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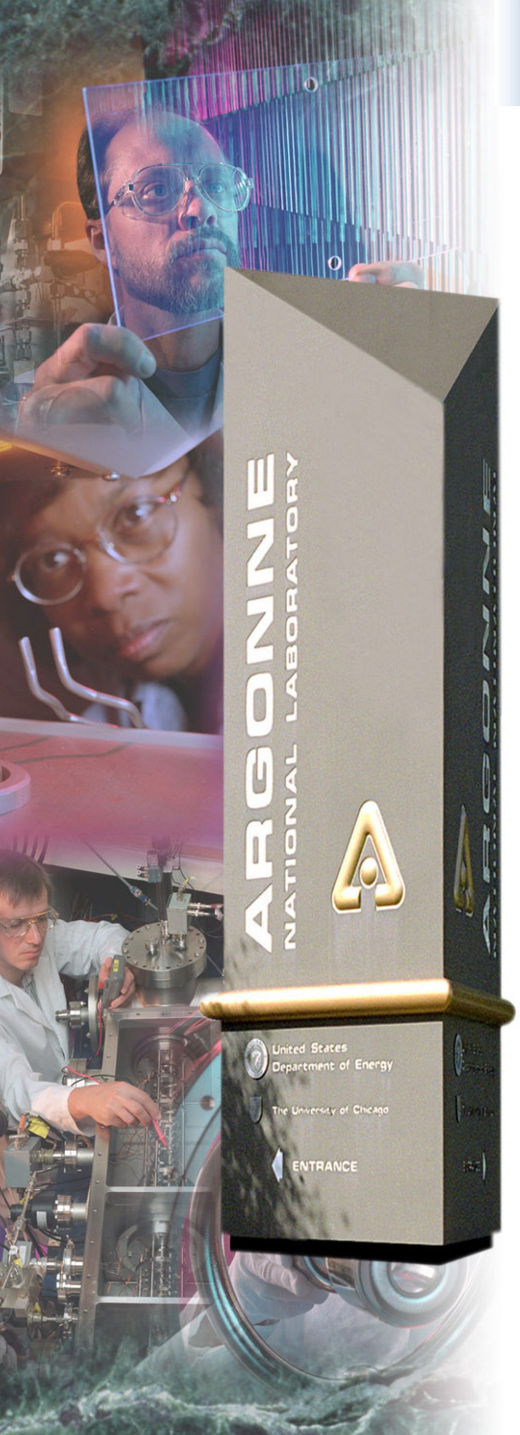

# U.S. Work on Hydrogen Production Using Light-Water Reactors

## *Mark C. Petri*

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

THE UNIVERSITY OF CHICAGO
Office of Science
U.S. DEPARTMENT OF ENERGY

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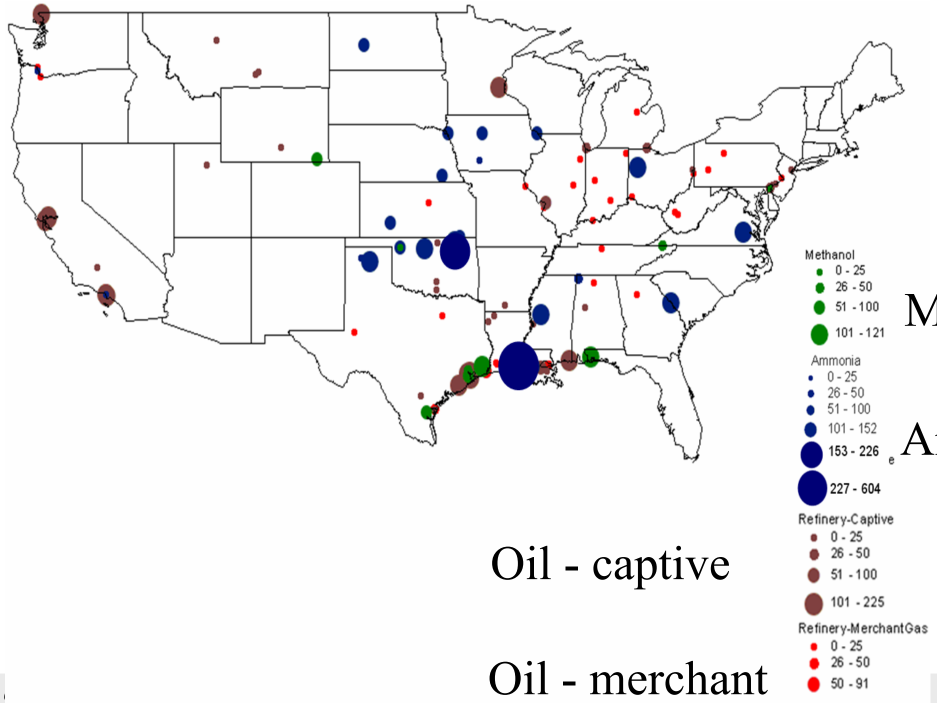
# Current U.S. Hydrogen Markets

