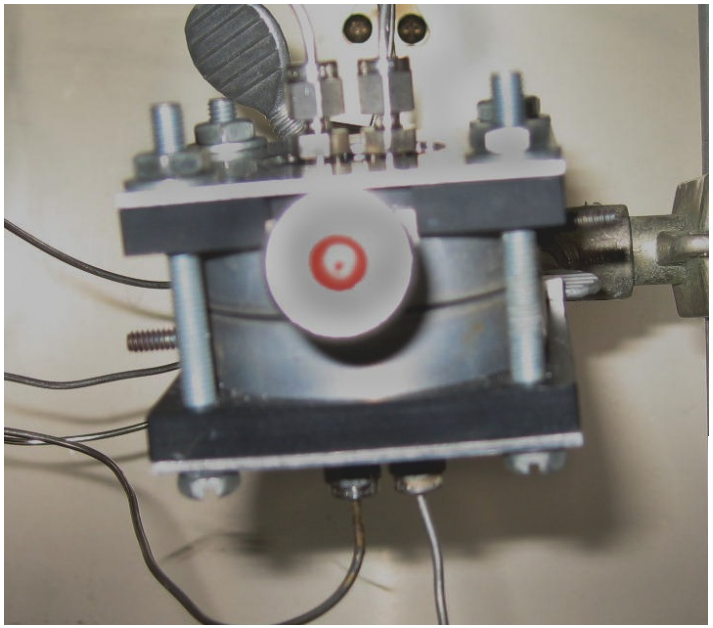
Experimental Cell

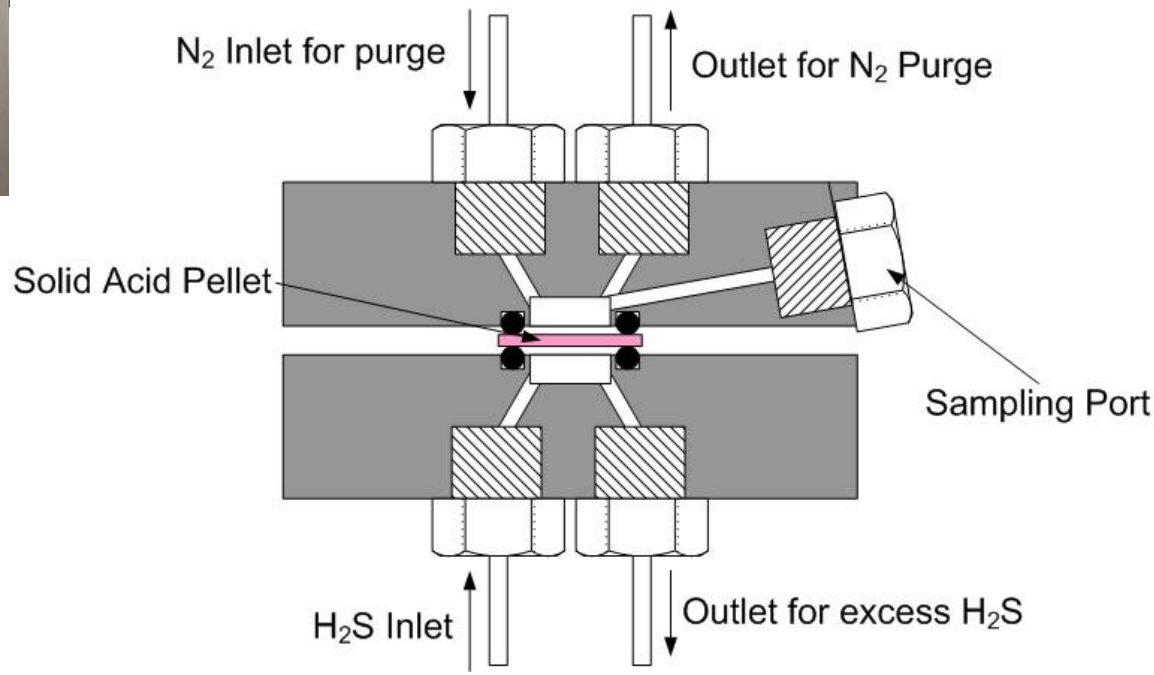


