Idaho National Engineering and Environmental Laboratory

#### Almquist Lecture 2004

## Hydrogen Production using Nuclear Energy

#### Dr. Steve Herring

Consulting Engineer Advanced Nuclear Energy Systems

Departments of Chemistry and Chemical Engineering University of Idaho March 25, 2004 Idaho National Engineering and Environmental Laboratory



#### World Energy Demand













## The Emerging Needs for Hydrogen

"The Hydrogen Economy"

- The "transportation fuel of the future"
  - 28% of US energy used for transportation
  - Essential for overall CO<sub>2</sub> reduction
- Distributed power neighborhood fuel cells
- Aviation/Aerospace Fuel

#### But even today.....



## **Present US Hydrogen Consumption**

- Petroleum refining
  - Sulfur removal
  - Opening of Benzene rings
  - Breaking of long-chain hydrocarbons
  - trends will continue in the future, e.g. Athabasca oil sands
- Anhydrous Ammonia Production
- Chemical Industry
- 2002 US consumption: 12 million t H<sub>2</sub>/yr (47 GWth if burned)
- 95% produced by steam reforming of methane (5% of US natural gas use) Releases 74 million t CO<sub>2</sub>/yr [World consumption: 50 million t H<sub>2</sub>/yr] (50 million t H<sub>2</sub>/yr would require 390 GWth input to a thermochemical process)
- Standard size of steam reformer is 300 million ft<sup>3</sup>/day, i.e. the output of a 2000 MWth reactor.



#### A Large Demand for Hydrogen is due to the Declining Quality of Available Crude Oil





## The Nuclear Hydrogen Outlook

- DOE Hydrogen Fuel Initiative, DOE-NE Nuclear Hydrogen Initiative
- Long-term, a 30 million t/yr U.S. hydrogen supply would be able to serve one-quarter of our transportation fuels use
- Nuclear energy required for this production is 234 GWth per year

The energy from one pound of nuclear fuel could provide the hydrogen equivalent of 250,000 gallons of gasoline without any carbon emissions.



"Within the scope of today's technology, nuclear fission is the only viable, clean source of large quantities of energy."



– Geoffrey Ballard Founder, Ballard Power





#### **Carbon Dioxide Emissions Avoided**

Herring, H<sub>2</sub>, March 25, 2004 7



#### **Potential for Nuclear in Transportation**



Growing U.S. Transportation Sector Energy Demand and Imports

Source: 2003 Annual Energy Outlook

- Transportation sector growth leads electricity & heating
- Outlook is for a disproportionate increase in imports
- Increasing dependence on imports clouds the outlook for energy security and stability
- Hydrogen can contribute if production-distribution-end use issues can be successfully addressed Herring, H<sub>2</sub>, March 25, 2004 8



# Methods for hydrogen production using nuclear energy

- Steam methane reforming using nuclear energy for the endothermic heat of reaction
- Conventional electrolysis using nuclear-generated electricity
- Thermochemical cycles for water splitting
- Hybrid cycles combining thermochemical and electrolytic steps
- High temperature electrolysis using nuclear electricity and heat



# Steam methane reforming using nuclear energy for the endothermic heat of reaction

 $CH_4 + 2 H_2O + 185 kJ \ll CO_2 + 4 H_2$ 

(80% of  $CH_4$  converted at 800° C)

- Advantages
  - Existing technology
  - Avoids methane use to produce steam
  - Easier to sequester  $CO_2$
- Disadvantages
  - Still uses large quantities of methane (natural gas)
  - Releases large amounts of CO<sub>2</sub>
  - Nuclear input is about 20%



