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
Current U.S. Hydrogen Markets

- Oil refining (4.1M tonnes H₂).
- Ammonia (2.6M tonnes H₂).
- [Canadian oil sands (0.5M tonnes H₂)].
- Methanol (0.4M tonnes H₂).
- Chemical, metal, food, etc. (0.1M tonnes H₂).

[Map showing current U.S. hydrogen markets with locations for 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
- Fertilizers
- Refining

Mid-term markets
- Coal Liquefaction
- Tar Sands

Long-term markets
- Remote Power
- Transportation

Each market will have different hydrogen needs. Nuclear H₂ 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 H₂ markets and their requirements.

• Assess configuration options for each nuclear H₂ method within each market.
  —E.g., dedicated H₂ production vs. multiple energy products.

• Identify the key parameters and their thresholds and uncertainties for nuclear H₂ market viability.
  —H₂ production costs, construction times, H₂ output, H₂/electricity production efficiency, scaling factors.

• Perform studies to forecast market viability for nuclear H₂ configurations.
Hydrogen Market Characteristics Example: Oil Refining

- Current U.S. market size.
  - 4.36 million tonnes H₂/yr.
- Market characteristics:
  - Merchant liquid and compressed H₂.
  - Captive (on-site production).
- Distribution:
  - 62 refineries in 22 states with current H₂ 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 H₂ 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 H₂ 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

<table>
<thead>
<tr>
<th>Parallel Heat Loads (PHL)</th>
<th>Series Heat Loads (SHL)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Direct Cycle (DC)</strong></td>
<td><strong>Indirect Cycle (IC)</strong></td>
</tr>
<tr>
<td>Core</td>
<td>Core</td>
</tr>
<tr>
<td>H₂ process heat</td>
<td>H₂ process heat</td>
</tr>
<tr>
<td>Recuperator</td>
<td>Recuperator</td>
</tr>
<tr>
<td>Heat sink</td>
<td>Heat sink</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Characteristics of Many Near-Term H₂ Markets

- Captive, on-site production.  
  — Oil refining, tar sands, coal liquefaction.
- Steady-state operation.
- On-site H₂ storage.
- Demand that varies from site to site.
- Growing overall demand.

Characteristics of Nuclear H₂

- Large-scale, centralized systems. (Small-scale, distributed systems?)
- Limited plant siting.
- Capital intensive, long construction times.
- Potential for variable H₂, co-generation.
- Process heat plus H₂.
- CO₂, import benefits.
## Prospects for Nuclear Hydrogen Markets

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil Refining</td>
<td>4,084</td>
<td>Strong growth.</td>
<td>Market suitable to dedicated hydrogen production at local sites.</td>
<td>Standardized nuclear reactor with fixed-capacity hydrogen plant customized for site; excess electricity for site or grid sales.</td>
<td>Thermochemical or electrolysis with co-generation.</td>
</tr>
<tr>
<td>Ammonia Industry</td>
<td>2,616</td>
<td>Market stalled by high natural gas and hydrogen costs.</td>
<td>Market suitable to dedicated hydrogen production at local sites.</td>
<td>Standardized nuclear reactor with fixed-capacity hydrogen plant customized for site; excess electricity for site or grid sales.</td>
<td>Thermochemical or electrolysis with co-generation.</td>
</tr>
<tr>
<td>Methanol Industry</td>
<td>393</td>
<td>Market stalled by high natural gas and hydrogen costs and MTBE phase-out.</td>
<td>Market suitable to dedicated hydrogen production at local sites, but possibly shrinking market.</td>
<td>Co-generation plant to switch to electricity if methanol demand falls.</td>
<td>Electrolysis.</td>
</tr>
</tbody>
</table>
## Prospects for Nuclear Hydrogen Markets (cont’d)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Other Industries</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Electrolysis.</td>
</tr>
<tr>
<td>— Edible fats and oils</td>
<td>22</td>
<td>Modest growth.</td>
<td>Market suitable to scaleable regional production centers.</td>
<td>Dedicated or co-generation plant that can be scaled for market growth.</td>
<td></td>
</tr>
<tr>
<td>— Metals</td>
<td>48</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>— Electronics</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>— Other</td>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal Liquefaction and Shale Oil</td>
<td>Medium-to-long term</td>
<td>Potentially significant.</td>
<td>Market suitable to dedicated hydrogen production at local sites.</td>
<td>Standardized nuclear reactor with fixed-capacity hydrogen plant customized for site; excess electricity for site or grid sales.</td>
<td>Thermochemical or electrolysis with co-generation.</td>
</tr>
</tbody>
</table>
### Prospects for Nuclear Hydrogen Markets (cont’d)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak Electricity</td>
<td>Medium-to-long term</td>
<td>Potentially significant.</td>
<td>Market suitable to dedicated hydrogen production at local sites.</td>
<td>Standardized nuclear reactor with fixed-capacity hydrogen/oxygen plant customized for site.</td>
<td>Thermochemical or electrolysis.</td>
</tr>
<tr>
<td>Transportation</td>
<td>Long term</td>
<td>Potentially significant.</td>
<td>Depending on market scenario, may be suitable to scaleable regional production centers.</td>
<td>Dedicated or co-generation plant that can be scaled for market growth.</td>
<td>Electrolysis.</td>
</tr>
</tbody>
</table>
Hydrogen Production Options

• Almost all H₂ today comes from steam reforming of CH₄.
  – Costs rising with natural gas prices. — >750°C. — CO₂ 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.
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: \( \text{H}_2\text{O} + \text{energy} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2 \).

