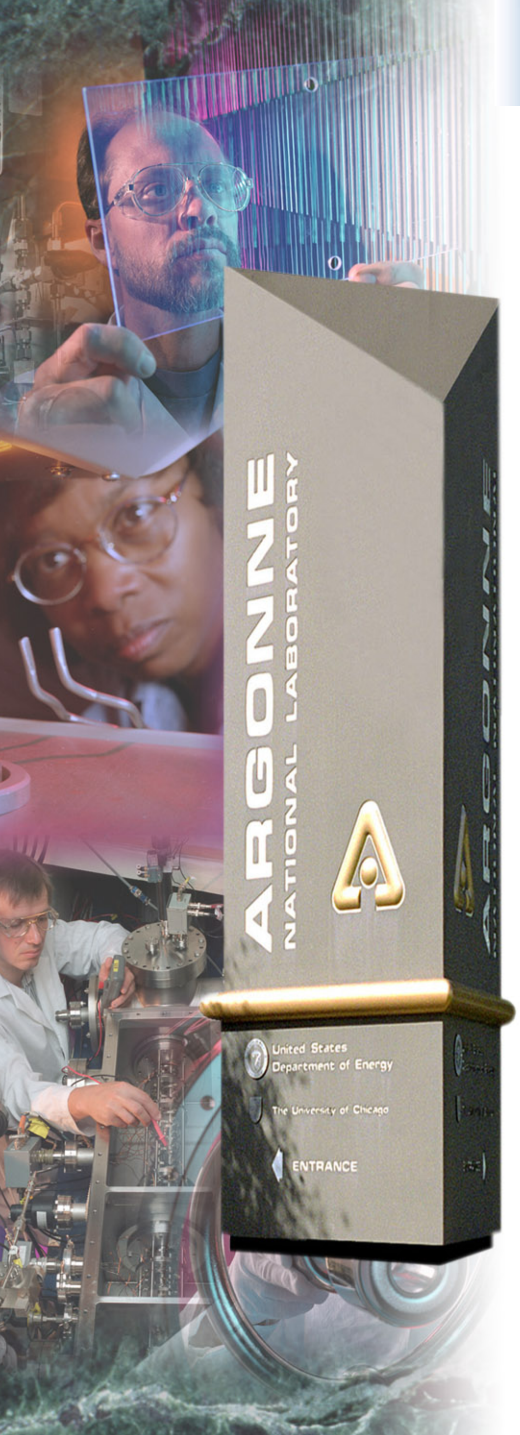

ARGONNE NATIONAL LABORATORY

U.S. Work on Hydrogen Production Using Light-Water Reactors

Mark C. Petri

IAEA Technical Meeting on
Advanced Applications of
Water-Cooled Nuclear Power Plants
October 11-14, 2005
Vienna, Austria

THE UNIVERSITY OF CHICAGO

Office of Science
U.S. DEPARTMENT OF ENERGY

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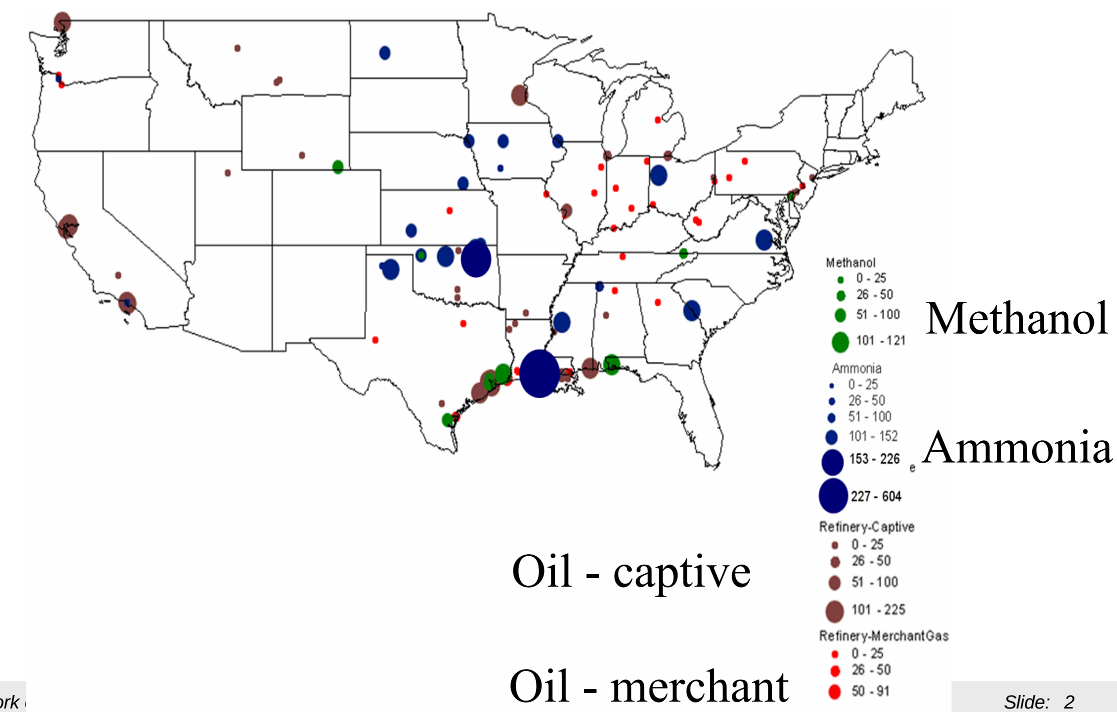
Current U.S. Hydrogen Markets