#### **Top-ranked Thermal Cycles**

- Sulfur-Iodine, GA, JAERI, Sandia and others
  - $-850^{\circ}C$  2  $H_2SO_4$   $\otimes$  2  $SO_2$  + 2  $H_2O$  +  $O_2$
  - $-450^{\circ}C$  2 HI  $\otimes$   $I_2 + H_2$
  - $-120^{\circ}C$   $I_2 + SO_2 + 2H_2O \otimes 2HI + H_2SO_4$
- UT-3, University of Tokyo
  - $-600^{\circ}C$  2Br<sub>2</sub> + 2CaO  $\otimes$  2CaBr<sub>2</sub> + O<sub>2</sub>
  - $-600^{\circ}C$  3FeBr<sub>2</sub> + 4H<sub>2</sub>O  $\otimes$  Fe<sub>3</sub>O<sub>4</sub> + 6HBr + H<sub>2</sub>
  - $-750^{\circ}C$  CaBr<sub>2</sub> + H<sub>2</sub>O  $\otimes$  CaO + 2HBr
  - $300^{\circ}C$   $Fe_{3}O_{4} + 8HBr \otimes Br_{2} + 3FeBr_{2} + 4H_{2}O$

Idaho National Engineering and Environmental Laboratory



## **The Sulfur-Iodine Process**





#### Top-ranked Hybrid Cycles (thermal/electrochemical)

#### Westinghouse

 $-850^{\circ}C$  2  $H_2SO_4$   $\otimes$  2  $SO_2 + 2 H_2O + O_2$  (thermal)

(Japanese are proposing dividing above reaction into 2 electrochemical steps at 400-450° C)

- 77°C SO<sub>2</sub> + 2  $H_2O$   $\circledast$   $H_2SO_4$  +  $H_2$  (electrochemical) Ispra Mark 13
- $-850^{\circ}C$  2  $H_2SO_4$   $\otimes$  2  $SO_2$  + 2  $H_2O$  +  $O_2$  (thermal)
- $-77^{\circ}C$  2 HBr  $\otimes$  Br<sub>2</sub> + H<sub>2</sub> (electrochemical)
- $-77^{\circ}C Br_2 + SO_2 + 2H_2O \otimes 2HBr + H_2SO_4$  (thermal)

# High temperature electrolysis using nuclear electricity and heat

- Advantages
  - Builds on existing Solid Oxide Fuel Cell technology
  - Lower operating temperatures than thermochemical cycles
  - Less corrosive operating conditions
- Disadvantages
  - May have lower efficiencies than thermochemical cycles
  - Cells are relatively small (100 mm x 100 mm)







Theoretical Efficiency of High Temperature Electrolysis

900



#### High Temperature Electrolysis Plant







Herring, H<sub>2</sub>, March 25, 2004 17

#### **Ceramatec "button cell" for initial single-cell testing:**

- Anode: Nickel zirconia cermet (cathode in electrolysis mode)
- Cathode: Strontium-doped lanthanum manganite (anode)
- Electrolyte: YSZ, 175 µm thickness
- Active cell area: ~ 3.2 cm<sup>2</sup>
- Includes an electrically isolated electrode patch for monitoring of reference open-cell voltage





#### LSGM Reversible Fuel Cell & Hydrogen Generator





### Major Issues in HTE Materials Needs

- Cost of materials and cell fabrication
- Lifetime of the module
  - Performance lifetime tradeoff
  - Limiting number of thermal cycles/transients
- Uniformity and quality of cell manufacturing
- Maximum temperature of interconnects
- Sealing, especially in planar configuration
- Manufacture of thin electrolytes
- Matching coefficients of thermal expansion
- Shrinkage during manufacture



#### Interconnect Plate and Electrolyte for Stack Testing





#### **Ten-Cell Stack Experiment**





## Most recent 6-cell stack results, produced 30.8 normal liters of $H_2$ per hour for the 918 hours of electrolysis operation





#### Ceramatec test Oct-Nov, 2003

#### Hydrogen Production in 6-cell stack





## Planar design SOFC long-term stability – cell potential versus time.



Herring, H<sub>2</sub>, March 25, 2004 25



#### Side Issue: Hydrogen Storage on vehicles

Methods:

Compressed gas: 10,000 psi tanks Cryogenic liquids: 20 K, 1/3-2/3 energy density of gasoline metals, 2-5% H<sub>2</sub> Hydrides: Carbon nanotubes Sodium Borohydride: aqueous solution, 7-10 wt% H2 released, 50-70% energy density of gasoline  $NaBH_4(aq) + 2H_2O \longrightarrow NaBO_2(aq) + 4H_2(g)$  $NaBO_2 + 4H_2 + heat + electricity \longrightarrow NaBH_4 + 2H_2O$ 



