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CHEMICAL/HYDROGEN ENERGY STORAGE SYSTEMS

ANNUAL REPORT
JANUARY 1, 1979 TO DECEMBER 31, 1979

May 1980

MASTER

Work supported by the
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OFFICE OF ADVANCED CONSERVATION TECHNOLOGIES
UNITED STATES DEPARTMENT OF ENERGY

DEPARTMENT OF ENERGY AND ENVIRONMENT

BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973

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(Energy Storage-Chemical -TID-4500)

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May 1980

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ENERGY TECHNOLOGY PROGRAMS
DEPARTMENT OF ENERGY AND ENVIRONMENT
BROOKHAVEN NATIONAL LABORATORY
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ABSTRACT

This report describes the progress made in 1979 in the Chemical/Hydrogen Energy Storage Systems Program. The program is managed by Brookhaven National Laboratory for the Division of Energy Storage Systems of the Department of Energy. The program consists of research and development activities in the areas of Hydrogen Production, Storage and Materials, End-Use Applications/Systems Studies, and in Chemical Heat Pumps. The report outlines the progress made by key industrial contractors such as General Electric in the development of SPE water electrolyzers; INCO in the studies of surface poisoning (and reactivation) of metal hydrides; and Air Products and Chemicals in the evaluation of hydrogen production at small hydropower sites. The BNL inhouse supporting research, as well as that at universities and other national laboratories for which BNL has technical oversight, is also described.

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1.0 INTRODUCTION AND SUMMARY

Brookhaven National Laboratory (BNL) management and technical support activities in 1979 have been broadened in focus to include Chemical Energy Storage/Chemical Heat Pump (CES/CHP) technology development within the scope of the Hydrogen Energy Storage Program. In midyear, DOE/STOR transferred CES/CHP management responsibility from Sandia Livermore Laboratories (SLL) to BNL. The resulting programmatic framework will permit a more comprehensive treatment of energy storage technology development and applications.

Early efforts in Electrolysis-Based Hydrogen Energy Storage Systems aimed toward utility load leveling. Requirement projections were associated with the exercise of the nuclear power generation option. The deferral of these prospects has led to a restructuring of activities calling for a shift in emphasis toward the longer-term payoff of renewable resource conversion. For the nearer term, opportunities for application of energy storage technology to conservation and resource recovery are being identified. Programmatically, 1978 and 1979 have been viewed as transition years wherein the stage has been set for redirecting the program to address specific markets which would drive base technology and systems development activities.

1.1 Program Overview

Hydrogen production represents the major programmatic thrust. In restructuring the program, the areas of investigation have been divided into functional elements of: Electrochemical Systems; Storage Systems and Materials; Chemical Heat Pumps; and End-Use Applications/Systems Studies. Each of the areas of investigation is examined with regard to the prospects of a given technology or innovation to make a substantial contribution to our energy situation in a timely manner.

Electrochemical Systems

Engineering development of solid polymer electrolyte (SPE) water electrolysis maintains the highest priority in the program. Base technology advances have been applied to the designs and fabrication of test modules and systems. It remains for the projected systems cost and performance benefits to be verified and for commercialization opportunities to be identified in order to focus further development such as scale-up to large multimegawatt (50 MW) systems. Modest efforts in advanced alkaline systems have been pursued whereby advanced components have been tested for effect on system efficiency improvements. These improvements will be equated to cost and used as baseline comparison for other advanced systems such as SPE water electrolysis.

Project formulation and planning activities identify Fuel Cell/Hydrogen Storage Systems development as a strong project candidate targeted to long-term transportation applications. The fuel cell's high energy conversion efficiency can compensate for the relatively low energy storage density of hydrogen storage systems by effecting improvements of two to threefold in fuel utilization. Hydrogen, available in its pure form, permits consideration of high efficiency alkaline fuel cells which do not require noble metal catalysts in the electrode components. The promise of lower capital cost, lower weight, rapidly refueled hydrogen storage/conversion systems suggests strong potential as alternative traction power in the future.

Storage Systems and Materials

Metal hydrides have been identified as safe and effective storage materials for hydrogen, suitable for incorporation into systems as required, over a wide range of energy storage applications. Evaluation of current materials available for near-term applications show that bulk hydride hydrogen storage is not practical, in general, because of the high cost. Metal hydrides appear in a much more favorable light when viewed as short-term storage media operated in a rapid cycling mode. Mobile storage systems, compressors, separation/purification systems, and chemical heat pumps surface as potentially economically attractive systems development objectives.

Metal hydrides may assume a new resource recovery role resulting from technology spin-off from earlier investigations into metal hydrides poisoning mechanisms and high capacity storage materials. The resource derives from industrial process off gases and refinery gas which contain 12-60% hydrogen mixed with methane and various contaminants such as CO, H_2S, and NH_3. In 1978, this valuable commodity in refineries was used as fuel or flared in amounts estimated as in excess of 0.1 Quad. Techniques such as pressure swing absorption, cryogenic separation, and membrane separation schemes suffer from technical or economic limitations which can be overridden by application of selective hydrogen absorption by poison-resistant or restorable metal hydrides. Process cost projections indicate that hydrogen can be recovered at $1.25 per million standard cubic feet (including fuel replacement cost at $0.80/MSCF).

A new material for hydrogen storage systems (commercially available as a plastic filler) promises to take on the role of hydrogen bulk storage and transport media. The material is in the form of hollow glass microspheres (approximately 40 microns) that can be filled to pressures up to 6000 psi. The diffusion characteristics of the hydrogen through the sphere walls are such that release of hydrogen is finite but negligible at normal temperatures, while rapid at higher temperatures. Preliminary characterization of these materials verifies their potential for hydrogen storage with more than double the weight fraction of hydrogen stored compared to hydrides.

Efforts to determine the viability of underground storage of hydrogen have been completed and the results are positive from a technical and engineering standpoint with some cost constraints due in large part to the cost of hydrogen, per se.

End-Use Applications and Systems Studies

Procurement actions have been taken and completed regarding the demonstration of hydrogen production from small hydropower sites. All indications are that specific sites are identifiable in proximity to merchant hydrogen markets and the cost of producing hydrogen using advanced water electrolysis technology is consistent with current market requirements.

This effort has been implemented in cooperation with the DOE Division of Hydroelectric Resource Development and hopefully sets the stage for other interdivisional, intradivisional and even interagency efforts. Hydrogen does have logical ties with technology development in solar, transportation, ocean thermal energy conversion, and synfuels technology.

Chemical Heat Pumps

In the last quarter of FY 79, BNL agreed to assume responsibility for technical management of the Chemical Energy Storage/ Chemical Heat Pump activities previously managed by Sandia Livermore Laboratories (SLL). Projects undertaken by SLL as active and/or worthy of continued pursuit included: (1) Development of a Sulfuric Acid/Water Chemical Heat Pump (CHP) at Rocket Research Corp.; and (2) Development of Calcium Chloride/Methanol CHP at the EIC Corporation. Other projects considered to be potentially viable included

BNL efforts in the last quarter of FY 1979 were directed toward planning new actions with industry and universities, familiarization with project status, and maintaining the thrust of development activities at selected contractor facilities where such action was warranted. By the end of FY 79, BNL had set in place a continuation contract at EIC involving the debugging, testing, and evaluation of a CHP prototype system [$CaCl_2/CH_3OH$] designed and fabricated under previous contract. Also following in-depth discussions with technical and management staff at Rocket Research Corp. (RRC), a follow-on statement of work to the H_2SO_4/H_2O CHP system was prepared as part of a contract package to be executed in early FY 80.

Due consideration was given at BNL to the restructuring of the Chemical Energy Storage/Chemical Heat Pump Program in order that it be integrated effectively within the hydrogen energy storage activities. The integrated program will be broadened in focus such that the chemical storage option of hydrogen production, storage, and use would be extended to energy storage in all chemical systems which would offer substantial benefits through the use and upgrade of low-grade solar or waste heat as well as to conserve and/or recover conventional energy resources.

1.2 FY 80 Programmatic Guidelines

Activities for FY 80 will focus on technology developments with potential for the accrual of near-to-midterm benefits via early technology transfer and commercialization. In addition, exploratory and applied research will be continued to provide a sound base for further development in the longer term.

Project activities for FY 80 are summarized as follows:

- Hydrogen production will retain programmatic priority but key decisions regarding future direction and budget outlays will be made based upon cost/performance evaluations and market projections.
- Resource conversion, especially renewable resources, will be assigned a lead priority with efforts extending from small hydropower to other targets-of-opportunity such as ocean thermal energy conversion (OTEC) and wind energy

conversion system (WECS). Hydrogen's relationship to synfuels from coal resources requires greater in-depth exploration.

- Storage systems and materials development will focus on near-to-midterm applications with cost effectiveness being a major criterion in selecting options and establishing project priorities.
- Systems studies will complement technology development specifically in the area of economic benefits. Value from an energy conservation standpoint will be equated to costs, and where negative disparities are identified programmatic or technical redirection will be recommended.
- Chemical heat pump investigations have continued initially along the lines previously established by SLL. Examination of cost/performance projections made for the systems currently under development point to design/performance tradeoffs as they pertain to thermal input (solar, waste heat, fuel-fired); coefficient of performance vs storage; space conditioning and/or waste heat management applications.

1.3 BNL Program Management Perspective

Budget allocations to FY 79 project activities are delineated in Fig. 1.1 and include projections made for FY 80. The continued emphasis on electrolytic hydrogen production is shown to prevail in FY 80 with the substantial overall budgetary increase attributed to CES/CHP activity which will be restructured in 1980. For example, new or extended efforts pertinent to the application of storage technology to conservation and resource recovery may derive support from CES/CHP funding sources.

FY 80 will be highlighted by critical decision points related to commitments to selected projects supported in prior years as well as to new starts which spin off from earlier developments. Project activities which will be examined in depth include:

- SPE Electrolyzer (Scale-up)
- Advanced Alakline Electrolyzer System
- Microcavity Storage Systems

FIGURE 1.1

CHEMICAL/HYDROGEN STORAGE SYSTEMS PROJECT
BUDGETARY BREAKDOWN

FY 79			FY 80		
	Budget $4435K*	$K		Budget $5200K*	$K
H_2 Production 1940	GE$^+$	1590	Electrochemical Systems 1970	GE$^+$	1200
	Teledyne	100		Teledyne	100
	Univ. of Va.	20		Univ. of Va.	50
	Brooklyn Coll.	15		Brooklyn Coll.$^+$	60
	BNL	215		State Univ. of New York$^+$	20
				LASL (Fuel Cells)	70
				BNL (incl. Fuel Cells)	300
				TBD	170
H_2 Storage Sys. 505	Foster Wheeler	20	Storage Systems & Materials 980	EDRI	150
	ORNL	40		Billings	30
	IGT	100		R.J. Teitel	180
	EDRI	40		MPD/Air Products	300
	Billings	60		BNL	200
	BNL	245		TBD (Auto Stor. Appl.)	120
H_2 Storage Mat. 430	DRI$^+$	100	End-Use Applications Sys. Studies 340	Air Products	50
	INCO	30		NYSERDA	160
	Air Products	50		Factory Mutual	30
	R.J. Teitel	90		BNL	20
	BNL	160		TBD	80
End-Use Appl. 855	NYSERDA	655	Chem. Heat Pumps 1410	Rocket Research	400
	Air Products	170		EIC	160
	BNL	30		Argonne$^+$	130
				Tech. Econ. Assess.	80
Chem. Heat Pumps 295	RRC	125		RFP MH_x Heat	250
	EIC	170		BNL	45
				TBD	345
Program Mgmt.	BNL	410	Program Mgmt. 500	BNL	400
				Courtesy	25
				Consultants	50
				Misc.	25

*Figures include DOE/BHO held contracts and carryover commitments.
$^+$DOE/BHO held contracts

- Metal Hydrides as Resource Recovery and Separation/ Purification Systems
- Chemical Heat Pumps Tied to Solar Heating and Cooling

Several projects which represent substantial DOE/STOR budgetary commitments are funded and administered directly by the DOE Brookhaven Area Office (BHO). BNL provides technical support and oversight to these projects which include:

- SPE Water Electrolysis Development at General Electric
- Hydrogen Production from Small Hydro at NYSERDA
- Metal Hydride CHP Development
- Special Research Supporting Agreement at Several Universities

The Program Organization Chart, Fig. 1.2, identifies the lines of communication as well as the specific areas of functional responsibility assumed by BNL staff. The Program Manager serves as the single point contact for the Chemical/Hydrogen Energy Storage Program. Each Area Manager maintains technical responsibility for contracted and in-house efforts falling within the purview of the identified areas of technology.

Area Managers and support staff function as a technological resource for the Program Management staff. An estimated level of effort of two man-years is allocated to providing technical oversight of contracted activities. This support is drawn from scientific and engineering personnel at BNL. These represent the full range of disciplines engaged in complementary in-house R&D within the scope of the overall program.

Budget Summary (Fig. 1.3) provides breakdowns for BNL technical and management support for each of the budget control areas.

Fig. 1.4 provides a summary of the objectives and accomplishments in 1979 for the individual project activities that comprise the program. The accomplishments and pacing problem areas are described in more detail in the later sections of the report.

1.4 The Master Plan

The thrust of the current DOE/BNL program is aimed toward the applications of Chemical/Hydrogen Energy Storage Systems technology as a renewable resource conversion option. The broader focus of the program now includes chemical energy storage options other than hydrogen production and storage;

thus, activities can point more comprehensively toward the conservation of our conventional resources. It is recognized that base technology and systems development are driven, more often, by market needs. Therefore, the master plan seeks to define criteria for markets identification and to establish programmatic courses of action which best promise to penetrate those markets. The criteria are:

- relevance to the technological base under development;
- potential for substantive impact within a near- to midterm time frame;
- integration potential with the existing energy infrastructure.

Consistent with these criteria, the markets to be addressed include:

- chemical feedstocks via electrolytic hydrogen production;
- energy conservation in the residential/commercial/industrial sectors via chemical storage, chemical separation, and chemical heat pumps;
- transportation--tying mobile storage systems to efficient energy conversion systems; and
- natural gas supplementation as the means for transporting and distributing hydrogen within distribution systems now in place.

Project activities at BNL have been divided into program elements comprising: Electrochemical Systems; Storage Materials and Systems; Chemical Heat Pumps; and End-Use Applications/Systems Studies. These subdivisions are consonant with the technical disciplines assigned to provide technical and management oversight to complementary in-house and subcontracted activities. In reality, the Work Breakdown Structure deals with three interrelated functions: (1) Base Technology Development; (2) Systems Development and Engineering; (3) Markets Field Test and Demonstration. The Work Breakdown Structure and activities within each component are summarized in Fig. 1.5.

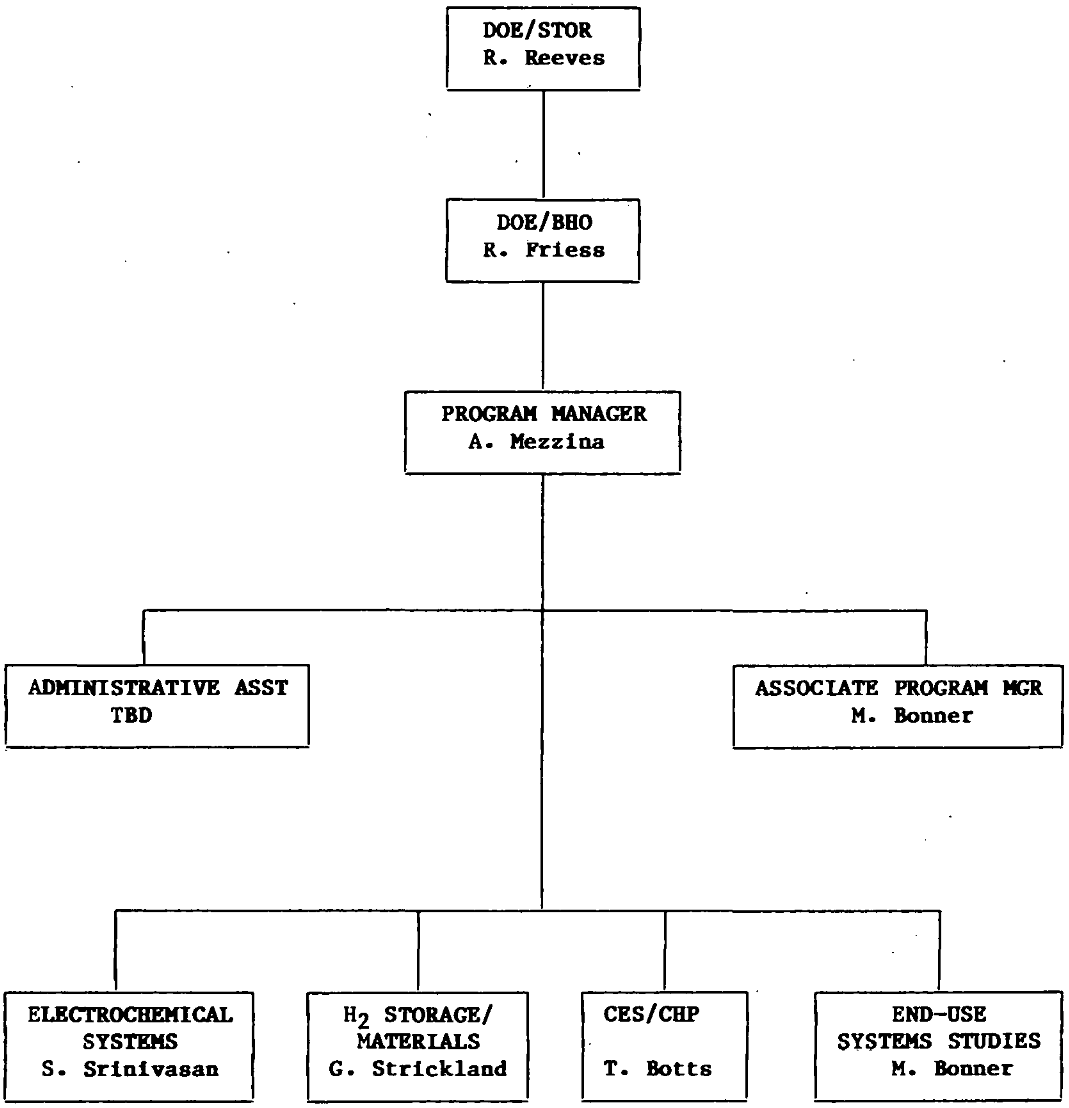


Figure 1.2. Program Organization Chart

FIGURE 1.3

BUDGET/ACTIVITY SUMMARY FOR FY 1979

Total Budget	$3,800,000
Contracts	2,200,000
Carry-over from FY 78	600,000
BNL Technical/Management Support	1,000,000
BNL	
In-house R&D	480,000
Technical Monitoring	170,000
Program Management	350,000

Activities
- Managed 18 R&D contracts (including CES/CHP)
- Evaluated 14 proposals
- Issued one major competitive procurement

Documents
- Summary Progress Plan/Annual Operating Plan
- Monthly Progress Reports
- Annual Report
- Formal Program Reviews
- Supported LLL's Automotive Storage Study

Other
- Conducted FY 79 Contractors' Review Meeting
- Supported DOE/STOR in IEA activities
- Interaction with public and private sector

Figure 1.4

CHEMICAL/HYDROGEN ENERGY STORAGE SYSTEMS PROGRAM
1979 OBJECTIVES AND ACCOMPLISHMENTS

1. ELECTROCHEMICAL SYSTEMS

ACTIVITY	OBJECTIVES	ACCOMPLISHMENTS
GE SPE Electrolyzer Development	● Assemble & Test 12-cell, 50kW Module (2.5 ft^2 cells) ● Fabricate 200kW system ● Initiate development of 10 ft^2 cells	● Extensive testing was completed and a number of engineering problems uncovered and solved (2.5 ft^2 cells) ● 200kW system fabricated and checked out ● Design of 10 ft^2 cell completed--further development delayed pending scale-up decision ● Key problems: cell sealing and electrochemical performance
BROOKLYN COLLEGE Ruthenium & Iridium Oxide Catalyst Studies	● To grow single crystals of RuO_2 ● To elucidate mechanism causing decrease in current density and in electrocatalytic performance in oxygen evolution reaction	● Large single crystals grown and electrocatalytic activity investigated ● Voltammetry curves provide much information on electrocatalytic process
BNL Electrocatalyst Studies for SPE Water Electrolysis	● Evaluate Ru-based mixed oxides as electrocatalysts for SPE electrolysis ● Ellipsometric studies of Ru-Ir alloys	● Mixed-oxide $RuIr_{0.5}T_{0.5}\ O_x$ identified as significantly better than E-50, WE-3 or other mixed oxides ● Data obtained providing insight into time variation of overpotential problem

(Cont.)

Figure 1.4

CHEMICAL/HYDROGEN ENERGY STORAGE SYSTEMS PROGRAM
1979 OBJECTIVES AND ACCOMPLISHMENTS

1. ELECTROCHEMICAL SYSTEMS (Cont.)

ACTIVITY	OBJECTIVES	ACCOMPLISHMENTS
TELEDYNE Advanced Alkaline Electrolysis	• Evaluate performance of cell components/materials at high temperature (125°C) in KOH. • Develop computer model to investigate H_2 cost vs electrolysis system parameters and economics	• Tests indicated voltage efficiency improvements from 72% to 80-85% on new cathode (TES-C-AN) • Testing of new separators was inconclusive because of test anomalies • Computer program completed and tested and near delivery to BNL --Provides visibility into cost factors
UNIVERSITY OF VIRGINIA Materials Studies for Alkaline Electrolysis	• To evaluate whisker electrodes • To investigate mechanisms of time dependent energy losses	• Whisker electrodes showed 10% efficiency improvement over conventional nickel screens • Energy losses attributed to formation of hydride on cathode but unable to detect because it is too unstable
BNL Evaluation of Materials for Alkaline Systems	• Evaluate high surface area nickel anode/cathode electrocatalysts • Test composite separators	• Nickel deposited on mild steel electrodes from INCO showed lowering of overpotential and merits further work--others not conclusive • Separator studies indicated no significantly better materials than asbestos-based materials

(Cont.)

Figure 1.4

CHEMICAL/HYDROGEN ENERGY STORAGE SYSTEMS PROGRAM
1979 OBJECTIVES AND ACCOMPLISHMENTS

2. STORAGE SYSTEMS & MATERIALS

ACTIVITY	OBJECTIVES	ACCOMPLISHMENTS
Storage Systems		
EDRI Chemical Compressor	• Complete design, fabrication and performance testing of bench-scale hydrogen compressor	• Design and fabrication of two modules completed after some assembly problems--One module performance tested at 800 psi and 50 SCFM
IGT Underground Storage of H_2	• Determine technical and economic feasibility of underground storage of hydrogen	• Study completed, no real technical problems; may be pressure limit of 1200 psi due to H_2 embrittlement--Storage will be costly because of cost of H_2 cushion gas
BILLINGS (BEC) Hydrogen Homestead Operation	• To evaluate storage system operational and safety characteristics	• Progress delayed because of move by BEC to Missouri
BILLINGS/MERADCOM Hydride Storage/Fuel Cell Fork Lift Truck	• Demonstrate that fuel cell/battery-powered fork lift truck with hydride storage is superior to battery truck with gas cylinder storage	• Design of storage system completed • Some problems in assembly • Testing will be delayed
BNL HYTACTS and VPTU-2 Storage vessel	• To complete construction of the HYTACTS Hydrogen Test Facility • To complete basic engineering tests on VPTU-2 H_2 storage vessel incorporating latest designs	• HYTACTS completed and approved for operations by DEE Safety Committee • The VPTU-2 was tested and met design points of 50kW, 500kWh, and 15 SCFM and yielded much information on vessel design and operation

(Cont.)

Figure 1.4

CHEMICAL/HYDROGEN ENERGY STORAGE SYSTEMS PROGRAM
1979 OBJECTIVES AND ACCOMPLISHMENTS

2. STORAGE SYSTEMS AND MATERIALS

ACTIVITY	OBJECTIVES	ACCOMPLISHMENTS
Storage Systems (Cont.) BNL Heat/Mass Flow Studies	• To obtain information on heat/mass flow enhancement for rapid cycle hydride vessel applications (mobile, compressor, separation systems)	• Data obtained showing significant enhancement when aluminum foam is used over just copper particles or mesh--Dramatic enhancement with introduction of pressurized hydrogen (20-50x)
LLL Automotive Storage Systems Study (BNL Tasks)	• Continue to investigate and compare candidate storage systems including hydrides, microspheres, and use of alkaline fuel cell for automotive use • Update projections on H_2 storage in hydrides and microspheres	• Increase of 15 to 40% in available H_2 based on Daimler-Benz data for fast charge hydride vessel similar to BNL design • Projections for microspheres somewhat less than originally expected--weigh about 40% of dual hydride at twice the volume; storage about 6-8 wt % • Preliminary projections on alkaline fuel cell use are positive
Storage Materials R. J. TEITEL Glass Microspheres for Automotive Applications	• To develop data base on glass microsphere performance for later applications	• Test equipment was assembled and is operational (laboratory scale) • Preliminary results indicate some variability in microsphere manufacturing processes and characteristics; engineering analysis determined that it was unrealistic to identify a cost at this time (Cont.)

