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CHEMICAL/HYDROGEN ENERGY SYSTEMS

ANNUAL REPORT
JANUARY 1, 1981 TO DECEMBER 31, 1981

April 1982

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PHYSICAL AND CHEMICAL ENERGY STORAGE DIVISION
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DEPARTMENT OF ENERGY AND ENVIRONMENT

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CHEMICAL/HYDROGEN ENERGY SYSTEMS

ANNUAL REPORT
JANUARY 1, 1981 to DECEMBER 31, 1981

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April 1982

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ABSTRACT

This report describes progress made in 1981 in the Chemical/Hydrogen Energy Systems Program for which Brookhaven National Laboratory provides management support and technical oversight for the Department of Energy (DOE). The technical and management responsibilities are discharged on behalf of the Office of Energy Systems Research, Division of Physical and Chemical Energy Storage, acting in accordance with DOE policy and budgetary guidance. The program addresses research and development activities conducted by selected private sector contractors and supported by BNL as well as other National Laboratory and university researchers. Efforts are summarized for projects in: (1) Electrolytic Hydrogen Production, primarily directed toward SPE and advanced alkaline water electrolysis; (2) Hydrogen Storage Systems, Materials and End-Use Technology, which includes hydrogen embrittlement studies; (3) Chemical Energy Storage/Recovery Systems, which address hydrogen recovery from H_2S and waste gas streams; (4) Chemical Heat Pumps, covering the use of reversible chemical reactions for industrial heat upgrade and space conditioning; and (5) Thermochemical Production of Hydrogen. The progress in each of these areas is discussed and compared with competing alternatives. The plans and proposed funding for future activities are also presented.

TABLE OF CONTENTS

Page

TABLE OF CONTENTS (Cont.)

TABLE OF CONTENTS (Cont.)

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (Cont.)

LIST OF FIGURES (Cont.)

1.0 INTRODUCTION AND EXECUTIVE SUMMARY

Brookhaven National Laboratory (BNL) provides management, technical oversight, and in-house research support for the Chemical/Hydrogen Energy Systems (C/HES) Program sponsored by the Department of Energy, Office of Energy Systems Research, Division of Physical and Chemical Energy Storage. This effort, which has been performed since 1975, has been conducted consistent with federal policy and budgetary guidance factors, which have resulted in programmatic changes of content, direction, and emphasis over the years. In 1981, program direction and emphasis were shifted from systems development toward more fundamental and exploratory research, and additional responsibilities were given to BNL via the transfer of the thermochemical water decomposition projects from the DOE Brookhaven Area Office.

1.1 Programmatic Guidelines

In response to revised policy and concomitant budgetary constraints programmatic planning and implementation began to address long-term, high-risk, high-payoff ventures. Activities which previously looked to near-to-midterm spinoffs of base technology, and close interaction with the private sector for cooperative process and systems development are now deferring to more basic pursuits.

Typical of actions taken in 1981 which carry over to planning for future years are the redirection and/or discontinuation of two major projects:

(1) The SPE electrolyzer development at General Electric has been virtually stopped. This project had progressed to the design, fabrication, and testing of a 200-kW advanced water electrolysis system. Plans had called for value engineering efforts to reduce capital costs and for demonstrating improved operating efficiencies as a prerequisite to scale-up to multi-megawatt systems. New programmatic guidelines have resulted in project redirection toward analyses of cost versus performance tradeoff based upon the identification of key pacing problems and their solutions. It is anticipated that the results of analyses will set the stage for

independent private sector pursuits consistent with their perspectives regarding commercialization and marketing prospects.

(2) Hydrogen separation/purification processes under development at Air Products and Chemicals Incorporated and International Nickel Company will not proceed in accordance with the original plan for joint ventures in pilot plant design, fabrication, and demonstration at an industrial site. The contractors have been progressing toward the definition of a chemical process based upon metal hydrides hydrogen storage technology. Materials characteristics regarding kinetics, poisoning resistance, and restoration were being applied to resource recovery options as identified for industrial waste streams and refinery gases. Project redirection now calls for contractors' delivery of process flowsheets including design, engineering, and capital/operating cost factors as an end-item. Technical and economic risks versus benefits as identified by the contractors should set the stage for future independent pursuits in the private sector.

New project directions will emphasize base technology and exploratory developments of innovative concepts which promise step-jump improvements in cost and performance characteristics of components, subsystems, and systems. The program organization and structure will incorporate a Technology Assessment and Planning function to identify and evaluate R&D targets in terms of:

- Long-term impact on the U.S. energy supply situation
- R&D costs weighed against potential benefits
- Milestone schedules versus needs of the long-term user markets

1.2 Program Overview and Summary

The C/HES Program in 1981 was impacted substantially by budget rescissions and changes in policy, with the Hydrogen Technology Program element in particular undergoing major adjustment. The following summarizes the status and highlights of major activities.

1.2.1 Hydrogen Production

- The SPE Water Electrolysis Project at General Electric (GE) was curtailed and redirected in February 1981. Pacing problems as pertaining to demonstrating operating efficiency of 80% with low catalyst loadings were being addressed at the time a "stop work" order was issued. The project continued to indicate uncertainties with respect to meeting cost and performance goals. These uncertainties were further compounded by added concerns with regard to life and reliability factors due to potential SPE membrane degradation and the system's high degree of susceptibility to low level impurities in water. GE is now engaged in independent activities funded in part by Empire State Electric Energy Research Corporation and Niagara Mohawk Power Company. Engineering design and cost/performance improvements are being tested in a 20-cell system (1.0-ft^2 cells) with the aim of resolving uncertainties and pacing problems as identified in efforts previously sponsored by DOE.
- The Static Feed Water Electrolysis concept pursued at Life Systems, Inc. (LSI) continued to show promise as a low cost - high efficiency alternative to conventional as well as SPE systems. Modest efforts indicate the capability of operating at high current densities with either pure or brackish water. The system design promises the elimination of most of the parasitic power for operating pumps and water-cleanup subsystems and greater flexibility for matching power conditioning output at maximum efficiency. In 1981 LSI demonstrated the viability of cell scale-up from 0.1 to 1 ft^2 without loss of performance.
- Advanced Alkaline Electrolysis component testing at Teledyne Energy Systems identifies improved electrode, catalyst, and separator systems capable of operating in the 120°C temperature regime can compete with the more realistic projections of SPE electrolyzer cost and performance characterization.
- The Production of Hydrogen From Small Hydropower at NYSERDA/Potsdam has been stopped short of commitment to construction. New PURPA regulations suggest that the probable revenues from direct sales of electricity to the local utility will make required hydrogen

revenues noncompetitive with current market prices for merchant hydrogen.