- 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 $H_2$).



Methanol

Ammonia

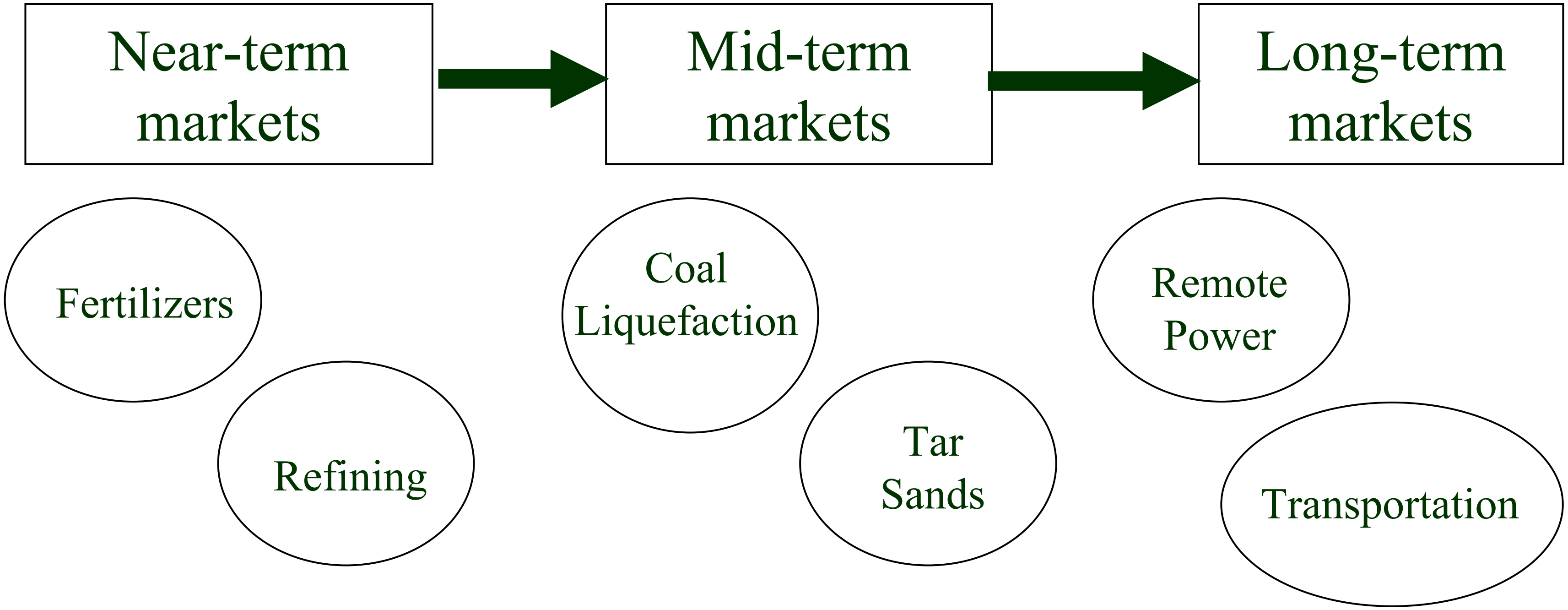
Oil - captive

Oil - merchant

# 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



Near-term markets → Mid-term markets → Long-term markets

- Fertilizers
- Refining
- Coal Liquefaction
- Tar Sands
- Remote Power
- Transportation