Figure 1.4

CHEMICAL/HYDROGEN ENERGY STORAGE SYSTEMS PROGRAM
1979 OBJECTIVES AND ACCOMPLISHMENTS

2. STORAGE SYSTEMS AND MATERIALS (Cont.)

ACTIVITY	OBJECTIVES	ACCOMPLISHMENTS
Storage Materials (Cont.) DENVER RESEARCH INSTITUTE (DRI) Search for Optimal Hydrides	• To develop 3 wt % hydrides with proper PCT. characteristics using DRI predictive technique	• Some Ti-based alloys (Ti-V-Mn, Ti-V-Cr) attractive if temperature of 200-250°C available--others no better than FeTi • DRI predictive technique is limited and at best qualitative
AIR PRODUCTS H_2 Storage Systems for Automotive (Phase I)	• To develop hydrides with > 3 wt % H_2 Storage at dissociation levels of 175°C and 1 atm pressure	• Identified Mg_2Al_3 as most promising alloy (3 wt % and 1 atm) but dissociation temperature is 230°C and kinetics too slow for automotive use
AIR PRODUCTS H_2 Storage (Phase II)	• To investigate kinetics of Mg_2Al_3 reaction and use of nickel catalysts to improve rates	• Slow reaction rates in 200°-250°C range due to disproportionation--Study indicated that nickel improved H_2 desorption rate but not absorption, implying different limiting factors
INCO Hydrides Surface Poisoning Studies	• To determine mechanisms of poisoning of FeTi, $LaNi_5$ hydrides by CO, O_2, and H_2O • Investigate methods of reactivation and development of poison resistant alloys	• Completed comprehensive study with significant results indicating that all alloys can be reactivated using simple procedures • Some alloys more susceptible to specific poisons, e.g., CO and $LaNi_5$, O_2, H_2O, and FeTi or (FE, Mn) Ti, poison resistance can be designed into alloy

(Cont.)

Figure 1.4

CHEMICAL/HYDROGEN ENERGY STORAGE SYSTEMS PROGRAM
1979 OBJECTIVES AND ACCOMPLISHMENTS

2. STORAGE SYSTEMS AND MATERIALS (Cont.)

ACTIVITY	OBJECTIVES	ACCOMPLISHMENTS
Storage Materials (Cont.)		
BNL H_2 Storage Materials Work	• To conduct research to develop special purpose metal hydrides • To investigate potential for using hydrides for gas separation	• Identified high temperature $TiCr_2$-H hydride system that may have application in chemical compressors • Low temperature $TiCr_2$-D system suitable for H_2-D_2 separation • Identified $LaNi_5$, $LaCuNi_4$ as suitable for separating H_2 from natural gas streams system cycled 20 times with no loss in kinetics or H_2 capacity

3. END USE APPLICATIONS/SYSTEMS STUDIES

ACTIVITY	OBJECTIVES	ACCOMPLISHMENTS
AIR PRODUCTS H_2 from Small Hydropower	• To determine commercial feasibility of producing H_2 from small hydropower using "over the fence" approach	• Systems analysis and site selection activities completed--Study determined that over-the-fence approach is not economically attractive--No match between site and customer--Small-user merchant market not attractive either for specific area and study conditions
NYSERDA H_2 from Small Hydropower	• Initiate project to demonstrate H_2 production from small hydropower at Potsdam, N. Y.	• Project delayed in getting underway because of administrative/contractual problems--rescheduled to begin April 1980

Figure 1.4

CHEMICAL/HYDROGEN ENERGY STORAGE SYSTEMS PROGRAM
1979 OBJECTIVES AND ACCOMPLISHMENTS

4. CHEMICAL ENERGY STORAGE/CHEMICAL HEAT PUMPS

ACTIVITY	OBJECTIVES	ACCOMPLISHMENTS
ROCKET RESEARCH H_2SO_4/H_2O System	• Identify requirements for Chemical Heat Pumps beyond solar applications • Design, build and test Verification Test Unit incorporating commercial requirements	• Requirements analysis has been completed identifying several applications including industrial waste heat utilization • VTU conceptual design completed and detail design has begun
EIC CORPORATION Methanol-Calcium Chloride Heat Pump System	• Verify system design on engineering test unit and initiate prototype design for methanol-calcium chloride system	• Testing with partial salt loading has been completed satisfactorily--Full-scale testing has been delayed because of lack of adequate quantities of +25-40 mesh salt
BNL/ARGONNE Metal Hydride/Chemical Heat Pump	• To develop work statement for competitive procurement for a Metal Hydride CHP based on prior Argonne work	• Determined that sufficient interest exists in industry for Metal Hydride CHP for industrial/commercial/residential space conditioning

FIGURE 1.5

WORK BREAKDOWN STRUCTURE CHEMICAL/HYDROGEN ENERGY STORAGE

Base Technology Development	Systems Development and Engineering	Markets Field Test Demonstration
● Electrochemical	● Electrolyzers	● Feedstocks
● Energy Conversion	● Fuel Cells	● Space Conditioning
● Energy Storage	● Chemical Compressors	● Industrial Waste Heat Management
● Materials	● Chemical Separation	● Natural Gas Supplementation
	● Chemical Heat Pump	● Transportation
	● Mobile Storage	
	● Stationary Storage	

2.0 ELECTROCHEMICAL SYSTEMS

The major accomplishments in the Electrochemical Systems area during 1979 are as follows:

- SPE Water Electrolysis Development - At General Electric, in the 2.5-ft^2 cell development task, a total of 18 modules consisting of 1 to 12 cells were tested for a total operating time of 4000 hours. This testing resulted in design modifications aimed at improving performance, water flow, and sealing, which are being incorporated in the 2.5-ft^2 hardware. The reasons for the loss in performance by about 100 mV at 1 amp cm^{-2} are being investigated. During the year, the assembly and checkout of the 200-kW system (with 2.5-ft^2 electrodes) were completed. The design of the next scale-up cell (2.5, 10 ft^2) was finalized. The cell is to be rectangular in shape with dimensions of approximately 75" x 24" or a 6-foot by 2-foot configuration. Fabrication development of the 10-ft^2 components is planned for 1980 after performance of the 2.5-ft^2 cells in the 200-kW system.

- Supporting Research - With the aim of stabilizing ruthenium-based electrocatalysts for SPE water electrolyzers, mixed oxides of ruthenium with Ta, Zr, Hf, Ir, W, La, Mn, Pb, and Sr were examined as electrocatalysts for the oxygen evolution reaction at BNL. The most promising of these oxides is the tantalum-based oxide, $Ta_{0}.{}_{5}Ir_{0}.{}_{5}RuO_{x}$, which exhibits a Tafel slope of only 30 mV throughout the entire range. Specifically, this electrocatalyst represents substantial improvement over the current WE-3 proprietary catalyst used by GE in the SPE electrolyzer. In a parallel project, large single crystals of RuO_2 were grown by the vapor transport method at Brooklyn College. Investigations are being made on these materials to determine effects of crystal orientation on electrocatalytic activity of oxygen evolution.

- Development of Advanced Alkaline Water Electrolyzers - Materials for cell components were evaluated in the 5-cell ARIES (Applied Research Industrial Electrolysis System) test rig at Teledyne Energy Systems. There was a more marked improvement in cell performance with improved cathodes as compared with improved anodes. A 1000-hour test was conducted in the 5-cell module with a proprietary platinum-catalyzed cathode, a PTFE-bonded nickel powder anode, and a chrysotile electrode separator. The cell potential of 1.855 volts decayed slightly to 1.877 volts (78.8% energy efficiency) at a current density of 500 mA cm^{-2} after 1000 hours. Material testing was carried out at temperatures up to 125°C. A computer-assisted engineering design study aimed at calculation of hydrogen production costs in advanced electrolyzers was initiated in September 1979.

- Advanced Alkaline Water Electrolysis: Supporting Research - The selection and evaluation of materials for advanced water electrolyzers operating at temperatures of up to 125°C was continued at BNL. High surface area nickel-based materials show promise as electrocatalysts for the hydrogen and oxygen evolution reactions. Preliminary results indicate the usefulness of composite materials (e.g., asbestos sandwiched between Teflon-bonded potassium titanate as separators). At the University of Virginia, examination of nickel whisker electrocatalysts disclosed a 10% improvement in cell performance over conventional nickel screens, attributed to the high surface area nickel whisker electrodes. The time variation of hydrogen overpotential on nickel was investigated using x-ray diffraction, electrochemical, and scanning electron microscopic techniques and data suggest the formation of an α and/or a β nickel hydride which requires further study.

2.1 Design, Development and Testing of 50- and 200-kW SPE Water Electrolyzers - General Electric Company

Objective:

During 1979, the General Electric Company continued development of the SPE water electrolysis technology for large-scale hydrogen generation under the sponsorship of the Department of Energy (DOE), the New York State Energy Research and Development Authority (NYSERDA), Niagara Mohawk Power Corporation (NMPC), Empire State Electric Energy Research Corporation (ESEERCO), Gas Research Institute (GRI), and the General Electric Company (GE).

The general goals of the program were:

- Overall system efficiency: 85-90%
- System capital cost (battery limits) - \$150/kW equivalent (1980 dollars)
- Life - Cells: 40,000 hr
- System Life - 20 years
- Scale-up: 2.5 ft^2, 10 ft^2
- Program Goal: 5-MW Demonstration System

The overall milestone chart for the program is shown in Fig. 2.1, the heavy lines indicating the present status.

Tasks:

Task 1. Operation Evaluation of the Scaled-up Cell (2.5-ft^2 active area) in Modules of up to 12 Cells (500 SCFH hydrogen output).

Task 2. Complete Assembly and Operate a 200 kW (2000 SCFH) System.

Task 3. Design a Cell with a 10-ft^2 Active Area and Module.

Task 4. International Energy Agency Participation

Technical Progress:

Task 1. 2.5-ft^2 Cell Evaluation: The operational evaluation of full-sized 2.5-ft^2 cells in a 50-kW test bed system, which had begun in 1978, continued throughout 1979. A total of 18 modules, containing from 1 to 12 cells each were tested with more than 4000 operational hours logged during FY Fig. 2.2 shows a 2.5-ft^2 module on test in the 50 kW test system. As a result of this testing, design modifications aimed at improved performance, improved water flow, and improved sealing were identified and are being incorporated into the 2.5-ft^2 hardware.

Performance: Fig. 2.3 summarizes the performance demonstrated by full-sized, 2.5-ft^2 cells at 180°F during FY 79. The initial cells utilized molded carbon current collectors which contained a phenolic resin binder. The phenolic resin was found to be a source of electrode contaminant which caused significant performance loss in the range of 1000-A/ft^2 current density, as shown in Fig. 2.3. Short periods of operation at high current density (2000 A/ft^2), as indicated by the dashed line, would temporarily restore the cells to baseline performance. An alternative fluoropolymer binder was identified under the Technology Development Program which eliminated the contamination and offered a significantly shorter molding cycle and thus reduced cost. Full-sized 2.5 ft^2 collectors utilizing the fluoropolymer/carbon mixture were successfully molded and demonstrated stable and improved performance in the range of 1000 A/ft^2, as seen in Fig. 2.3. However, the resistance of the initial fluoropolymer collectors was relatively high, with the protective foil-to-carbon/fluorocarbon interface being a major contributor. This interface is currently being optimized.

Water Flow: In the 2.5-ft^2-size modules, it was found that the 1-mil-thick perforated titanium foil anode support allowed sufficient deflection into the oxygen/water flow field to cause increased pressure drop and reduced water flow. This in turn restricted operation at the higher current densities. Under the Technology Development Program, techniques to fabricate an alternative porous titanium plate anode support were developed. This type of support provides significantly improved anode support and, as shown in Fig. 2.4, greatly reduced oxygen side pressure drop and improved water flow.

Cell Sealing: With the initial collector configuration, practical flatness tolerances in the molded collector led to marginal sealing, even with extensive application of heat and compression pressure. The use of force amplifiers (sealing ridges) around the internal manifold ports and around the periphery of the collector was shown to improve sealing. The collector molds were modified to produce molded-in force amplifiers, shown in Fig. 2.5. Evaluation of collectors molded with force amplifiers is in progress.

Task 2. 200-kW System: During FY 1979, assembly and checkout of a 200-kW (2000 SCFH) system was completed. System diagrams are shown in Fig. 2.6 and 2.7. A photograph of the main fluid control console is shown in Fig. 2.8. The system is fully monitored (see Fig. 2.9) and configured with automatic shutdown provisions for safe, unattended operation. During 1979, the system was operated using 6-cell and 12-cell modules over 1500 hours with no major difficulty. The majority of this operation has been unattended. It is planned that a full 200-kW module be tested in this system early in 1980.

Task 3. 10-ft^2 Cell Design: Design of the next step in cell scale-up with 10 ft^2 active area was completed in 1979. Drawings of the cell component and compression hardware were prepared. The cell is rectangular with overall dimension of approximately 75" x 24". The rectangular shape was selected based on anode side pressure drop, manufacturing process, and material availability considerations. Fabrication development of the 10-ft^2 components is planned for 1980 after demonstration of the 2.5-ft^2 cell in a full 200-kW module.

Technical Problems:

The following technical problem areas are currently being addressed by GE:

- Verification of cell sealing
- Verification of cell's electrochemical performance
- Maintaining seal/electrochemical performance at scale-up dimensions (i.e., 10 ft^2)

Publications:

During 1979, papers on the Solid Polymer Electrolyte Water Electrolysis Program were presented to:

- The Joint American Chemical Society/Chemical Society of Japan General Meeting in Honolulu, Hawaii in April 1979.
- The IEEE Power Engineering Society summer meeting at Vancouver, British Columbia, July 1979.
- The Intersociety Energy Conversion Engineering Conference at Boston, Massachusetts, August 1979.
- The DOE Chemical/Hydrogen Energy Systems Contracts Review at Reston, Virginia, November 1979.
- The International Conference on Alternative Energy Sources at Miami, Florida, December 1979.