- Photolytic Water Decomposition studies at BNL have aimed toward the development of low cost, high efficiency heterojunctions. BNL investigations have shown that improved semiconductor heterojunctions can exhibit optimal compromise of bandgap response and stability by appropriate preparation of substrates with good photoresponse and thin-film overlays with good stability characteristics. Further investigations geared toward optimizing heterojunction fabrication will set the stage for advanced water-splitting systems development. Techniques developed in thin-film deposition may extend to other semiconductor applications.
- Anode Depolarization investigations applied to advanced water electrolysis were initiated at BNL late in 1981. These studies will investigate the use of coal or other carbonaceous materials as the oxidizable species which may produce valuable by-product as synfuels "building blocks" as well as hydrogen at low voltages. Early experiments using formates as the depolarizing agent demonstrated the ability to dissociate water at low voltages (<1 V) while operating at current densities in the range of 200 to 500 mA/cm^2.
- High Temperature Water Electrolysis studies at BNL were introduced as a long-term activity with initial modest efforts directed toward characterization and upgrade of candidate solid oxide electrolytes. Plans call for evaluation of Westinghouse's state-of-the-art advances in High Temperature Fuel Cell operated in the reverse mode and to determine the mechanisms for potential electrode degradation and means for achieving optimal materials characteristics suited to high temperature electrolyzers interfaced with HTGR, Fusion and possibly Solar Systems.

1.2.2 Hydrogen Storage/Transport

- Microcavity Storage Systems investigated by Robert J. Teitel Associates were found unsuitable for the cost-effective storage of hydrogen in either bulk or mobile storage applications. This conclusion relates to commercial-grade material now being marketed. Findings have suggested that "customized" microspheres could provide improved "fill/release" characteristics as well as recyclability to reduce cost.

- Natural Gas Supplementation as a hydrogen transport option was reexamined at BNL. Consideration was given to the possibility of separating the hydrogen at user sites consistent with needs of merchant hydrogen and larger user markets to determine if the separation option would compete with delivery/storage alternatives of a conventional nature. The current analysis reinforced the earlier findings that the concept was economically unfavorable primarily because of the price disparities between H_2 and natural gas. The separation/purification incentive can only be pursued if the natural gas is not returned to the network for credit; however, the steel industry offers a strong potential market for direct reduction of iron ore as scrap iron sources become depleted. Economics control the viability of such an application.
- The use of ammonia as a hydrogen transport/storage option was examined at BNL. This option was evaluated for OTEC plantship application but findings suggest that as electricity prices escalate, storage/transport alternatives to hydrogen liquefaction appear more attractive, independently of the resource converted. Current state-of-the-art technology can be applied to the catalytic cracking of ammonia and purification of H_2 for most user applications. Low temperature catalysts and improved purification schemes would enhance the ammonia transport/storage alternative to H_2 liquefaction/Dewar storage. The possibilities extend to use of NH_3-derived H_2 as a fuel alternative in selected user sectors, e.g., in agricultural vehicles and machinery and maritime application.

1.2.3 Chemical Energy Systems

- Hydrogen Separation/Purification from Industrial Waste Streams is under investigation at Air Products & Chemicals, Inc. (APCI)/Ergenics. Emphasis is being placed on identifying metal hydrides and their poison-resistant characteristics. Such definition will then permit process development and designs including stream precleanup in the form of process flow sheets. The DOE-funded effort addresses hydrogen recovery from refinery gases as a major target. A parallel self-sponsored effort has been ongoing at APCI/Ergenics for recovering hydrogen from ammonia process off-gases. The latter activity has enjoyed a level of success and will progress to the prototype stage shortly. Spinoffs of findings will apply to the DOE/BNL-sponsored activity. DOE/BNL does not plan to proceed to pilot plant design and operation at an industrial site.

- H_2 Recovery from H_2S investigations at SRI have proceeded successfully, having demonstrated that H_2S bubbled through molten copper results in a high purity (~99%) H_2 product and the molten reactant can be easily recycled. Energy balance evaluations applicable to process designs focusing on sour gas or sour petroleum treatment appear to have technical merit; however, BNL systems analyses suggest that SO_2 or H_2SO_4 by-product can be detrimental to the economic viability of this process.
- The H_2SO_4/H_2O Chemical Heat Pump development at Rocket Research Corporation has progressed on schedule. A 150,000-Btu/hr, 10^6-Btu storage system is currently undergoing performance verification testing in the industrial chemical heat pump temperature amplification mode of operation. Test results of this first-of-a-kind closed-loop operation of an industrial chemical heat pump have demonstrated the ability to raise 195°F residual process heat to the level of 50 lb steam (~300°F). The initial series of continuous tests to provide a performance mapping of operations have been completed in compliance with milestone schedule requirements. Revised policy will forestall plans to test a 10^6-Btu/hr system at an industrial site in favor of continued performance mapping considering dual reject heat input which promises to drive output temperatures to 400°F. The test option for characterizing the system operated in the HVAC mode will be deferred and possibly eliminated.
- Metal Hydride CHP development at Southern California Gas/Solar Turbine International was initiated in February 1981 following a competitive procurement. Efforts have stressed identification of the application and configuration prior to commitment to component and subsystem design, development, and test. Pacing problems being

addressed by the contractor relate to arriving at designs which permit rapid cycling of the selected metal hydride pairs at minimal rapid cycling of the selected metal hydride pairs at minimal tradeoff of COP due to sensible heat factors. Resolution of the technical and budgetary uncertainties will determine actions to be taken following completion of the initial design and evaluation phase of this project.

1.3 Future Program Directions

The C/HES Program at BNL in 1982 will be structured in accordance with DOE fiscal and policy guidance. Planning actions will be based upon a nominal budget authority of $4 million; but due consideration will be given to possible funding reductions or increases dependent on actions taken by the Congress relative to DOE's overall budget request.