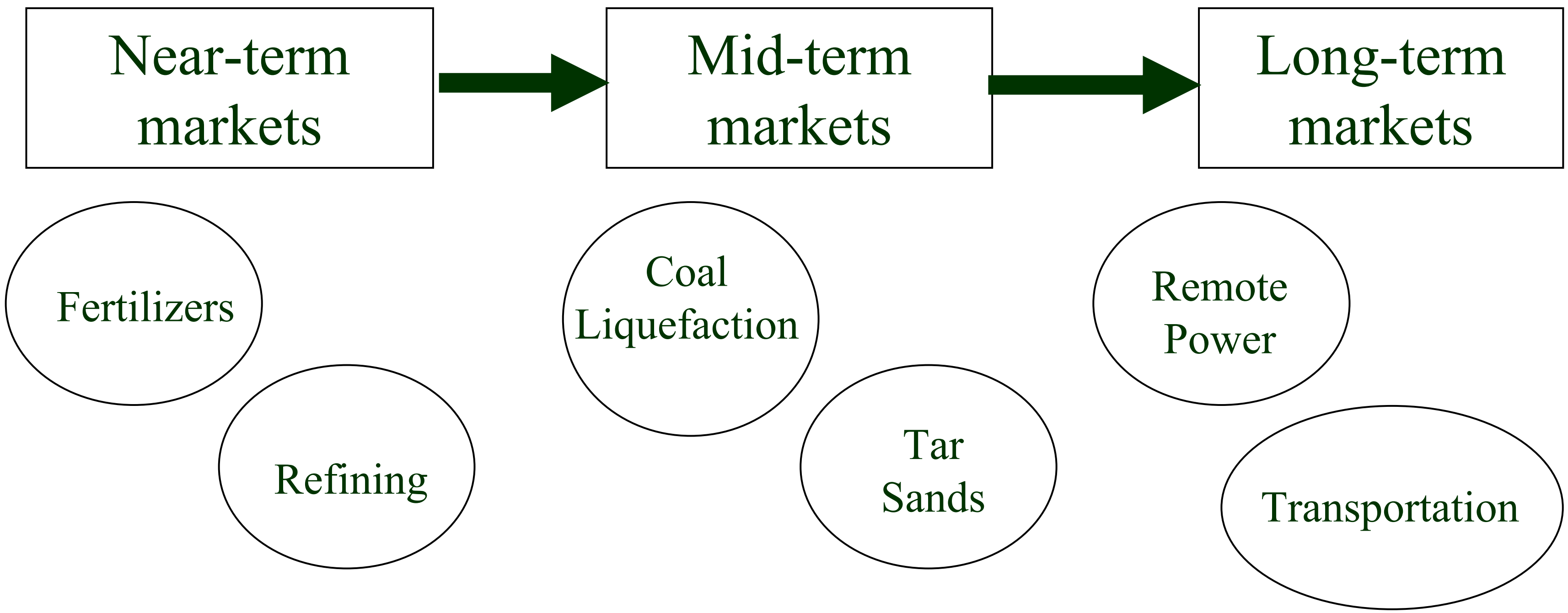
- Oil refining (4.1M tonnes H_2).
- Ammonia (2.6M tonnes H_2).
- [Canadian oil sands (0.5M tonnes H_2)].
- Methanol (0.4M tonnes H_2).
- Chemical, metal, food, etc. (0.1M tonnes H_2).



Medium and Long-Term U.S. Hydrogen Markets

- Transitional transportation fuels (5 - 15 years).
  - Coal liquefaction.
  - Shale oil.
- Ultimate solution (> 15 years).
  - Direct use of hydrogen for transportation (150M tonnes would be needed by 2040 to fuel all cars and light trucks).

Nuclear Options in an Evolving Hydrogen Economy



Each market will have different hydrogen needs.

Nuclear H_2 must compete with alternative technologies in each market.

The Need for System Integration Analyses

- Technical feasibility is insufficient to guarantee the adoption of any nuclear hydrogen option.
- Nuclear power must compete with other technologies in various hydrogen markets.
  - —Cost
  - —Risk
  - —Operability
  - —Environmental impact

All influenced by the specific hydrogen market being considered

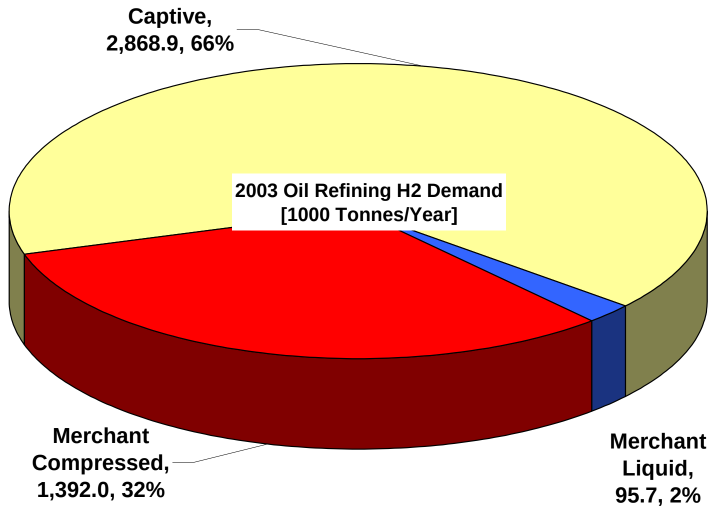
- As markets evolve, nuclear hydrogen's ability to compete will change.

