Nuclear Hydrogen?
Current Methods of H₂ Production

![Pie chart showing the distribution of primary energy sources for hydrogen production.](image)

Fig. 1. Present distribution of primary energy sources for hydrogen production. Ewan IJHE 2005, 30, 809

SMR is not clean!!! So we should try for better solution

![Bar chart showing full cycle emissions.](image)

Full Cycle Emissions!!

The options are clear

Joop F. Van de Vate *Energy Policy* 1997, 25, 1
SMR = Steam Methane Reforming
Factors included in OFM include cost ($/tonne H₂), area/MW H₂–Km², Kg CO₂/GJ
Nuclear Hydrogen Production Technologies


Hydrogen Production

Thermochemical (TC) Processes

Hybrid Processes

Electrolysis (ES)

S-MR
S-I
UT-3

WSP

Water ES

High T. Steam ES (HTSE)

MHR
AHTR

STAR

MHR
AHTR

GT-MHR
S-CO\textsubscript{2}-AGR
SCWR
ALWR

S-CO\textsubscript{2}-AGR
GT-MHR

SMR = Steam Methane Reforming
WSP = Westinghouse Sulfur Process
ES = Electrolysis
HTSE = High Temperature Steam Electrolysis
Possible Processes

• Electrolysis (conventional <100°C) – uses electricity only. Process is mature. Efficiency limited to ~ 70-80% (25-30% coupled HTR).

• HTSE (750-1000°C) ~45% efficiency (coupled to HTR). Reverse SOFC

• Thermochemical methods - make use of the process heat from advanced reactors. Potentially more efficient.

More than 1000 systems have been proposed. Most considered are:

Zinc-Oxygen 1500 °C
Sulfur-Iodine (S-I) 850 °C
Calcium-bromine (UT-3) 750 °C
Copper-Chlorine 550 °C

1. I₂(l) + SO₂(g) + 2H₂O(l) → 2HI(aq) + H₂SO₄(aq)
2. H₂SO₄(aq) → H₂O(g) + SO₂(g) + 1/2O₂(g) 850 °C
3. 2HI(g) → H₂(g) + I₂(g)

1. CaO + Br₂ → CaBr₂ + 1/2O₂  \( \Delta G^0 (800K) = -40.9 \text{ KJ/mol} \)
2. CaBr₂ + H₂O → CaO + 2HBr  \( \Delta G^0 (1000K) = +104.0 \text{ KJ/mol} \)
3. Fe₃O₄ + 8HBr → 3FeBr₂ + 4H₂O + Br₂  \( \Delta G^0 = -119.9 \text{ kJ/mol} \)
4. 3FeBr₂ + 4H₂O → Fe₃O₄ + 6HBr + H₂  \( \Delta G^0 (900K) = +117.5 \text{ kJ/mol} \)
Capabilities of Next Generation Nuclear Reactors for Hydrogen Production – Not Just a Load of Hot Air

VHTR – DOE-GIF Gen IV reactor concept

Nominal Hydrogen production capacity 80,000 m$^3$/h ~1000 MW VHTR

Massive Hydrogen Production Possible!!

HTTR - 30 MW reactor in Japan with 950 °C outlet coolant temperature

Already in advanced stage

<table>
<thead>
<tr>
<th>Major specification of the HTTR</th>
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<tbody>
<tr>
<td>Thermal power (MW)</td>
<td>30</td>
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<tr>
<td>Coolant</td>
<td>Helium gas</td>
</tr>
<tr>
<td>Outlet coolant temperature (°C)</td>
<td>850 (rated operation)</td>
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<td></td>
<td>950 (high temperature test operation)</td>
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<tr>
<td>Inlet coolant temperature (°C)</td>
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<td>Primary coolant pressure (MPa)</td>
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<td>Fuel</td>
<td>Low-enriched UO$_2$</td>
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<tr>
<td>Fuel element type</td>
<td>Prismatic block</td>
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<tr>
<td>Moderator</td>
<td>Graphite</td>
</tr>
<tr>
<td>Plant lifetime (years)</td>
<td>20</td>
</tr>
</tbody>
</table>

Fig. 5. Schematic drawing of the HTTR hydrogen production system.
High Temperatures Enable a Range of Process Heat Applications

- Iron manufacture
- Electricity generation (Gas turbine, Coal gasification)
- Styrene (Ethylbenzene)
- Petroleum refineries
- Desulfurization
- Wood pulp manufacture
- Desalination, District heating