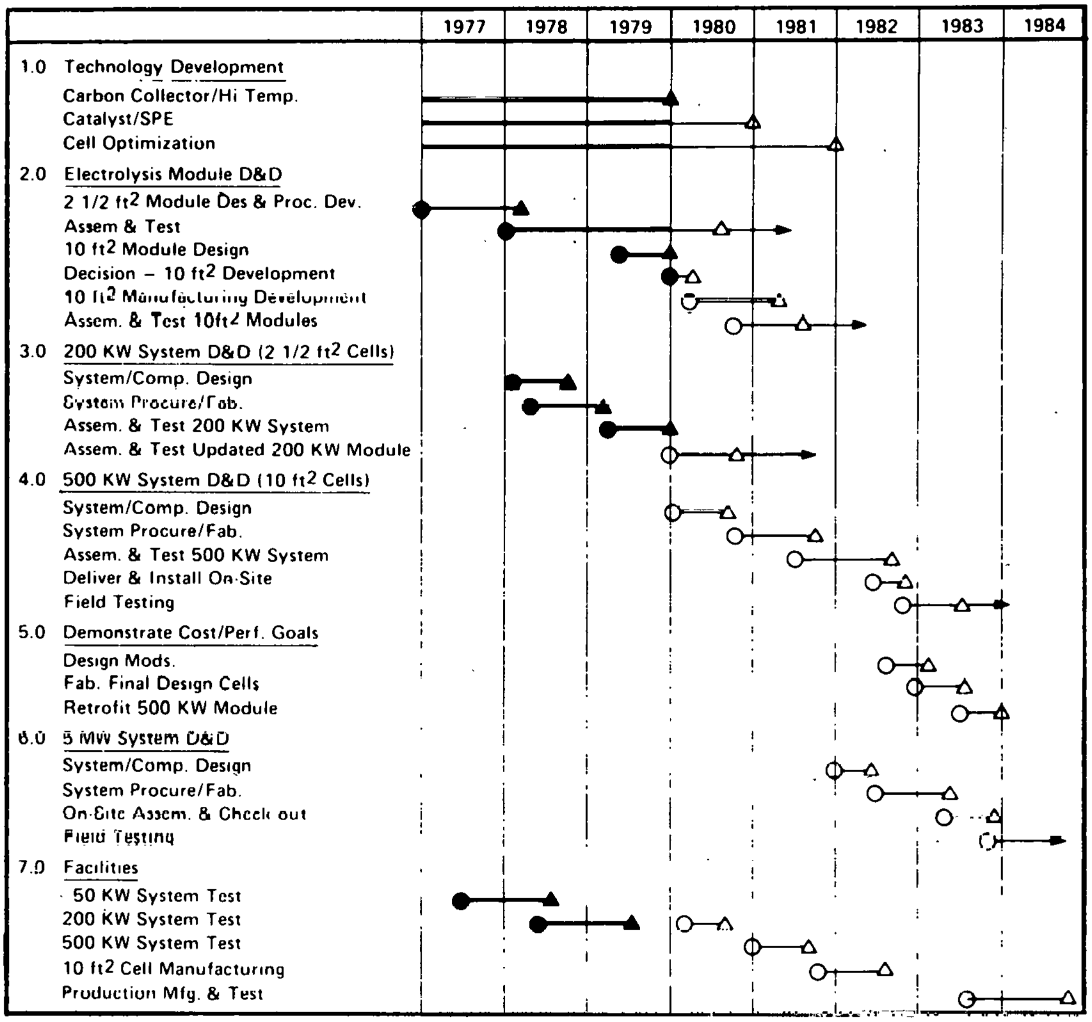


Figure 2.1. Major Milestones - Bulk Hydrogen Generation Program

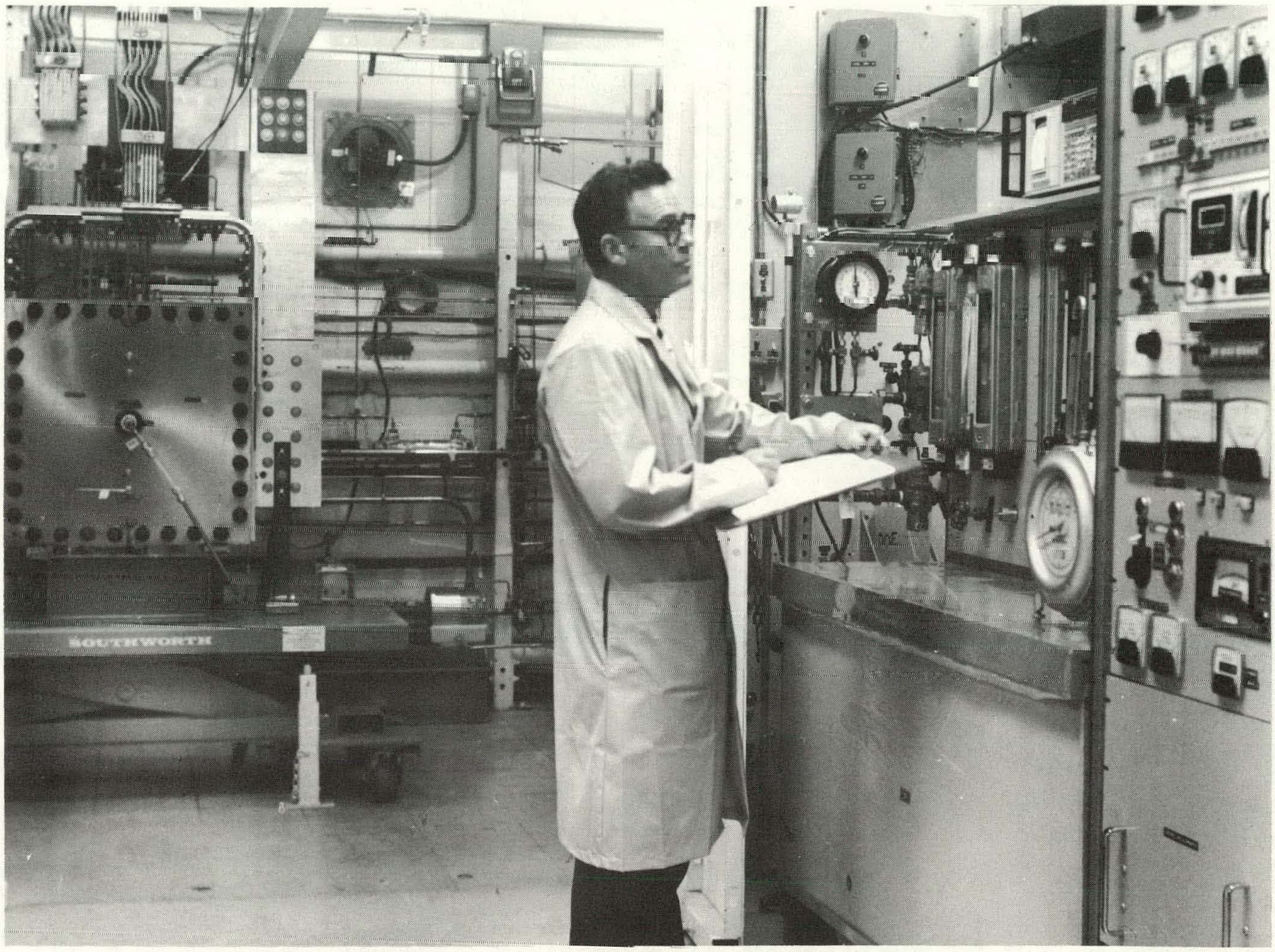


Figure 2.2. 2.5 ft^2 Module on Test in 50-kW Test Bed System

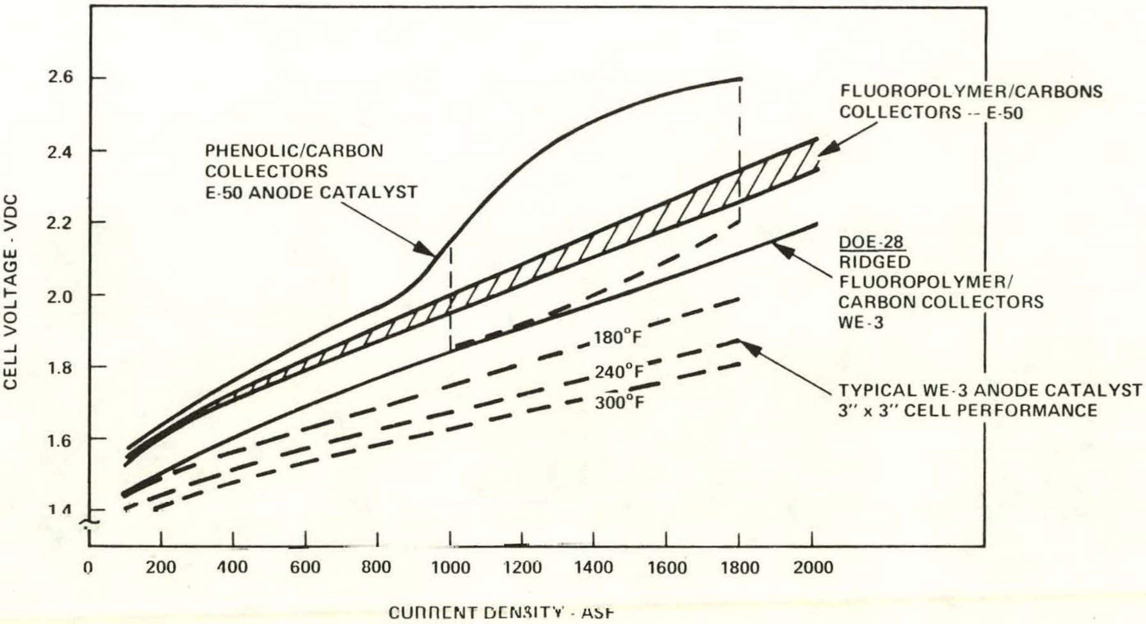


Figure 2.3. 2.5 ft^2 Cell Performance Comparison

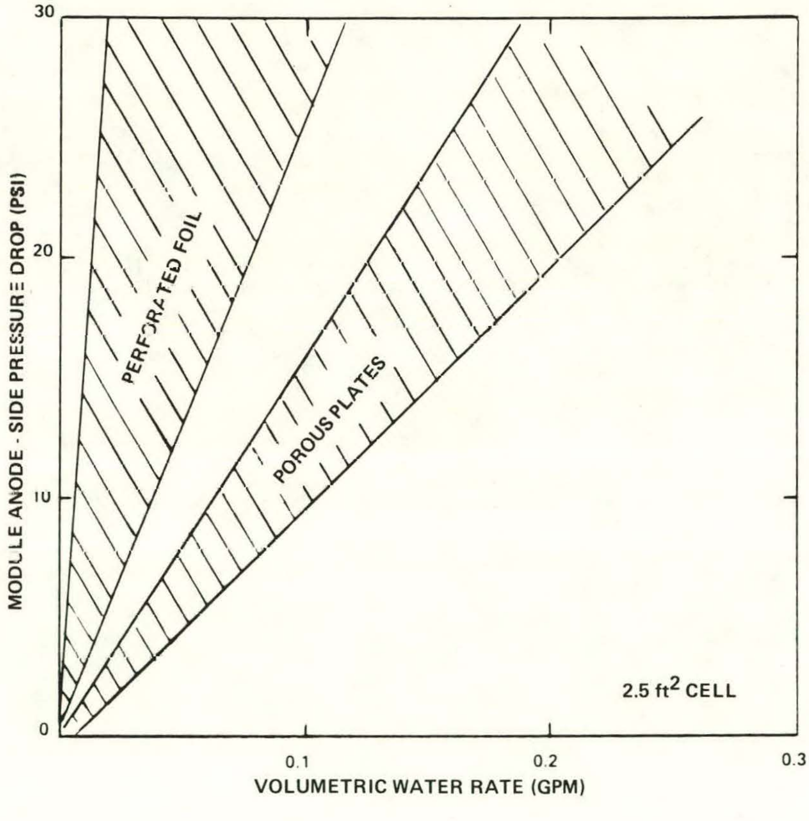


Figure 2.4. Effect of Various Anode Supports on Feed Water Flow

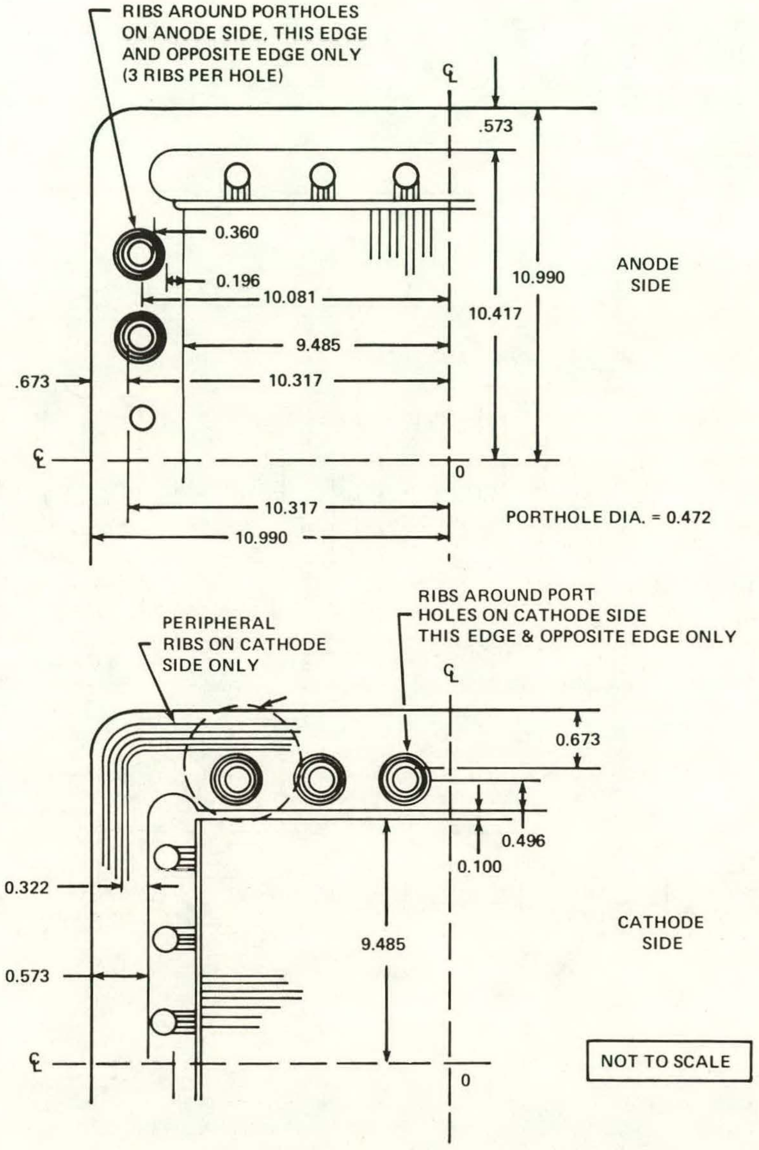


Figure 2.5. Collector Dimensions and Rib Locations

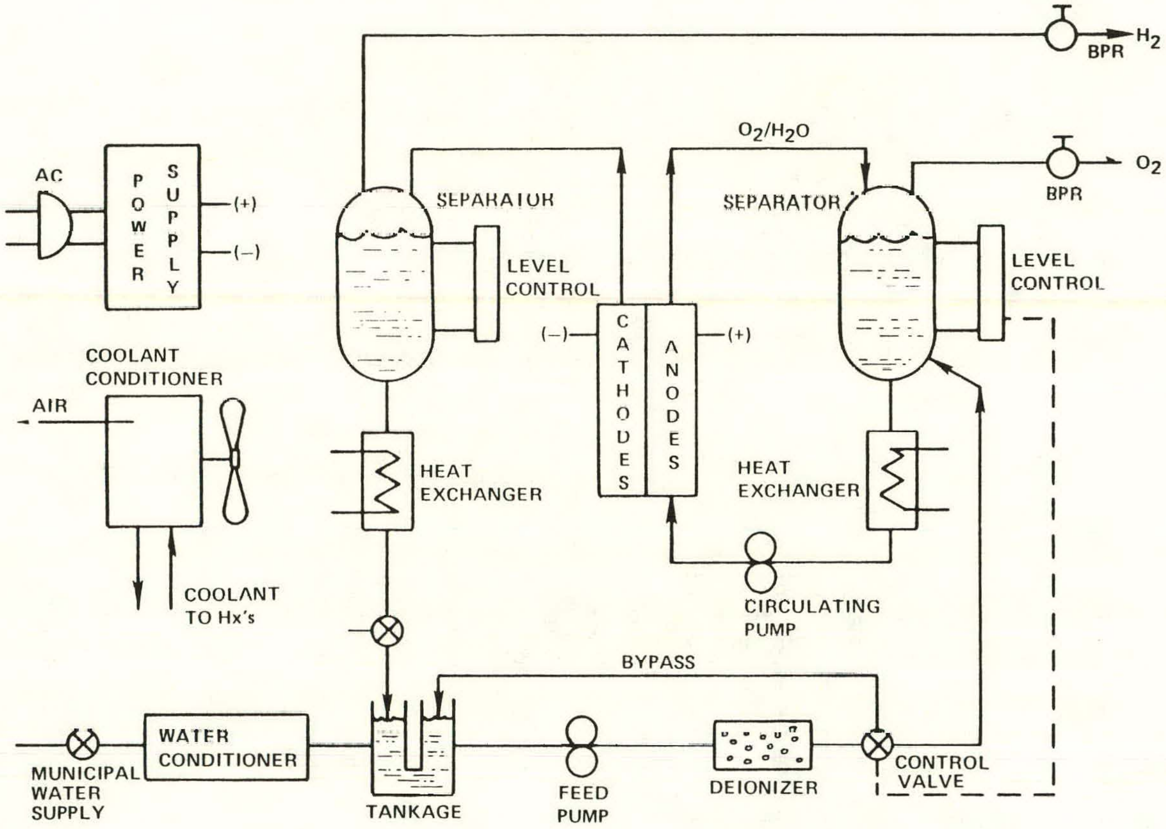


Figure 2.6. 200-kW System Schematic

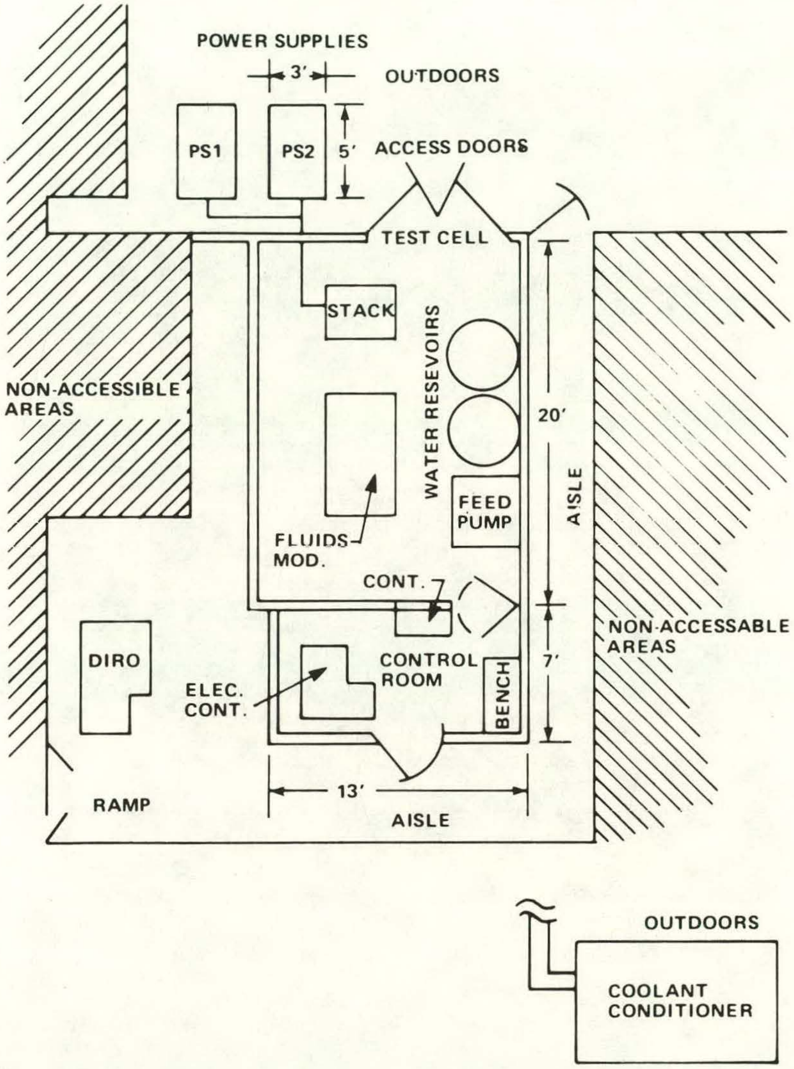


Figure 2.7. 200-kW System Layout Scale Drawing

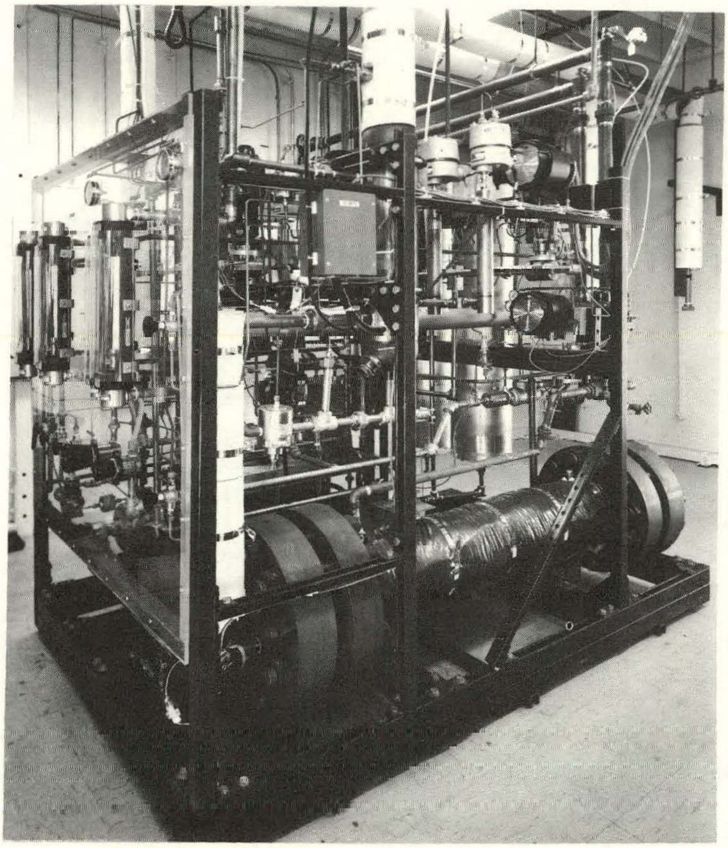


Figure 2.8. Fluid Component Subassembly

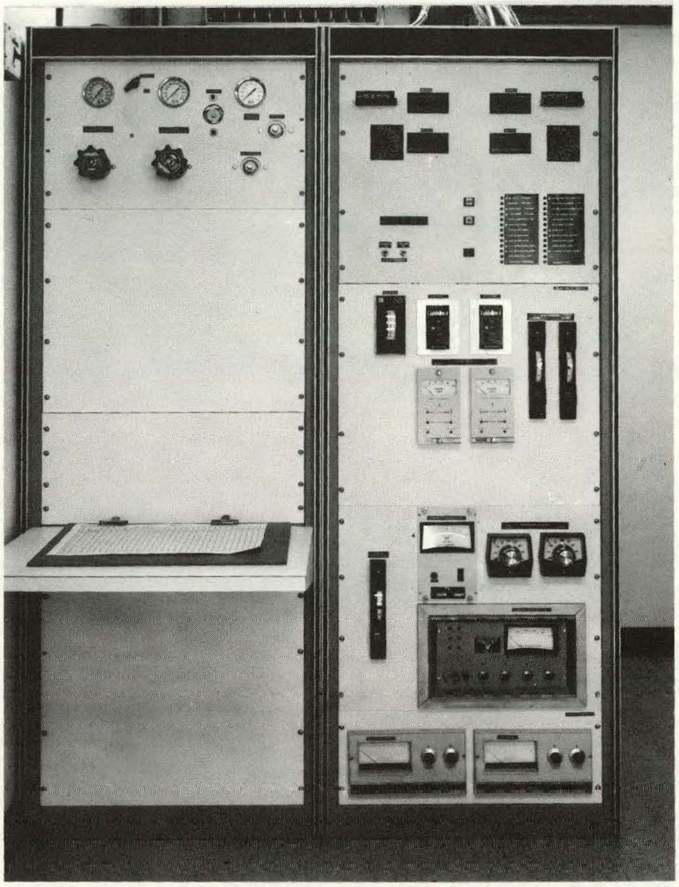


Figure 2.9. Electrical Control Console

2.2 Electrochemical and Ellipsometric Studies on Anode Electrocatalysts for SPE Water Electrolyzers - Brookhaven National Laboratory

Objective:

The objectives of the program at BNL are to identify low cost, high performance, and more stable electrocatalysts for the General Electric Company SPE Water Electrolyzer and to draw correlations between the optical properties of oxide films (formed on noble metals and their alloys) and their electrocatalytic activities for oxygen evolution.

Tasks:

Task 1. Evaluation of Ruthenium-Based Mixed Oxides as Anode Electrocatalysts for SPE Water Electrolyzers.

Task 2. Electrochemical and Ellipsometric Studies on Ru-Ir Alloy.

Technical Progress:

Task 1. Ruthenium-Based Mixed Oxides: It has been found that the electrocatalytic activity of ruthenium is improved and stabilized by alloying with oxides of tantalum and iridium. With the aim of stabilizing ruthenium-based electrocatalysts for SPE water electrolyzers, mixed oxides of ruthenium with Ta, Zr, Hf, Ir, W, La, Mn, Pb, and Sr were prepared by the thermal decomposition method on a titanium substrate and were examined as oxygen evolution electrocatalysts in 1.0 N H_2SO_4 at 25°C. With some of these oxides, the current-potential plots, obtained using the slow potential sweep technique, exhibit hysteresis, as shown in Fig. 2.10 for $WRuO_x$. This behavior is characteristic of electrodes at which there is a time variation of overpotential. The mixed oxide $LaRuO_x$ behaved in a similar manner while the hysteresis was not observed with the other mixed oxides. The current-potential relations for oxygen evolution on RuO_x, IrO_x, $TaRuO_x$, $Ta_{0.5}Ir_{0.5}O_x$ and $TaIr_{0.5}Ru_{0.5}$ were obtained using steady state techniques and the Tafel lines are shown in Figs. 2.11 and 2.12. Fig. 2.12 also shows that the electrocatalytic behavior of the mixed oxide $Ta_{0.5}Ir_{0.5}RuO_x$ is superior to that of the proprietary anode electrocatalyst WE3 used in the General Electric Solid Polymer Electrolyte Water Electrolyzer (i.e., a lower Tafel slope for the former which will result in a lower oxygen overpotential at the desired current densities than for WE3). The time variation of overpotential at a constant current density of 50 mA cm^{-2} is considerably less on the binary and ternary oxides than on RuO_2.

Task 2. Electrochemical and Ellipsometric Studies on Ru-Ir Alloy: A combined electrochemical-ellipsometric method was used with the aim of (i) drawing correlations between electrocatalytic and optical properties of oxide films formed on surfaces, and (ii) elucidating the mechanism of the time variation of overpotential. Investigations were made on a Ru-Ir alloy (50-50 atomic percent) in 1.0 M H_2SO_4. Preliminary results showed that oxygen evolution kinetics can be improved by multicycling of the electrode between 0.1 to 1.5 volts vs RHE. Similar effects were observed with multicycling of Pt and Ir electrodes. A Tafel slope of 60 mV/decade was obtained, as shown in Fig. 2.13. The performance improvement is attributed to the growth of oxide layer with thickness of about 30 Å. This layer is enriched in $Ir(OH)_3 \cdot XH_2O$ due to preferential dissolution of Ru. The oxide layer dissolved when oxidized at higher anodic potentials (say, 2.1 volts vs RHE) and the resulting oxide layer is a poorer electrocatalyst. A Tafel slope of 80-85 mV/decade was observed on this oxide layer. In contrast to the oxide formed on Ir metal, this oxide layer on the Ru-Ir alloy cannot be reduced completely even at high cathodic potential which indicates the presence of ruthenium oxide. However, the composition of Ru in the oxide layer is lower than that in the bulk material.

Technical Problems:

There are no major problems with this work.

Publications:

Lu, P. W. T. and S. Srinivasan. Advances in water electrolysis technology with emphasis on use of the solid polymer electrolyte. J. Appl. Electrochem. 9, No. 3, 269-83 (1979).

Srinivasan, S. Selection and evaluation of materials for advanced water electrolyzers. Proc. of the DOE Chemical/Hydrogen Energy Systems Contracts Review, Reston, Virginia, November 13-14, 1979. Conf-781142.

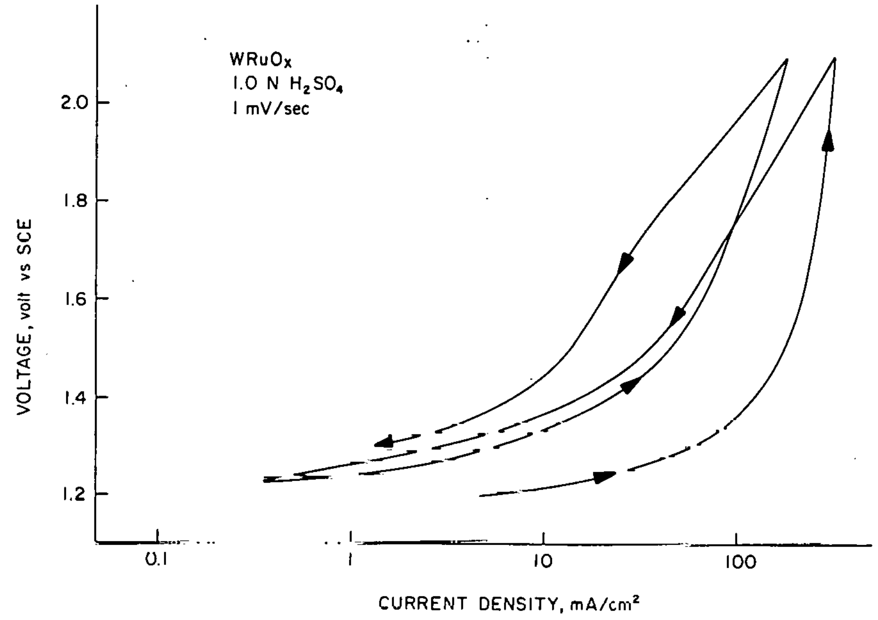


Figure 2.10. Voltage-current relationship for oxygen evolution Reaction for $WRuO_x$ in 1.0 N H_2SO_4 at 25°C. Sweep Rate: 1 mV/sec

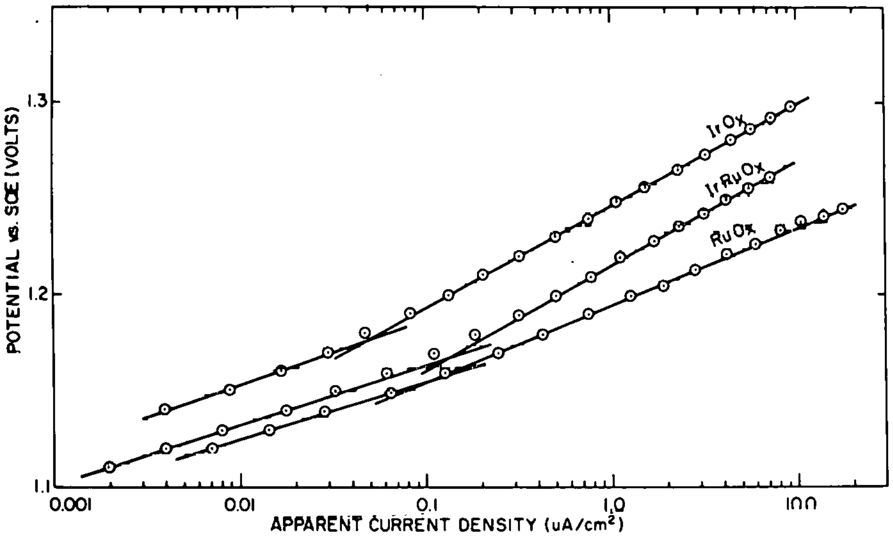


Figure 2.11. Tafel Plots for Oxygen Evolution on IrO_x, $IrRuO_x$, in 1N H_2SO_4 at 25°C

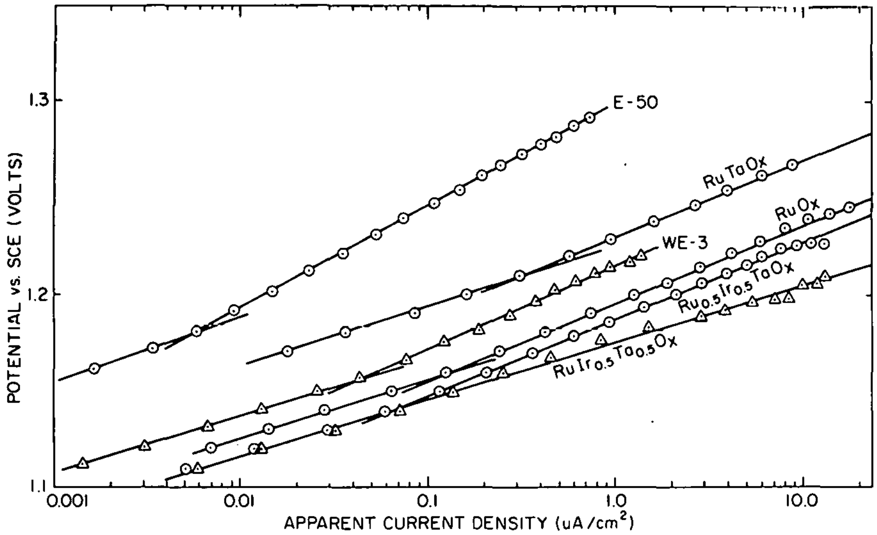


Figure 2.12. Tafel Plots for Oxygen Evolution on RuO_x, $RuTaO_x$, $Tu_{0.5}Ir_{0.5}TaO_x$ and $RuIr_{0.5}Ta_{0.5}O_x$ in 1 N H_2SO_4 at 25°C

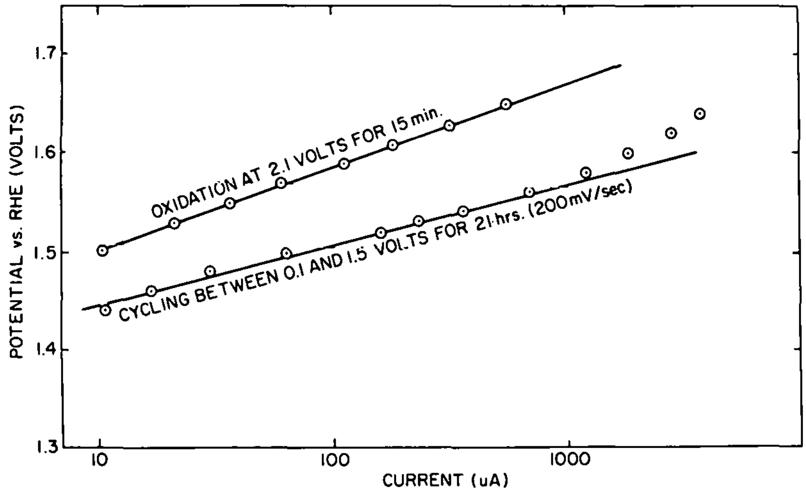


Figure 2.13. Tafel Plots for Oxygen Evolution on Oxides Formed on Ru-Ir Alloy in 1 N H_2SO_4 at 25°C

2.3 Optical and Electrochemical Investigation of Ruthenium, Iridium and Their Oxides in Relation to Their Electrocatalytic Activity - Brooklyn College of CUNY

Objective:

The performance of Ir, Ru, and their alloys has been found to be much superior to that of pure Pt as an electrocatalyst for the oxygen evolution reaction. A major difficulty is the continuous decrease of current density with time. It has been suggested that this fundamental problem is connected with the continuous growth of a poorly conducting oxide film on the catalyst surface. For example, the BNL group has concluded that the performance degradation for oxygen evolution on a RuO_x catalyst is presumably due to the gradual accumulation of a RuO_2 film on the surface of the RuO_x particles by a dissolution/precipitation process. Efforts are underway at the General Electric Company and Brookhaven National Laboratory to further develop Ru-based electrocatalyst.