Planning for the 1982 C/HES Program is summarized as follows:

- Hydrogen production technology development will seek out novel approaches. Past efforts into activities such as GE SPE electrolysis system, GA sulfur/iodine thermochemical cycles, and TES component testing, will be deemphasized in deference to advanced concepts such as novel approaches to thermochemical water decomposition, anode depolarization, high-temperature electrolysis, photolytic water decomposition, and continued pursuits in static feed water electrolysis.
- Resource recovery activities will be restricted to process definition associated with H_2 recovery from H_2S with substantial deemphasis of the gas separation investigations as might apply to H_2 recovery from supplemented natural gas or from refinery gases.
- Hydrogen storage/transport options will be reexamined with emphasis placed on high risk/high payoff technology.
- Chemical heat pump development will retain a high programmatic priority carrying through engineering evaluation test of first generation systems. Second generation CHP's will seek out alternative reversible reactions which circumvent limitations identified in the earlier development activity.

- In recognition of budget limitations, milestone schedules will be defined accordingly, stressing evolutionary development of fundamental concepts targeted for long-term application in the U.S. Energy System.
- Although systems and process engineering and testing of commercializable technology will defer to private sector involvement, the program will retain the option for conducting small-scale technology demonstrations and performance verification testing.

1.4 BNL Management Perspective

The program management perspective at BNL is reflected in the program's organizational structure and comparative budgetary commitments made to projects within the major elements of the CHES Program.

1.4.1 Program Organization

The Program Organization Chart (Figure 1.1) displays the division of activities within the program, and reflects a change from previous years wherein the program was organized strictly by technical discipline. The focus of the program is in the technology research area, supported by a separate and defined assessment and planning function to identify promising and relevant research problems; and a third area, designated exploratory systems development, to evaluate the research concepts in working hardware. An Area Manager is assigned to each function reporting to the Program Manager. The in-house BNL research staff provides the technological resource to the management staff as well as conducting specific R&D in each of the technical areas.

The BNL technical management and oversight perspective which has been applied to subcontracted activities will be extended to BNL in-house R&D efforts. In past years, intellectual and technological resources at BNL were pooled to serve as complementary and support functions to contracted private sector pursuits associated with various systems developments. Within the new structure, specific in-house projects will be identified including plans and schedules. Each project will be assigned a separate account number and technical progress vs budget outlays will be evaluated accordingly.

Individual projects within each area are listed, along with FY 1981 and 1982 funding in Figure 1.2.

1.4.2 Budget Considerations

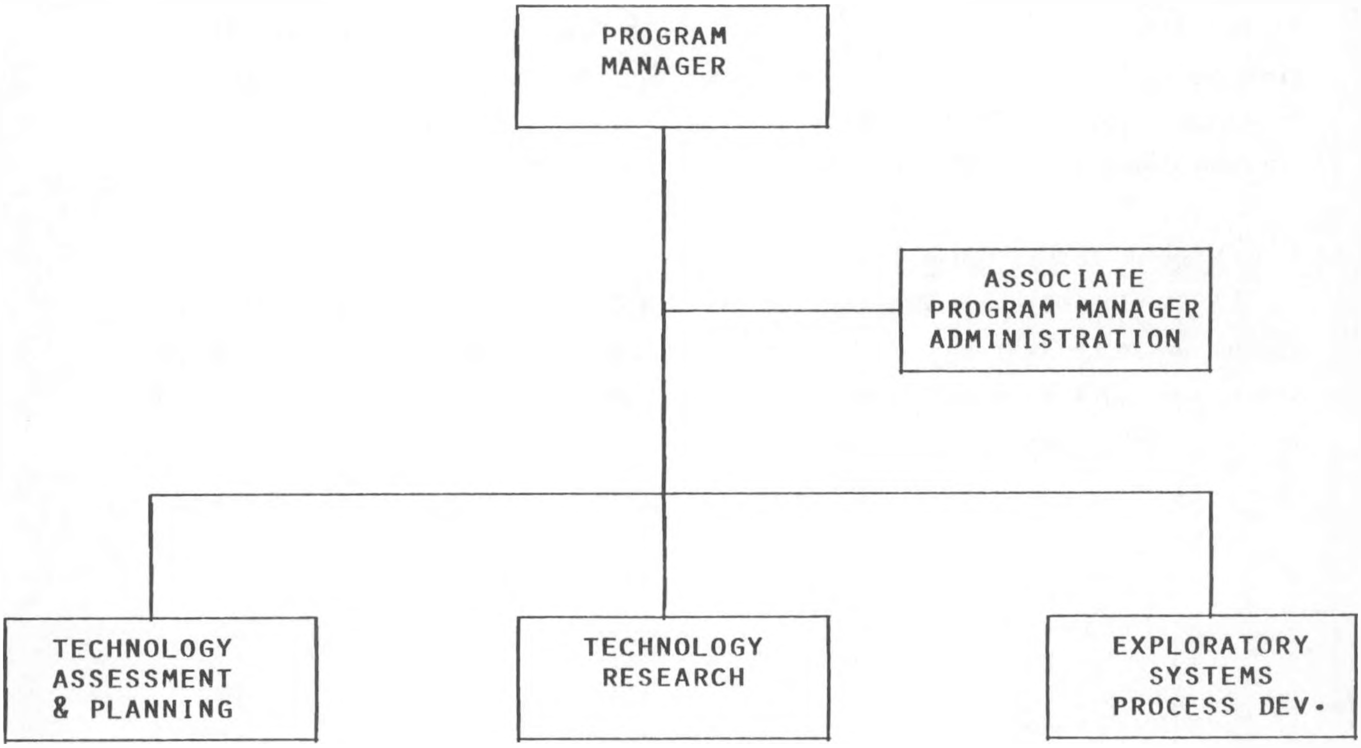
The FY 1982 budget outlay reflects a significant decrease (~40%) over the previous year's funding. This funding decrease is compounded even further when considered in the context of an inflationary economy. Activities presented in this budget are consistent with current administration guidelines that suggest a departure from prototype demonstration activities towards an increased emphasis on fundamental research which addresses high risk/high payoff technologies and greater private sector participation in systems demonstration/development.

1.5 Program Accomplishments

A listing of the specific objectives and accomplishments for the individual projects is provided in summary format in Figure 1.3. Those events which were considered critical to the program and identified by either DOE or BNL as milestones, are shown in Figure 1.4.