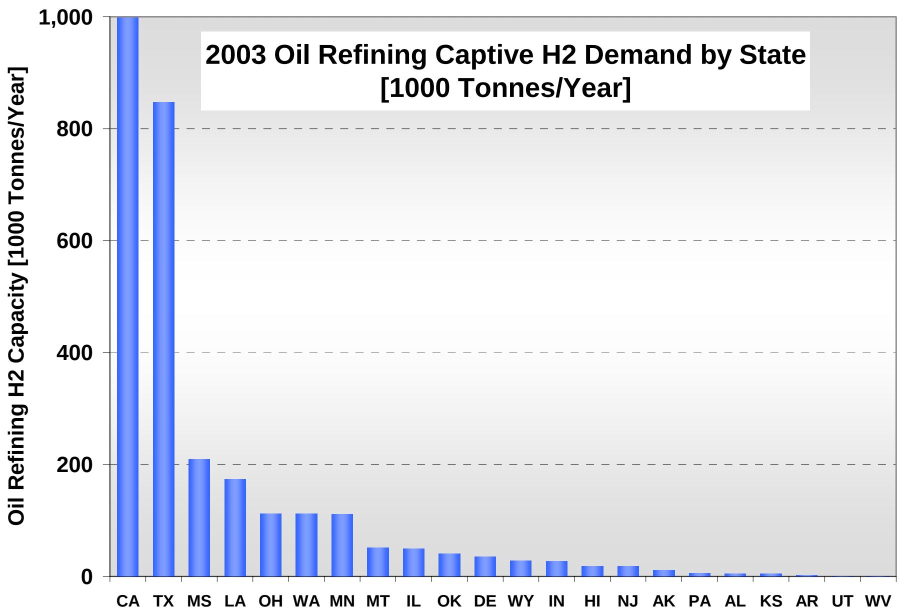
Nuclear Hydrogen System Study Components

- Identify H_2 markets and their requirements.
- Assess configuration options for each nuclear H_2 method within each market.
  - —E.g., dedicated H_2 production vs. multiple energy products.
- Identify the key parameters and their thresholds and uncertainties for nuclear H_2 market viability.
  - —H_2 production costs, construction times, H_2 output, H_2/electricity production efficiency, scaling factors.
- Perform studies to forecast market viability for nuclear H_2 configurations.

Hydrogen Market Characteristics Example: Oil Refining

- Current U.S. market size.
  - —4.36 million tonnes H_2/yr.
  - —Market characteristics:
    - Merchant liquid and compressed H_2.
    - Captive (on-site production).
  - —Distribution:
    - 62 refineries in 22 states with current H_2 demand (captive).
    - CA and TX account for 64% of current captive demand.





Hydrogen Market Characteristics Example: Oil Refining (cont'd)

- Main growth drivers.
  - —Growth in domestic gasoline refining.
  - —Increasing share of processed sour crude oil.
  - —More stringent environmental constraints (desulfurization needs).
- Potential market inhibitors/threats.
  - —Corporate Average Fuel Economy (CAFE) standards; shift to hybrid cars: slowing gasoline demand.
  - —Growth in *gasoline* imports.
- Marketing and business model.
  - —On-site production (captive demand):
    - 66% of oil refinery demand is captive, 32% merchant compressed, 2% merchant liquid.
  - —On-site merchant-owned plants.
  - —Long-term (15-year) contracts between merchant and refiner.