Electrolyte Conductivity and Sulfur Viscosity



Permeability Cell





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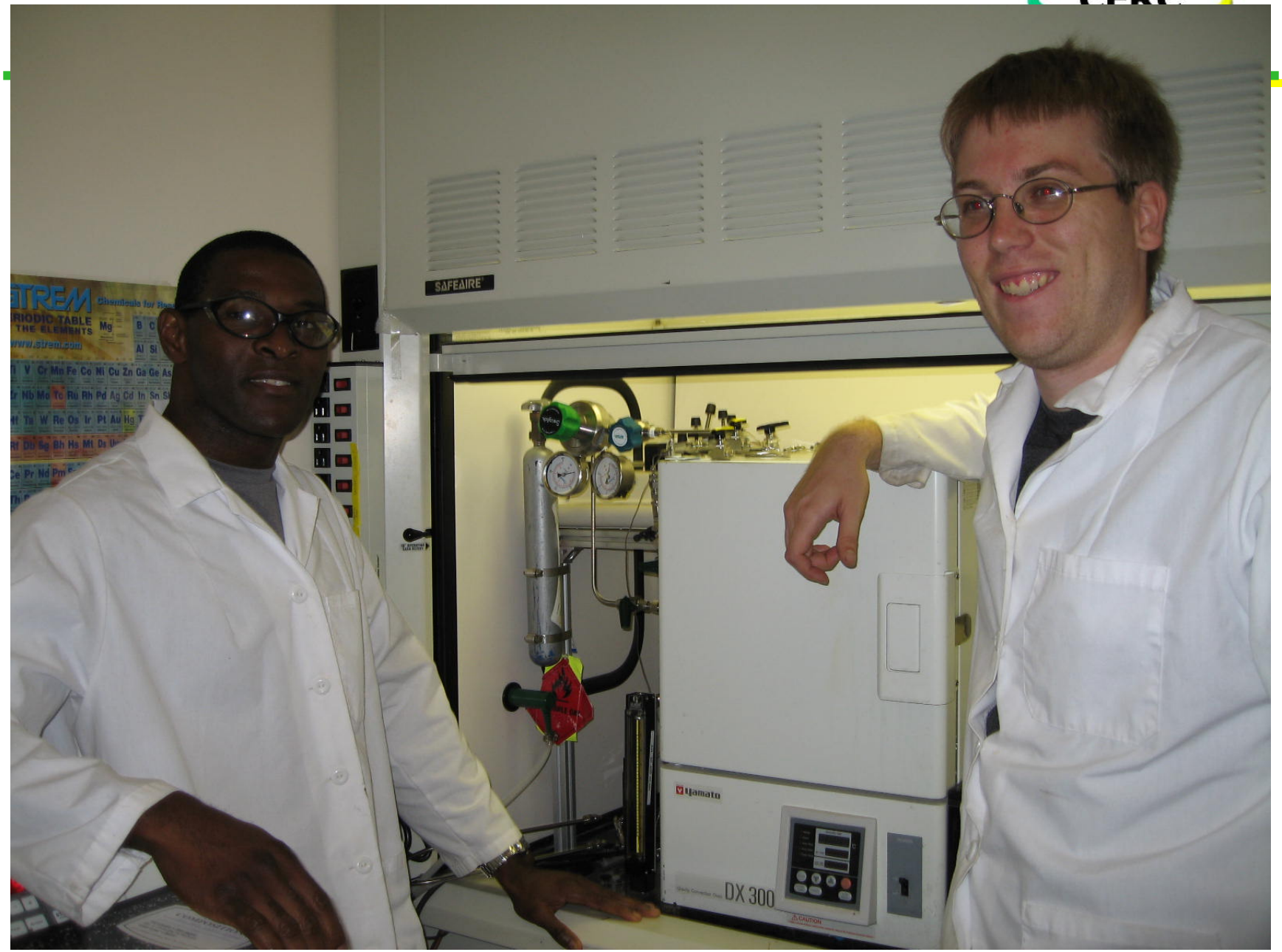
