IV.G.6 Materials for High-Temperature Thermochemical Processes

D. F. Wilson
Oak Ridge National Laboratory
P.O. Box 2008
MS-6156
Oak Ridge, TN 37831-6156
Phone: (865) 576-4810; Fax: (865) 241-0215; E-mail: wilsondf@ornl.gov

DOE Program Manager, Nuclear Hydrogen Research: David Henderson
Phone: (301) 903-3097; Fax: (301) 903-5057; E-mail: David.Henderson@nuclear.energy.gov

Start Date: FY 2004
Projected End Date: FY 2008

Objectives

- Assure a focused integrated materials evaluation program to establish engineering feasibility

Technical Barriers

This program addresses the following technical barrier of the Nuclear Hydrogen Initiative (NHI):

- High temperature, corrosion resistant materials

Approach

- Coordinate materials planning for NHI and monitor evolving research and development activities
- Assess range of service conditions for NHI thermochemical (TC) processes (Sulfur cycles, Ca-Br, and others
- Identify candidate materials of construction for cycle components (alloys, ceramics, refractories)
- Develop materials testing approach and priorities to support NHI TC cycle development

Accomplishments

- Completed assessment of NHI TC cycle service conditions and associated candidate materials
- Issued report: Materials Requirement for Nuclear Hydrogen Generation Systems
  - Identifies chemistry and temperatures for key process steps
  - Identifies candidate materials for major components in NHI TC cycles
  - Identifies testing approach and prioritizes materials R&D needs

Future Directions

- Revise and update materials selection
- Develop a prioritized, integrated materials evaluation program to establish an engineering feasibility

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Introduction

The NHI is investigating both high temperature electrolysis (HTE) and TC cycles as candidate technologies for the nuclear hydrogen production systems. The focus of TC cycle R&D is on the sulfur-based cycles – sulfur-iodine and hybrid sulfur, which involve temperatures in the range of 800 to

1,000°C and corrosive environments. The calcium-bromine cycle is also being evaluated, which involves lower peak temperatures (~760°C). High temperature electrolysis involves temperatures up to 1,000°C in a steam environment. The multiple technologies provide methods of hydrogen production that could be coupled to the fairly wide range of operating conditions of the different Gen IV reactor concepts, while at the same time providing multiple, potentially redundant paths to minimize risk. Each technology has unique materials challenges that must be addressed to enable its successful deployment.

This task is focused on planning and coordinating a focused approach to establishing engineering feasibility.

Approach

In the past year, an assessment of the proposed hydrogen production technologies and their associated materials requirements has been performed. Extensive input has been obtained from commercial, academic, and national laboratory experts regarding both the anticipated configurations and operating conditions for each technology as well as the resulting materials challenges. In the first iteration of the materials R&D plans for NHI, only high-level materials needs and approaches to addressing them were identified, along with a general priority for the work. The priorities were jointly derived from the criticality of the issue for establishing the viability of the process and the necessity for early identification of candidate materials to meet that need.

Results

The initial evaluation uncovered a wide range of materials issues that must be addressed before any of the systems proposed for nuclear hydrogen production can be deployed. These issues include materials compatibility, high-temperature strength and stability of materials, and fabrication technologies. A number of these issues were identified as of particularly high priority and must be addressed early in the program. These areas are summarized in Table 1.

Table 1. Summary of High Priority Materials Research Issues of the NHI Program

System	Component	Research Focus	Comment
SI	H_2SO_4 Concentrator	Corrosion Screening	Technical Viability Issue
	H_2SO_4 Vaporizer	Corrosion Screening	Technical Viability Issue
		Corrosion Screening	Technical Viability Issue
	HI Reactive Distillation Column	Corrosion Screening	Technical Viability Issue
	Inorganic Membranes	Performance and Corrosion Screening	Technical Viability Issue
Ca-Br	Reaction Bed Heat Exchanger (HX)	Corrosion Screening	Technical Viability Issue
	Ca-Br/HBr HX	Corrosion Screening	Technical Viability Issue
	Reaction Bed Vessel	Corrosion Screening	Technical Viability Issue, if not internally insulated
HTE	Metallic Interconnects	Protective Surface Layer Modifications	Economic Viability Issues
	Steam-Hydrogen Separator	Corrosion Screening	Economic Viability Issues
	Oxygen HX	Corrosion Screening	Economic Viability Issues
	Hydrogen HX	Corrosion Screening	Economic Viability Issues
	Inorganic Membranes	Performance and Corrosion Screening	Economic Viability Issues