FIGURE 1.1

PROGRAM ORGANIZATION



- PORTFOLIO ANALYSIS
- PROGRAM RATIONALE
- R&D TARGETS EVALUATION
- COST/BENEFIT ANALYSIS
- RISK ASSESSMENTS

- ADVANCED ELECTROLYSIS
- HIGH TEMP. ELECTROLYSIS
- ALT. MAT./SURFACE SCI.
- ANODE DEPOLARIZATION
- PHOTOLYTIC H_2O DECOMP.
- H_2 EMBRITTLEMENT

- CHEMICAL HEAT PUMPS
- RECOVERY/SEP. PROCESSES
- ADV. THERMOCHEM. PROC.
- ENERGY MGT. SYSTEMS
- PV/ELECTROL. INTERFACE

Figure 1.2

CHEMICAL/HYDROGEN ENERGY SYSTEMS BUDGETARY BREAKDOWN

Activity	Contractor	$\$10^3$	
		FY 1981	FY 1982
• Technology Assessment & Planning			
- CHP Sys. Anal.	- TRW	91	50
- Chem. Sys. Anal.	- ERG	0	50
- R&D Portfolio Anal.	- BNL	0	30
- Cost/Benefit Anal. Supp.	- BNL	0	30
- Technology Assess.	- BNL	120	30
		211	190
• Technology Research			
- SPE Technology Development	- GE	1260	0
- Static Feed Water Electrolysis	- LSI	217	250
- Adv. Alk. Sys. (PV/Elect.)	- TES	196	150
- AWE Matl's. Dev.	- U. Va.	45	0
- Adv. T/C (Zeolites)	- CCS	0	50
- H_2 Embrittlement of Pipelines	- BMI	143	150
- High Temp. Electrolysis	- BNL	130	150
- Anode Depolarizers	- BNL	0	100
- Anode Depolarizers Support	- TA&M*	0	0
- Photolytic Water Decomp.	- BNL	100	100
- Photoelectrolysis Support	- BU *	0	0
- Photoelectrolysis	- SUNY*	0	0
- Tech. Support/IEA	- ANL/LANL	100	50
		2191	1000
• Exploratory Systems Development			
- H_2SO_4/H_2O CHP	- RRC	396	400
- MH_x CHP HT/Mass XFER	- SOCAL	331	200
- Chemical Compressor	- MPD	110	0
- MH_x/H_2 Separation	- ERG/APCI	288	0
- H_2 Storage/Safety	- RJTA/FMI	77	0
- Elect. Tech. Eval.	- ADL	61	0
- PV/Electrolysis	- BNL/CONTR.	340	340
		1589	940
• Program Management Technical Oversight			
- Pgm./Admin. Mgt.	- BNL	607	370
- ACT/BHO-D.C. Liaison		0	200
		640	570
• Bailments, Closeouts/Consult.	- TBD	42	200
	GRAND TOTAL:	4663	2900

*FY 81 SRSA Funding

Figure 1.3

CHEMICAL/HYDROGEN ENERGY SYSTEMS PROGRAM
1981 OBJECTIVES AND ACCOMPLISHMENTS

1. INTRODUCTION (see text)

2. ELECTROLYTIC HYDROGEN PRODUCTION

ACTIVITY	OBJECTIVES	ACCOMPLISHMENTS
GE SPE Electrolyzer Development	● Performance improvements in 2.5 ft^2 cells in the areas of: - Cell Sealing - Purity/Distribution - Reduced Cell Impedance ● Determine optimum system design/operating parameters and their effects on cost of gas	● Demonstrated cell design modifications for improved sealing (inboard and outboard) in both 2.5 ft^2 and 1.0 ft cell stacks. ● Satisfactory water purity and distribution after incorporating modified deionizer and preformed Ti foil in water distribution grooves. ● Completed techno-economic study which showed dominance of electric power cost in the cost of gas, signifying that higher catalyst loading and lower current density operation (~600 ASF) would be tolerable. (Cont.)

Figure 1.3

CHEMICAL/HYDROGEN ENERGY SYSTEMS PROGRAM
1981 OBJECTIVES AND ACCOMPLISHMENTS

2. ELECTROLYTIC HYDROGEN PRODUCTION (Cont.)

ACTIVITY	OBJECTIVES	ACCOMPLISHMENTS
TELEDYNE ENERGY SYSTEMS Advanced Alkaline Electrolysis	● Develop improved alkaline cell components (for operation at 100° to 125°C in KOH focusing primarily on the separator.	● Satisfactory separator developed consisting of mixture of 70-80 v/o potassium titanate, 20-30% polybensimidazole (PBI). Tested only to 75°C but promises longer life than asbestos at 100-125°C. ● High surface area electrodes (anode) demonstrated improvements through use of perovskite coatings.
LIFE SYSTEMS, INC. Static Feed Water Vapor Electrolysis	● Demonstrate operation with contaminated or impure water. ● Verify scale-up in 1.0 ft^2 cell size. ● Conduct study of scale-up and economics.	● Satisfactory performance demonstrated in 1.0 ft^2 cells using advanced (older tech. electrode). ● Cell run for over 100 hours on impure water with little voltage increase. ● Scale-up sequence defined and cell design improvements initiated. (Cont.)

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Figure 1.3

CHEMICAL/HYDROGEN ENERGY SYSTEMS PROGRAM
1981 OBJECTIVES AND ACCOMPLISHMENTS

2. ELECTROLYTIC HYDROGEN PRODUCTION (Cont.)

ACTIVITY	OBJECTIVES	ACCOMPLISHMENTS
UNIVERSITY OF VIRGINIA Evaluation of Advanced Alkaline Materials	● Electrochemical characterization of hydrogen evolution on nickel whisker electrodes.	● Experiments verified that enhanced electrocatalytic activity of nickel whisker electrodes was due to extremely high surface area only. ● Novel technique for determining true electrode surface area developed.
STATE UNIV. OF NEW YORK AT STONY BROOK AND BNL Photoelectrochemical Characterization of Oxide Materials in Electrolyte Systems	● To apply photoelectrochemical techniques to characterize transition metal oxides for developing better electrode materials.	● TiO_2/Fe_2O_3 heterojunctions fabricated and tested to verify hole injection taking place. Promises stability and good bandgap response. ● TiO_2 photo anodes properties modified by doping with BaF_2 (ionic conductor).
BROOKLYN COLLEGE Optical/Electrochemical Studies of Ru and Ir Oxides as Electrocatalysts	● To define mechanism of electrocatalysis using single RuO_2 crystals.	● Significant findings on the importance of crystal orientation as a factor in electrocatalysis. (Cont.)