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Primary nuclear application considered for VHTR - H2 production

Thermochemical cycles for Hydrogen production >750 C
Other reactor concepts with high outlet temperatures also potentially useful

**Modular Helium Reactor (MHR) Reference Concept for VHTR Concept Set**

- Based on prismatic (GT-MHR) design connected to steam reformer/steam generator -- non electric
- High temperature source for range of process heat applications
- High Temperature Considerations
  - Advanced particle coatings for FP retention at elevated temperatures
  - Advanced fuel materials (carbides, nitrides, composites, etc)
  - Fuel element design for reduced temperature drop - fuel to coolant
  - Control materials and design
  - Structural materials
  - Heat exchanger / recuperator materials and design

A GT-MHR is at an advanced stage as part of a joint Russian-US initiative
The S-I Process – Membranes for H₂ Separation

Hwang (JAERI) AIChe 2000, 46, 92

Needed
Catalysts for lower temperature H₂SO₄ decomposition
Membranes for separation of H₂ from HI, H₂O, I₂ products
Solid Oxide High Temperature Steam Electrolysis

A SOFC Operating in Reverse

Nanoporous Ceramic Membranes

Herring et al. *Int. J. Hydrogen Energy* 2007, 32, 440

Cathode = Nickel Zirconia CerMet; Anode – Manganese
Electrolyte = YSZ or ScSZ
VHTR Hydrogen Production Efficiency Steam Electrolysis

Efficiencies of High Temperature Electrolysis

[Graph showing efficiencies of high temperature electrolysis with reactor outlet temperature (C) on the x-axis and efficiencies on the y-axis, with lines indicating electrical generation efficiency and hydrogen production efficiency]
Nanoporous Oxide Membranes are important components of a potential hydrogen Economy

1. Fuel Cells
2. Hydrogen gas purification (pure hydrogen required for some fuel cells)
3. Hydrogen gas separation from reaction products
4. Membrane electrodes for electrolysis and photoelectrolysis

The Development of such membranes requires expertise in their preparation and microstructural and structural determination as well as providing mechanistic understanding of formation processes that are necessary for rational design.

X-ray and Neutron Scatter techniques very useful in this regard
Classes of Open Framework Materials Under Study

**Layered Oxides**
(10-24 Å)

**Mesoporous**
30 < d < 100 Å
Supramolecular templates

**Microporous**
(e.g. Zeolites, AlPO’s)
2 < d < 20 Å
Single molecule template for synthesis

**Supramolecular templates**

**Macroporous**
100 < d < 1000 Å

**Microporous Q-lattices**
(e.g. ETS-10)
2 < d < 20 Å
Hydrated Cation Templates

**Microemulsions or Infiltration polymer Networks/microspheres**

**Hybrid Networks**
Nanoporous Materials as Adsorbents for Nuclear Separations

Step 1: Granular mesoporous Substrates

Step 2: Functionalization

Step 3: MA, Tc Selective adsorbent

Step 4: Immobilization in Ceramic matrix

Step 5: Multicycle Transmutation

Mesoporous ZrTi₂-oxide in granular form with uniform Zr and Ti distribution should lead to synroc-like ceramics at low temperatures.

To Fast Reactor/Burner
or Advanced PWR

5 mm Porous Monolith

Repository Option

Transmutation Option
Zr$_x$Ti$_{1-x}$O$_2$ Oxides with Controlled Porosity

The use of small angle scattering for monitoring evolution of porosity

$x = \frac{Zr}{Zr+Ti} = 0 - 1$

The precise control of porosity is possible
Simple Methods for Producing Hierarchical WO$_3$ with High Photoactivity (ANSTO-NHMA/CSIRO)

Varying electrolyte pH gives dramatically films with vastly textures and porosities which give quite different photoresponse. Photocurrent response depends of porosity

Enhanced Photocatalytic Activity of Sol-gel Mesoporous Tungsten Trioxide Films
Bin Yang, Yingjie Zhang, Piers R. F. Barnes and Vittorio Luca

Structure of Highest Performing Film

Macropore

Mesopore
Conclusions

• High Temperature and Advanced High Temperature Reactors appear particularly suitable for massive hydrogen production.

• Production rates are expected to be comparable to the largest steam reforming plants but without the CO₂ emissions.

• Prototypes are in construction (HTTR, Japan) while other reactors in design stage.

• New materials are required for both the reactors and the hydrogen production systems which ultimately need to be coupled.

• Membranes needed??? Scattering techniques important!