Nuclear Hydrogen Production Plant Configuration Options

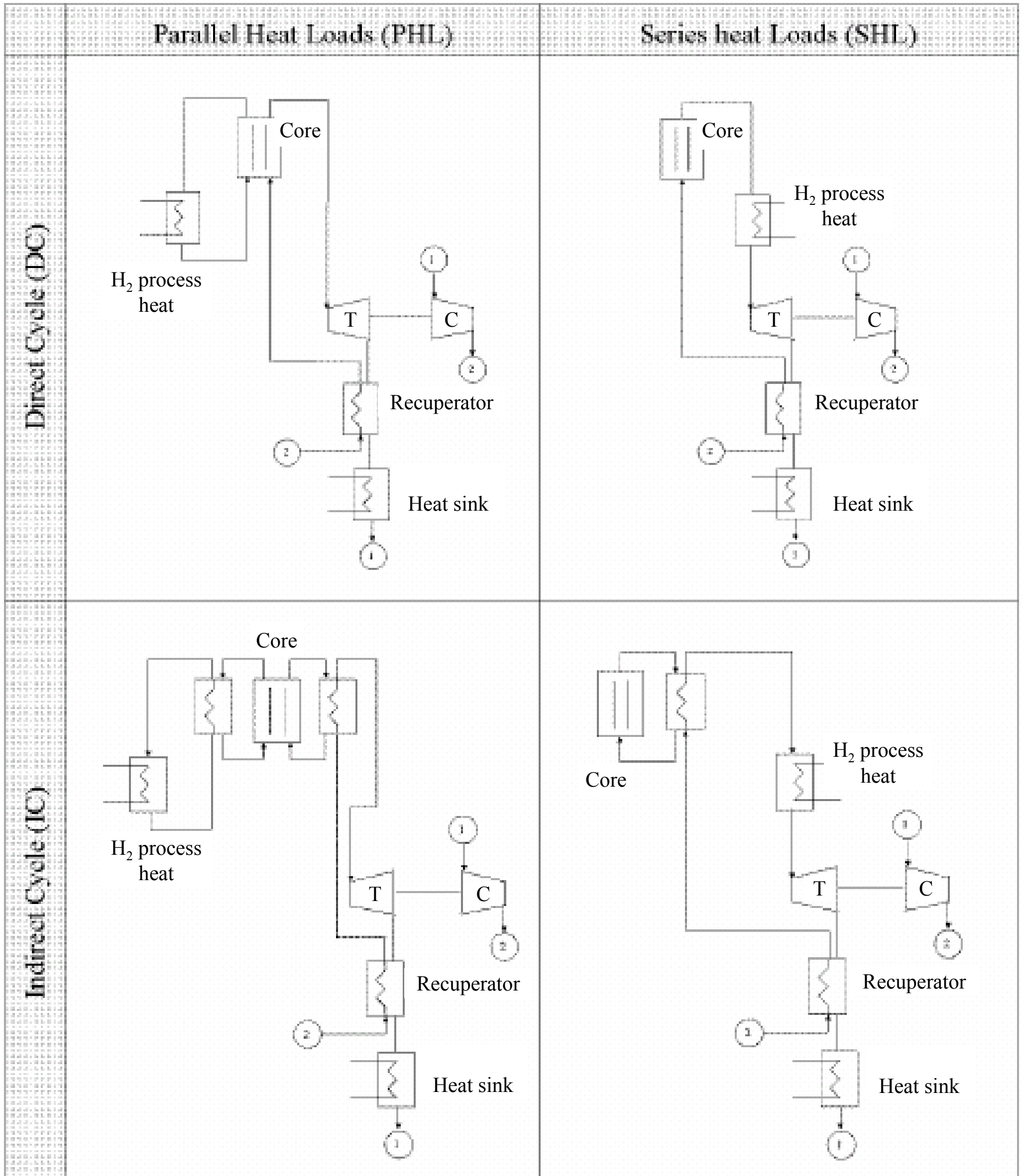
- Multiple energy products.
  - — Dedicated H_2 vs. hydrogen plus electricity.
- Plant size.
  - — Large-scale vs. modular/distributed.
- Flexibility of changing product output rate in co-generation.
  - — Load following on either electricity or hydrogen rate without changing the reactor power.
- Direct vs. indirect heating of the electricity production cycle (if electricity is produced).
- Parallel vs. series arrangement of heat loads.
  - — Heat transfer to the H_2 production process at the exit of the reactor or elsewhere in the plant (e.g., at the exit stream from the turbine).

Implications for

- —Efficiency
- —Cost
- —Location requirement

for the specific technology in a specific market.

Interface Configurations for a Nuclear Hydrogen Production Plant



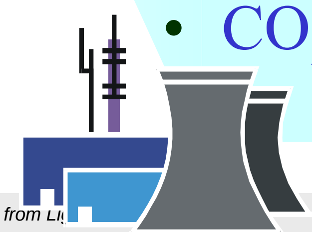
Nuclear Hydrogen Characteristics and Needs of Expanding Hydrogen Markets

Characteristics of Many Near-Term H_2 Markets

- Captive, on-site production.
  - Oil refining, tar sands, coal liquefaction.
- Steady-state operation.
- On-site H_2 storage.
- Demand that varies from site to site.
- Growing overall demand.

Characteristics of Nuclear H_2

- Large-scale, centralized systems. (Small-scale, distributed systems?)
- Limited plant siting.
- Capital intensive, long construction times.
- Potential for variable H_2, co-generation.
- Process heat plus H_2.
- CO_2, import benefits.



Prospects for Nuclear Hydrogen Markets

Hydrogen Market	2003 U.S. Market Size (1000 tonnes H_2)	Outlook	Hydrogen Production Implications	Nuclear Technology Implications	Nuclear Hydrogen Technology Options
Oil Refining	4,084	Strong growth.	Market suitable to dedicated hydrogen production at local sites.	Standardized nuclear reactor with fixed-capacity hydrogen plant customized for site; excess electricity for site or grid sales.	Thermochemical or electrolysis with co-generation.
Ammonia Industry	2,616	Market stalled by high natural gas and hydrogen costs.	Market suitable to dedicated hydrogen production at local sites.	Standardized nuclear reactor with fixed-capacity hydrogen plant customized for site; excess electricity for site or grid sales.	Thermochemical or electrolysis with co-generation.
Methanol Industry	393	Market stalled by high natural gas and hydrogen costs and MTBE phase-out.	Market suitable to dedicated hydrogen production at local sites, but possibly shrinking market.	Co-generation plant to switch to electricity if methanol demand falls.	Electrolysis.