Figure 1.3

CHEMICAL/HYDROGEN ENERGY SYSTEMS PROGRAM
1981 OBJECTIVES AND ACCOMPLISHMENTS

2. ELECTROLYTIC HYDROGEN PRODUCTION (Cont.)

ACTIVITY	OBJECTIVES	ACCOMPLISHMENTS
BNL Selection/Evaluation of Materials for SPE Electrolysis	● To elucidate interface reaction at SPE/catalyst interface and investigate membrane degradation.	● Modern electrochemical techniques applied and showed interactions of sulfonic anions and the absorption/desorption of H_2 atoms on platinum electrode current collector; corrosion reaction mechanism elucidated.
A. D. LITTLE Techno-economic Assessment of Water Electrolysis Techniques	● Assessment of SPE technology compared to current state-of-the-art and future program goals.	● Detailed technology and cost data assembled but study has not been completed.
BNL/DOE/INTERNATIONAL ENERGY AGENCY (IEA) Annex IV Working Group	● To stimulate exchange of information and collaboration in alkaline and SPE water electrolysis.	● Considerable amount of research underway throughout the world in both alkaline and SPE technology. Major programs in Japan and Canada. (Cont.)

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H/81 98.3

Figure 1.3

CHEMICAL/HYDROGEN ENERGY SYSTEMS PROGRAM
1981 OBJECTIVES AND ACCOMPLISHMENTS

3. HYDROGEN STORAGE SYSTEMS, MATERIALS, AND END-USE TECHNOLOGY

ACTIVITY	OBJECTIVES	ACCOMPLISHMENTS
BNL Ammonia as a Hydrogen Storage Medium	● To evaluate ammonia as an H_2 storage/transport option.	● Study concluded that NH_3 is a cost effective H_2 distribution and storage medium for H_2 demands up to 40 MSCFY; separation of N_2 from H_2 still a problem.
BNL Photovoltaics Array/Advanced Technology Electrolyzer Testing	● To illustrate interface technology between PV array and an advanced electrolyzer for H_2 production.	● Preliminary plan completed including plot plan, layouts, sizing, and equipment specifications. Power conditioner is main item yet to be designed.
BATTELLE COLUMBUS LABORATORIES Effects of H_2 on Low Cycle Fatigue Life and Slow Crack Growth in Pipeline Steels	● To complete investigations initiated by Sandia on H_2 embrittlement of pipeline steels. The two remaining areas to be characterized were low cycle fatigue life and slow crack growth in weldments.	● Test materials selected and characterized (X42, X60, A106B and A516-70 to be used). ● Equipment to conduct pipe section and compact tension specimen testing assembled and checked out. ● Testing started at the end of year. (Cont.)

Figure 1.3

CHEMICAL/HYDROGEN ENERGY SYSTEMS PROGRAM
1981 OBJECTIVES AND ACCOMPLISHMENTS

3. HYDROGEN STORAGE SYSTEMS, MATERIALS, AND END-USE TECHNOLOGY (Cont.)

ACTIVITY	OBJECTIVES	ACCOMPLISHMENTS
NYSERDA H_2 Production from Small Hydropower	● To verify the commercial prospects for merchant H_2 production from small hydro sites.	● Study completed and project terminated primarily because of latest power reimbursement rates (PURPA) and lack of ready markets making H_2 production economically unattractive at the Potsdam site.

4. CHEMICAL ENERGY STORAGE/RECOVERY SYSTEMS

ERGENICS/AIR PRODUCTS H_2 Separation Using Metal Hydrides	● To develop H_2 recovery/separation system based on metal hydrides.	● Several waste gas streams identified with potential H_2 recovery of $2x10^9$ SCFD. ● Economic study shows no clear advantage over steam reforming of waste gas stream.

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Figure 1.3

CHEMICAL/HYDROGEN ENERGY SYSTEMS PROGRAM
1981 OBJECTIVES AND ACCOMPLISHMENTS

4. CHEMICAL ENERGY STORAGE/RECOVERY SYSTEMS (Cont.)

SRI H_2 Recovery from Hydrogen Sulfide	● To investigate cost-effective process for recovery of H_2 from hydrogen sulfide currently being produced in the desulfurization of sour crude oil and natural gas.	● Bench-scale experiments bubbling H_2S through molten copper completed. ● By-product is SO_2 which can best be converted to sulfuric acid already in excess on the market. Limits prospects for concept.
BNL H_2 Recovery from Natural Gas	● To develop cost effective process for recovery of H_2 from "H_2 supplemented" natural gas.	Metal hydride process identified to recover 80% of H_2 in a transmission line supplemented with 20% H_2. CO_2 must be removed and no odorant present.
BNL Systems Analysis Activities	● To evaluate H_2 recovery and process options.	● Three studies completed: 1. Natural gas supplementation/separation attractive but H_2 must compete economically with natural gas. 2. H_2 recovery from H_2S little advantage in SRI process because of unmarketable H_2SO_4. 3. Metal hydrides for H_2 separation. Economics critically dependent on cost of MH_x alloy.

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Figure 1.3

CHEMICAL/HYDROGEN ENERGY SYSTEMS PROGRAM
1981 OBJECTIVES AND ACCOMPLISHMENTS

4. CHEMICAL ENERGY STORAGE/RECOVERY SYSTEMS (Cont.)

R. J. TEITEL ASSOCIATES Microcavities for Hydrogen Storage	● To develop/evaluate commercial grade microspheres for H_2 storage.	● Work completed and final report published. (Commercial grade microspheres not viable, but customized product might be more suitable.)

5. CHEMICAL HEAT PUMPS

ROCKET RESEARCH CORP. Sulfuric Acid Water System	● To develop an H_2SO_4/H_2O CHP system incorporating mass producible design features. ● Demonstrate performance in verification test unit (VTU).	● VTU tested successfully in industrial waste heat upgrade mode. Temp. amplification of 113°F achieved (input 195°F output 308°) ● Operation/design problems dictated going to Carpenter 20 steel for reaction trays.