High-Priority Materials R&D for the SI System

High priority areas of materials compatibility research which were identified for the SI system include:

- Screening of materials for service in both the concentrator and vaporizer portions of the sulfuric acid concentration and decomposition section and those used in the reactive distillation column of the hydrogen iodide decomposition section. At the present time, candidate materials have been identified for these service conditions, but the environments are known to be extremely aggressive and performance of even the most promising materials is not adequately established to ensure system viability.
- Assessment of high-temperature inorganic membranes for separation of decomposition products of sulfuric acid to potentially reduce peak required temperatures, and associated structural materials requirements, in the hydrogen generation plant and the nuclear reactor providing the process heat.

High-Priority Materials R&D for the Ca-Br System

High priority areas of materials compatibility research which were identified for the Ca-Br system include:

- Corrosion screening of the materials for the internal heat exchanger within the reaction beds. The wide range of high operating temperatures and widely varying reactants in which these heat exchangers will operate as the beds change from modes of production, where HBr is replaced by steam, to regeneration, where bromine is replaced by pure oxygen, will create a significant challenge for the heat exchanger materials.
- Investigation of the corrosion resistance of materials for the heat exchanger that will cool the process stream from the reaction beds prior to its introduction into the plasmatron, where the combination of the HBr, bromine, and water must be accommodated is also a very high priority.
- Selection of materials for the vessel that will enclose the reaction beds if the vessel is not insulated from the operating temperatures. If the decision is made to internally insulate this vessel, the reduction in temperature will allow the use of nickel-clad, low-alloy steel.

High-Priority Materials R&D for the HTE System

High priority areas of materials compatibility research which were identified for the HTE system include:

- Investigation of the use of inorganic membranes to enable nearly isothermal (and hence much more economical) separation of hydrogen from steam in the output stream from the cell.
- Materials for metallic interconnects of the electrolytic cell, as well as materials to enable higher temperature operation of the steam-hydrogen separator and the recuperators for hydrogen and oxygen cooling. However, alternate approaches such as ceramic interconnects or partial adiabatic cooling, are available. Hence, these issues should not affect the operational viability of the system and, thus, were not judged to be a high technical priority. If the economic consequences of using the more expensive or less efficient alternate approaches are later judged to affect the overall viability of the system, these issues should be given a high priority in the NHI materials program.

Conclusions

As a result of extensive discussion with industrial and national laboratory personnel, prioritized issues were identified that must be resolved in order to establish engineering viability and allow for down selection of the TC processes for hydrogen production using nuclear process heat. Technical viability issues are, in general, associated with high temperature/corrosive environments associated with these processes. For the sulfur cycles (S-I, Hybrid S), the major material issues are associated with:

- H_2SO_4 concentrator, vaporizer
- HI reactive distillation column
- Inorganic membranes
  - Potential for increased product formation
  - Potential for reduced operating temperature

For the Ca-Br cycle:

- Reactive bed HX
- Ca-Br/HBr HX

- Reaction bed vessel

For the HTE:

- Inorganic membranes
  - Potential for enabling nearly isothermal (and hence much more economical) separation of hydrogen from steam in the output stream from the cell.

FY 2005 Publications/Presentations

1. D. F. Wilson, *Candidate Materials for a High Temperature Intermediate Loop with Molten Salt Working Fluids*, ORNL TM 2005, draft report issued.
2. D. F. Wilson et al., *Materials for High-Temperature Thermochemical Processes*, DOE Hydrogen Program Annual Review, Crystal City, Virginia, May 23-26, 2005
3. W. R. Corwin et al., *Materials Requirements for Nuclear Hydrogen Generation Systems*, ORNL TM, 2004, draft report issued
4. W. R. Corwin, High Priority Materials R&D for NHI, NHI Materials Program Review Meeting, ORNL, February 10, 2005