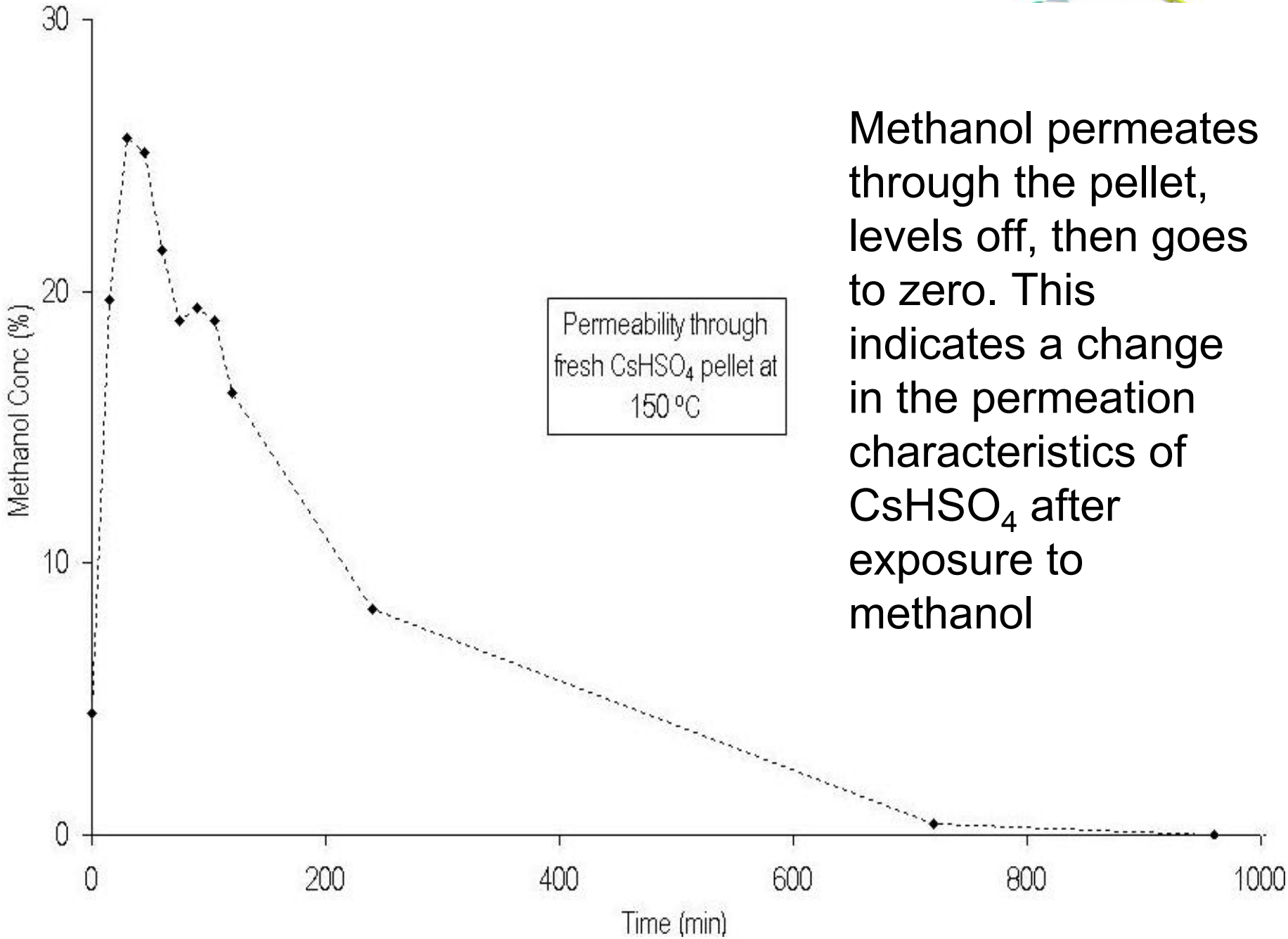
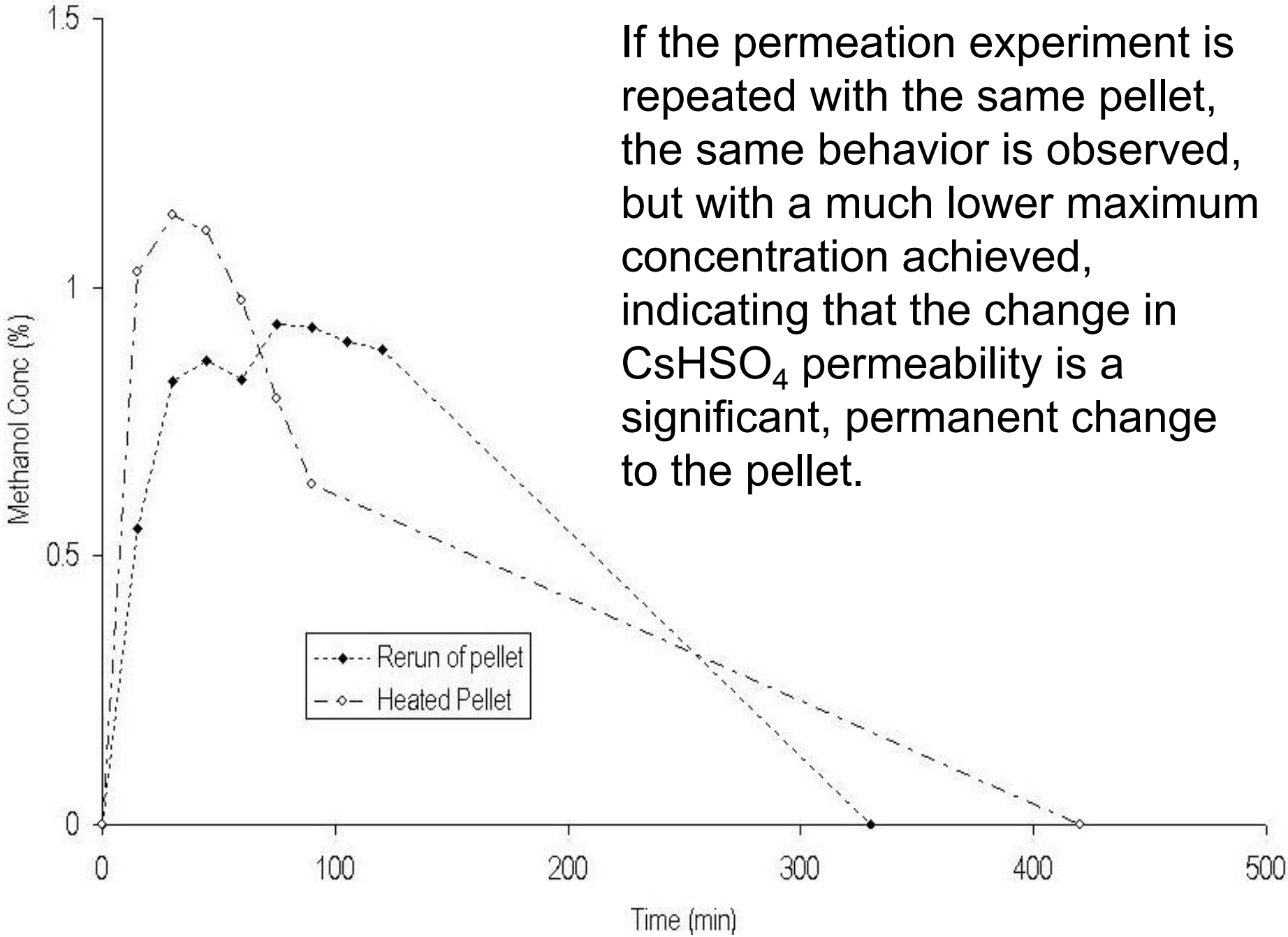