Prospects for Nuclear Hydrogen Markets (cont'd)

Hydrogen Market	2003 U.S. Market Size (1000 tonnes H_2)	Outlook	Hydrogen Production Implications	Nuclear Technology Implications	Nuclear Hydrogen Technology Options
Other Industries		Modest growth.	Market suitable to scaleable regional production centers.	Dedicated or co-generation plant that can be scaled for market growth.	Electrolysis.
— Edible fats and oils	22				
— Metals	48				
— Electronics	14				
— Other	11				
Tar Sands	(515 in Alberta in 2004)	Strong growth (Canada).	Market suitable to dedicated hydrogen production at local sites.	Standardized nuclear reactor with fixed-capacity hydrogen plant customized for site; heat for process steam.	Thermochemical or electrolysis with process heat generation.
Coal Liquefaction and Shale Oil	Medium-to-long term	Potentially significant.	Market suitable to dedicated hydrogen production at local sites.	Standardized nuclear reactor with fixed-capacity hydrogen plant customized for site; excess electricity for site or grid sales.	Thermochemical or electrolysis with co-generation.

Prospects for Nuclear Hydrogen Markets (cont'd)

Hydrogen Market	2003 U.S. Market Size (1000 tonnes H_2)	Outlook	Hydrogen Production Implications	Nuclear Technology Implications	Nuclear Hydrogen Technology Options
Peak Electricity	Medium-to-long term	Potentially significant.	Market suitable to dedicated hydrogen production at local sites.	Standardized nuclear reactor with fixed-capacity hydrogen/oxygen plant customized for site.	Thermochemical or electrolysis.
Transportation	Long term	Potentially significant.	Depending on market scenario, may be suitable to scaleable regional production centers.	Dedicated or co-generation plant that can be scaled for market growth.	Electrolysis.

Hydrogen Production Options

- Almost all H_2 today comes from steam reforming of CH_4.
  - Costs rising with natural gas prices. — >750°C. — *CO_2 emissions.*
- Low-temperature water electrolysis.
  - Energy intensive (i.e., costly).
  - Precious-metal catalysts.
- Thermochemical cycles.
  - Most require high temperatures (800°C - 2000°C) and aggressive chemicals.
- High-temperature steam electrolysis.
  - Solid-oxide fuel cell technology. — Durability?
- Solar hydrogen.
  - Direct solar production: photo-electrochemical cells; artificial photosynthesis.
  - Biomass as feedstock.
- Other options under investigation:
  - Biological/biomimetic hydrogen production.
  - Coal gasification.
  - Direct ceramic membrane separation of water.

U.S. DOE Nuclear Hydrogen R&D Plan

- Sulfur-based thermochemical cycles:
  - —Sulfur-iodine. — Hybrid sulfur.
- High-temperature steam electrolysis.
- Calcium-bromine thermochemical cycle.
  - —ANL cycle with H-Br separation.
- System interface, including heat exchangers.
- Alternative cycles.
- System integration analysis.
  - —Hydrogen economy evolution and infrastructure needs.
  - —Economic framework for market penetration.

Low-Temperature Water Electrolysis

- Commercially available.
  - —Solid-polymer / proton exchange membrane (PEM) cells.
  - —Liquid-electrolyte (e.g., KOH) cells.
- Energy intensive.
  - – Cell efficiency: 65 - 90%.
  - – LWR electrical generation efficiency: 32%.
  - – Total water electrolysis efficiency: 21 - 30%.
- Noble metal catalysts (e.g., Pt).
  - —A strong U.S. program to find alternative catalysts.
- Higher-pressure PEM systems (35 MPa?) can reduce hydrogen compression costs.

Supercritical water reactors can reach 44%

Low-Temperature Water Electrolysis

- DOE research goals:
  - —Capital cost: $300/kW for a 250 kg/day plant with 73% efficiency.
  - —$2.00/kg hydrogen.
- Implications for nuclear power:
  - – No process heat needed, in general.
  - – Hydrogen production can be decoupled from electricity generation.
  - – Hydrogen/electricity co-generation and off-peak production is possible.

Lower-Temperature Hybrid Thermochemical Cycles

- Hundreds of thermochemical and thermo-electrochemical hydrogen production cycles have been identified.
  - —Net reaction: H_2O + energy → H_2 + ½O_2.
- A recent review found 11 with maximum reaction temperatures below 550°C.
  - —Some additional cycles have been considered, but are proprietary and can't be discussed.
- Three cycles are openly being pursued.
  - —Copper-chloride.
  - —Magnesium-chloride.
  - —Heavy-element halide.

Lower-Temperature Hybrid Thermochemical Cycles

- Lower temperatures give more flexibility.
  - —Heat sources are more readily available, including alternative reactor designs.
  - —Higher-temperature reactors can use excess heat for efficient electric power.
- Operating conditions are less severe.
- Potentially simpler material issues (e.g., heat exchangers).