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

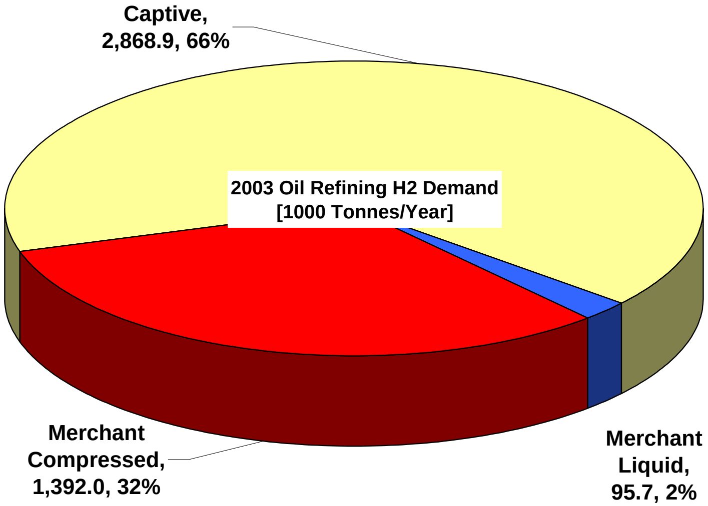
- As markets evolve, nuclear hydrogen's ability to compete will change.

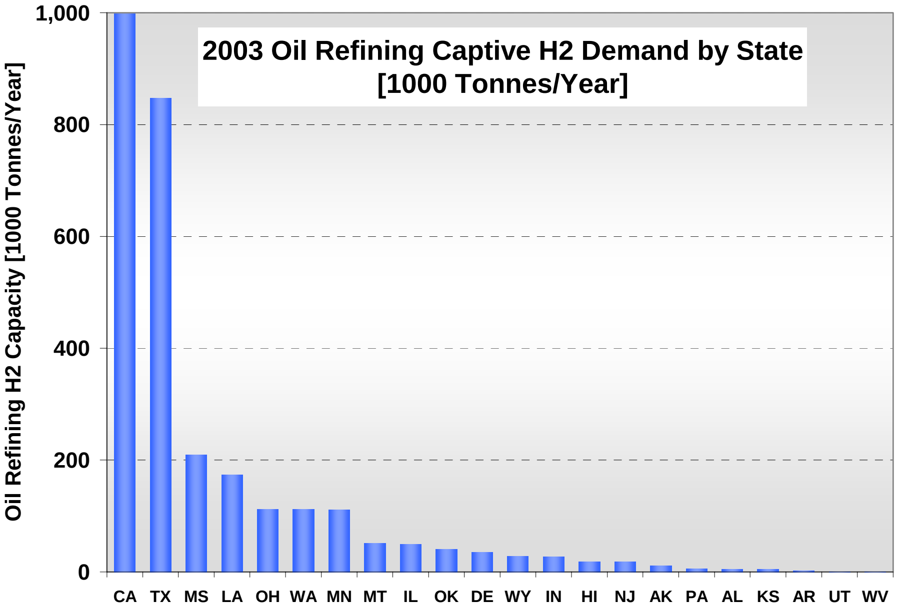
# Nuclear Hydrogen System Study Components