Figure 1.3

CHEMICAL/HYDROGEN ENERGY SYSTEMS PROGRAM
1981 OBJECTIVES AND ACCOMPLISHMENTS

5. CHEMICAL HEAT PUMPS (Cont.)

SOCAL Metal Hydride/Chemical Heat Pump Development	● To develop a cost-effective heat pump based on metal hydride technology.	● Conceptual design and preliminary market survey completed. ● Hydride pair selected: $LaNi_5/LaNi_{4.5}Al_{.5}$ ● Industrial waste heat upgrade looked promising with applications in food, paper/pulp, and chemical industries.
ARGONNE NATIONAL LABORATORY Metal Hydride CHP Engineering Support	● To provide support in development of metal hydride chemical heat pump.	● Engineering analysis of thermal design of SOCAL metal hydride CHP completed.
TRW CHP Cost-Effectiveness Study	● To evaluate CHP's in relation to current and emerging competing technologies.	● Study phase completed: - CHP's in industrial heat upgrade mode more cost effective than vapor compression systems. - In residential HVAC, only solar-driven systems looked promising. - Commercial HVAC did not look favorable because of cooling load.

Figure 1.3

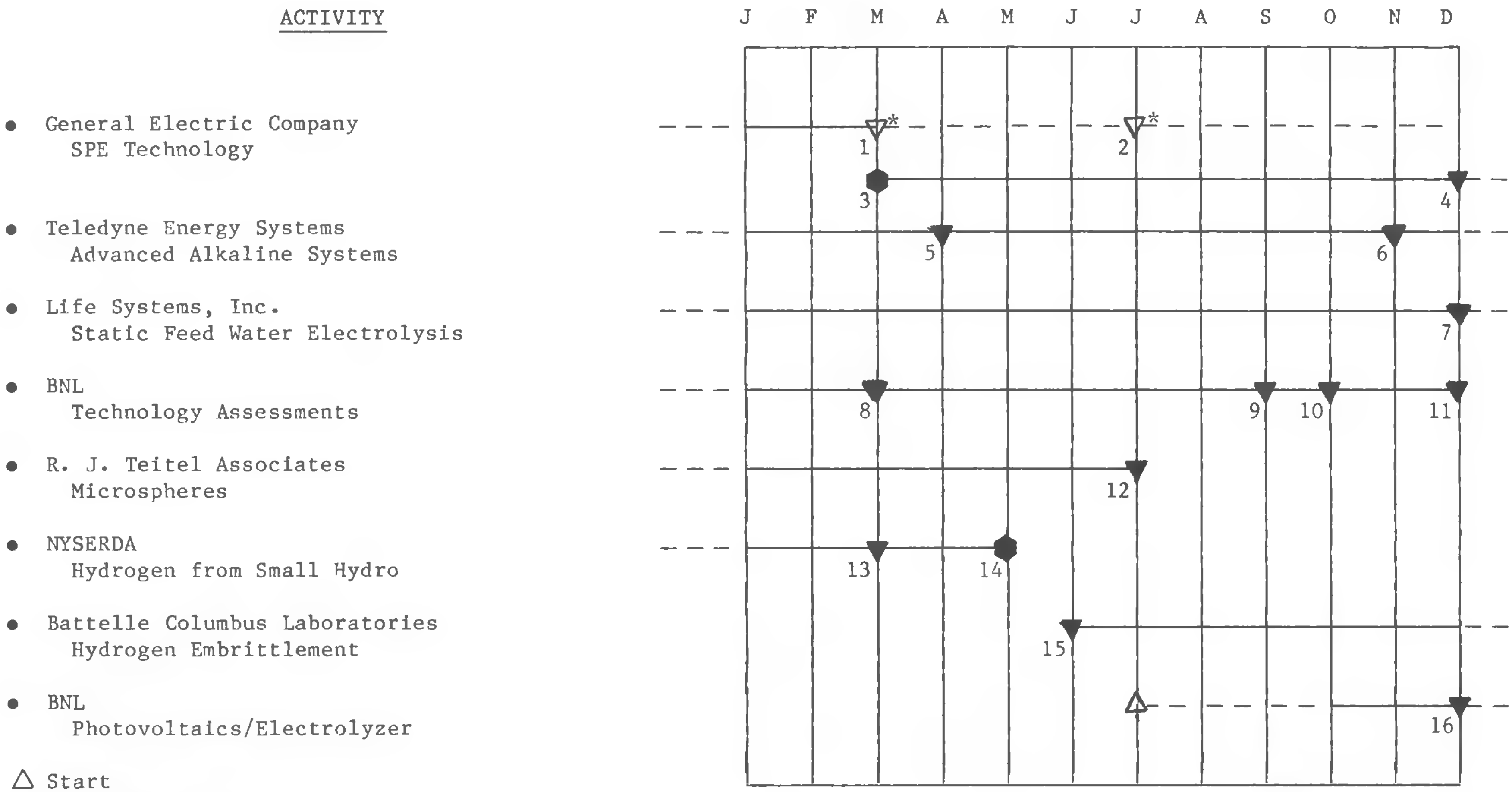
CHEMICAL/HYDROGEN ENERGY SYSTEMS PROGRAM
1981 OBJECTIVES AND ACCOMPLISHMENTS

6. THERMOCHEMICAL HYDROGEN PRODUCTION

GENERAL ATOMIC Sulfur-Iodine Water Splitting Cycle	● To demonstrate the viability of the sulfur/iodine thermochemical water splitting cycle.	● Completed engineering studies on the sulfuric acid/iodine cycle. ● Developed less energy-intensive approach to decomposition of hydrogen iodide.
LOS ALAMOS NATIONAL LABORATORY Thermochemical Processes for H_2 Production	● To address basic chemistry problems associated with thermochemical H_2 production processes.	● Other candidate thermochemical cycles were identified and alternate steps for existing processes were proposed.
JET PROPULSION LABORATORY Advanced H_2 Production Concepts and Processes	● To investigate alternate methods of H_2 production with ties to coal, fusion, or other high temperature systems.	● Critical process parameters in the decomposition of sulfuric acid were identified. ● Preliminary experiments conducted in reacting coal with H_2SO_4.