Tasks:

- To grow single crystals of RuO_2
- To elucidate mechanism of the electrocatalytic process of oriented single crystals

Technical Progress:

Large single crystals of RuO_2 have been grown by the vapor transport method. Electochemical investigations have been carried out on various oriented surfaces of the single crystal material as well as on a sample of unoriented single crystal material. A number of significant similarities and differences have been observed between the various faces that have been studied. The results have revealed considerably more structure in the cyclic voltammetry curves than reported by other investigators. Thus the work on oriented single crystal RuO_2 contains important information concerning the electrocatalytic process.

Shown in Figs. 2.14, to 2.17 are the cyclic voltammetry curves for single-crystal RuO_2 with (100), (110), (111), and unoriented surfaces, respectively. The measurements were performed in a N_2-saturated solution of 1 N H_2SO_4 for several different scan rates. Below about 1.5 V vs RHE, the four curves are qualitatively similar with major features at 0.4 and 0.7 V vs RHE in the cathodic region. The potentials of these features are independent of sweep rate.

For the (100) case (Figure 2.14) the first anodic peak (0.4 V vs RHE) consists of a well defined doublet and there is some structure on the cathodic peak at 0.2 V vs RHE. For the (110) crystallographic face (Figure 2.15) the second anodic peak (0.75 V vs RHE) is a doublet and there is structure on either the anodic or cathodic peaks at voltages below 1.5 V vs RHE. It is of interest to note that the two anodic peaks are at the same voltage for the three orientations while there are small differences (0.1 V vs RHE) for the cathodic features averaging out the structure in each case. For the unoriented sample (Figure 2.17) no structure is seen on either the anodic or cathodic peaks. In addition, the voltage difference between corresponding anodic and cathodic peaks is less than for the oriented samples. We attribute the observed structure in the cyclic voltammograms below 1.5 V vs RHE to the Ru_2O_3/Ru (lowest voltage anodic-cathodic pair) and the Ru_2O_3/RuO_2 couple.

In terms of the oxygen evolution reaction (OER) potential the (111) face shows no dependence on sweep rate (Figure 2.16), while for the other cases there are shifts to higher voltages with decreasing scan speed. We have also investigated cyclic voltammetry for Ru metal in a 1 N H_2SO_4 solution saturated with N_2 for the same scan speeds used in the RuO_2 cases. In the case of the Ru metal the OER potential does not depend on scan rate, similar to our observations for the (111) face. Although we do not completely understand these differences, it is interesting to note that for the (111) orientation of rutile (the crystal structure of RuO_2) it is possible to have a crystal face free of oxygens, i.e., only metal atoms. Thus the (111) case may be closer to the metallic situation.

Publications:

Berger, L. I., Fred H. Pollak, Y. Caniver, and W. O'Grady. The oxygen and hydrogen evolution reaction on oriented single crystals of ruthenium dioxide. Proc. of the DOE Chemical Energy Storage and Hydrogen Energy Systems Contracts Review, Reston, Virginia, November 13-14, 1979.

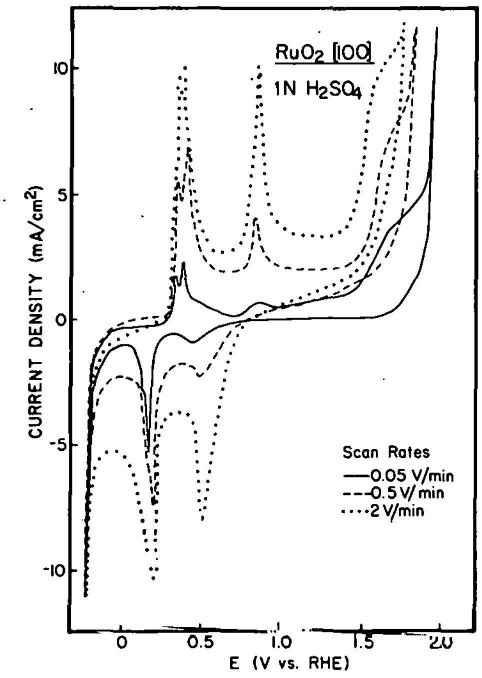


Figure 2.14. Cyclic Voltammetry Curve for Single Crystal RuO$_2$ (100) Surface

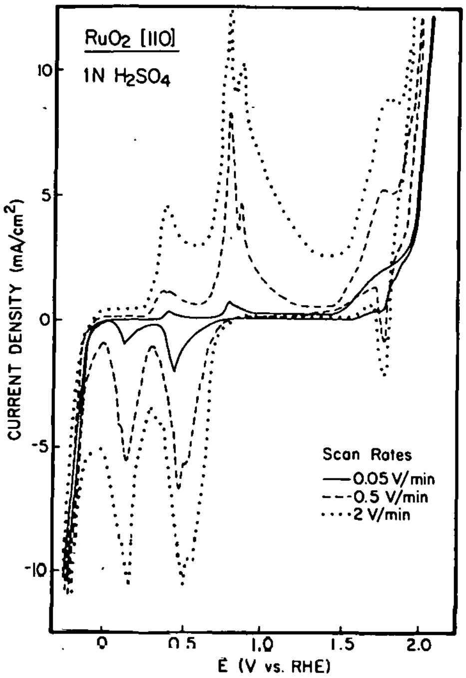


Figure 2.15. Cyclic Voltammetry Curve for Single Crystal RuO$_2$ (110) Surface

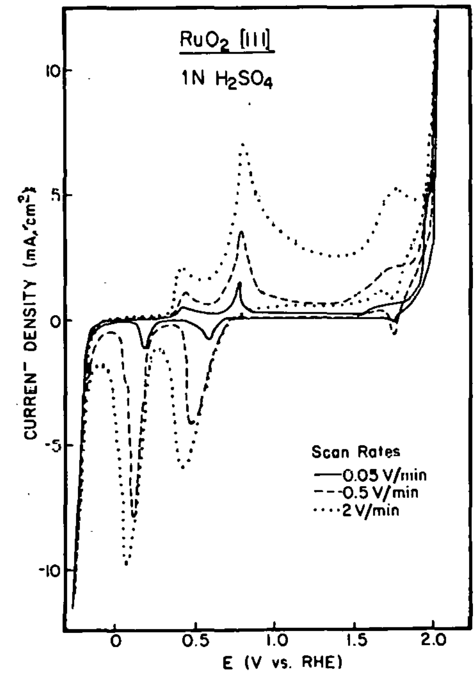


Figure 2.16. Cyclic Voltammetry Curve for Single Crystal RuO$_2$ (111) Surface

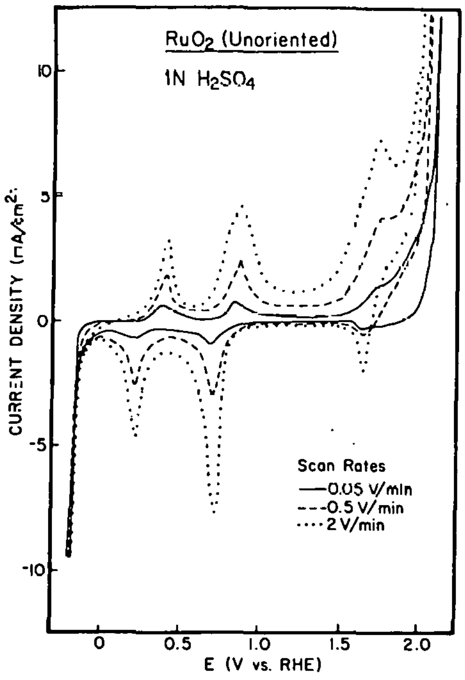


Figure 2.17. Cyclic Voltammetry Curve for Single Crystal RuO$_2$ (Unoriented) Surface

2.4 Evaluation of Materials for Cell Components in 5-Cell Test Rig and Development of Computer Program for Technoeconomic Assessment of Electrolytic Hydrogen Production - Teledyne Energy Systems

Objectives:

The overall objectives of this program are to increase the efficiency of hydrogen production via electrochemical processing from the conventional state-of-the-art (60%) to a goal of 100% at cell operating current density of at least 500 mA/cm^{-2} and to demonstrate the stability of the improvements in a useful full-sized system.

Tasks:

The tasks for calendar year (CY) 1979 were to:

Task 1. Continue investigations on improved electrolysis cell components in 5-cell testing with emphasis on cathode technology.

Task 2. Develop Fortran-coded computer program to optimize the hydrogen system design and determine the cost of hydrogen given a wide variety of possible energetic and economic inputs.

Technical Progress:

Task 1. Testing of Materials for Cell Components: The test facility in these investigations is a complete water electrolysis system in which one can evaluate performance of the electrolysis cell components under a variety of conditions at temperatures up to 150°C. The unit was designed and constructed during an earlier contract phase and identified as ARIES (Applied Research Industrial Electrolysis System). The 300 cm^2 active area electrolysis cell, designed previously at Teledyne Energy Systems (TES), can be subjected to continuous operation at current densities up to 2.5 A/cm^2. A 5-cell module (see Fig. 2.18) has been used for the various evaluations and data are presented as averaged values for operation at 450 mA/cm^2 at 100°Cunless otherwise indicated.

The initial evaluations of the conventional wire screen electrode technology in early 1978 showed the baseline technology to require 2.075 volts per cell or have a voltage efficiency of 71% (assuming 100% thermal efficiency equivalent to 1.48 volts). The decrease of cell voltage with increase of operating temperature was found to be between 3 and 4 mV/°C. In order to achieve the desired goal of 100% efficiency, new electrocatalytic materials were required and they were the objective of this investigation.

Evaluation of the effect of using improved electrodes was carried out by operating the 5-cell screening modules in ARIES for periods up to 500 hours. The volt-amp (V-A) data were recorded periodically throughout the test period. The general cell operation can be expressed as a thermal response coefficient and three voltage factors--the internal cell resistance voltage loss, a summed anode and cathode psuedo-Tafel slope voltage term, and a base input voltage "constant."

The testing of anodes was limited to the evaluation of (a) higher surface area nickel electrodes, (b) composite structures containing nickel and Teflon (PTFE), and (c) the $NiCo_2O_4$ electrocatalyst prepared via the "freeze-drying" technique by Dr. A.C.C. Tseung (City University of London). In general, little, if any, voltage differences or improvements were observed comparing the candidate test anodes to the baseline wire screen anode. The thermal response coefficients of all the cells were also found to be nearly identical and no significant differences were observed in the cell pseudo-Tafel slope value of 230 mV/decade of current.

The substitution of improved cathode electrocatalysts was considerably more successful in lowering the input voltage requirements. Four distinct approaches were chosen. Increasing the surface area of the baseline nickel screen electrode allowed an improvement from the normal input voltage of 2.075 V/cell to 1.96 V/cell. The addition of Ni_2B (courtesy Deutsche Automobilgesellshaft) to the standard wire screen or the addition of small quantities (≤ 1 mg/cm^2) of noble metal to the cathode surfaces (the TES-C-110 structure) resulted in cell voltages of 1.88 and 1.84 volts, respectively. Recently, a new cathode electrocatalyst made available to TES and designated as the TES-C-AN structure was tested, with the resulting input of 1.73 V/cell which corresponds to a thermal efficiency of 86% (see Fig. 2.19). Regressing analysis of the V-A data sets from the various effective electrocatalysts showed the cell pseudo-Tafel slope to have been lowered to approximately 105 mV/decade current.

In order to improve the thermal efficiency at higher current densities beyond 85%, the cell internal resistance term must be further reduced. In the TES cell designs, this term is quite small and is, in effect, influenced by the porous interelectrode separator in the electrolyte between the anode and cathode. The use of chrysotile asbestos separators has been shown to be satisfactory up to at least 80°C. However, only two alternative materials have been identified which satisfy the TES design requirements for a substitute for high temperature operation. Since potassium titanate electrode separators are not made commercially available, investigations are being limited to the second material, polybensimidazole (PBI). Earlier TES-funded work indicated that PBI had reasonable stability at 125°C. Preliminary evaluations in the 300 cm^2, 5-cell ARIES screening module showed satisfactory initial performance. The module behavior during the next 25 operating hours was, however, quite erratic and no particular satisfactory reasons have been identified for the shifts in the input cell voltages during this period. By the 35th operating hour, the PBI separator cells had apparently stabilized. A 60-mV higher input voltage was required for the TES-C-110 cathode/ PBI cells, whereas approximately a 120-mV higher input voltage was observed with the plain nickel wire screen PBI cells. The input voltage to these four cells was improving slowly at the end of the test period. Further testing to determine if a significant change in the PBI separator porosity occurred is scheduled as part of the next task.

One moderately long-term test was conducted with advanced components (See Fig. 2.20). In this test, a 5-cell module contained the TES-C-110 cathodes (with less than 1 mg/cm^2 noble metal electrocatalyst), the PTFE- bonded nickel powder (TES-010-00) as the anode electrode structures and the conventional chrysotile electrode separators. The stability of the cathode electrocatalyst, the mechanical integrity of the PTFE-bonded anode electrocatalyst structure, and the change in electrical input characteristics with time were the areas of major concern. The cell potential 1.855 volts (79.8% energy efficiency) decayed slightly to 1.877 volts (78.8%) after 60 days of testing, involving over 1000 hours of operating time. It was encouraging to note that the psuedo-Tafel slope of the cell remained constant throughout the test period. The module and/or system was restarted over 35 times from ambient (25°C), as well as standby conditions (100°C), and was operated at various current densities up to 2 A/cm^2 with temperature excursions up to 125°C. The general pattern of the module input voltage varying linearly with the logarithm of the continuous operating time was again observed throughout the test period. However, the module voltage loss rate was found to be only approximately 10 mV/decade of time after the system came to equilibrium.

Further electrode, as well as module testing, is required to identify why these results are superior to published data on individual electrodes.

Task 2. Technoeconomic Assessment of Electrolytic Hydrogen Production: The new task started in September 1979, is the establishment of a refined computer-assisted engineering design study aimed at identification of optimized costs for electrolysis plants utilizing various advanced electrocatalysts. For any given set of input design constraints such as plant size, economic factors, plant utilization profile, and materials for use at various proposed operating temperatures, this model will optimize the electrolysis plant design current density and subsequently calculate the resulting cost of product hydrogen gas. The effectiveness of various electrocatalysts as well as projected advanced operating conditions will be subsequently determined. Part of the output will include optimized key system component sizings for such items as power conditioning, heat exchangers, electrolyte pump(s), as well as gas product conditioning equipment. The writing of the specific codes was finished by the end of the reporting period with program debugging and initial studies to be completed by the end of January.

Technical Problems:

Minor problems associated with the required electrolyte filter maintenance and with recalibration of the control transducer DPX-2 were identified. Modifications to ARIES are scheduled prior to start of the next test phase. Clearly, further work with the PBI electrode separator is required to understand both the constructional requirements and the operational procedures which may be distinct from the previous work with the chrysotile asbestos separators.

Publications:

TES-BNL-39, Electrolysis Cell Material Development Task No. 3 Summary Report, Characterization of Commercially Available Components in the Applied Research Industrial Electrolysis System (ARIES), March 1979.

Murray, J.N. and M.R. Yaffe. Testing aqueous caustic electrolyzers at high temperatures. Int. J. Hydrogen Energy 4, No. 3, pp 193-205, June 1979.

Murray, J.N. and M.R. Yaffe. High efficiency alkaline electrolysis technology. Proc. 14th IECEC, Boston, Massachusetts, August 1979.

TES-BNL-45, Electrolysis Cell Material Development Task No. 4 Summary Report, High Efficiency Electrode Screening Tests, August 1979.

Yaffe, M.R. and J.N. Murray. New developments in alkaline water electrolysis. *Proc. DOE Chemical Energy Storage and Hydrogen Energy Systems Contracts Review*, Reston, Virginia, November 13-14, 1979.

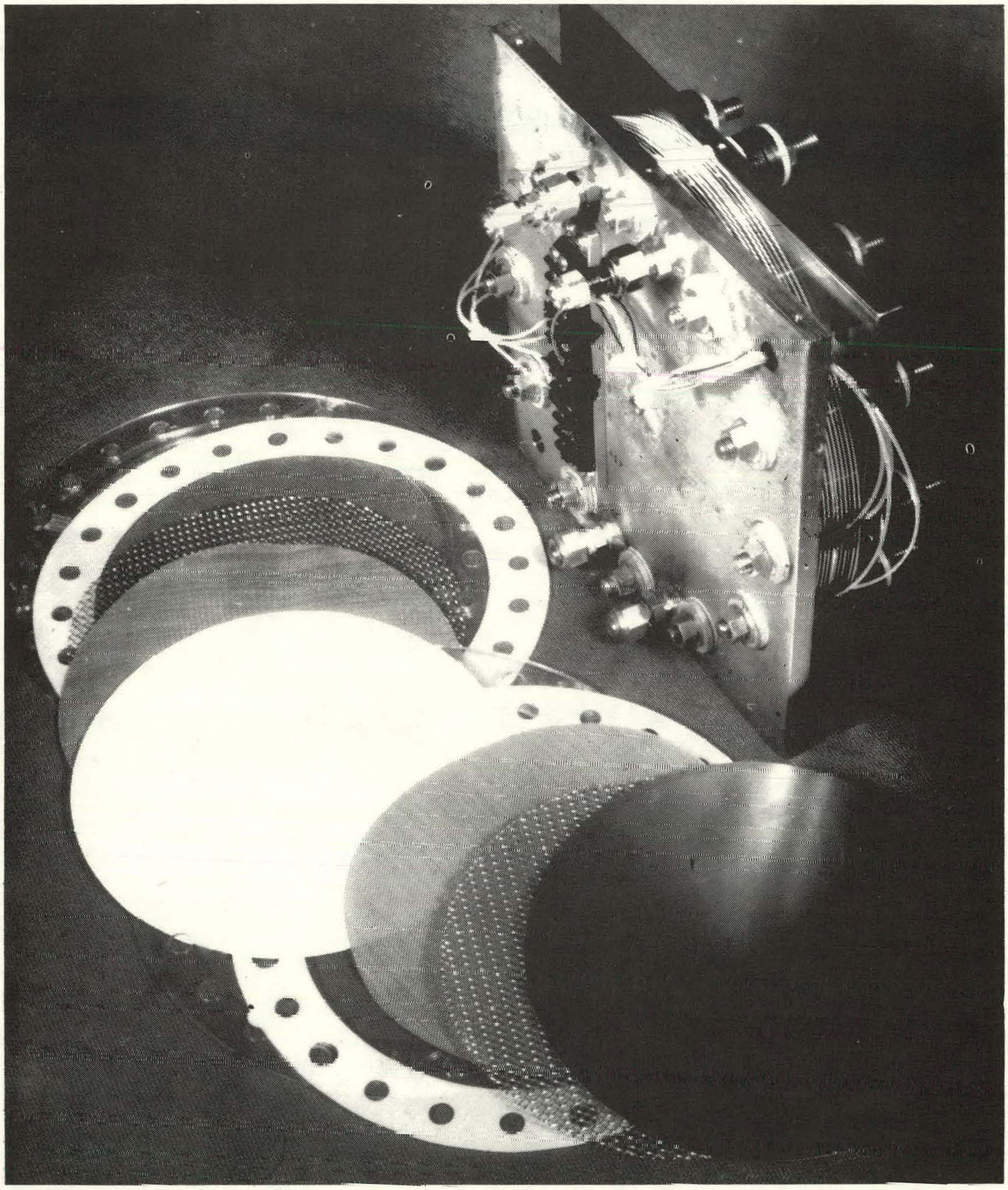


Figure 2.18. Assembled ARIES Module and Components

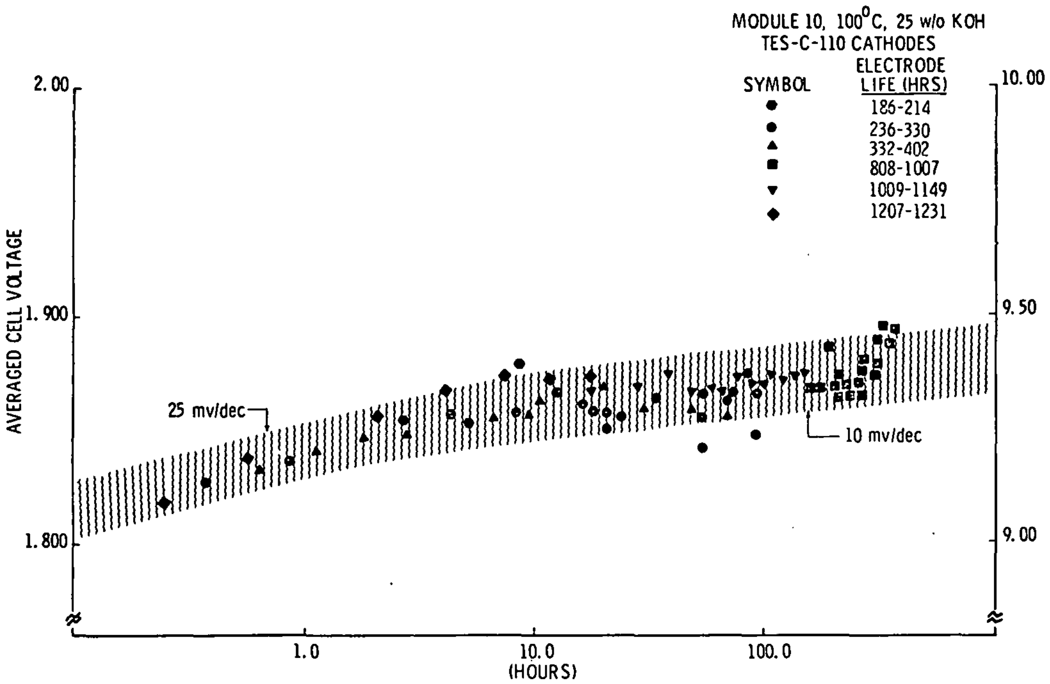


Figure 2.19. Module No. 10, Average Cell Voltage vs. Log Continuous Operating Time

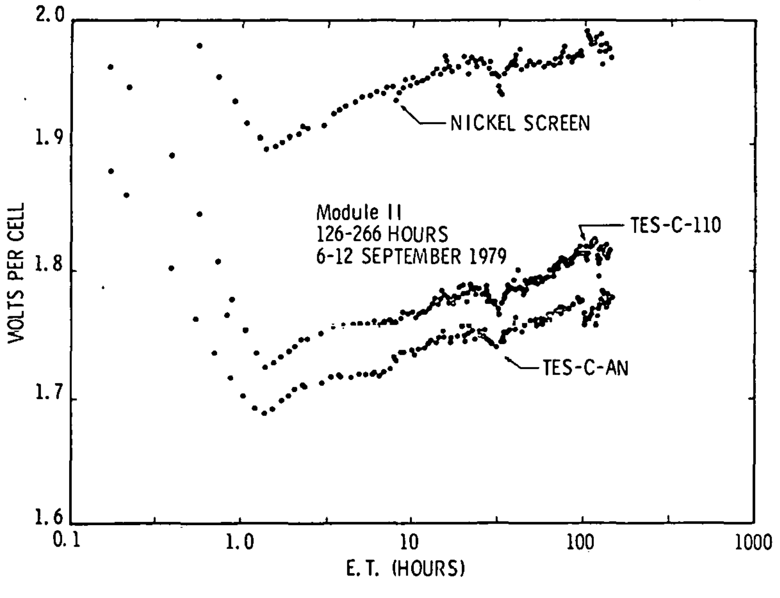


Figure 2.20. Module 11, Comparison of Cathode Voltages vs Log Continuous Operation

2.5 Selection and Evaluation of Materials for Advanced Alkaline Water Electrolyzers - Brookhaven National Laboratory

Objectives:

The objectives of this program are to identify materials for cell components (electrodes, separators, gaskets, seals) for advanced alkaline water electrolyzers operating at temperatures above 100° and below 150°C, at current densities of close to 500 mA/cm^{-2} with energy efficiencies approaching 100%.

Tasks:

The tasks during CY 1979 were:

Task 1. Evaluate high surface area nickel-based materials as anode and/or cathode electrocatalysts.

Task 2. Develop and test composite materials as separators.

Technical Progress:

Task 1. Anode and Cathode Electrocatalysts: During the reporting period, beryllium copper nickel alloy (0.44 Be, 30.25 Ni, 69.31 Cu), obtained from Kawecki Berylac Industries (KBI), high surface area nickel deposited on mild steel (from International Nickel Company-INCO) and nickel whisker electrodes with a high surface area deposited on mild steel from UVA were evaluated as electrocatalysts. The beryllium copper nickel alloys exhibited higher anodic and cathodic overpotentials than nickel. The high surface area nickel electrodes from INCO and from UVA were tested only as anodes. The deposited electrodes should be on nickel screens to be evaluated as cathodes. These high surface area nickel electrocatalysts showed a lowering of activation overpotential and merit further investigations at BNL in small cells and at TES in the 5-cell test rig. The whisker electrodes showed a peculiar behavior in that there was a lowering of hydrogen overpotential, which further decreased with time. This was attributed to the observation that black deposits of nickel were found on the cathode. This process could have occurred only by disintegration or dissolution of the nickel particles from the high surface area whisker anodes and subsequent deposition of the nickel ions or particles in the electrolyte on the cathode.