- 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

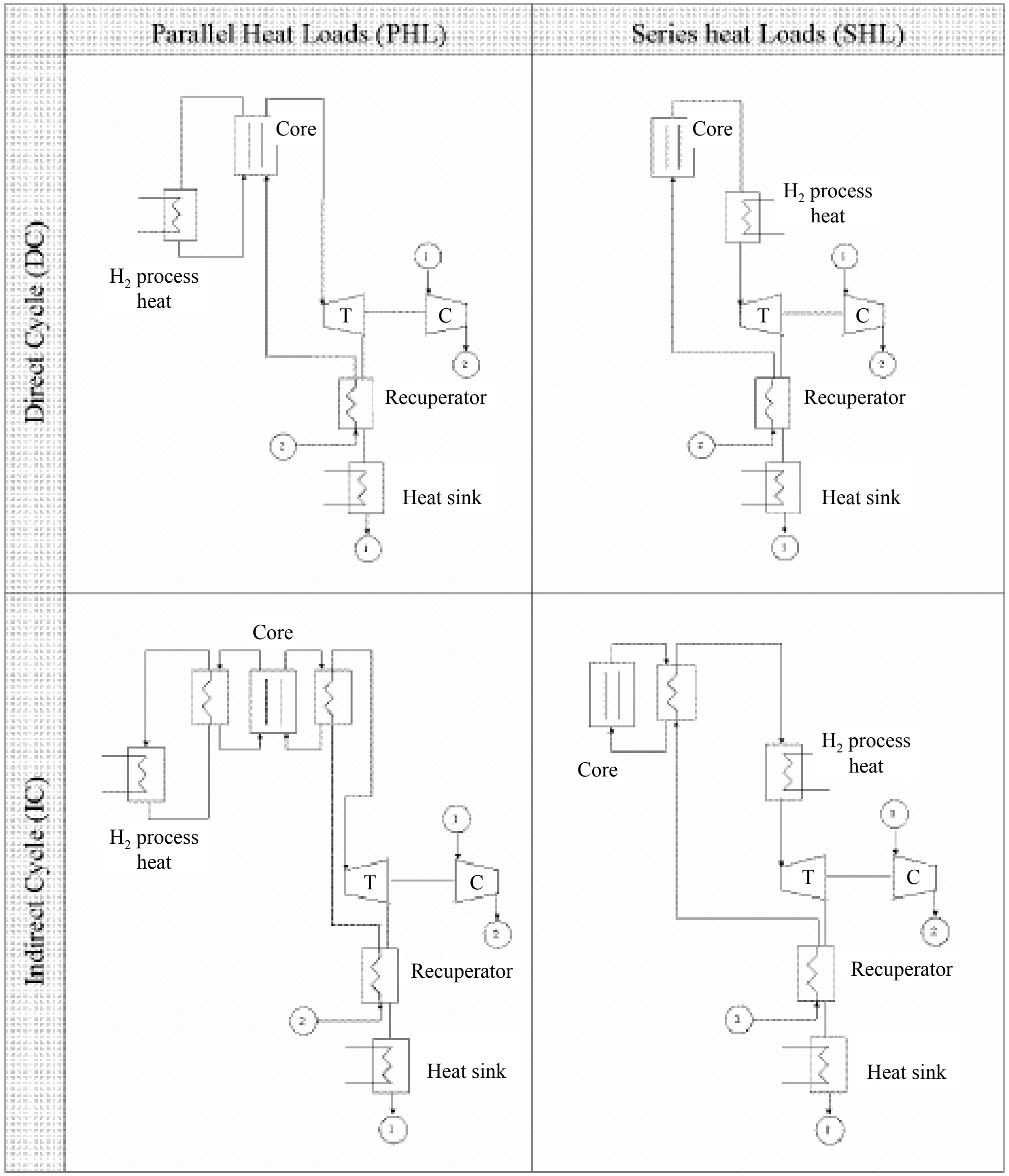
- Multiple energy products.
  - Dedicated $H_2$ vs. hydrogen plus electricity.
- Plant size.
  - Large-scale vs. modular/distributed.
- Flexibility of changing product output rate in co-generation.
  - Load following on either electricity or hydrogen rate without changing the reactor power.
- Direct 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*