Magnesium-Chloride (Reverse Deacon) Cycle

- Three primary steps:
  - $MgCl_2 + H_2O \rightarrow 2HCl + MgO$, $T = 450^oC$.
  - $MgO + Cl_2 \rightarrow MgCl_2 + \frac{1}{2}O_2$, $T = 500^oC$.
  - $2HCl \rightarrow H_2 + Cl_2$, Electrolytic.
- Zeolite support structure for $MgCl_2$ reactions.
- Limited testing so far.
- Side products may require higher reaction temperatures.

U-Eu-Br Heavy-Element Halide Cycle

$$2UO_2Br_2 \cdot 3H_2O(s) \xrightarrow[300\ ^\circ C]{\Delta} 2UO_3 \cdot H_2O(s) + 4HBr + 2H_2O \quad (1)$$

$$4EuBr_2 + 4HBr \rightarrow 4EuBr_3(s) + 2H_2(g) \quad (2)$$

$$4EuBr_3 \xrightarrow[300\ ^\circ C]{\Delta} 4EuBr_2(s) + 2Br_2 \quad (3)$$

$$2UO_3 \cdot H_2O(s) + 2Br_2 + 4H_2O \rightarrow 2(UO_2Br_2 \cdot 3H_2O(s)) + O_2(g) \quad (4)$$

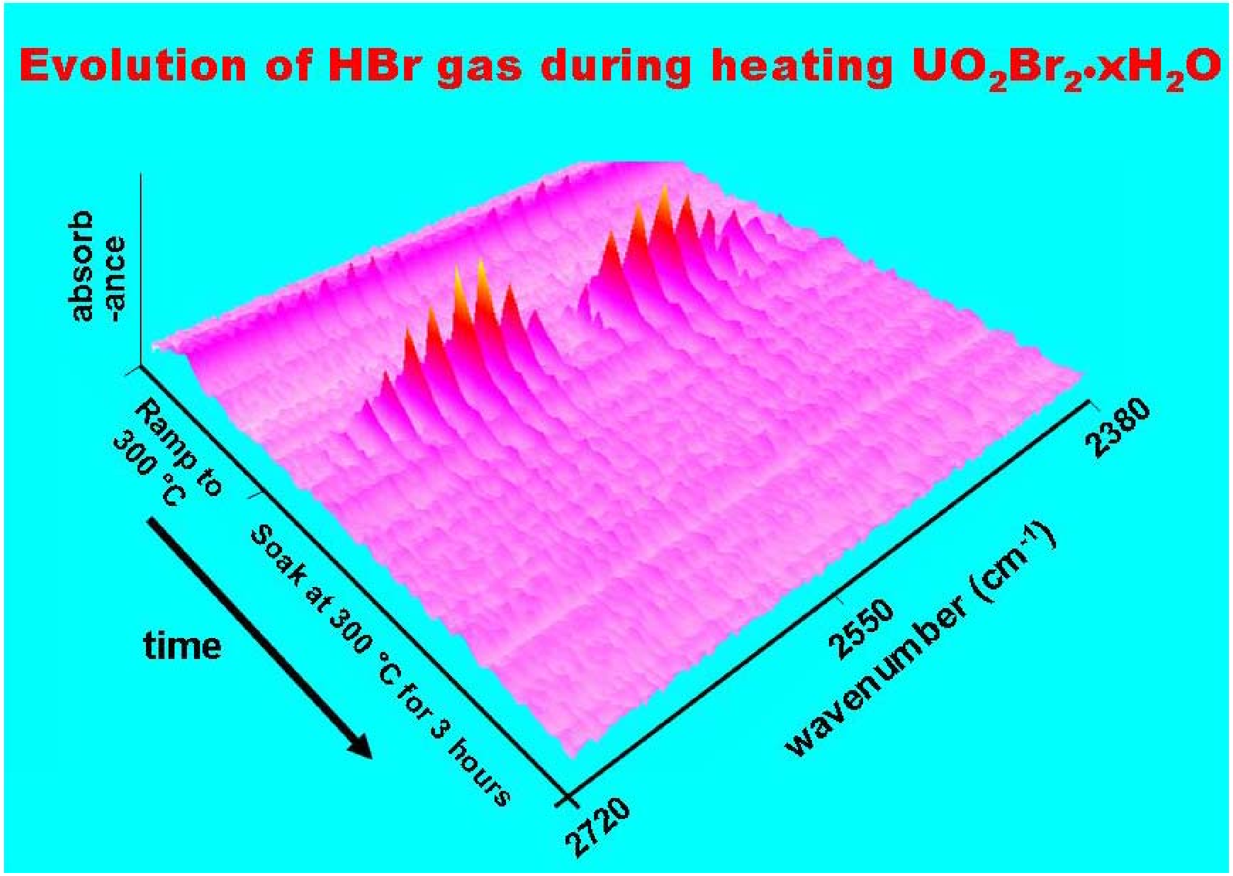
Net reaction: $2H_2O \xrightarrow[300\ ^\circ C]{\Delta} 2H_2 + O_2$

- Purely thermochemical — no electrolysis step.
- Maximum temperature = 300°C.