• A recent review found 11 with maximum reaction temperatures below 550\(^\circ\)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:
  - \( \text{MgCl}_2 + \text{H}_2\text{O} \rightarrow 2\text{HCl} + \text{MgO}, \quad T = 450^\circ\text{C}. \)
  - \( \text{MgO} + \text{Cl}_2 \rightarrow \text{MgCl}_2 + \frac{1}{2}\text{O}_2, \quad T = 500^\circ\text{C}. \)
  - \( 2\text{HCl} \rightarrow \text{H}_2 + \text{Cl}_2, \quad \text{Electrolytic}. \)

- Zeolite support structure for \( \text{MgCl}_2 \) reactions.
- Limited testing so far.
- Side products may require higher reaction temperatures.
U-Eu-Br Heavy-Element Halide Cycle

2UO$_2$Br$_2$·3H$_2$O(s) $\xrightarrow{\Delta 300^\circ C}$ 2UO$_3$·H$_2$O(s) + 4HBr + 2H$_2$O \hspace{1cm} (1)

4EuBr$_2$ + 4HBr $\rightarrow$ 4EuBr$_3$(s) + 2H$_2$(g) \hspace{1cm} (2)

4EuBr$_3$ $\xrightarrow{\Delta 300^\circ C}$ 4EuBr$_2$(s) + 2Br$_2$ \hspace{1cm} (3)

2UO$_3$·H$_2$O(s) + 2Br$_2$ + 4H$_2$O $\rightarrow$ 2(UO$_2$Br$_2$·3H$_2$O(s)) + O$_2$(g) \hspace{1cm} (4)

---

Net reaction: 2H$_2$O $\xrightarrow{\Delta 300^\circ C}$ 2H$_2$ + O$_2$

- Purely thermochemical — no electrolysis step.
- Maximum temperature = 300$^o$C.
**U-Eu-Br Heavy-Element Halide Cycle: Proof of Concept Reaction 1**

\[
UO_2Br_2\cdot3H_2O(s) \xrightarrow{\Delta} UO_3\cdotH_2O(s) + 2HBr(g) + H_2O(g)
\]

- 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**

\[ 4\text{EuBr}_2 + 4\text{HBr} \rightarrow 4\text{EuBr}_3 + 2\text{H}_2(\text{g}) \]

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

\[ \text{Eu}^{2+} + \text{H}^+ + \text{e}^- \rightarrow \text{Eu}^{2+} \]

\[ \text{H}^+ + \text{e}^- \rightarrow \text{H}_2(\text{g}) \]

- Catalysis is being considered to improve the kinetics.
U-Eu-Br Heavy-Element Halide Cycle: Proof of Concept

Reaction 3

\[ 2\text{EuBr}_3 \xrightarrow{\Delta 300 \, ^\circ \text{C}} 2\text{EuBr}_2(s) + \text{Br}_2(g) \]

- 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

\[ 2\text{UO}_3\cdot\text{H}_2\text{O}(s) + 2\text{Br}_2 + 4\text{H}_2\text{O} \rightarrow 2(\text{UO}_2\text{Br}_2\cdot3\text{H}_2\text{O})(s) + \text{O}_2 \]

- \( \text{Br}_2 \) and water can react to form HBr and HOBr ("bromine water"):
  \[ \text{Br}_2 + \text{H}_2\text{O} \rightarrow \text{HBr} + \text{HOBr} \]

- 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:

  - $2\text{Cu} + 2\text{HCl}(g) \rightarrow \text{H}_2(g) + 2\text{CuCl}$, $T = 450^\circ\text{C}$.
  - $4\text{CuCl} \rightarrow 2\text{Cu} + 2\text{CuCl}_2$, Electrolytic.
  - $2\text{CuCl}_2 + \text{H}_2\text{O}(g) \rightarrow \text{CuO}^*\text{CuCl}_2 + 2\text{HCl}(g)$, $T = 325^\circ\text{C}$.
  - $\text{CuO}^*\text{CuCl}_2 \rightarrow 2\text{CuCl} + \frac{1}{2}\text{O}_2(g)$, $T = 530^\circ\text{C}$.
## Technical Progress for Thermal Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Kinetics</th>
<th>Conversion</th>
<th>Separations</th>
<th>Possible Competing Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ generation</td>
<td>√</td>
<td>√</td>
<td>H₂ and unreacted HCl</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100% Cu → CuCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCl generation</td>
<td>√</td>
<td>Still optimizing parameters</td>
<td>HCl and H₂O?</td>
<td>Yes (Cl₂ formation)</td>
</tr>
<tr>
<td>(Preliminary)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂ generation</td>
<td>√</td>
<td>√</td>
<td>None</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100% O₂ recovered</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**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.

Source: Platts

California electricity prices vary by 3000%

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 H₂.
  - 100 kg/day system: $8.09/kg H₂.
  - 1000 kg/day system: $4.15/kg H₂.

- 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.