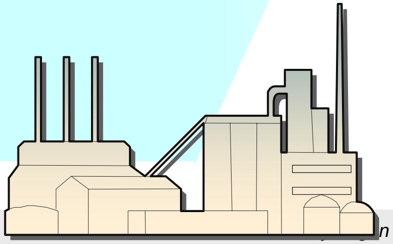
# *Nuclear Hydrogen Characteristics and Needs of Expanding Hydrogen Markets*

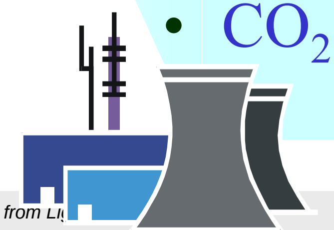
## Characteristics of Many Near-Term $H_2$ Markets

- 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: $H_2O + \text{energy} \rightarrow H_2 + ½O_2$.
- A recent review found 11 with maximum reaction temperatures below 550$^o$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:
  - $MgCl_2 + H_2O \rightarrow 2HCl + MgO$, $T = 450^{o}C$.
  - $MgO + Cl_2 \rightarrow MgCl_2 + ½O_2$, $T = 500^{o}C$.
  - $2HCl \rightarrow H_2 + Cl_2$, 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

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

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

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

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

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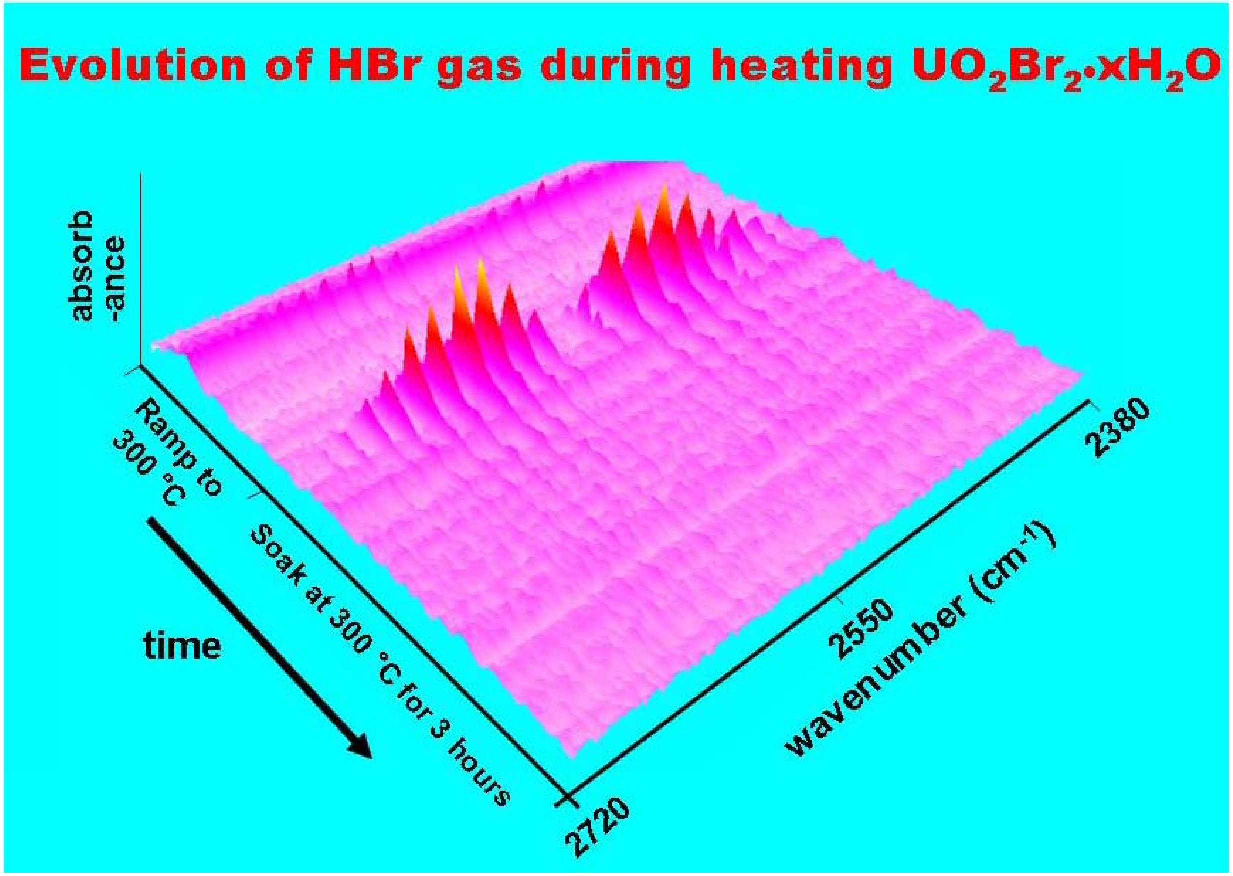
Net reaction: $2H_2O \xrightarrow[300\ ^\circ C]{\Delta} 2H_2 + O_2$