SAFEAIRE
Yamato
DX 300

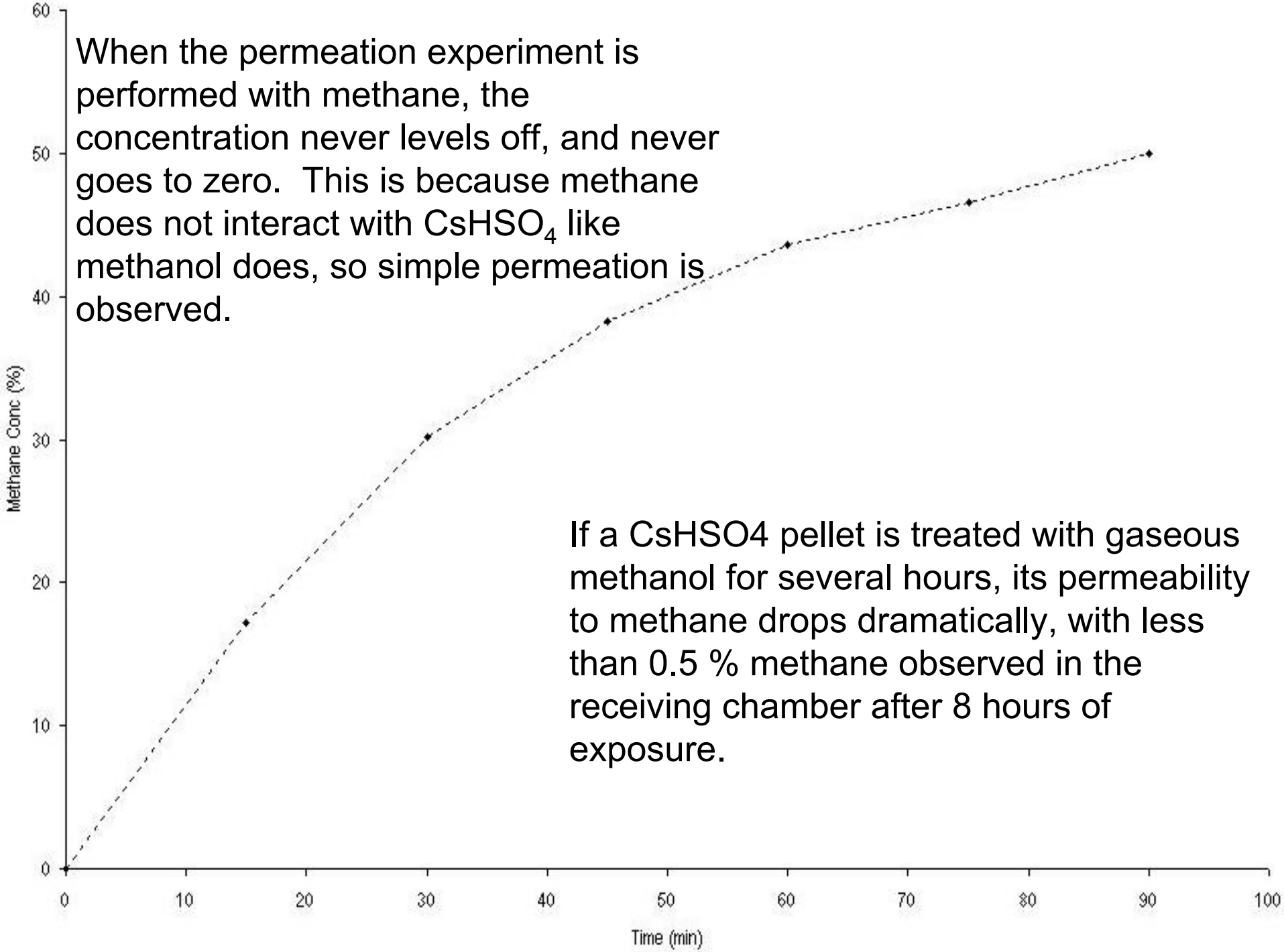


Methanol permeates through the pellet, levels off, then goes to zero. This indicates a change in the permeation characteristics of $CsHSO_4$ after exposure to methanol



If the permeation experiment is repeated with the same pellet, the same behavior is observed, but with a much lower maximum concentration achieved, indicating that the change in $CsHSO_4$ permeability is a significant, permanent change to the pellet.

When the permeation experiment is performed with methane, the concentration never levels off, and never goes to zero. This is because methane does not interact with $CsHSO_4$ like methanol does, so simple permeation is observed.