Figure 1.4

FY 1981 MILESTONE EVENTS

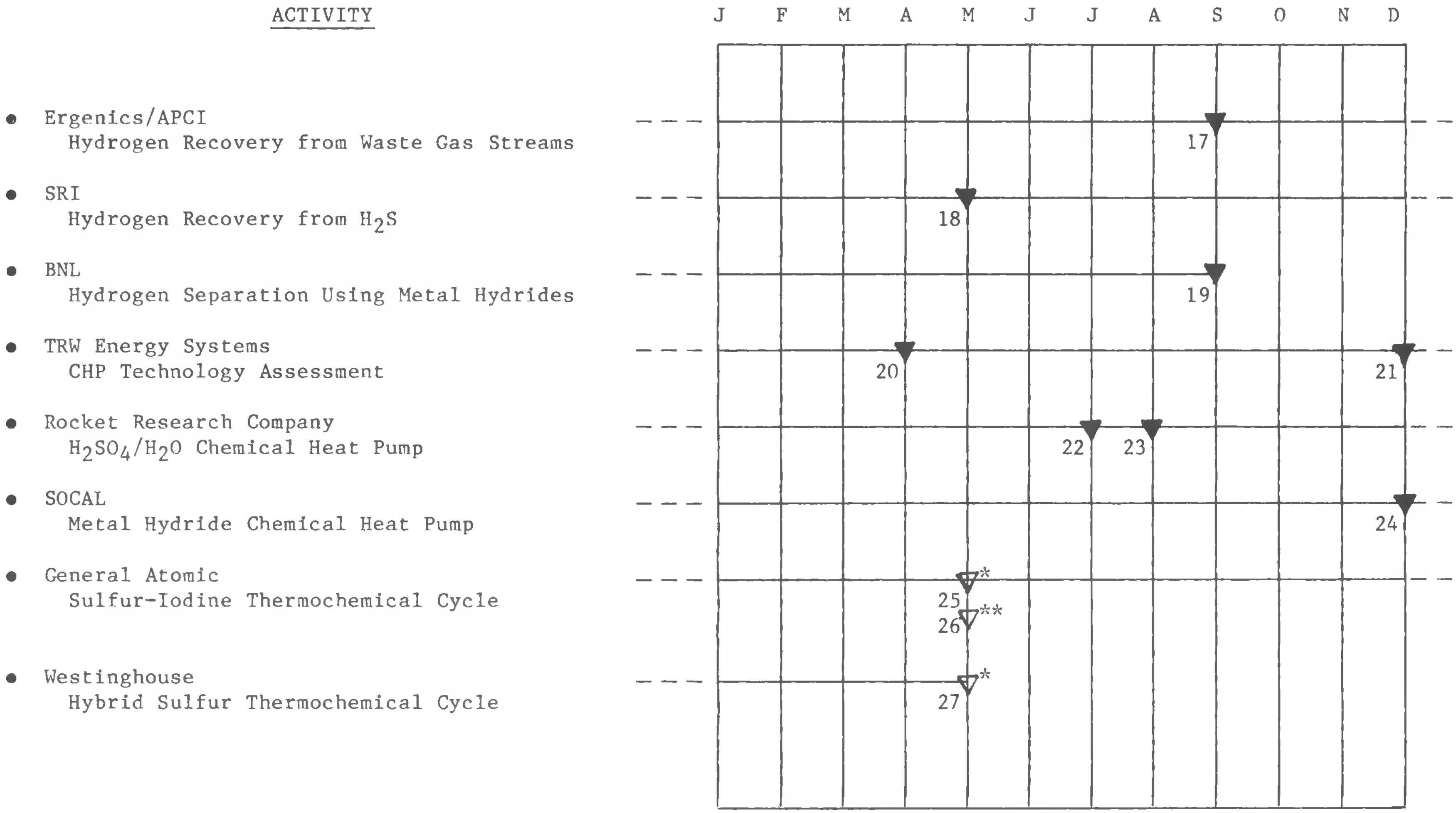


△ Start
▼ Completed
▽ Pending
⬡ Decision
* Milestone deleted because of program redirection
** Milestone deleted because of stop work order
\- Dashed line indicates ongoing program

(See Milestone Legend, pp 24-25)

Figure 1.4

FY 1981 MILESTONE EVENTS



(See Milestone Legend, pp 24-25)

B86
H/81/MS

FY 1981 MILESTONE LEGEND

Milestone No.	Description	Organization
1	Complete fabrication and checkout of 2.5 ft^2 cells with low cost/low loading catalyst	GE
2	Demonstrate improved performance of SPE cells (2.5 ft^2, 50 kW, 1.80 VDC) [Director-controlled milestone]	GE
3	Decision by DOE to redirect GE program, withdraw support for technology developent but continue with SPE technology system study	GE
4	Complete SPE technology system study (GE hardware work continues using DOE-owned equipment)	GE
5	Complete anode/separator testing of advanced alkaline components	TES
6	Define optimum separator for high temperature alkaline systems	TES
7	Demonstrate scale-up potential of static feed concept in 1.0-ft^2 cells	LSI
8	Conduct workshop on natural gas supplementation/ separation concept	BNL
9	Complete systems analysis of natural gas supplementation/H_2 separation concept	BNL
10	Complete limited techno-economic assessments of H_2 recovery from H_2S	BNL
11	Complete limited techno-economic assessments of H_2 separation from waste gas streams	BNL
12	Complete characterization of glass microspheres and issue final report	RJTA
13	Complete site evaluation and engineering design for small hydropower. Final report to be issued through DOE.	NYSERDA
14	Decision not to proceed with small hydro project	NYSERDA
15	Award contract and initiate work to continue H_2 embrittlement of pipeline steels	BNL/BCL

FY 1981 MILESTONE LEGEND (Cont.)