Task 2. Separators: There was a modest effort to develop sandwich barrier materials of asbestos coated on both sides with Teflon-bonded potassium titanate. This type of approach may serve a twofold purpose--mechanically stabilize asbestos--in advanced alkaline water electrolyzers operating at temperatures above 100°C. A configuration suggested by Mallory of asbestos sandwiched between Permion 300 showed a high electric resistance. Tin hydrosol-treated asbestos from UVA increased the cathode overpotential. Polybenzimidazole (PBI), although acceptable as far as electrolyte resistance is concerned, showed poor physical stability.

Technical Problems:

Methods to increase the hydrogen generation rates (and hence to lower capital costs) and the efficiency of alkaline water electrolyzers were first identified at Brookhaven National Laboratory with the experimental work initiated in 1974. The main recommendations which have been made were to increase the operating temperature to about 150°C, use high surface area electrodes (e.g., nickel boride cathodes, nickel cobalt oxide anodes) with good and stable electrocatalytic activities, and substitute potassium titanate for asbestos as separator. Though some progress has been made, continuing effort is still required on electrocatalysts and separator materials, and in verifying the performance at 125°C and higher temperatures. The long-term stability of materials for cell components in concentrated KOH containing H_2 or O_2 has to be determined.

Publications:

Davidson, C. R., and S. Srinivasan. Influence of nickel oxide transformation reaction on oxygen evolution kinetics as ascertained by temperature effects, J. Electrochem. Soc. 127, 1060-63 (May 1980).

Yeo, R. S., J. McBreen, G. Kissel, F. Kulesa, and S. Srinivasan. Perfluoro sulfonic acid (Nafion) membrane as separator for advanced alkaline water electrolyzer. J. Applied Electrochem., in press.

2.6 Selection and Evaluation of Materials for Advanced Alkaline Water Electrolyzers - University of Virginia

Objectives:

The overall objectives are to investigate the use of nickel whiskers as electrode materials and to determine the mechanism(s) of time-dependent energy losses.

Tasks:

Task 1. Whisker Electrode Studies

Task 2. Time Effects Studies

Technical Progress:

Task 1. Whisker Electrodes: Whisker electrodes characterized by their high porosity and relatively high surface area were shown to give an apparent improvement of 10% in efficiency over conventional nickel screens. These whisker electrodes show good mechanical stability and produce gas of smaller bubble size. When shipped to BNL for evaluation, the whisker electrodes also appeared to reduce cathode time effects when whisker anodes were employed. This phenomenon requires further investigation.

Task 2. Time Effects: This part of the project is considered the major scientific thrust of this contract. Time effects represent not only a steady energy loss but an operational difficulty when electrolyzers are shut down and restarted. The original work in this area confirmed the fact that time effects were primarily a cathode phenomenon. Furthermore, it was suggested that the formation of some kind of nickel hydride was responsible or involved as a causative mechanism. Attempts to confirm this hypothesis have involved studies of cathodically polarized electrodes by x-ray diffraction, electrochemical transients, and scanning electron microscopy. All data at this point are consistent with the formation of an α and/or a β nickel hydride. However, this hydride, if it exists, is too unstable in KOH to detect by normal analysis. Therefore, further work is needed to "prove" or "disprove" the hydride theory.

Technical Problems:

Task 1. The problems here were twofold: (1) there has been a delay in the production of these whiskers at Virginia because of the need to satisfy strict OSHA requirements; (2) specific catalytic ability of these whiskers has still not been determined on a true surface area basis. The next phase of our project will determine the current-potential characteristics of individual whiskers whose true surface area has been determined.

Task 2. The major problem here has been associated with the fact that nickel hydride is too unstable to detect in KOH, although it lasts for a measurable period in acid solutions.

Publications:

Moran, P.J., G.L. Cahen, Jr., and G.E. Stoner. Energy losses occurring in and new electrode concepts for alkaline electrolyzers. Presented at the Spring Meeting of the Electrochemical Society, Boston, Massachusetts, May 1979.

3.0 STORAGE SYSTEMS AND MATERIALS

The major accomplishments in the Storage Systems and Materials area are as follows:

Storage Systems

- A bench-scale hydride-hydrogen chemical compressor successfully passed initial tests, thus potentially providing a way to substantially lower hydrogen compression costs. (Ergenics/DRI)
- A fuel cell/battery-powered fork lift truck was modified by Billings to operate on hydride hydrogen supplied to the fuel cell, for which rapid refueling and extended operating time are major system advantages. (Joint Billings/BNL/MERADCOM project)
- IGT underground hydrogen storage study was completed indicating no technical constraints but there will be a storage pressure limitation of 1200 psi due to hydrogen embrittlement.
- BNL HYTACTS - The BNL HYTACTS hydrogen test facility was made operational and testing was completed on a 50-lb metal hydride storage vessel (VPTU-2).
- BNL contributed to LLL's study on energy storage systems for automotive use, with analysis showing favorable projections of hydrogen-air fuel cell/battery system in comparison with alternative systems.
- BNL/ORNL modeling studies - heat and mass transfer modeling studies on hydride beds showed good correlation for predicting pressure temperature, capacity behavior. Experimental work showed that an aluminum foam matrix will enhance heat transfer by a factor of 2.6.

Storage Materials

- R. J. Teitel Associates - Glass microspheres - high pressure hydrogen storage of 6.5 wt % was achieved with about 70% recovery. Scale-up tests are planned to study attrition, filling/dispensing, and associated cost factors.
- Surface poisoning studies at INCO - comprehensive study has been completed showing AB and AB_5 hydrides could be reactivated, after poisoning, by simple procedures. Study showed $LaNiH_x$ most resistant to O_2, H_2O and modified $TiFeH_x$ most resistant to CO.
- Further studies by Air Products on MgAl alloys for automotive use showed that reaction kinetics are limited by disproportionation even with Ni

catalyst. Tradeoff to lower temperature operation (300° to 250°C) results in reduction of H_2 content (7 to 3 wt %) which has limited value.

- Use of DRI's predictive technique to develop hydrides with specific characteristics was generally unsuccessful in identifying hydrides better than FeTi or Mn-modified FeTi. Project has been completed.
- BNL studies showed TiCr-based hydrides have most potential for H_2/D_2 separation and hydride chemical compressor applications.

A. STORAGE SYSTEMS

3.1 Design, Construction, and Evaluation of a Portable Hydrogen Chemical Compressor - Ergenics Division of MPD Technology Corp.

Objective:

The goal of the program is to develop a commercial-size, hydride-hydrogen chemical compressor. The objective of Phase I is to complete the design and construction, and then evaluate the performance of a bench-scale (portable) unit. Phase II deals with a pilot-scale unit for a specific application.

Tasks:

Phase I of the program is comprised of four tasks.

Task 1. Program Plan.

Task 2. Design Effort: Previous work on design of the unit will be completed, with special consideration given to the heating technique. If tests show that the proposed auto-resistive technique is not suitable or safe, an alternative method will be selected. The materials of construction are to be suitable for the expected operating conditions, at a minimum safety factor of four (based on ASME Code on Unfired Boilers and Pressure Vehicles). The hydride used in Phase I should also be suitable for the application identified in Phase II.

Task 3. System Construction and Characterization Tests: The parts remaining to be fabricated are to be completed and assembled in accordance with the approved design. Tests include measurement of: peak and average power requirements; peak and average temperatures; fan-cooling rates; and temperature history during heating and cooling.

Task 4. Performance Testing and Evaluation: The assembled two-module unit is to be tested to establish the hydrogen pressure/flow rate relation for comparison with the design values. Performance stability is to be assessed during operational aging for a minimum of 100 cycles. During testing for a minimum of 500 cycles, appropriate pressure, temperature, and flowrate data are to be taken. Subsequently, one of the hydride tubes is to be sacrificed for physical examination. Performance is to be evaluated, and needed system modifications identified--particularly those related to hydride expansion, particle migration, and heat transfer.

Technical Progress:

Task 1. The Program Plan was received and approved by BNL.

Task 2. Design of the unit was completed, and is based on the exponential dependence of hydride-hydrogen pressure on hydride temperatures, using two batches of the same hydride which are cycled out of phase in order to obtain a reasonably steady flow of hydrogen. Auto-resistive heating of the tubular containers is used as a convenient way to simulate waste heat input, and air cooling is provided by fans. As shown in Fig. 3.1, each hydride module or tube bundle (two), is comprised of an array of tubes connected to inlet and outlet headers which serve as gas manifolds and current carriers (bus bars). The hydride is packaged in 0.5-in.-diam x 3-in.-long capsules which fit tightly in the tubes. The capsules are insulated from the tubular container by their anodized coating. Plain and coated capsules are shown in Fig. 3.2; the end of the plain capsule will be rolled over to retain the filter. Capsule packaging, as experience has shown thus far, avoids container deformation caused by hydride expansion, and minimizes pressure drop due to migration and packing of the hydride. The aluminum capsules have end filters made of porous metal discs (stainless steel) and are fluted to allow axial hydrogen flow. The hydriding alloy selected for use has a composition close to that desired, $LaNi_{4.5}Al_{0.5}$. Its hysteresis, plateau flatness and equilibrium hydrogen content are satisfactory, the latter being about 9% less than the maximum attainable.

Task 3. Two modules were assembled by brazing the stainless-steel tubes to the copper headers. It was necessary to copper plate the tube ends in order to obtain high-integrity joints. Testing of the auto-resistive heating technique showed that anodizing of the capsules provided sufficient insulation to avoid hot spots. Gold plating of the bus-bar ends was necessary to avoid oxidation at the electrical connections. The control panel and power supply were also completed.

Task 4. During initial testing of the serviceable module at pressures up to 800 psig, the expected capacity of 50 SCFH was achieved. This module will be tested until a second one is available to begin out-of-phase cycling.

Technical Problems:

The tube-to-header joint leak in one module was apparently due to blistering and poor wetting by the brazing alloy which resulted from temporary loss of atmosphere control during furnace brazing and an unusually high oxygen level in the copper.

Publications:

Snape, E. and F. E. Lynch. Design, construction and testing of a thermally activated hydrogen chemical compressor. Proc. of the DOE Chemical Energy Storage and Hydrogen Energy Systems Contracts Review, Reston, Virginia, November 13-14, 1979.

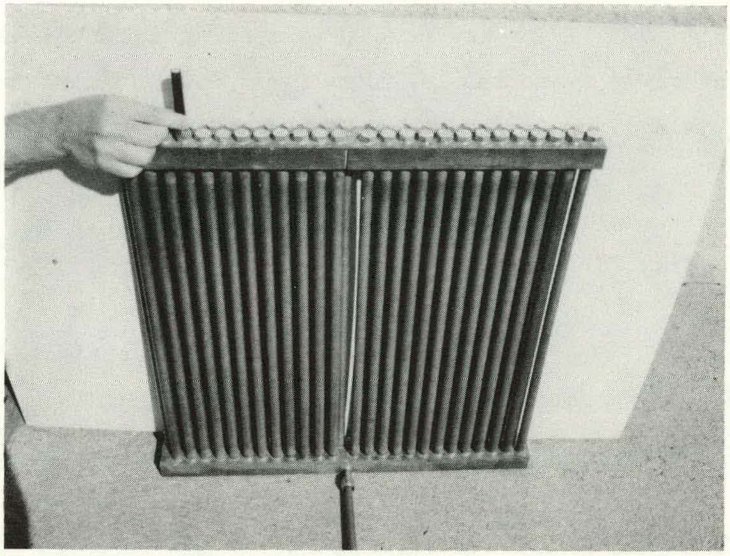


Figure 3.1. Module for Hydride-Hydrogen Chemical Compressor and Typical Hydride Capsule in the Tubes

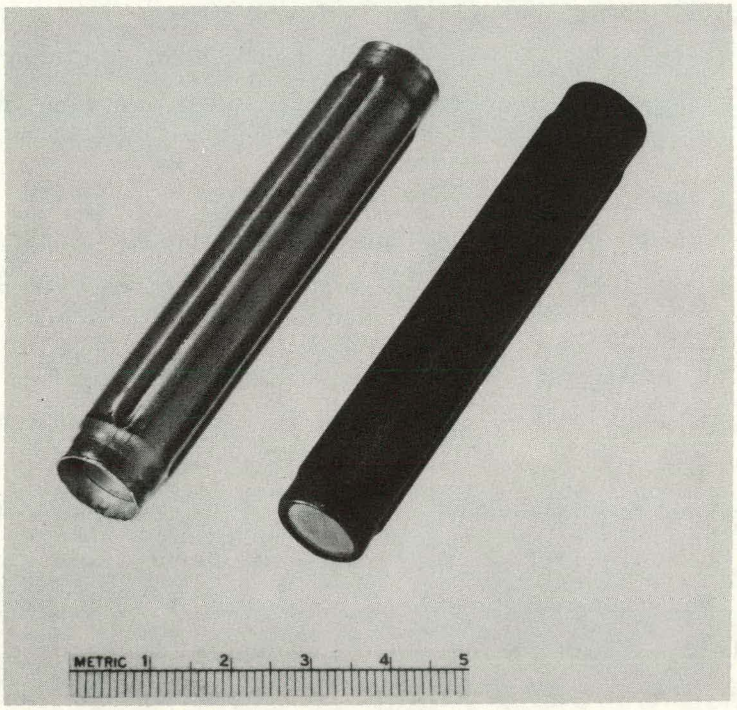


Figure 3.2. Plain and Anodized Capsules

3.2 Underground Storage of Hydrogen - Institute of Gas Technology

Objective:

The objective of the program is to complete a technical and economic assessment of storing hydrogen in four types of underground cavities: a depleted field, an aquifer, a washed salt cavern, and an excavated cavern.

Tasks:

The program is comprised of five tasks.

Task 1. Program Plan

Task 2. Feasibility Based on Current Practice: The objective of this task is to establish the technical feasibility of storing hydrogen underground by developing practical specifications and operating conditions that can be used for the engineering of the four types of storage reservoirs. This characterization will establish technical criteria for selection and development of suitable sites.

Task 3. Current Cost of Underground Gas Storage: The objective is to determine the economics for those types of reservoirs in which hydrogen storage is technically suitable. The economics of at least one porous and at least one nonporous formation will be analyzed.

Task 4. Estimated Costs for Underground Hydrogen Storage: The objective is to develop and analyze the economics of converting an existing gas storage reservoir to hydrogen.

Task 5. Research and Development Requirements: The purpose is to organize and document several study conclusions that are major program objectives, including the identification of any necessary required R&D.

Technical Progress:

Task 1. The submitted Program Plan was approved by BNL.

Task 2. Although all types of reservoirs cannot be used at all times for any type of service, there are no technical constraints that prohibit the storage of hydrogen in underground reservoirs. Some pressure limitations and constraints on how the fields are cycled make some fields more attractive than others. The strongest technical constraint is hydrogen embrittlement, which limits the reservoir pressures to 1200 psi with commonly used materials of construction. At higher pressures, the major capital cost items (wells, gas compression systems, and pipe fields) will probably require replacement in converting to hydrogen service because it may not be cost effective to locate and repair hydrogen-sensitive defects (flaws, hard spots, and plastic deformation).

Task 3. Costs of Service ($\$/10^6$ Btu) for the storage of both natural gas and hydrogen were calculated for four specific reservoirs that are examples of four different types of storage (depleted field, aquifer, washed salt cavern, and an excavated cavern). A graphical summary of the calculated base-case costs of service for both natural gas and hydrogen storage is shown in Fig. 3.3. For natural gas storage, somewhat different base-case costs were assumed in each case in order to test the economic model against actual practice; thus the natural gas base cases are not directly comparable. Plant and operating costs for hydrogen are 2 to 4 times that for natural gas because of the reduced Btu throughput for hydrogen. Likewise, the base-gas costs are higher because of the difference in assumed costs ($\$6/10^6$ Btu for H_2 vs $\$.30$ to $\$1.60/10^6$ Btu for natural gas). As shown for the depleted-field case, hydrogen's cost of service is extremely sensitive to pressure (I is high, III is low). A lower field pressure requires less base gas and permits use of a greater fraction of the stored gas. The plant cost increases, though, because more compression equipment and wells are needed to compensate for the lower pressure. Even so, the overall cost decreases because of the higher fraction of usable gas and the reduced cost for base gas.

Task 4. A depleted field was selected as the type of existing gas storage reservoir to be converted to hydrogen use. As in the final report, the case is discussed under Task 3.

Task 5. The basic conclusions are presented in Tasks 2 to 4. Several areas worthy of further investigation were identified in this study. The key recommendations are as follows:

1. Research on hydrogen environment embrittlement is required in the range of 1000-5000 psi in order to identify cost-effective materials of construction.
2. The present study dealt only with the delivery of pure hydrogen; however, practical considerations will require dealing with the economics of mixtures of natural gas and hydrogen.

3. Use of a shallow salt cavern in a water-compensated mode could be the most cost effective; an investigation of the experience in the United Kingdom at Teeside should be initiated.

Technical Problems:

Areas requiring further investigations are listed under Task 5.

Publications:

Foh, Stephen M., Martin Novil, Philip L. Randolph and Evelyn M. Rockar. Underground storage of hydrogen. Proc. of the DOE Chemical Energy Storage and Hydrogen Energy Systems Contracts Review, Reston, Virginia, November 13-14, 1979.

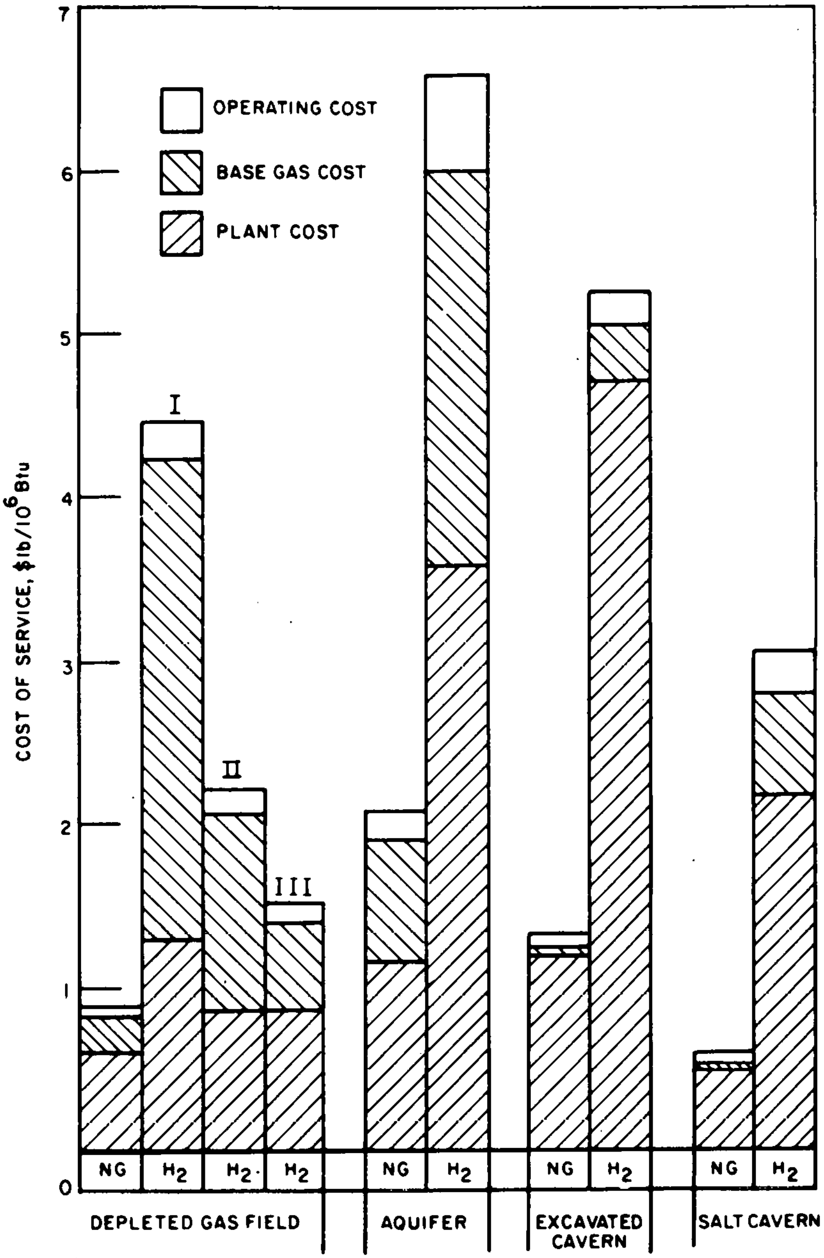


Figure 3.3. Cost of Service - Natural Gas vs Hydrogen for Four Types of Fields

3.3 Modification and Operation of the Hydrogen Homestead Hydride Vessel Energy Storage System - Billings Energy Corporation (BEC)

Objective:

This project is part of a larger BEC effort to determine the feasibility of using hydride hydrogen as a domestic fuel. The present objective was to characterize storage system performance, relate the results to hydrogen demand at one or more Homesteads, and to assess the requirements for safe functioning of the Homestead complex.

Tasks:

The program is divided into three tasks.

Task 1. Performance Tests of Storage Vessel: With the storage vessel fully charged, determine the length of time that discharge rates of 12, 6, 3, and 2 lb of H_2/24 hours can be sustained, starting with the hydride bed at pressure and temperature equilibrium in each case.

Task 2. Hydrogen Demand Evaluation: Determine the capability of the storage vessel to satisfy the hydrogen demands at one or more Homesteads.

Task 3. Hydrogen Safety at the Homestead Complex: Determine the measures necessary to assure safe use of hydrogen at the complex; detail the cost of needed items; evaluate any failure experience of system components; determine ways of evaluating performance in order to assure fail-safe conditions; and issue the Safety Report previously outlined.

Technical Progress:

Tasks 1 through 3. The relocation of BEC's energy-related activities to Independence, Missouri, necessitated a six-month, no-cost extension to the program. The storage vessel and associated equipment were moved and reassembly of the equipment and modifications to the instrumentation were just recently started.

Technical Problems:

No problems evident even after relocation.

Publications:

Billings, R. E., L. D. Hadden, G. L. Kimball, and R. L. Woolley. Program review and continuation plan. Proc. of the DOE Chemical Energy Storage and Hydrogen Energy Systems Contracts Review, Reston, Virginia, November 13-14, 1979.

3.4 Conversion of Hybrid MERADCOM Fork Lift Truck from Gaseous Hydrogen Fuel Storage to a Hydride-Hydrogen Storage - Billings Energy Corporation

Objective:

The objective of this work is to show that a hydride-hydrogen storage system coupled with a fuel cell/battery-powered propulsion system will provide performance superior to that of a battery-powered system, including extended operating time and short recharge time.

Tasks:

The program is comprised of seven tasks.

Task 1. Shipment of Fork Lift Truck from MERADCOM at Fort Belvoir, Virginia, to BEC at Provo, Utah.

Task 2. Design and Fabricate Hydride Hydrogen Storage System: the storage vessels are to be designed in accordance with the ASME code, contain a suitable heat exchanger, and are to contain $TiFe_{0.9}Mn_{0.1}H_x$. The delivery system is to provide reduced-pressure hydrogen to the fuel cells by utilizing waste heat from the cells, or by means of an electrical heating technique.

Task 3. Component Testing: Any necessary component testing to insure reliability of the fuel delivery system will be performed.

Task 4. Install the Storage System: The rear portion of the fork lift truck will be modified as required, and the storage system will be installed.

Task 5. Shake down Test: A preliminary test will be made of the modified fork lift truck to assure proper operation of the hydride-hydrogen storage system, and to verify compatibility of related components.

Task 6. Final Report: Details of the work performed are to be described in the final report.

Task 7. Shipment of Fork Lift Truck: Upon completion of the described work, and any required modifications, the fork lift truck is to be delivered to MERDADCOM at Fort Belvoir from Provo, Utah.

Technical Progress:

Task 1. The fork lift truck was delivered to BEC at Provo, Utah.

Task 2. Design of the hydride-hydrogen storage system was completed. The storage vessels are to be made from carbon-steel vessels originally fabricated for compressed-gas storage. Modification by shortening and welding of the parts is planned. Production of the hydride was started.

Tasks 3 through 7. After some delays these tasks remain to be completed in early 1980.

Technical Problems:

The use of welding-modified compressed-gas cylinders as the storage vessels requires further study. Advice on the proposed welding modification will be obtained from Sandia Livermore Laboratories.

Publications:

There were no publications on this program.

3.5 Hydrogen-Technology Advanced Component Test System (HYTACTS) - BNL

Objective:

- To construct a test system that will provide means for controlling hydrogen flow-rates, temperatures and pressures applicable to studies and tests of hydrogen transport and storage systems.
- To utilize the HYTACTS and its associated data acquisition system for testing of the Bulk Hydrogen Storage Vessel (VPTU-2).

Tasks:

This program is divided into five tasks.

Task 1. Initiate Testing of the VPTU-2: After the final hook-up and hydride filling operation, the Bulk Storage Vessel will be leak and pressure tested using an inert gas. The vessel will be made operational.