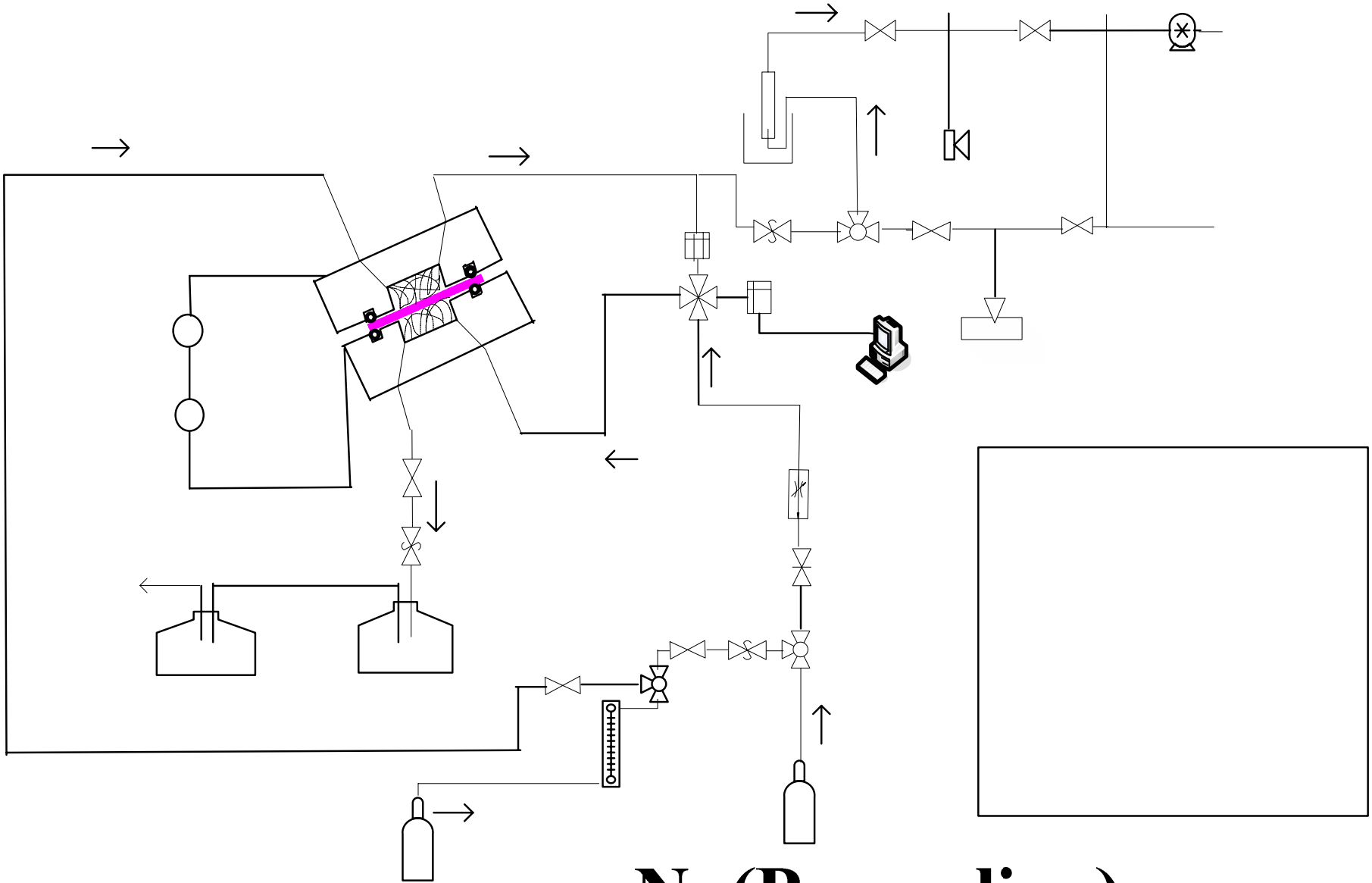


If a CsHSO4 pellet is treated with gaseous methanol for several hours, its permeability to methane drops dramatically, with less than 0.5 % methane observed in the receiving chamber after 8 hours of exposure.

Permeability Results

Type of Experiment	Max Conc Observed (mol %)
Methanol, fresh pellet	25%
Methanol, treated pellet	1.5%
Methane, fresh pellet	100%
Methane, treated pellet	<0.5%

- $CsHSO_4$ displays improved impermeability after exposure to gaseous methanol
- This impermeability is dramatic even in gases that do not interact with $CsHSO_4$, like methane
- This suggests that treatment with methanol may improve $CsHSO_4$ impermeability to H_2S



N_2 (Purge line)

Status of Phase 1 SOW

- **Task 1.0 Preparation of Apparatus**
- **1.1 Fabricate electrochemical cell. Two done.**
- **1.2 Set up apparatus for handling H2S flow. Almost done.**
- **1.3 Install electrodes for H2S. On immediate agenda.**
- **1.4 Set up hydrogen and sulfur collection systems. Done.**

- **Task 2.0 Electrolysis**
- **2.1 Decomposition of H2S. Will closely follow 1.2 and 1.3.**
- **2.2 Analyze H2 and S produced. To be done in conjunction with 2.1.**
- **2.3 Verify impermeability of pellets. Started and will continue.**

- **Task 3.0 Reporting. Reports will be provided as they become due.**

Phase 2 Plans

- **Once principal is proven, the process will need refinement before commercialization.**
- **Advanced electrode materials and contacting techniques will be developed. Attachment of electrodes during electrolyte fabrication will be investigated.**
- **Catalysts and surface treatments will be applied to attempt to increase power densities.**
- **New electrolyte materials will be sought and investigated in a search for better electrical and mechanical properties.**
- **Better pellet fabrication techniques will also be sought.**
- **Thin pellets will be fabricated.**

Acknowledgement

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- The authors would also like to thank Don Payne and Paris Wiley for their help with the work.