#### Inevitable Conclusion:

Liquid hydrocarbons are very good fuels for transportation

- Liquid over range of ambient temperatures
- Pumpable: gas pump: 20 gal/min = 43  $MW_{th}$
- Energy dense: 34 MJ<sub>th</sub>/liter at 0.1 MPa
  - $H_2$  gas: 9.9  $MJ_{th}$ /liter at 80 MPa,
  - $H_2$  120  $MJ_{th}/kg$ , gasoline: 40  $MJ_{th}/kg$
- Storable: little loss, small explosion hazard
- Transportable by pipeline: 36 in oil pipeline: 70 GW<sub>th</sub>

Hydrogen will be used primarily to enhance gasoline, diesel and jet fuel production until the on-board storage problem can be solved.



### The Biomass-Hydrogen Combination

- Biomass is a great way to collect carbon but the overall energy gain may be small.
- Hydrogen produced using nuclear energy is an energy-rich carrier, but is difficult to transport long distances and store on-board.
- Hydrogen as a transportation fuel requires a whole new infrastructure.

Therefore hydrogen needs a carbon source.

 Ethanol plants (corn or cellulose), CO<sub>2</sub> sequestration, FutureGen, MSW, ...



#### The interface between Nuclear Engineering and Chemical Engineering

- Temperature requirement for chemical plant exceeds practical maximum temperature for nuclear plant?
- Chemical plant built to nuclear standards?
- Improved reliability, availability, maintainability (RAM) of chemical plant must be better than conventional chemical plants to avoid frequent shutdowns of nuclear reactor?
- Integrated safety demands due to co-location and integration of nuclear and chemical plants more severe?



#### Intermediate Heat Exchanger (IHX)

- Assume an IHX will be required between the nuclear and chemical processes
- Design problems
  - Higher reliability required
  - Unusually severe temperature
  - Delta T must be minimized because temperature requirement for chemical process approaching limit of nuclear reactor coolant temperature
  - Hydrogen/tritium permeation must be prevented
  - Preventing pressurization of either side due to IHX failure
  - Large size assumed because of small delta T requirement and low heat capacity of assumed gas reactor coolant
  - Ability to replace components with minimum radiological exposure



#### Very-High-Temperature Reactor (VHTR)

#### **Characteristics**

- Helium coolant
- 1000°C outlet temperature
- Water-cracking cycle

#### **Benefits**

- Hydrogen production
- High degree of passive safety
- High thermal efficiency
- Process heat applications





## Very High Temperature Reactor Systems (VHTR)

- Four concepts submitted
- General features of VHTR--
  - ~1000° C coolant core exit temperature
  - 600 MW<sub>th</sub>, LEU once-through cycle
  - could be pebble bed or prismatic core
- Shows promise for
  - Gains in sustainability and flexibility
  - Significant advance towards safety goals
  - Comparable economics
  - Bridge to hydrogen economy





## High Temperature engineering Test Reactor, JAERI, O-arai, Japan



Using HTTR for NPH demonstration



#### Gas-Cooled Fast Reactor (GFR)

#### **Characteristics**

- Helium coolant
- 850°C outlet temperature
- Direct gas-turbine cycle
- 600 MW<sub>th</sub>/288 MW<sub>e</sub>

#### **Benefits**

• Waste minimization and efficient use of uranium resources





#### Safety and Marketing Considerations

- Plants may have large inventories of SO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, HI, HBr, ... at high temperatures and moderate pressures
- Interaction between nuclear reactor and chemical plant transients will have to modeled and tested
- Contamination of the product is a much bigger issue than in the generation of electricity
- There may have to be an intermediate loops between a fission heat source and the hydrogen product to minimize tritium permeation and migration, especially if Li or Be salts are used for heat transfer



## Conclusions

- Demand for hydrogen is large today and growing 4-10% /yr
- Petroleum and chemical industries represent concentrated demands,
- Thermochemical cycles have highest efficiency but most daunting operating conditions.
- Electrolysis shows promising particularly in the near-term
- Conventional liquid fuels will be difficult to displace
- Biomass Hydrogen combination is promising
- Tritium production and migration are issues that require close attention