Task 2. System Hardware and Instrumentation Completion: The HYTACTS will be brought to a state of readiness with the completion of the construction and installation of all operating instrument consoles, associated alarm circuits, and data recording instrumentation.

Task 3. System Check-Out: The HYTACTS with the VPTU-2 will be checked out using an inert gas to confirm that all components are functioning properly and to gain operating experience before introducing hydrogen to the system.

Task 4. VPTU-2 Hook-up and Test of the Bed-Loosening Tube: The high hydrogen flow-rate system for the periodic fluidization of the hydride bed will be completed and tested.

Task 5. VPTU-2 Charge/Discharge Performance Testing: The VPTU-2, Bulk Storage Vessel, will be tested to determine its hydrogen absorption/desorption capability as a function of hydrogen flow-rate.

Technical Progress:

Task 1. The Variable Parameter Test Unit-2 (VPTU-2) bulk storage vessel was filled with 3825 lb of $TiFe_{0.85}Mn_{0.15}$ alloy, leak and pressure tested. It was declared ready for operation.

Task 2. The fabrication and installation of the instrument panel, data collection units, alarm systems, and remote valve actuators were completed and the units tested and declared ready for operation.

Task 3. The HYTACTS was checked out using an inert gas (nitrogen) to 1) test the functioning and reliability of all remote acting valves; 2) calibrate pressure, temperature, and flow-rate measuring devices; 3) purge all water vapor and oxygen from the system before admitting hydrogen; 4) gain system operating experience. The HYTACTS was declared ready for operation. See Fig. 3.4.

Task 4. The bed-loosening system was hooked up, but was not tested. Recommendations made by a Safety Review panel discouraged the visual monitoring of the bed surface. Since with the present instrumentation it would not be possible to monitor bed motion, it was decided to defer this test until some later date.

Task 5. The bed was activated to only ∿80% of its theoretical capacity but, because of time constraints, performance testing was initiated. The results indicate that the heat exchanger design is adequate during the charge cycle for hydrogen flow-rates at least as high as 30 SCFM (143 kW) for a period of 3.6 hours during which 6450 SCF (34.3 lb) of hydrogen was charged (514 kWh). See Fig. 3.5.

The vessel was not able to maintain the same hydrogen flow-rate during the discharge cycle and fell below the 30 SCFM set point after 1.2 hours and the flow-rate continued to decline to ∿15 SCFM which is the 10-hour (design) flow-rate. During the 4.4-hour discharge run, 5900 SCF (31.3 lb) of hydrogen was liberated (473 kWh). This poorer performance was attributed to two factors: 1) the hydride was not completely activated and, therefore, the vessel pressure was lower than anticipated, greatly reducing the driving force; and 2) the heat exchanger does not appear to be suitable for flow-rates that high, as demonstrated by the large temperature difference between the bed and the thermal transfer fluid(20°-30°F). If the water temperature were raised from 122°F to 150°F, the system would probably perform adequately.

The design hydrogen flow-rate run (15 SCFM, 72 kW) was completed with the following results. The hydrogen flow-rate of 15 SCFM was maintained for the full charge cycle time (7.2 hours). During that period 6500 SCF (34.5 lb) of hydrogen was charged (521 kWh). This performance is well within the design points of 50 kW, 500 kWh; and in addition, it is expected that the vessel will exhibit improved performance if the time is taken to fully activate the alloy.

Because of time constraints, no data were collected on the 10-hour discharge (design) flow-rate run. Intuitively, it is felt that the design parameters (50 kW, 500 kWh) will be easily attained at this flow-rate, even at a circulating fluid temperature of 122°F (e.g., from fuel cell waste heat).

Technical Problems:

The use of ultra-high purity hydrogen in large quantities for continued HYTACTS operations necessitates the completion of the compression-purification-drying system, since the gas purity required can presently be purchased only in 1A (1 lb) cylinders.

The use of the HYTACTS to test components now in construction at various other contractor locations will require minor modifications. The system, in its present configuration, is useful only when the hydrogen flow-rates are in the range of 10-6000 SCFM. Under present plans most of the components that might be tested in the HYTACTS require hydrogen flow-rate control well below 10 SCFM. Purchase of an additional flow control valve in the range of 0.1-10 SCFM and the associated installation will enable testing of these components.

Publications:

Rosso, M. J. Jr. and G. Strickland. Hydride beds: engineering tests. Proc. of the DOE Chemical Energy Storage and Hydrogen Energy Systems Contracts Review, Reston, Virginia, November 13-14, 1979.

Strickland, G. and M. J. Rosso, Jr. Bulk hydrogen storage using metal hydrides. Proc. of the 2nd Miami International Conference on Alternative Energy Sources, Miami Beach, Florida, December 10-13, 1979.

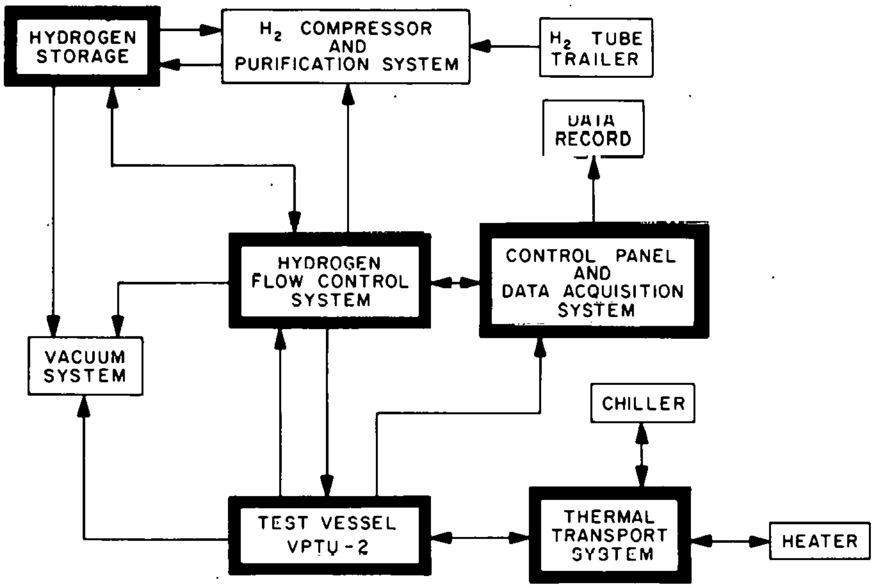


Figure 3.4. Block Diagram of HYTACTS

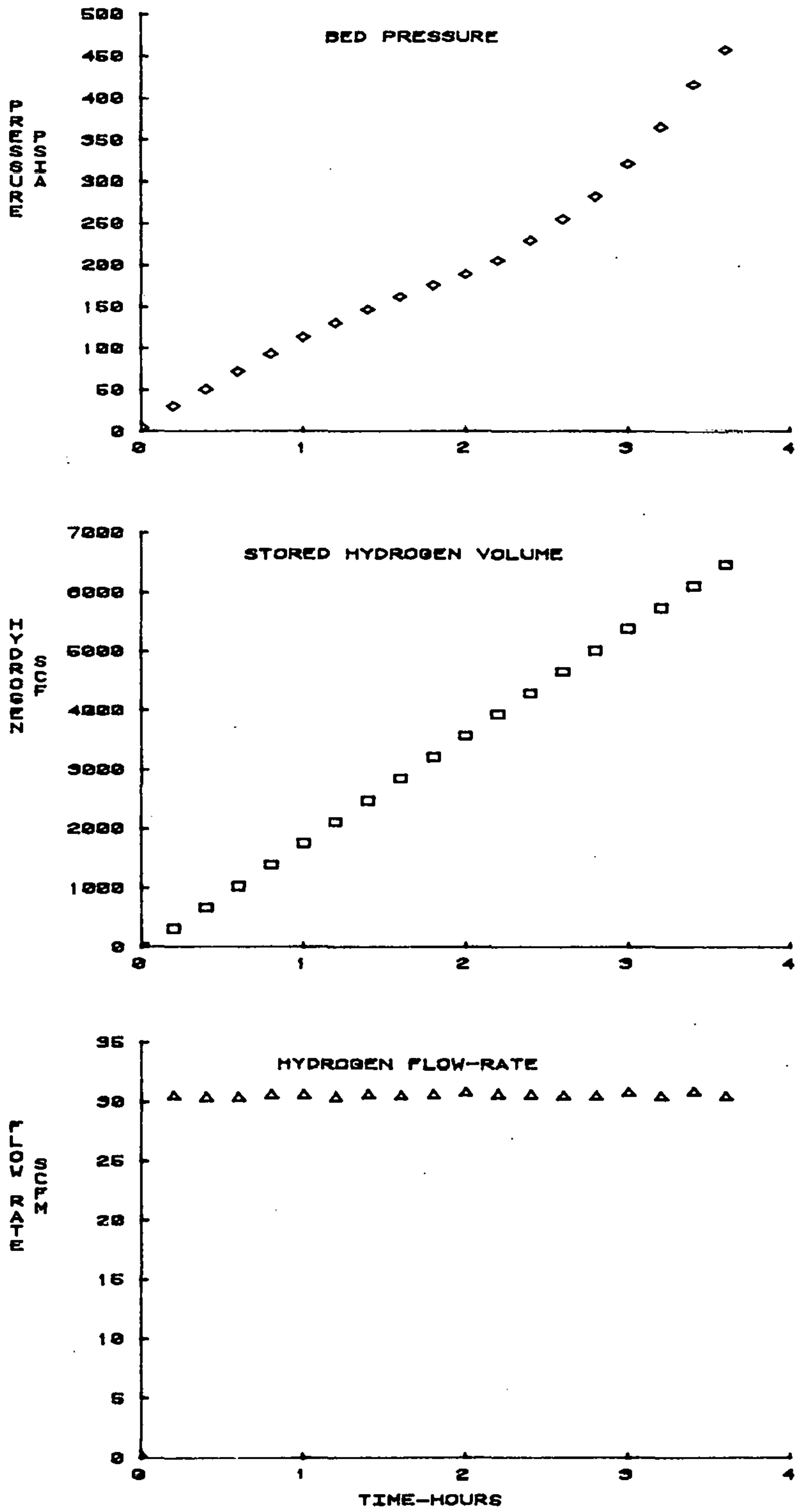


Figure 3.5. VPTU-2 Plot of 30 SCFM Hydrogen Flow Rate Charge Run

3.6 Heat/Mass Flow Enhancement Studies - BNL

Objective:

The objective is to provide information on heat and mass flow enhancement for attaining rapid charge/discharge cycles for storage and/or supply reservoirs consistent with applications ranging from rapid refueling of mobile onboard storage subsystems to chemical compressor systems.

Tasks:

Task 1. Design Heat Transfer Apparatus: The heat transfer test vessel will be designed using a standard-cylindrical geometry to simplify the data analysis and in such a way that the bed is the primary resistance to heat-mass flow.

Task 2. Test Program: Choose the enhancement materials to be tested and evaluate relative improvement to the bed's effective thermal conductivity for each material.

Task 3. Data Analysis and Final Report: Data will be treated to yield the effective thermal conductivity for each system.

Technical Progress:

Task 1. The effects of adding small amounts of high conductivity material to the hydride bed in an attempt to enhance the heat transfer wereinvestigated. The experimental apparatus included a thin-walled (2.45-in. i.d. x 0.095-in. wall) cylindrical copper vessel 11-1/4 inches long, rated at 200 psia, and flanged at both ends. Two temperature-controlled baths (30° and 80°C) were used to provide the constant temperature environment at the outside wall of the test vessel. Heat flow was radial with end effects minimized, and temperatures were measured by a thermocouple centered both axially and longitudinally in the bed.

Task 2. For each set of experiments the test vessel was assembled, filled with hydride (2365 grams), and machine packed by raising and dropping the vessel with its holder (total weight 25 lb) in a prescribed manner to eliminate variances in the bed's void fraction. The bed's void fraction was computed using bed height measurements.

The test vessel was cycled between a low temperature (30°C) bath and a high temperature (80°C) bath and the data measurement started. The rate at which the data were recorded was chosen so as to provide a minimum of fifty data points for each run. Generally, each run was repeated three times and the results were extremely reproducible.

Cooling runs were accomplished by allowing the vessel to come to equilibrium at 80°C (within 0.2°C) and transferring it to the low temperature bath. The data for the cooling runs, except for minor variations at low pressure, produced thermal conductivities that agreed very well with the heating runs. The variation in all cases was less than 5%.

Three experimental configurations were used: (1) no enhancement, 2365-g packed bed of -30 +80 mesh deactivated FeTi hydride; (2) the same bed with 5 wt % of the hydride removed and replaced with an equal weight of copper in the form of a loosely knitted mesh; (3) the same bed with 5.6% of aluminum in the form of a 10-pore-per-inch reticulated foam. Each of these configurations was tested at 150 μm, 1.0-psia, and 200-psia hydrogen pressure.

Task 3.

When the temperature data are plotted as in Fig. 3.6 the improvement in thermal conductivity by a small addition of high conductivity material in the right form becomes obvious. The results presented in Fig. 3.7 show the improvements possible using the aluminum foam enhancement over the copper mesh or no enhancement at all.

The introduction of hydrogen, even at pressures as low as 1.0 psia improves the thermal conductivity of the unenhanced configuration dramatically (∿20 times). Increasing the vessel's pressure to 200 psi results in a further improvement of 2.5. At 200-psia hydrogen pressure, the addition of a loosely knitted copper mesh material had a slightly negative effect, although aluminum, in the form of a 10-pore-per-inch reticulated foam with a density of 5.6%, enhanced the heat transfer by a factor of 2.6.

The poor performance of the copper addition is attributed to two factors; a slight increase in the system void fraction and the long heat transfer path through the copper wires that make up the mesh material.

Technical Problems:

In future studies, a procedure should be developed to insure that the contact resistance between the inside vessel wall and the enhancement material is standardized.

Vessel modifications should be made to extend testing to include the more useful case where the heat is generated in the bed by the absorption of hydrogen into the hydride.

Publications:

Rosso, M. J. Jr. and G. Strickland. Heat transfer enhancement in metal hydride systems. Proc. of the 2nd Miami International Conference on Alternative Energy Sources, Miami Beach, Florida, December 6-10, 1979. (BNL 27347).

Rosso, M. J. Jr. and G. Strickland. Hydride beds: engineering tests. Proc. of the DOE Chemical Energy Storage and Hydrogen Energy Systems Contracts Review, Reston, Virginia, November 13-14, 1979.

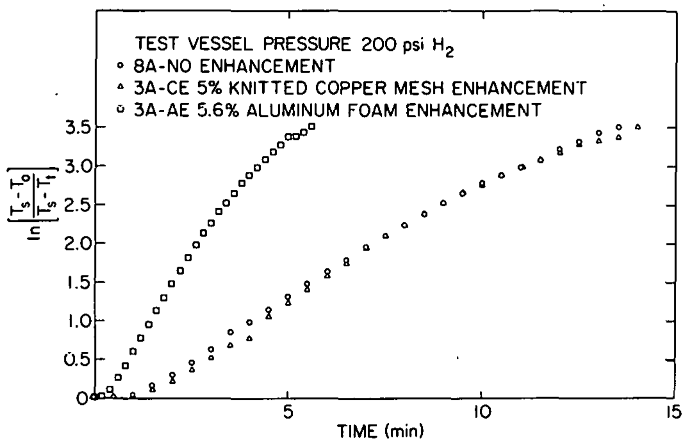


Figure 3.6. Effect of Additions of High Conductivity Materials to Beds of Hydride Particles

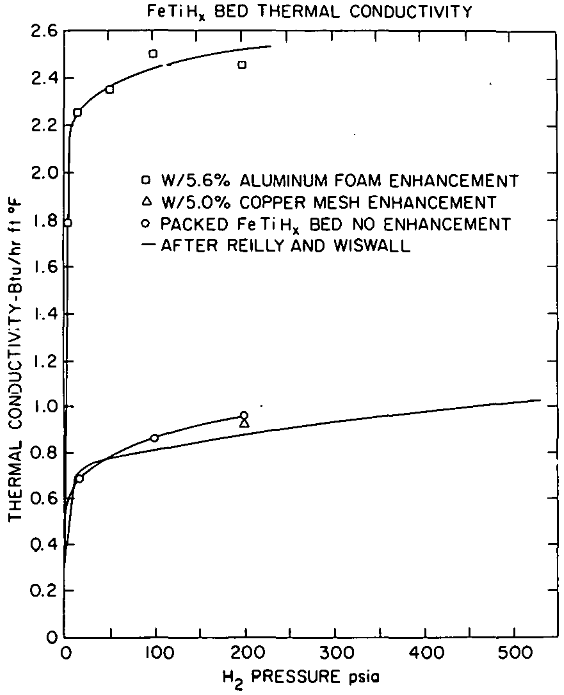


Figure 3.7. Increased Thermal Conductivity Using Reticulated Aluminum Foam Enhancement

3.7 Hydride-Bed Heat-Transfer Modeling Study - Oak Ridge National Laboratory

Objective:

To develop an analytical model that accurately describes the heat-transfer characteristics of beds of hydride particles. The model will correlate the data taken at BNL on a 6-in.-diam bed and a 2-in.-diam bed.

Tasks:

Task 1. Use of the Model to Investigate the Performance of Metal Hydride/Hydrogen Storage Beds Based on BNL Data: The basic model developed in the FY 78 effort will be tested by comparing the model's performance predictions to the actual experimental data measured at BNL.

Task 2. Investigation of Discharging Rates: The model's sensitivity to small changes in the hydrogen flow-rate during charge/discharge cycles will be assessed as a means of predicting the performance of faster systems for such applications as the chemical compressor and chemical heat pump.

Task 3. Measure Sensitivity of Model to Changes in Parameters, Heat Transfer Characteristics, Bed Size Diffusivity, etc.: The effect of small changes, density, bed void fraction, and particularly changes in the hydride's equilibrium isotherm in dynamic conditions will be evaluated.

Task 4. Alterations of Code to Approximate Large Multitube Cooled Beds: The model will be modified to include multitube heat exchange systems and the predictions compared to selected data.

Technical Progress:

Task 1. The model produces bed pressures and temperatures (as shown in Figs. 3.8 and 3.9) which are in good qualitative agreement with the BNL supplied experimental data; however, maximum (or minimum) pressure and centerline temperature are shifted somewhat in time. This discrepancy is attributed to effects of chemical kinetics and hysteresis (which occur when switching from adsorption to desorption).

Task 2. Higher loading rates were investigated; however, the results were inconsistent and more work is required to refine the existing model to reliably predict "fast system" performance.

Task 3. The thermal conductivity and the shape of the equilibrium sorption isotherm appear to be the most sensitive parameters; even a 20% change in the heat capacity, the heat transfer coefficient, or the heat of reaction produces less than 1% change in predicted loading times and bed pressure.

Task 4. The model was altered to investigate the behavior of storage vessels with internal cooling tubes rather than external cooling. Bed pressure (rather than the maximum temperature or loading time) proved to be the most difficult parameter to match between external and internal cooling configurations. The results show that a bed with cooling tubes designed on the basis of these criteria to meet or exceed performance of the externally cooled 6.4-in.-i.d. bed would require six 0.25-in.-o.d. tubes, four 0.5-in.-o.d. tubes, or three 1-in.-o.d. tubes. Note that as the diameter of the tube decreases the number of tubes increases but the total heat transfer surface area actually decreases.

Technical Problems:

Modification of the model to include very fast systems would require additional effort.

The problem of time shift of events between the experimental data and the model prediction must be solved before the model can be considered for use as a diagnostic tool or storage vessel design aid.

Publications:

Fisher, P. W. and J. S. Watson. Modeling solid hydrogen storage beds. *Proc. of the DOE Chemical Energy Storage and Hydrogen Energy Systems Contracts Review Meeting*, Reston, Virginia, November 13-14, 1979.

Fisher, P. W. and J. S. Watson. Modeling and evaluation of transport in solid hydrogen storage beds. Presented at the National Meeting of AIChE, San Francisco, California, November 26-29, 1979.

Watson, J. S. and S. D. Clinton, Compilors. ORNL Semiannual Progress Report for Period 10/1/78 - 3/31/79, Advanced Technology Section, Vol. II, Energy Science Progress, ORNL-TM-6891/BT.

Watson, J. S. and J. S. Clinton, Compilors. ORNL Semiannual Progress Report for Period 4/1/79 - 9/30/79, Advanced Technology Section, in preparation.

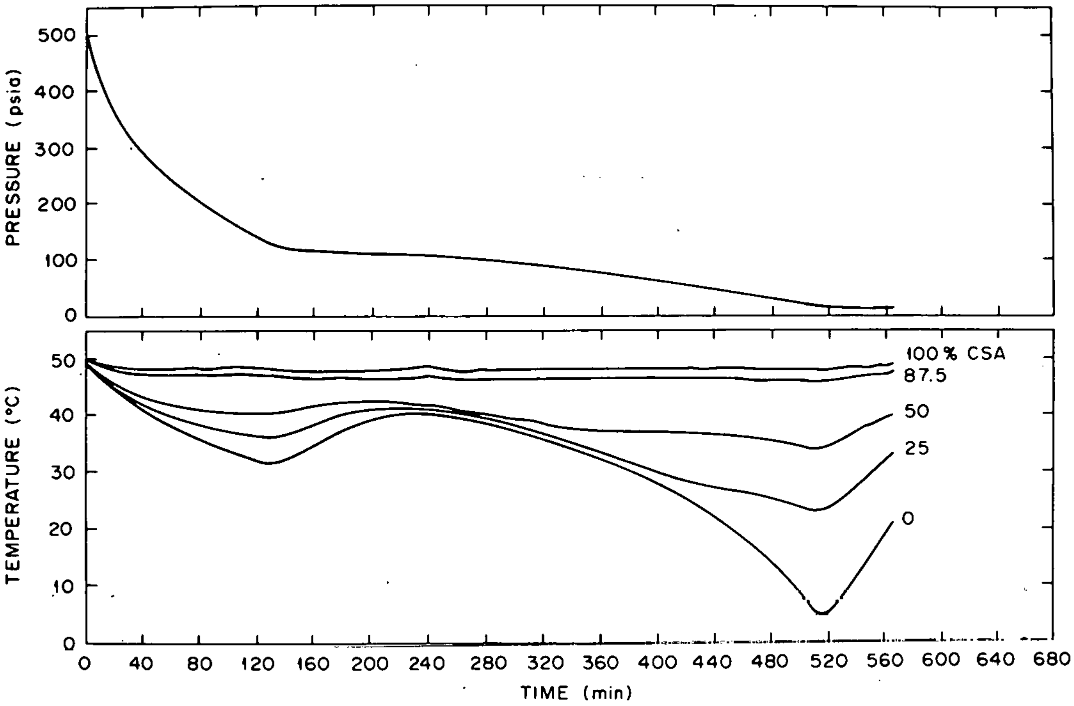


Figure 3.8. BNL Experimental Data for ESEERCO Discharge Run E08-D1 With Hydrogen Flow Rate at 10 liters/min. From 6.4 Inch Diameter Externally Heated FeTi Bed (Water Temperature 50°C)

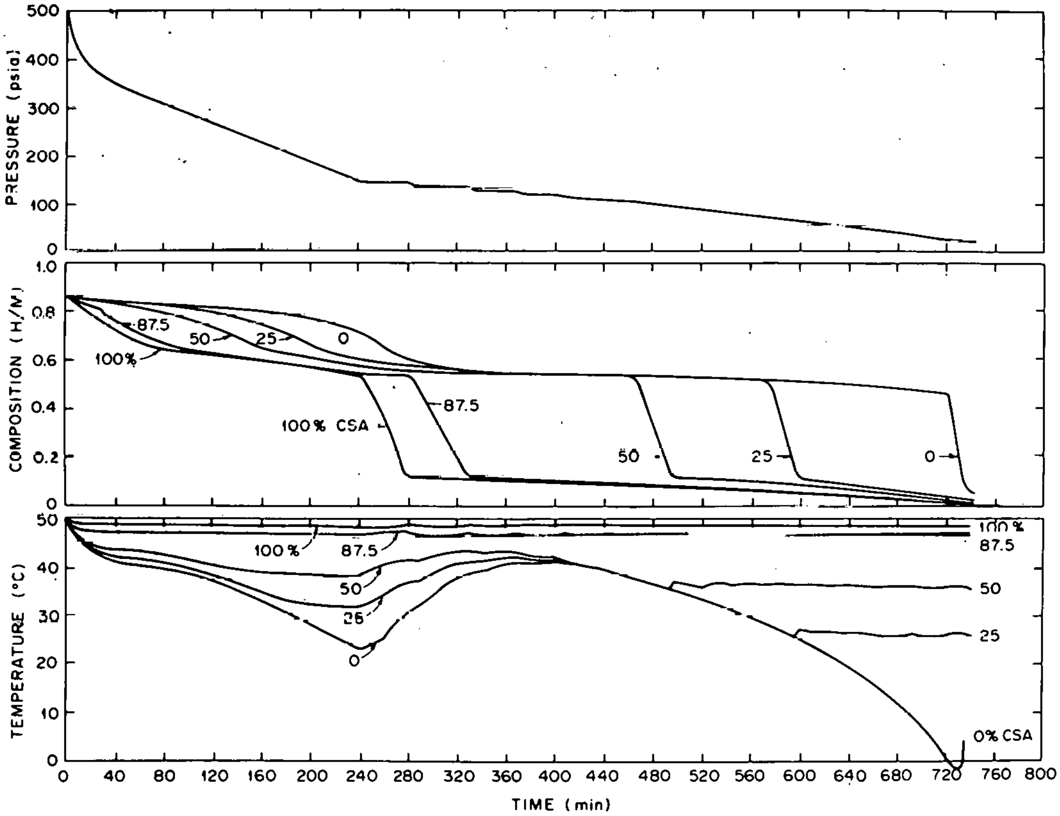


Figure 3.9. Vessel Performance Prediction Based on ESEERCO Discharge Run E08-D1 Conditions

3.8 Energy Storage Systems for Automobile Propulsion

Lawrence Livermore Laboratory - Brookhaven National Laboratory

Objective:

The program goal is to identify storage systems that will reduce our dependence on oil and will be suitable candidates for automotive propulsion use in the remaining years of the century. The 1979 objective is to continue analyzing comparative cost/performance tradeoffs among the candidate systems, electrochemical (including fuel cells), mechanical, chemical, and hybrids, which are used in computer-modeled vehicles of various sizes and performance capabilities.