- 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.

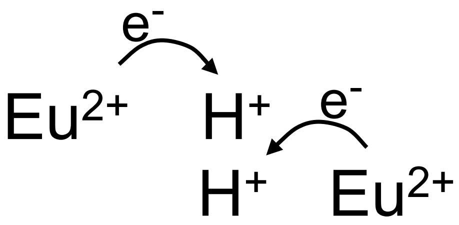


# U-Eu-Br Heavy-Element Halide Cycle: Proof of Concept

## 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:



$e^-$

$Eu^{2+}$ $H^+$ $e^-$

$H^+$ $Eu^{2+}$

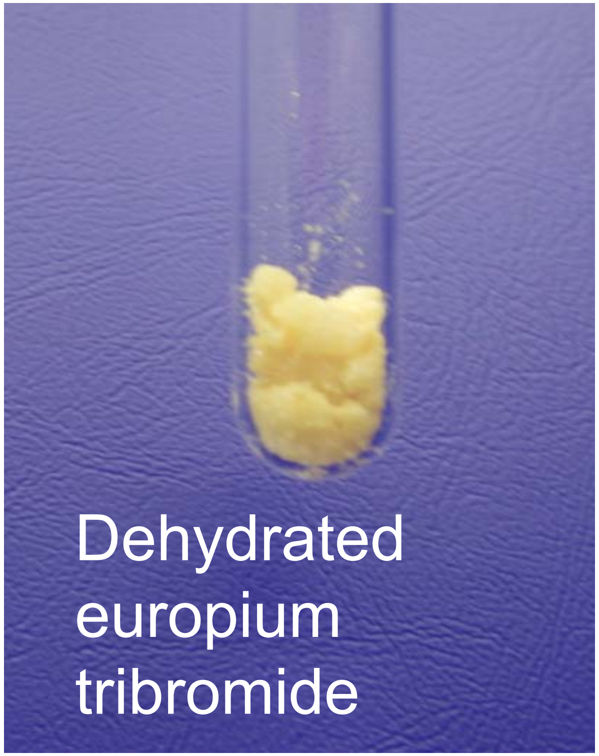
- Catalysis is being considered to improve the kinetics.

$H_2$ 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.


Dehydrated europium tribromide


Europium dibromide

# *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°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:
  - $2Cu + 2HCl(g) \rightarrow H_2(g) + 2CuCl$, $T = 450^{o}C$.
  - $4CuCl \rightarrow 2Cu + 2CuCl_2$, Electrolytic.
  - $2CuCl_2 + H_2O(g) \rightarrow CuO{*}CuCl_2 + 2HCl(g)$, $T = 325^{o}C$.
  - $CuO{*}CuCl_2 \rightarrow 2CuCl + \frac{1}{2}O_2(g)$, $T = 530^{o}C$.