U-Eu-Br Heavy-Element Halide Cycle: Proof of Concept Reaction 1

$$UO_2Br_2 \cdot 3H_2O(s) \xrightarrow{\Delta} UO_3 \cdot H_2O(s) + 2HBr(g) + H_2O(g)$$

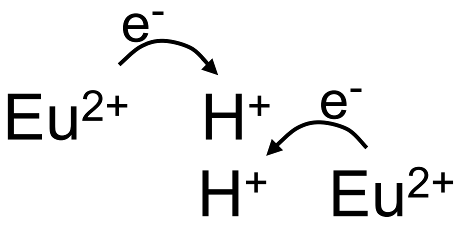
- Fourier Transform Infrared Analysis confirms that the reaction goes to completion at 300°C.



U-Eu-Br Heavy-Element Halide Cycle: Proof of Concept Reaction 2

$$4EuBr_2 + 4HBr \rightarrow 4EuBr_3 + 2H_2(g)$$

- Hydrogen generation has been demonstrated, but the reaction rate is slow.
- Evidence for a simultaneous, concerted four-center reaction:



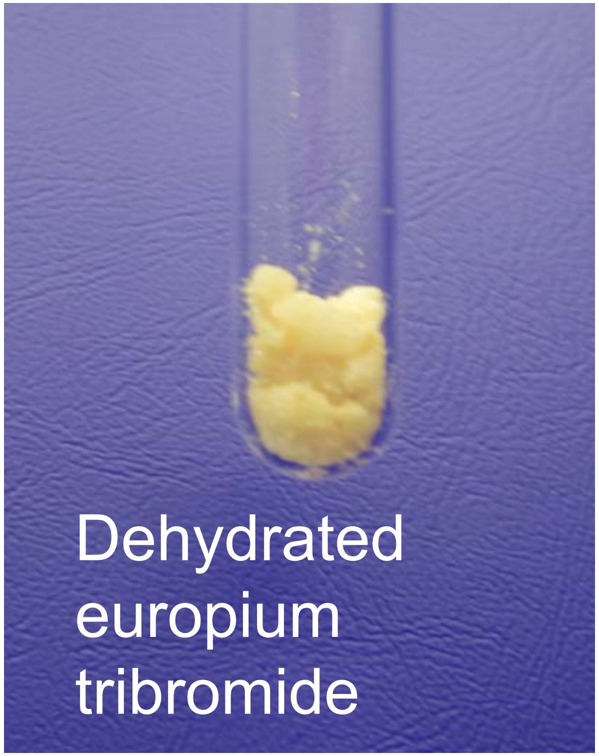
- Catalysis is being considered to improve the kinetics.

H_2 gas bubble evolution from the heavy metal halide reaction

U-Eu-Br Heavy-Element Halide Cycle: Proof of Concept Reaction 3

$$2EuBr_3 \xrightarrow[300\ ^\circ C]{\Delta} 2EuBr_2(s) + Br_2(g)$$

- Vacuum pyrolysis allows the reaction to proceed without the complications that can arise from entrained water.



U-Eu-Br Heavy-Element Halide Cycle: Proof of Concept Reaction 4

$$2UO_3 \cdot H_2O(s) + 2Br_2 + 4H_2O \rightarrow 2(UO_2Br_2 \cdot 3H_2O)(s) + O_2$$

- Br_2 and water can react to form HBr and HOBr ("bromine water"):

$$Br_2 + H_2O \rightarrow HBr + HOBr$$

- HOBr can interfere with the desired reaction.
- Such side reactions are the subject of current investigation.

U-Eu-Br Heavy-Element Halide Cycle: Additional Research Needs

- Thermodynamic data
  - —Needed to assess cycle efficiency.
- Corrosion-resistant structural materials.
  - —Corrosion should be more tractable at 300^{o}C than at higher temperatures.
- Engineering process design.
  - —Optimization of a process flowsheet.

Copper-Chloride Cycle

- The most mature of the lower-temperature cycles.
- Four primary steps:
  - $2Cu + 2HCl(g) \rightarrow H_2(g) + 2CuCl$, T = 450°C.
  - $4CuCl \rightarrow 2Cu + 2CuCl_2$, Electrolytic.
  - $2CuCl_2 + H_2O(g) \rightarrow CuO{*}CuCl_2 + 2HCl(g)$, T = 325°C.
  - $CuO{*}CuCl_2 \rightarrow 2CuCl + \frac{1}{2}O_2(g)$, T = 530°C.

Technical Progress for Thermal Reactions

Reaction	Kinetics	Conversion	Separations	Possible Competing Reactions
H_2 generation	√	√ 100% $Cu \rightarrow CuCl$	H_2 and unreacted HCl	No
HCl generation	√ (Preliminary)	Still optimizing parameters	HCl and H_2O?	Yes (Cl_2 formation)
O_2 generation	√	√ 100% O_2 recovered	None	No