The program is directed and funded by Lawrence Livermore Laboratory (DOE/STOR funds) and is assisted by other national laboratories, industrial organizations, universities, and consultants.

Tasks:

The BNL program is comprised of four tasks.

Task 1. Contribution of the Chemical Energy Storage Panel: BNL will continue to be responsible for the work of this panel and its required interaction with the other panels.

Task 2. Update Projections for the Hydride Systems: Revisions to the projected energy and power densities are to be made for Ti-based hydride and the Ti-Mg-based (dual) hydride systems.

Task 3. Develop Projections for the Microcavity Storage System: The first quantitative projections for energy and power densities are to be made for the high-pressure storage of hydrogen in glass microspheres. Revised projections are to be made for the complementary Ti-based storage component used for start-up and for hydrogen absorption after shutdown.

Task 4. Introduction of the Alkaline Fuel Cell: The use of this energy-efficient conversion device, in combination with a battery, is to be described and characterized in terms of energy and power densities, and scaling factors.

Technical Progress:

Task 1. A staff member from BNL served as Chairman of the Chemical Energy Storage Panel. Duties included the integration of panel-member input for the contribution to LLL's Annual Report, participation in meetings and activities of the Panel Chairmen, and participation in the annual workshop conducted by LLL.

Task 2. Increases of 15 to 40% were made in projections for the available hydrogen content of the BNL Fast-Charge Reservoir design, based mainly on performance data that Daimler-Benz AG (West Germany) obtained with their reservoir of similar design (hydride in tubes). This improvement is reflected in higher energy densities for the single- and dual-hydride systems and in reduced system and vehicle weights and costs.

Task 3. Projections made for 6000-psi hydrogen stored in hollow glass microspheres, at a level of 10 wt %, show that at best the system could weigh about 40% less than the dual-hydride system, cost about half as much, and occupy close to twice the volume. The storage concept is based on the high and selective permeability of hydrogen through glass at elevated temperatures, and a very low leakage rate at ambient temperatures. Filling is performed in a series of discrete increases in temperature and pressure; only sensible heat is required. Filled microspheres can be handled in a low-pressure container. (See Section 3.9 of this report for further details.)

Task 4. In the fuel cell/battery system, the fuel cell is used for cruising and battery charging, whereas the battery (Ni-Zn in this case) is used for start-up and power surges such as acceleration and hill climbing. Details of the fuel cell section were described and also presented in terms of component weights, volumes, and related scaling factors--including those for the range-controlling Ti-based hydride-hydrogen storage system. Range is a function of the fuel weight carried on board, and rapid charging is featured. Results of the study show that the optimistic projections made for the fuel cell/battery system generally compare favorably with those made for alternate systems.

Publications:

Strickland, G. Hydrogen storage for automobiles. Proc. of the DOE Chemical Energy Storage and Hydrogen Energy Systems Contracts Review, Reston, Virginia, November 13-14, 1979.

Forsberg, H. C., et al. Energy Storage Systems for Automobile Propulsion: 1979 Study. Volume 1: Overview and Findings; Volume 2: Detailed Report; Volume 3: Battery/Flywheel Electric Vehicles Using Advanced Batteries; prepared for Division of Energy Storage Systems, U.S. Department of Energy, UCRL-52841, December 15, 1979.

B. STORAGE MATERIALS

3.9 Hydrogen Storage Using Glass Microspheres for Automotive Applications - R. J. Teitel Associates

Objective:

The objective of this project is to build a base of hydrogen diffusion-rate data (as a function of pressure, temperature, glass composition, coating material and thickness, glass sphere diameter and wall thickness and leak rate at ambient temperature). This information will enable accurate performance and cost estimates to be made of conceptual schemes for automotive storage and other applications.

Tasks:

Task 1. Assemble Microsphere Test Setup: A laboratory-scale apparatus for filling and dispensing hydrogen from 1 to 2-cc beds of glass microspheres will be assembled and made operational.

Task 2. Determine Temperature Pressure Characteristics: The temperature and pressure requirements for filling and dispensing hydrogen from selected grades of commercially available glass microspheres will be determined.

Task 3. Assemble Data Base on Microsphere Properties for the Storage Application: A data base of microsphere properties as applicable to their use as a hydrogen storage medium will be experimentally generated. The data are to include such considerations as the gravimetric and volumetric energy storage density, the crush strength, hydrogen dispensing rates, and the temperature and pressure schedules to produce the greatest storage capacity for each grade tested.

Task 4. Conduct Engineering Analysis of Filling Operation: An engineering analysis will be performed to more accurately estimate the microsphere filling cost as a function of capital equipment cost and financing, hydrogen compression and heating energy, and all other product handling and start-up costs.

Technical Progress:

Task 1. The laboratory equipment was constructed and is operating satisfactorily.

Task 2. The optional temperature and pressure requirements and the schedule at which they are increased are specific for each of the microsphere grades tested and, therefore, had to be determined by a time-consuming empir[illegible]l method.

Task 3. The data base, although incomplete, is presented in the R. J. Teitel Final Progress Report. A compilation of the best results obtained for the commercial grades tested can be found in Fig. 3.10 of this report.

Task 4. An engineering analysis based on a 40,000 lb moles H_2/hr filling plant concludes that the microsphere filling costs range between $1.05/MBtu to $2.13/MBtu. These estimates are based on two approaches (a fludized bed process and a plugged flow process) with a number of variations to each approach. The fixed bed system appears to be the less expensive scheme. It is to be noted, however, that the cost of the microspheres is not included in the reported filling cost projections. Because of uncertainties associated with the initial cost of the material, the hydrogen storage capacity and attrition loss as a function of cycling, it is unrealistic to apply a cost at this time. The FY 80 effort will address this point and a better estimate of total storage costs will be available.

Publications:

Teitel, R. J. Development status of microcavity hydrogen storage systems for automotive applications. Proc. of the DOE Chemical Energy Storage and Hydrogen Energy Systems Contracts Review, Reston, Virginia, November 13-14, 1979.

Teitel, R. J., T. M. Henderson, J. Powers, and J. E. Luderer. Microcavity hydrogen storage. Proc. of the 2nd Miami International Conference on Alternative Energy Sources, Miami Beach, Florida, December 10-13, 1979.

FIGURE 3.10

PERFORMANCE PROPERTIES OF 3M D32/4500 HYDROGEN STORAGE BED

CRUSH TEST

Pressure (psi)	Survivors (%)
3500	96
4500	66
6000	50
7740	33
10340	15

HYDROGEN PERMEABILITY

Temperature (^oK)	Permeability $\frac{cc(STP)mm}{cm^2 sec(cmHg)} \times 10^{-15}$
300	9.6
413	150
473	660
573	2300
623	3900
673	5800

STORAGE BED CHARACTERISTICS

Bulk Density (g/cc)	0.2
Average Microsphere Diameter (μm)	27.7
Microsphere Size Range (μm)	5-60
Surface Area (m^2/g)	0.77
Glass Density (g/cc)	2.15
Microsphere Density (g/cc)	0.32
Packing Fraction	0.63
H_2 Storage Weight Fraction (gH_2/g_{bed})	
Untreated	0.053
Annealed	0.065
H_2 Storage Volume Fraction (gH_2/cc_{bed})	
Untreated	0.012
Annealed	0.015
Dispensing Rates at Operating Temperature (T_o)	
$140^oC < T_o < 200^oC$ - - -(cc/min-cc_{bed})	0.71
Available Hydrogen Below 200°C (%)	∿ 55
Available Hydrogen Below 250°C (%)	∿ 70
Storage Half Life at Ambient Temperature (Days)	110
Filling Cost Estimate Range ($/$10^6$ Btu)	1.05 - 2.13
Projected Microsphere Cost ($/lb)	0.77 - 1.15

3.10 Development of Hydrogen Storage Materials for Application to Energy Needs - Denver Research Institute (DRI)

Objectives:

The principal objective of this program is to develop hydride materials with storage capacities of at least 3 wt % hydrogen with attention being given to optimizing the following properties: (1) decreased materials cost, (2) contamination resistance, (3) minimized hysteresis, (4) maximized kinetics, (5) good thermal conductivity, (6) safe handling properties, and (7) long-term recyclability. Additionally, the proper pressure-temperature-composition relationships of selected systems will be sought, nominally in the ambient pressure-temperature ranges (e.g., plateau pressure levels in the range of 1 to 10 atmospheres at 25°C with as extensive and flat compositional features as possible).

Tasks:

This program is divided into two main tasks.

Task 1. Alloy Development Studies: This task consists of seven subtasks each of which deals with a study of the hydriding properties of specific alloy types. These alloy types are: (1) Ti-based systems, (2) AB_2, Laves phase structure intermetallic compounds, (3) CrB (B_f) structure-type intermetallic compounds, (4) borides, (5) AB_3 and AB_4 types of combination alloys, (6) AB_5 intermetallics, and (7) calcium-based systems. Compounds from each of these seven structure types were selected employing the DRI size-stability correlation.

Task 2. Studies of the Relationship Between Intermetallic Compound Structure and Hydride Formation: Theoretical studies on the relationship between intermetallic compound structure and hydride formation were to be made from a geometric point of view. Four intermetallic compound structures were selected. The objective here is to see if hydriding sequence and storage capacity might be predicted on a geometrical basis.

Technical Progress:

Task 1. The research done in this task is similar for each of the seven subtasks, which compose the total task; therefore, a brief description of overall progress for the total task will be given here. The basic experiments performed on selected members of each structural-type intermetallic consisted of measuring hydrogen absorption capacity and, presuming the alloy absorbed a significant quantity of hydrogen, pressure-composition isotherms.

The borides and AB_3, AB_4 compounds were all poor hydride formers and are of no practical interest. Structures of the CrB (B_f) type, in general, formed hydrides with reasonable absorption capacity but all were too stable thermodynamically. Specific Ti-based alloys investigated were from the general systems: Ti-V-Mn and Ti-V-Cr. Modifications of the ratio of metal atoms for these systems allow a variation in their pressure-composition characteristics but, in general, such systems are too stable for use at or near ambient temperatures. However, if temperatures of 200°-250°C are available, these metal-hydrogen systems could be quite attractive from a storage standpoint. The other structural types investigated were also found to have possible uses as hydrogen storage media in certain selected applications, but none were really better than FeTi from an overall properties point of view.

Task 2. An analytical study was performed, concurrent with the experimental work, to better define the types and sizes of interstitial holes (tetrahedral) in different families of intermetallic compounds, in order to relate these holes, or clusters thereof, to positions actually occupied by hydrogen in the hydride phases. The four different families analyzed in this manner were: (1) Hexagonal AB_5($CaCu_5$ type) compounds, (2) cubic AB_2(C15) Laves phases, (3) hexagonal AB_2(C14) Laves phases, and (4) orthorhombic AB(CrB type) compounds. Where structures have been determined for hydride phases of these type intermetallics, this geometric analysis has had limited success in predicting the sequence of interstitial hole filling and maximum hydrogen capacities. The geometric approach for predicting absorption capacities for intermetallics and hydriding sequence appears overly simplistic and no electronic contributions are taken into account.

Technical Problems:

The DRI predictive technique, used in the selection of alloys to be investigated, is only a qualitative tool. It cannot predict quantitatively, from the interstitial hole sizes in starting intermetallics, what the stability of the resulting hydride will be. Additionally, it does not allow for any prediction on ultimate hydrogen uptake by alloys. In most cases, where stability of the hydride phase is as desired, hydrogen capacity is greatly reduced.

Publications:

Magee, C.B., C.E. Lundin, and J. Liu. Paper to be presented at the International Symposium on the Properties and Applications of Metal Hydrides, Colorado Springs, Colorado, April 1980. To be published in two special issues of J. Less Common Met.

FIGURE 3.11

SUMMARY OF EXPERIMENTAL RESULTS FOR BINARY Mg ALLOYS (INTERMETALLICS) TESTED BY AIR PRODUCTS & CHEMICALS, INC.

Alloy	Dissociated Temperature at 1 Atm H_2 (°C)**	Hydrogen Capacity (% by wt)
Objective	Less than 249°C	+3.0
$Mg_2Al_{3.35}$	231.9	2.5
Mg_2Ni	249.5	3.11
$Mg_{17}Al_{12}$	268.3	2.3
MgZn	285.0	1.17
Mg	288.7	7.25
Mg + 5% Li	293.4	3.4
Mg^2Ca	301.9	2.0
Mg_2Zn_3	*	*
Mg_2Si	*	*
Mg_2Sn	*	*

*Did not hydride

**Extrapolated from Van't Hoff plots.

3.11 Development of New Hydrogen Storage Systems for Automotive Hydrogen Fuel Storage (Phase I) - Air Products & Chemicals, Inc.

Objectives:

This program is aimed at developing new Mg-based hydrides for use in vehicular applications in which hydrogen serves as a fuel. The specific objective of the Air Products & Chemicals, Inc. (APCI) program (Phase I) is to develop a Mg alloy which possesses the following properties: (1) hydrogen storage capacity of at least 3 wt %, and (2) a hydrogen dissociation pressure of 1 atmosphere at a temperature of ∿175°C. Additionally, other properties of the intermetallic-hydrogen system should be attractive e.g., kinetics, cyclic stability, etc.

Tasks:

This program consists of three primary tasks.

Task 1. Project Plan in accordance with standard requirements.

Task 2. Development of New Mg-Based Alloy Hydrides with Lower Dissociation Pressures: APCI will assemble a hydrogen absorption apparatus (Sieverts apparatus) for thermodynamic and capacity studies of intermetallic-hydrogen systems. Candidate Mg-alloy samples will be prepared utilizing the APCI hypothesis which relates the stability of hydrides formed to the stability of the hydrides of the individual metals which comprise the starting intermetallic and also by utilizing the "rule of reversed stability." Once the candidate alloys have been prepared, they will be evaluated for storage capacity, physical stability, and kinetic and thermodynamic properties.

Task 3. Report and Definition of Follow-on Work: APCI will prepare a final report which will include all findings of significance for the 14-month contract period.

Technical Progress:

Task 1. A detailed project plan was submitted to BNL in accordance with time and procedural requirements.

Task 2. Several experimental alloys (binary and ternary, Mg intermetallics) were selected and prepared by utilization of the APCI stability hypothesis and the "rule of reversed stability." They were evaluated for the properties noted above. Effects of Ni additions, to the selected alloys, were also studied to determine if system kinetics and/or capacity could be improved. The most promising alloy identified, in this program, was the

Mg_2Al_3 system which exhibited a 1-atmosphere dissociation (hydrogen) pressure of 230°C with a storage capacity of nearly 3 wt %. Hydrogen absorption/desorption kinetics were, however, slow for temperatures less than 250°C. Nickel addition to most alloys aided in initial activation (first hydriding), and appeared to play a secondary role in subsequent hydriding.

Task 3. Final report was approved, and recommended follow-on work included research on catalytic techniques to enhance hydrogen absorption/ desorption. Both the use of metal catalysts and the role of surface morphology were suggested as possible areas to explore.

Technical Problems:

Several technical problems were identified during this program. They are as follows:

1. All alloys investigated showed unacceptable hydride kinetics at reasonable temperatures (200°-250°C).
2. A limited number of intermetallics exist among Mg and acceptable second or third metals (i.e., weight, cost, toxicity).
3. The relatively low melting points of most Mg alloys limit their use and are a concern if local hot spots develop.
4. The hydrogen capacity of the various Mg alloys is significantly below MgH_2 and can qualitatively, it appears, be assigned considering only hydriding of the Mg portion of an alloy (i.e., $Mg_2Al_3 + 2H_2 \rightleftarrows 2MgH_2 + 3Al$). Therefore, disproportionation may be the dominant reaction path, and explain the relatively poor reaction kinetics at lower temperatures.

3.12 Development of New Hydrogen Storage Systems for Automotive Hydrogen Fuel Storage (Phase II - Air Products & Chemicals, Inc.

Objectives:

On the basis of thermodynamic considerations (Phase I of this program) Mg_5Al_8 (Mg_2Al_3) was identified as a possibly attractive hydrogen storage candidate for automotive applications. However, the kinetics of this alloy/hydrogen system were slow. In order to more fully understand the phenomena associated with the slow kinetics, a short, 4-month program was initiated with Air Products & Chemicals, Inc. with the following objectives: (1) to define the products of the hydriding reaction of the Mg_5Al_8/hydrogen system, (2) to explore the role of Ni as a possible catalyst to improve the absorption/desorption kinetics in the Mg_5Al_8 system, and (3) to investigate the kinetics of hydrogen absorption/desorption for Mg_5Al_8 in the absence of any potential catalysts.

Tasks:

This short 4-month program consists of five tasks, as follows:

Task 1. Preparation of High Quality, Single Phase Mg_5Al_8: APCI was to prepare by either arc-melting or induction-melting a single-phase intermetallic compound of composition Mg_5Al_8.

Task 2. Investigations of the Mechanism of Hydrogen Reaction with Mg_5Al_8: The products of the reaction of hydrogen with the Mg_5Al_8 intermetallic will be determined by x-ray diffraction techniques. The principal question here is whether this intermetallic disproportionates to MgH_2 and Al upon hydriding or whether a ternary hydride is formed.

Task 3. Qualitative Determination of Hydrogen Reaction Rate with Mg_5Al_8: Samples of Mg_5Al_8 which have been activated will be subjected to hydrogen at a set temperature and the rate of hydrogen absorption will be evaluated. A volume of hydrogen will be used with a small sample size of intermetallic. Desorption rate data will be obtained by discharge of hydrogen into a vacuum.

Task 4. Investigations of the Effects of Catalysts on the Absorption-Desorption Kinetics: Nickel will be studied as a possible catalyst for hydrogen absorption/desorption in the form of a thin film coating, as an alloyed addition to the intermetallic, and simply as a powder admixed with the

Mg_5Al_8 compound. This is with the hope of improving the absorption/desorption kinetics.

Task 5. Qualitative Determination of the Change (Improvement) in Hydrogen Absorption/Desorption of Mg_5Al_8 in the Presence of Nickel Catalyst: The change in reaction kinetics by utilizing Ni as a catalyst will be determined as for Task 3 above.

Technical Progress:

Task 1. Single-phase intermetallics of Mg_5Al_8 were prepared in a Lepel induction furnace at APCI. These samples were shown to be single phase by x-ray diffraction, and electron microprobe, and by obtaining micrographs of the materials. Nickel alloyed Mg_5Al_8 of the composition $Mg_5Al_8Ni_{0.058}$ was also prepared at APCI.

Task 2. X-ray diffraction studies confirm the fact that when hydrogen reacts with the activated Mg_5Al_8 the alloy disproportionates to form MgH_2 and Al. No ternary hydride phase was formed. The reaction is $Mg_5Al_8 + 5H_2 \rightleftarrows 5Mg + 8Al$.

Task 3. Qualitative rates of hydrogen absorption/desorption were measured for the activated starting intermetallic Mg_5Al_8. These rates are very slow in the 200°-250°C temperature region and appear to be controlled by alloy disproportionation. This was confirmed, to some degree, by taking a rapidly desorbed alloy and a slowly desorbed alloy and subjecting them to hydrogen. The rapidly desorbed sample reacted much more quickly. Such an observation is consistent with disproportionation as the rate-controlling step since an alloy which is desorbed quickly is expected to be in a metastable state which consists of Mg and Al which have not had sufficient time to reform the starting intermetallic. Therefore, in the case of the quickly desorbed alloy, disproportionation does not have to take place and reaction with hydrogen (absorption) may proceed more quickly. These results are shown in Fig. 3.12.

Task 4. For the systems studied, Ni, either in the form of surface plating (or coating), an admixture to the alloy (Ni-powdered), or as a direct addition to the alloy (Ni-alloyed) does not significantly increase the rate of hydrogen absorption for high surface area Mg_5Al_8. This is the expected result if disproportionation is the rate-limiting step in hydrogen absorption. See Fig. 3.13 for comparison of H_2 absorption rates.

Nickel additions described above significantly enhanced the rate of hydrogen desorption for the high surface area Mg_5Al_8 samples. However, these three forms of Ni affect the desorption rates differently; therefore, the form of Ni incorporation is important here. Desorption of hydrogen is fastest for the Ni-plated, high surface area alloy and slowest for the control (straight high surface area alloy) plus Ni powder.

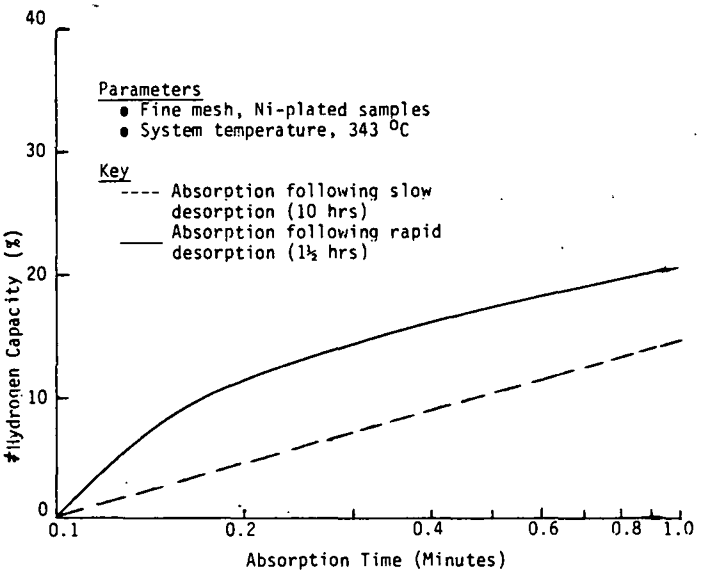
Task 5. See Tasks 3 and 4 above.

Technical Problems:

None.

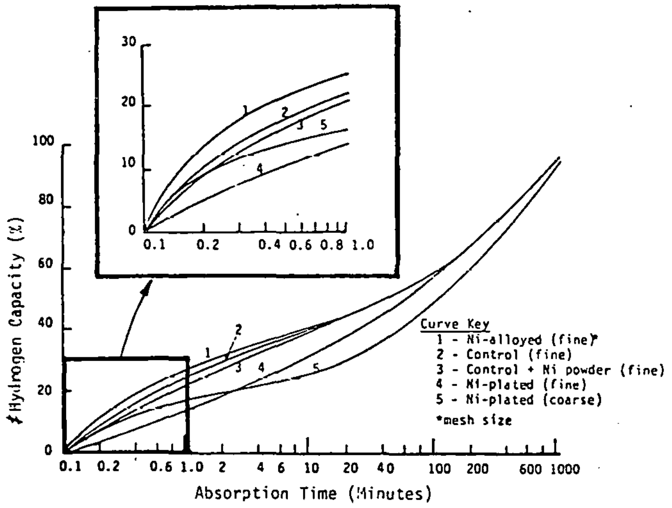
Publications:

Paper to be presented at the International Symposium on Properties and Applications of Metal Hydrides, Colorado Springs, Colorado, April 1980. To be published in two special volumes of J. Less Common Met.



‡NOTE: "Hydrogen Capacity" is the percentage of hydrogen absorbed by the alloy relative to the ultimate, experimentally observed, hydrogen capacity of the given alloy.

Figure 3.12. Hydrogen Absorbtion Rates for Mg_5Al_8 and "Disproportionated" Mg + Al as determined by Air Products & Chemicals, Inc.



‡NOTE: "Hydrogen Capacity" is the percentage of hydrogen absorbed by the alloy relative to the ultimate, experimentally observed, hydrogen capacity of the given alloy.

Figure 3.13. H_2 Absorbtion Rates for Mg_5Al_8 and Systems at 343°C as determined by Air Products & Chemicals, Inc.

3.13 Metallurgical Studies of Hydrogen Storage Alloys: Surface Poisoning of $LaNi_5$, FeTi, and $Fe_{0.85}Mn_{0.15}Ti$ by Co, O_2, and H_2O - International Nickel Company, Inc.

Objectives:

The objectives of this program were as follows:

1. Determine phenomenology and mechanisms of poisoning of FeTi, (Fe, Mn) Ti, and $LaNi_5$ by O_2, CO, and H_2O. Determine if there are substitution effects or fundamental differences between AB and AB_5 compounds.
2. Determine how easily poisoned samples can be reactivated and if there are any alloy effects.
3. Using the results of 1 and 2, assess the overall probability of successfully developing poison-resistant alloys or practical regeneration cycles.