# *Technical Progress for Thermal Reactions*

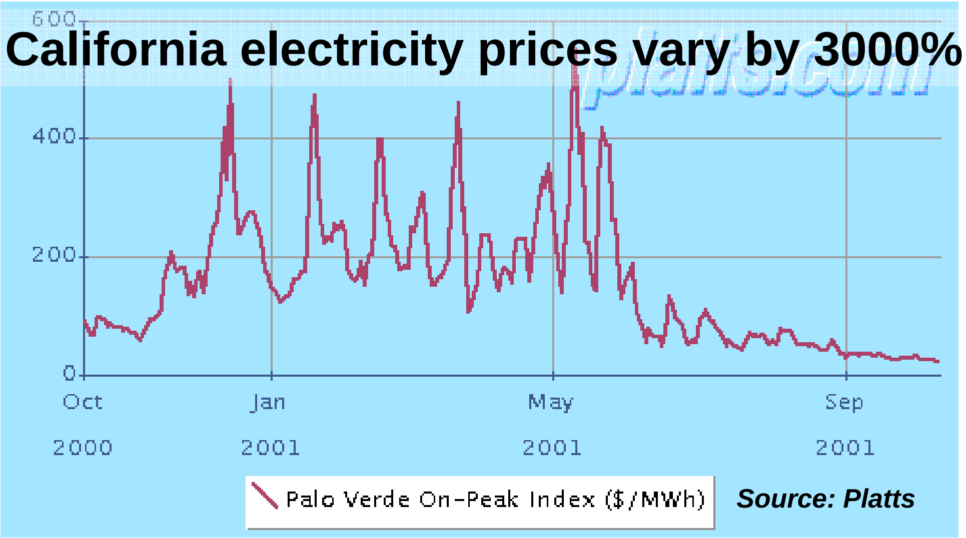
| *Reaction* | *Kinetics* | *Conversion* | *Separations* | *Possible Competing Reactions* |
|---|---|---|---|---|
| $H_2$ generation | √ | √<br>100%<br>Cu → CuCl | $H_2$ and unreacted HCl | No |
| HCl generation | √<br>(Preliminary) | Still optimizing parameters | HCl and $H_2O$? | Yes<br>($Cl_2$ formation) |
| $O_2$ generation | √ | √<br>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.

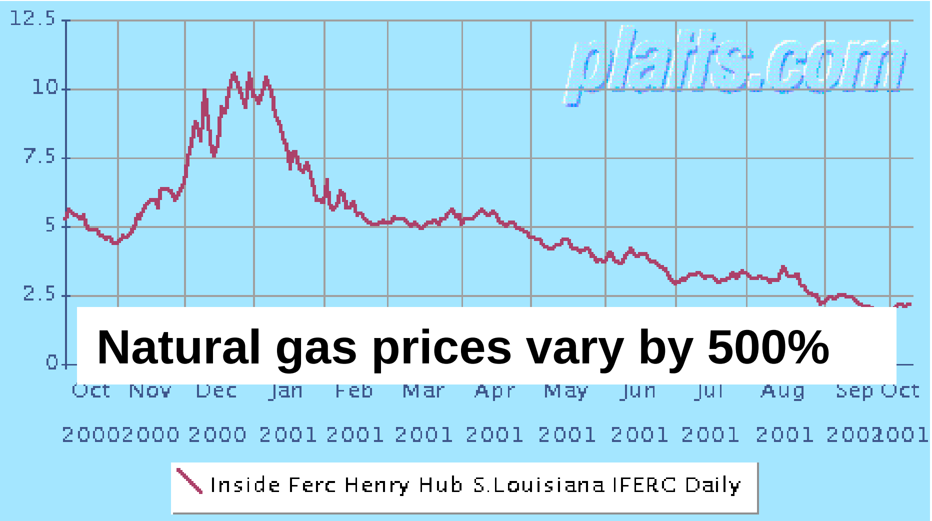
# Electricity (and Hydrogen) Costs Can Vary Widely

- 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.



**California electricity prices vary by 3000%**

***Source: Platts***



**Natural gas prices vary by 500%**

# *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.