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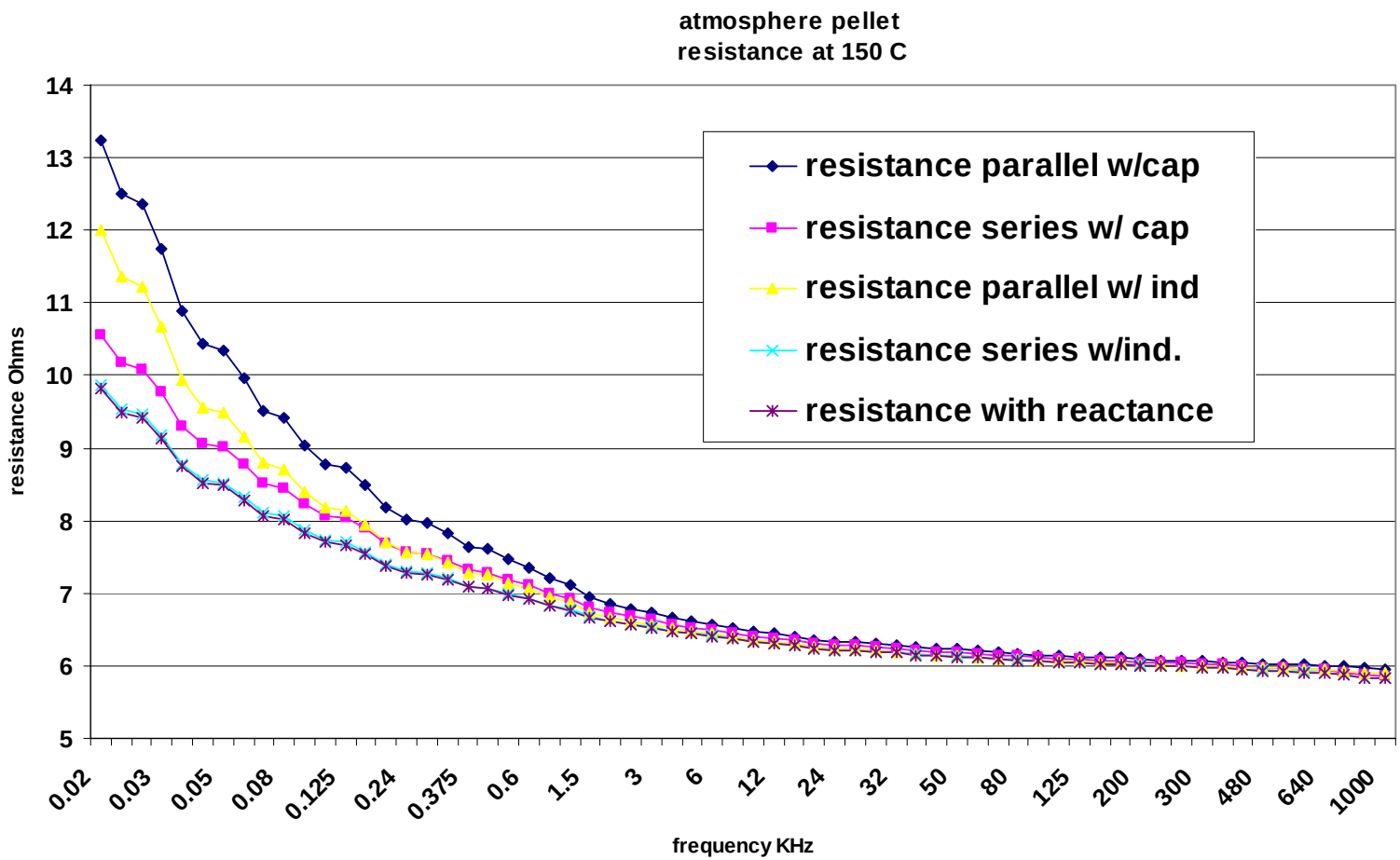
atmosphere pellet
resistance at 150 C
resistance Ohms
14
13
12
11
10
9
8
7
6
5
0.02
0.03
0.05
0.08
0.125
0.24
0.375
0.6
1.5
3
6
12
24
32
50
80
125
200
300
480
640
1000
frequency KHz
resistance parallel w/cap
resistance series w/ cap
resistance parallel w/ ind
resistance series w/ind.
resistance with reactance

Conclusions

- IGCC-Conventional cost difference: \$10-\$20/MWh
- Benefit from H_2 sales: \$0.63/MWh
- Possible benefit from CO_2 sequestration: \$0.86/MWh
- Sum of benefits: \$1.49/MWh
- $CsHSO_4$ has a superprotonic state at a temperature that makes it a well suited electrolyte for electrolytic production of molten sulfur and H_2 from H_2S
- Methanol exposure and heat treatment appear to reduce permeability of $CsHSO_4$ pellets