Tasks:

This program consists of three tasks.

Task 1. Poisoning Studies: The alloys FeTi, (Fe, Mn) Ti, and $LaNi_5$ will be subjected to mixtures of hydrogen containing gaseous impurities such as CO, O_2, and H_2O in order to carefully quantify the loss of kinetics (and ultimately capacity) as a function of alloy type, impurity type and level, and cycling. This will be followed by careful reactivation studies.

Task 2. Metallographic Examination of BNL Experimental Samples: INCO will examine BNL alloy samples on an "as needed" basis. Such examination can include chemical analysis, optical microscopy, scanning electron microscopy, etc.

Task 3. Preparation of Test Material for BNL: INCO will supply to BNL kilogram quantities of desired hydriding alloys for in-house testing. This will be on an "as needed" basis and will include metallographic and chemical analyses of all alloys.

Technical Progress:

Task 1. The mode of surface poisoning for each alloy in the presence of varying levels of CO, O_2, and H_2O gaseous impurities has been investigated by performing cyclic poisoning tests and adsorption tests. From such tests, mechanisms of surface poisoning have been deduced and it has been determined that all alloys can be reactivated after poisoning with procedures that are

From the point of view of practical applications, there are a number of obvious conclusions that can be drawn from this work.

1. If significant amounts of O_2 or H_2O are expected in the H_2, use $LaNi_5$ (or possibly some other AB_5 compound).
2. If CO is expected, use (Fe, Mn) Ti.
3. Binary FeTi will be a problem for any gaseous impurity.
4. All poisoned alloys can be reactivated quite easily. Some (e.g., FeTi) are harder to reactivate than others [e.g., $LaNi_5$ or (Fe, Mn) Ti.]

From a long-range development point of view, two conclusions can be ventured:

1. There are marked alloy-to-alloy variations giving hope for some day developing the understanding necessary to design specific poison resistance into an alloy.
2. If complete resistance to all poisoning is impossible (as it probably is), there should be ways to design reactivation cycles into the particular process or device involved.

Task 2. Samples of alloys and intermetallic compounds (mostly titanium-based materials) have been characterized metallographically by INCO for BNL on an "as needed" basis.

Task 3. INCO has supplied BNL with several kilogram melts of $LaNi_5$ and substituted $LaNi_5$ intermetallics as well as some titanium-based (Fe, Mn) Ti materials. These alloys represented state-of-the-art commercial metals and were characterized both chemically and metallurgically by INCO.

Technical Problems:

The major technical problem related to this contract resulted from the inability to measure baseline kinetic data for $LaNi_5$ and (Fe, Mn) Ti in the presence of super high purity hydrogen. This resulted, in the case of $LaNi_5$, from the fact that the hydrogen reaction is completely thermally controlled and in the (Fe, Mn) Ti systems, from complications introduced by the sloping reaction plateaus.

Publications:

Goodell, P.D. Thermal conductivity of hydriding alloy powders and comparisons of reactor systems. To be presented at the International Symposium on Properties and Applications of Metal Hydrides, Colorado Springs, Colorado, April 1980.

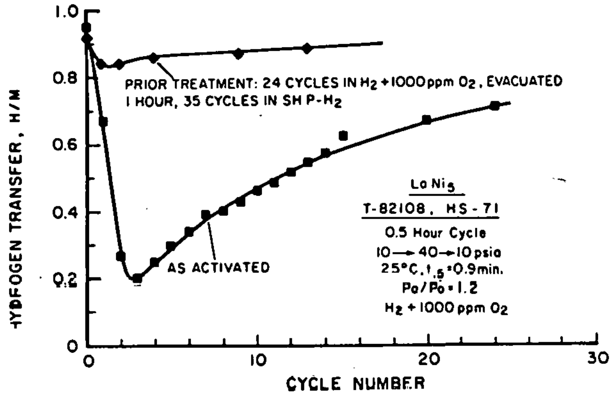


Figure 3.14. Cyclic Response of $LaNi_5$ in Hydrogen Containing 1000 ppm Oxygen. Data Compares Initial, As-Activated, Response with that after Prior Oxygen Exposure Treatment

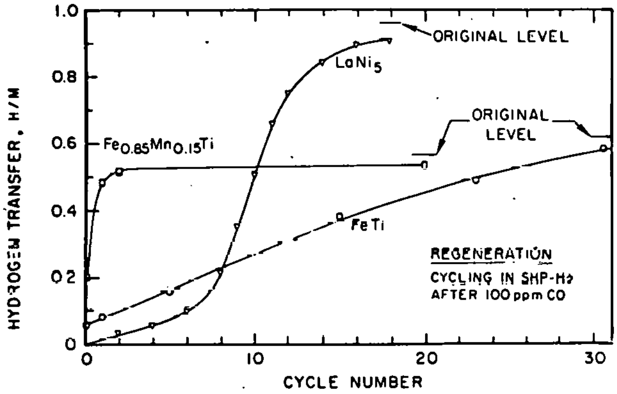


Figure 3.15. Recovery of Hydrogen Transfer Capability During Cycling in SHP-Hydrogen after Poisoning in Hydrogen Containing 100 ppm Carbon Monoxide

3.14 Hydrogen Storage Materials Research and Development Work at Brookhaven National Laboratory

Objective:

The objectives of the work performed at Brookhaven National Laboratory for FY 79 were severalfold. They were as follows: (1) Continuation of research in developing metal hydrides with attractive storage properties, (2) initiation of investigations into the technical and economic feasibility of using metal hydrides to remove hydrogen from mixed gas streams (this involves rapid turnaround times for hydrogen absorption/desorption as opposed to long term hydrogen storage), and (3) interaction with contractors to transfer this technology to industry.

Tasks:

This program consists of five tasks.

Task 1. Completion of Studies on the Low Temperature $TiCr_2$-D System: The purpose of this task is to complete the characterization of the physicochemical properties of this system.

Task 2. Completion of Studies on the High Temperature $TiCr_2$-H System: The purpose of this task is to gain a fuller understanding of the properties of this intermetallic-hydrogen system. This material stores 2(+) wt % hydrogen.

Task 3. Continuation of Hydriding Studies of $TiCr_{2-x}Mn_x$ Compounds and Defect $TiCr_{2-x}Mn_{x-y}$ Materials: Pressure-composition isotherms and hydrogen capacities are being measured by standard techniques. Hysteresis investigations are also being performed.

Task 4. Hydrogen Separation from Mixed Gas Streams: The objective of this task is to determine the technical and economic feasibility of using reversible hydrides for hydrogen removal in certain types of gas mixtures.

Task 5. Interaction with Contractors: The objective of this task is to coordinate certain DOE metal hydride projects, to interact on an advisory basis with the contractors, and to transfer this technology to private industry.

Technical Progress:

Task 1. Characterization of the physicochemical properties of the $TiCr_2$-D system was nearly completed. Isotherms have been measured and thermodynamic parameters calculated for the two deuterides formed in this system. The low temperature $TiCr_2$-D system is of interest since it exhibits a large reverse isotope effect which makes it attractive for H_2-D_2 separation.

Task 2. Studies of the physical and chemical properties of the high temperature $TiCr_2$-H system have been completed. Isotherms and hysteresis have been measured and a partial-phase diagram proposed. This system is too unstable for most hydrogen storage applications but could be useful for non-mechanical hydrogen compression or liquefaction.

Task 3. Hydriding studies have continued on the manganese-substituted $TiCr_2$ compounds. Manganese replaces chromium and greatly stabilizes the hydride phases formed while at the same time significantly reducing the alloy costs. Storage capacities in excess of 2 wt % can be obtained with these manganese-substituted systems. Finally, these systems (modified $TiCr_2$) may have more attractive features than the parent $TiCr_2/H_2$ system for nonmechanical compression or liquefaction of hydrogen.

Task 4. Hydrogen can easily be separated from natural gas (methane-hydrogen mixtures) by the use of the intermetallic compounds (activated) $LaNi_5$, $LaCuNi_4$, and $TiFe_{0.85}Mn_{0.15}$. The mixture used, to date, consisted of 10 volume percent hydrogen/90 volume percent methane. This is a typical gas mixture which could presently be transported in most existing natural gas pipelines without serious problems. Additionally, each of the above intermetallics has been cycled at least 20 times with no loss of transfer kinetics or ultimate hydrogen capacity. These alloys were selected on the basis of an extensive literature search and on the basis of previous poisoning studies done at BNL.

Task 5. Management and technical support on hydrogen storage materials contracts has been provided during FY 79 at the Denver Research Institute Air Products & Chemicals, Inc., and the International Nickel Company.

Technical Problems:

In applying metal hydride technology to hydrogen storage and conversion, basic and engineering research remains to be done in addressing two questions. These are: (1) What are the important factors which govern whether hydrogen will react with a given alloy or metal? (2) If reaction occurs, what will be the thermodynamic properties of the hydrides formed and what factors influence their ultimate storage capacities? Once a more complete understanding of these questions has been gained, it is very probable that better systems will be developed for specific applications (a variety of applications including straight bulk hydrogen storage).

Publications:

Johnson, John R. Hydrogen storage materials research and development work at Brookhaven National Laboratory. Proc. of the DOE Chemical Energy Storage and Hydrogen Energy Systems Contracts Review, Reston, Virginia, November 13-14, 1979.

4.0 END-USE APPLICATIONS/SYSTEMS STUDIES

The major accomplishments in the End-Use Applications/Systems Studies area related to the Hydrogen Production from Small Hydropower Projects are as follows:

- Air Products completed the systems analysis and site selection activities and was unable to find a suitable match between hydropower site and "over-the-fence" customer and recommended termination of their efforts.

- The NYSERDA project in Hydrogen Production from Small Hydropower, which was scheduled to begin in midyear, was delayed because of administrative/contractual problems. Work is expected to begin in March 1980.

4.1 Hydrogen Production from Small Hydropower Sites - New York State Energy Research and Development Authority (NYSERDA)

Objectives:

The purpose of this project is to verify the commercial prospects for merchant hydrogen production from a hydropower site in Potsdam, New York, leading to a field demonstration.

The NYSERDA team, consisting of Rist-Frost Associates, General Electric, and Chemetron, was selected for the project as a result of a competitive procurement. The key elements in the NYSERDA project which made it attractive are as follows:

- Completion of site analysis and submittal of FERC license application.
- Participation of a state entity (NYSERDA), a municipality (City of Potsdam), two cooperating divisions within DOE (STOR and Hydro/Resource Applications), as part of a larger program for small hydropower development.
- The availability of 5-mill "dump" power and the projection of capital costs in the range of $1000-$1500 per kW.
- The commitments of customers in the Potsdam area indicating a ready market for the hydrogen assuming it could be produced and distributed at competitive prices.

Tasks:

Phase I - Planning and Analysis: The tasks in Phase I consist of: planning and management activities; systems analysis and cost studies; and sensitivity analysis of factors affecting cost of hydrogen.

Phase II - Site Selection: The tasks in this phase consist of the documentation activities associated with legal, environmental, license applications, institutional problems, and overall rationale for selected site.

Phase III - Site Engineering - The tasks connected with site engineering include site restoration, development and design, hydrogen production, storage, and disposition including equipment selection, interfaces and operations,and a detailed cost estimate of the complete installation.

Phase IV - Construction and Operation Planning.

Phase V - Site/Facility Operations: These two phases will occur downstream following the work that is currently funded.

Technical Progress:

Final negotiations with NYSERDA have virtually been completed and the project start-up target date has been set as April 1, 1980. The project will be cost-shared by:

- DOE/STOR Division of Energy Storage Systems
- DOE/HRD Division of Hydroelectric Resource Development
- NYSERDA
- City of Potsdam

Technical Problems:

One incident occurred during the pre-contract phase involving a citizen's complaint on infringement of property rights due to the project. The incident was within the jurisdiction of the City of Potsdam and was resolved in favor of the City in going ahead with the project. No other problems have been identified at this time.

Publications:

Mathusa, P.D. and R.A. Wiley. Hydropowered electrolysis in New York State, Proc. of the DOE Chemical Energy Storage and Hydrogen Energy Systems Contracts Review, Reston, Virginia, November 13-14, 1979.

4.2 Hydrogen Production from Small Hydropower Sites - Air Products & Chemicals, Inc.

Objectives:

The purpose of this project is to conduct the analytical design and engineering investigations leading to the decision regarding the field demonstration of the commercial viability of hydrogen production from small hydropower sites. The project is focused on the "over-the-fence" approach whereby a match is obtained between an available site and a customer(s) such that the hydrogen could be delivered by short pipeline at a predetermined demand rate.

Tasks:

Phase I - Planning and Analysis: The tasks are to conduct a systematic engineering and economic analysis of a typical facility including a sensitivity analysis of major cost components in arriving at projected cost for hydrogen. This phase also included a detailed market and distribution analysis.

Phase II - Site Selection: The tasks are to select preferred site(s) which minimize the mixture of fixed and variable costs of production and distribution while providing a dependable balance of competitively priced hydrogen with market demand. This phase is to result in the selection of a specific site for development.

Phase III - Site Engineering and Economics: This task consisted of performing the preliminary engineering studies and analyses needed to arrive at a budgetary cost estimate for the entire facility and operations. Preliminary drawings, safety plans, and operating procedures were to be developed. A rationale and recommendation for continuation of the program was also to be provided.

Technical Progress:

As of March 1980, Air Products had completed the tasks associated with Phases I and II Planning/Systems Analysis and Site Selection. Based on the results of this work, their preliminary recommendation was that the study be discontinued for the following reasons: Air Products was unable to find a suitable match between small hydro site and customer for the "over-the-fence" approach; and an electrolytic hydrogen production facility would not be economically viable for the merchant hydrogen market in the New England area. A summary of the rationale for the recommendation is given below.

Summary

An on-site situation relying on a dam site customer match-up was not found. Under certain situations this alternative would have had favorable prospects for commercial development assuming a cost of service of approximately 31 mills. Air Products' base case analysis (see Fig. 4.1) indicated that 38 mills was the lower limit on cost of service from small dams, and would involve hydrologic conditions which are uncharacteristic of low head hydro.

The proposed facility, configured as a merchant plant, would be considerably smaller than the base case facility and would suffer scale penalties making it even more uncompetitive than the base case (see Fig. 4.2). As a general conclusion, an electrolytic hydrogen plant configured to serve the merchant market is more capital intense than originally presumed, reducing the importance of power costs on the overall cost structure.

The cost of service from small dams examined in Air Products' base case is likely to range from 38 to 110 mills depending on the degree to which existing generating equipment and civil works can be refurbished. Site selection activities by Essex Development Associates, Inc. failed to yield a site capable of producing power below 45 mills. An individual requirement for electricity can be satisfied more economically in Connecticut and Massachusetts from the grid where the cost of service, as an average, reflects older and lower cost generating facilities, especially nuclear.

FIGURE 4.1

ON-SITE HYDROGEN INVESTMENT AND PRODUCT COST

Production	
MMSCF/Year - 95% on-stream	99.36
10^9 Btu/year*	32.3
Investment - M$ (1979)	1,764.6
Power (kW)	1650
Operating Costs - Annual (1979$)	
Power - (31 mills/kW hr)	425,670
Make-up & Potable Water	1,500
Chems & Lubes - 1¢/100 SCF & electrolyte	10,140
Labor	13,000
Allocations & Site Overhead	11,520
G&A (20% on variable costs excluding power)	5,150
Subtotal	466,980
Fixed Costs	432,330
TOTAL	899,310
$/CSCF	.905
$/MMBtu	$ 28

*325 Btu/SCF HHV.

FIGURE 4.2

HYDROGEN PRODUCT COST CALCULATION
(Base case - 95% power availability)
Plant for Merchant Market

	GE Projected	Electrolyzer	Total
Production			
MMSCF/year - 95% on-stream	35.664	63.696	99.360
10^9 Btu/yr*	11.6	20.7	32.3
Investment - M$ (1979)	1709.7	2720.7	4430.4
Power (kW) Cells and Auxiliaries	558	1,054	1,612
Other	73	129	202
Total	631	1,183	1,814
Operating Costs - Annual (1979$)			
Power - (31 mills/kW hr)	162,790	305,190	467,980
Make-up & Potable Water - 1.50/1000 gal	800	700	1,500
C&L - 1¢/100 SCF & electrolyte	3,570	6,570	10,140
Labor - 1/2 man	4,700	8,300	13,000
Allocations & Site Overhead	8,960	14,300	23,260
G&A (Variable Costs) - 20% w/o power	1,900	3,2501	5,150
Subtotal	182,720	338,310	521,030
Fixed Costs	418,870	666,580	1,085,450
Total - $/yr	601,590	1,004,890	1,606,480
$/100 SCF	1.69	1.58	1.62
$/MMBtu*	51.86	48.55	**49.74

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*325 Btu/SCF HHV.

**Not competitive at $49/MMBtu.

5.0 CHEMICAL ENERGY STORAGE/CHEMICAL HEAT PUMPS

The major accomplishments in the CES/CHP section are as follows:

- Rocket Research has completed the analysis task for their H_2SO_4/H_2O system and sized it to 150,000 Btu/hr with 1,000,000 Btu of storage. The verification Test Unit (VTU) will operate in batch and continuous modes and will be capable of demonstrating space heating, cooling, and waste heat recovery.
- The EIC methanol-calcium chloride CHP has been taken through 12 charge/discharge cycles satisfactorily at partial salt loading and will soon be loaded with a full charge 400 lb of $CaCl_2$.
- Metal hydride heat pump - considerable interest has been displayed by the industrial community in this concept (indicated by response to CBD announcement) and a public solicitation (RFP) will be issued shortly.

5.1 $H_2SO_4H_2O$ Chemical Heat Pump/Thermal Energy Storage - Rocket Research Company

Objective:

The objectives of this project are to produce a H_2SO_4-H_2O chemical heat pump system, incorporating commercial mass-producible design features where possible and which can demonstrate scale-up and economic feasibility. The first unit produced to these requirements will be identified as the Verification Test Unit (VTU).

Tasks:

This program is divided into four tasks.

Task 1. Requirements Analysis: The major activity in this task is to identify and study generic requirements for various CHP/CES applications expanded beyond solar. Heat sources, applications, control requirements, safety requirements, and system performance will be identified and evaluated to determine the best markets and applications. A second part of this task is to determine the fuel savings payback period and amortized energy costs for selected VTU configurations. The last part of the task is to define VTU design requirements; size, operational modes, components, instrumentation requirements, control requirements, and operational limits for the VTU.

Task 2. VTU Design: This task will consist of conducting configurational tradeoffs; design of acid and water storage tanks, and conductingdetailed designs of fluid circuit and controls, generator and absorber, evaporator and condenser, and acid heat exchanger. It will include use of existing engineering model test system to investigate the use of atmospheric pressure acid and water storage tanks.

Task 3. VTU Fabrication and Assembly: The elements of this task are to acquire components, prepare the site, install the containment vessel, install acid and water tanks, install heat pump components, install instrumentation, and finalize assembly.

Task 4. VTU Testing: The VTU testing will check for leaks, verify controls using water, perform low temperature (100°F) check-out, verify drainage, load system with acid and water, perform a 150°F charge and discharge, demonstrate simultaneous charge and discharge, compare ambient and vacuum storage, and test with higher input temperatures (200°, 300°, and 400°F).

Technical Progress:

Task 1. The Requirements Analysis has been completed. Applications that have been identified include space conditioning, waste heat pumping, air/gas stream drying, steam accumulation, cogeneration, and energy storage. The VTU will perform heating and cooling on both batch and continuous modes as well as operate in a waste heat pumping mode. Energy delivery rate will be 150,000 Btu/hr and the energy storage capacity will be 1,000,000 Btu. Water and acid storage tanks have been identified which are inexpensive ($1.25/gal) and readily available. Three VTU configurations have been identified and will be compared in the next program phase.

Task 2. VTU design has been initiated following completion of the Requirements Analysis.

Task 3. VTU fabrication and assembly will be initiated upon completion of the design task.

Task 4. VTU testing will be initiated upon completion of fabrication and assembly.

Technical Problems:

Technical problems related to this investigation and to an H_2SO_4-H_2O system include:

- Demonstration that a reliable, corrosion-free system can be built economically.
- Proving that the low vapor pressures associated with pumping heat from low ambient pressures do not result in either excessively expensive piping or inhibited vapor transport by the introduction of noncondensibles.

Publications:

Hiller, C.C. Development of chemical heat pump/chemical energy storage systems for heating and cooling applications. Proc. of the 4th Annual Heat Pump Technology Conference, Oklahoma State University, Stillwater, Oklahoma. April 1979.

Clark, E.C. and C.C. Hiller. Development and testing of the sulfuric acid-water chemical heat pump/chemical energy storage system. Presented at the 14th Annual Intersociety Energy Conversion Engineering Conference, Boston, Massachusetts, August 1979.

Clark, E.C. and O.M. Morgan. Sulfuric acid and water chemical heat pump/chemical energy storage system. Proc. of the DOE Chemical Energy Storage & Hydrogen Energy Systems Contracts Review, Reston, Virginia, November 13-14, 1979. Conf-791127.

Clark, E.C. Sulfuric acid and water chemical heat pump/chemical energy storage system. Presented at the International Seminar on Thermochemical Energy Storage, Stockholm, Sweden, January 7-9, 1980.

5.2 Methanol-Based Heat Pump for Storage of Thermal Energy - EIC Corporation

Objective:

The objectives of this contract are to evaluate an engineering development test unit based upon $CaCl_2$-CH_3OH system fabricated under a previous contract, gather data necessary for the initiation of a first detailed prototype design (suitable for field testing), perform hardware check-out, perform cycling studies, and evaluate data.

Tasks:

The program is divided into two tasks.

Task 1. Testing and Operation of the Engineering Development Test Unit: The objective of this task is to verify system performance of the unit in a configuration simulating a possible commercial design in its basic features.

Task 2. Data Evaluation: The purpose of this task is to evaluate data from the engineering development test unit. Objectives include determining the operating characteristics of the $CaCl_2$-CH_3OH heat pump at a scale approaching that of a residential unit and evaluate design modifications directed toward lower system costs and improved system performance.

Technical Progress:

Task 1. Testing has been hampered by the inability to obtain adequate quantities of +20-45 mesh $CaCl_2$. Initial testing has been successfully completed with a partial salt loading. Suitable materials have been acquired and long-term cycling studies are being initiated.

Task 2. Using a single salt tray bed stability, heat, balance and initial heat exchanger performance were evaluated. Bed stability was found to be adequate. The overall heat transfer coefficient of the methanol heat exchanger was found to be 30 Btu/hr ft^2 ^oF for conditions approximating full system operation.

Technical Problems:

Technical problems related to this investigations and to $CaCl_2$-CH_3OH system include:

- Proof that long-term cycling can be accomplished in a system approximating a commercial configuration.
- Proof by economic analysis of this and other solid bed systems that they can survive in a competitive market framework.

Publications:

Offenhartz, P. O'D. Methanol-based heat pumps for storage of solar energy. Third Annual Proc. of Thermal Energy Storage Contractors' Information Exchange Meeting, Springfield, Virginia, December 5-6, 1979. Conf-781231.

Offenhartz, P. O'D. A chemical heat pump based on the reaction of calcium chloride and methanol for solar heating, cooling, and storage. Proc. of the DOE Chemical Energy Storage & Hydrogen Energy Systems Contracts Review, Reston, Virginia, November 13-14, 1979.

Offenhartz, P. O'D., F.C. Brown, R.W. Mar, and R.W. Carling. A heat pump and thermal storage system for solar heating and cooling based on the reaction of calcium chloride and methanol vapor. J. Solar Energy Engineering, Trans. ASME, 102(1), 59 (1980).

Offenhartz, P. O'D. Design of a chemical heat pump using calcium chloride and methanol for solar heating, cooling and storage. Presented at the International Workshop on Chemical Heat Pumps, Stockholm, Sweden, January 7-9, 1980.

5.3 Development of a Metal Hydride/Chemical Heat Pump

Argonne National Laboratory

Objective:

The goal of this program is to develop a marketable Metal Hydride/Chemical Heat Pump suitable for residential, commercial, or industrial space conditioning.

Tasks:

The program is comprised of three tasks.

Task 1. Heat Pump Analysis: Calculations are to be made on the coefficient of performance for a metal-hydride heat pump employing the tubular-heat-exchanger design developed by Ergenics Division of MPD Technology Corp.

Task 2. Hydride Heat Pump Evaluation: The Ergenics experimental heat pump configuration is to be tested and evaluated.

Task 3. Technical Support to BNL: Assistance is to be provided on planning, preparation, and proposal evaluation for a public solicitation (RFP) concerning work on development of a metal hydride/chemical heat pump.

Technical Progress:

Tasks 1 through 3. The present cooperative program began in FY 80 when ANL's hydride heat pump program was funded through BNL for various forms of technical assistance pertinent to the program goal. The first joint effort will be made in preparing a public announcement, to be advertised in Commerce Business Daily, seeking an expression of interest in developing the metal hydride/chemical heat pump. If there is sufficient interest by qualified organizations, an RFP will be issued.

Technical Problems:

None.

Publications:

None.

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