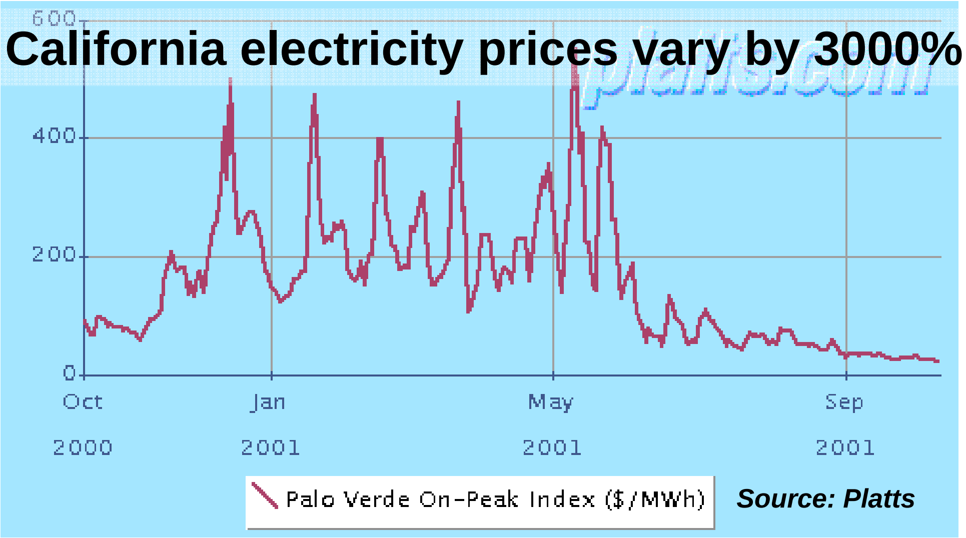
Cu-Cl Summary

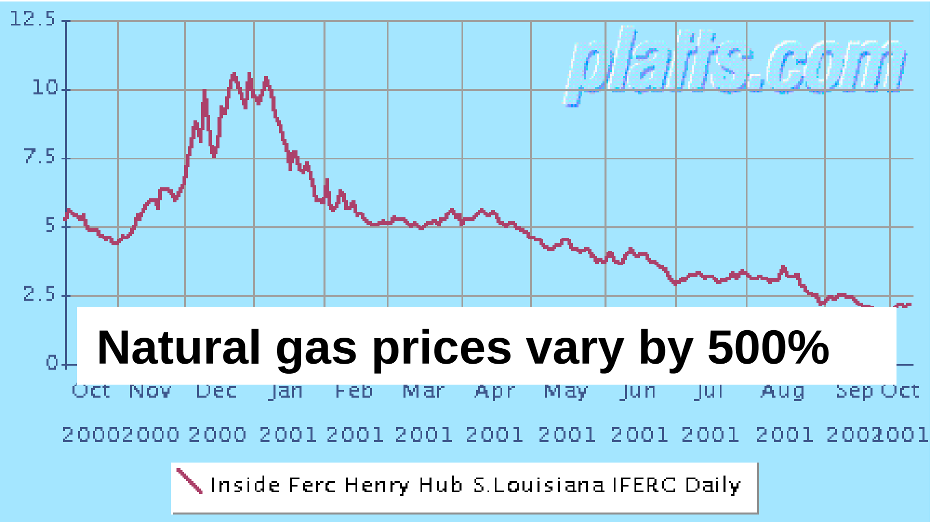
- All tests indicate that 530°C is the maximum required and Cu-Cl is a viable low temperature thermochemical cycle.

- Progress has been made:
  - —Kinetics measured for hydrogen and oxygen generation reactions.
  - —Operating parameters are being optimized for HCl reaction.
  - —Process flow modeling started.
  - —Additional research required for electrochemical cell development.

Electricity (and Hydrogen) Costs Can Vary Widely

- There's great promise in taking advantage of price fluctuations.
- But price variations are not predictable.
- A hydrogen production system based on off-peak (low-price) electricity would have to be flexible enough to adapt to changing market conditions.





Low-Temp. Electrolysis Base Load Hydrogen Production

- Nuclear hydrogen needs to compete with steam methane reforming.
  - For natural gas at \$4/MMBTU, hydrogen costs \$1.00 - \$1.29/kg.
  - For natural gas at \$12/MMBTU, hydrogen costs \$2.25 - \$3.58/kg.
- Two U.S. studies have looked at base load hydrogen production costs through low-temperature water electrolysis. At off-peak power prices:
  - 20 kg/day system: \$19.01/kg H_2.
  - 100 kg/day system: \$8.09 / kg H_2.
  - 1000 kg/day system: \$4.15 / kg H_2.
- Needs:
  - Cheaper electricity.
  - Cheaper electrolyzer systems; larger-capacity systems.

Off-Peak Nuclear Hydrogen Production

- Base-load operation maximizes the capital investment in low-temperature electrolyzer units.
  - —Studies presume 90 - 97% electrolyzer capacity factors.
  - —Off-peak power operation would result in ~40% capacity factor.
  - —Therefore, not $4/kg, but $7/kg.
  - —2.5-times larger plant needed to achieve the same daily production as a base load operation.
- A substantial off-peak electricity demand would affect off-peak pricing.

Summary

- The successful development of hydrogen production technologies is tied to the characteristics of the markets to be served.
- Different nuclear hydrogen technologies and system configurations are better suited to different markets.
- Low-temperature water electrolysis is a currently available technology for hydrogen production through nuclear power.

Summary (cont'd)

- A limited number of thermo-electrochemical cycles have heat requirements consistent with light-water reactor technology.
- Reductions in electricity and system costs would be needed (or a carbon tax) for low-temperature water electrolysis to compete with today's costs for steam methane reformation.
- The interactions between hydrogen and electricity *markets* and hydrogen and electricity *producers* are complex and will evolve as the markets evolve.