Milestone No.	Description	Organization
16	Establish conceptual design for photovoltaics/advanced electrolyzer integrated system	BNL
17	Complete process analysis of H_2 recovery from waste gas streams	Ergenics/ APCI
18	Establish reaction kinetics for H_2 recovery from H_2S	SRI
19	Complete process design for H_2 recovery from natural gas distribution systems using metal hydrides	BNL
20	Submit draft report on assessment of chemical heat pumps [Major Milestone]	TRW
21	Submit final assessment report on chemical heat pumps including RRC testing	TRW
22	Complete testing of verification test unit H_2SO_4/H_2O CHP	RRC
23	Define work scope for field test of H_2SO_4/H_2O chemical heat pump. [Major Milestone]	BNL/RRC
24	Complete conceptual design and identify metal hydrides for metal hydride chemical heat pump	SOCAL
25	Complete testing of bench-scale sub-unit III [Major Milestone]	GA
26	Complete flow sheet revision for total process sulfur-iodine cycle	GA
27	Review of data from the development of the sulfur dioxide electrolysis cell	Westinghouse

2.0 ELECTROLYTIC HYDROGEN PRODUCTION

Summary

This section describes the progress made by industrial contractors in developing water electrolysis technology, and also the supporting research efforts at BNL and universities. The industrial work includes General Electric's design improvements in the SPE system; Teledyne's identification of better separator for high temperature alkaline electrolysis; and the test results at Life Systems, Inc. on cells scaled up to 1.0 ft^2 using the static feed concept. The research work includes efforts at BNL/Stony Brook in fabricating heterojunction electrodes for photoelectrolysis; characterization of nickel whisker electrodes at the University of Virginia; and the investigation of the SPE/electrocatalyst interface reactions at BNL. The section also contains a summary of the IEA activities related to electrolytic hydrogen production for which BNL has a technical oversight responsibility for the United States through the Department of Energy.

2.1 Design, Development, and Testing of Solid Polymer Electrolyte Water Electrolyzers - General Electric Company

Objective:

During 1981, progress continued at General Electric in the development of Solid Polymer Electrolyte Water Electrolysis for Large Scale Hydrogen Generation. The program sponsored jointly by the Department of Energy, electric utilities, and General Electric Company, was aimed at performance improvement.

The general goals of the program which began in 1976 are:

- Overall system efficiency: 85 to 90%
- System capital cost (battery limits) - $150/kW equivalent (1975 $)
- Cell Life: 40,000 hr
- System life - 20 years
- Scale-up: 2.5 ft^2 to 10 ft^2
- Program Goal: Multi-MW demonstration system

DOE support for hardware scale-up was terminated in late February 1981. Effort on a techno-economic study, IEA participation, and preparation of a final report continued through 1981.

Tasks:

During FY 1981, DOE effort was directed toward performance improvement primarily in the areas of improved cell sealing, reduced cell impedance, and improved water quality and distribution. The tasks were:

1. Improved cell sealing
2. Improved water purity
3. Improved water distribution
4. Reduced cell impedance
5. Techno-economic study
6. IEA participation

Technical Progress:

Task 1 - Sealing

Modifications to the cell sealing configuration were made which incorporated increased collector sealing ridge height and silicone adhesive Teflon tape on the hydrogen side. Improved sealing with this configuration was demonstrated on modules containing six 2.5 ft^2 cells and up to twenty 1-ft^2 cells.

Task 2 - Improved Water Purity

Increased cation deionizer capacity downstream of the mixed bed deionizer was found to be highly effective in trapping any amines resulting from degradation of the anion beads in the mixed bed deionizer.

Task 3 - Improved Water Distribution

In previous 1.5-ft^2 modules, several local areas of membrane attack resulted from non-uniform water distribution which has been caused primarily by incomplete forming of the grooves in the oxygen side flow field of the current collectors. Pre-forming of the titanium foil prior to collector molding has led to significant improvement in the uniformity of the flow field and has reduced the module flow impedance by approximately 40%. A 20-cell, 1 ft^2 module containing these improved collectors is currently on test at 240°F with no indication of membrane attack after 150 hours of operation.

Task 4 - Reduced Cell Impedance

Significant performance improvements as a result of reduced membrane thickness and reduced collector impedance were demonstrated in GFY 81. These improvements are shown in Figure 2.1.

A six-cell module of 2.5-ft^2 cells (DOE 46) using 7-mil-thick solid polymer electrolyte versus the standard 10-mil-thick membrane showed a 75-mV improvement due to reduced membrane resistance plus an approximately 35-mV improvement due to collector resistance decrease.

Subsequently, a 20-cell, 1-ft^2 module (NMPC #1) was assembled utilizing standard 10-mil membrane, but with collectors which had been fabricated using optimized material control procedures. This module demonstrated a 70 mV improvement due to reduced collector resistance. This unit is currently under test at 240°F.

Task 5 - Techno-Economic Study

As part of the 1981 DOE program, a techno-economic study was performed to a) quantify the cost of hydrogen produced by SPE water electrolyzers as a function of design and operational parameters, b) establish the sensitivity of the hydrogen cost to the various parameters, and c) define the operating conditions for the optimum cost of hydrogen. From this study, projected cost information for a 2-MW system has been supplied to Arthur D. Little for a comparative analysis which is being performed by ADL under contract to DOE. A report of the techno-economic study is being issued.

Task 6 - IEA Participation

During 1981, support of the IEA Annex IV program continued through preparation of reports, preparation of information for London workshop, and participation in the IEA planning meeting.

Related Programs

Long-Term Life Testing

Under ESEERCO sponsorship, endurance testing of 1/20-ft^2 laboratory-sized cells has continued throughout the past year. Highlights of this testing are:

- More than 36,000 hours have been achieved to date on a carbon collector cell at 180°F.
- More than 16,000 hours have been accumulated to date on a 4-cell stack of present technology (fluoropolymer/carbon collectors and advanced WE3 oxygen side catalyst) cells at 180°F.
- More than 2,800 hours were achieved on a present technology cell at 240°F.

500-SCFH Prototype System

Figure 2.2 is a photograph of the prototype Model ES-1000 Electrolysis System developed under EPRI and PSE&G sponsorship. The system is designed to accommodate electrolysis modules of 100- 500-SCFH capacity. The prototype system utilizes a 200-SCFH module containing fourteen 1-ft^2 cells. The module is shown in Figure 2.3. The system has completed a 12-week in-house test sequence prior to being installed in the PSE&G Sewaren, New Jersey, facility for two years of field testing. Figure 2.4 shows the module performance to date. The system is designed to operate at 100-psi hydrogen delivery pressure at a current density of 1000 ASF and a 130^o to 140°F module operating temperature range.

Publications:

During 1981, papers on the Solid Polymer Electrolyte Water Electrolysis Program were presented to:

- DOE Chemical/Hydrogen Energy Storage Systems Program Contractors' Review at Arlington, Virginia, in May 1981.
- Input to the IEA London workshop in May 1981 (presented by F. J. Salzano).

- DOE Thermal and Chemical Storage Annual Contractors' Review at Tyson's Corner, Virginia, September 1981.
- Input to IEA Annual Report October 1981.

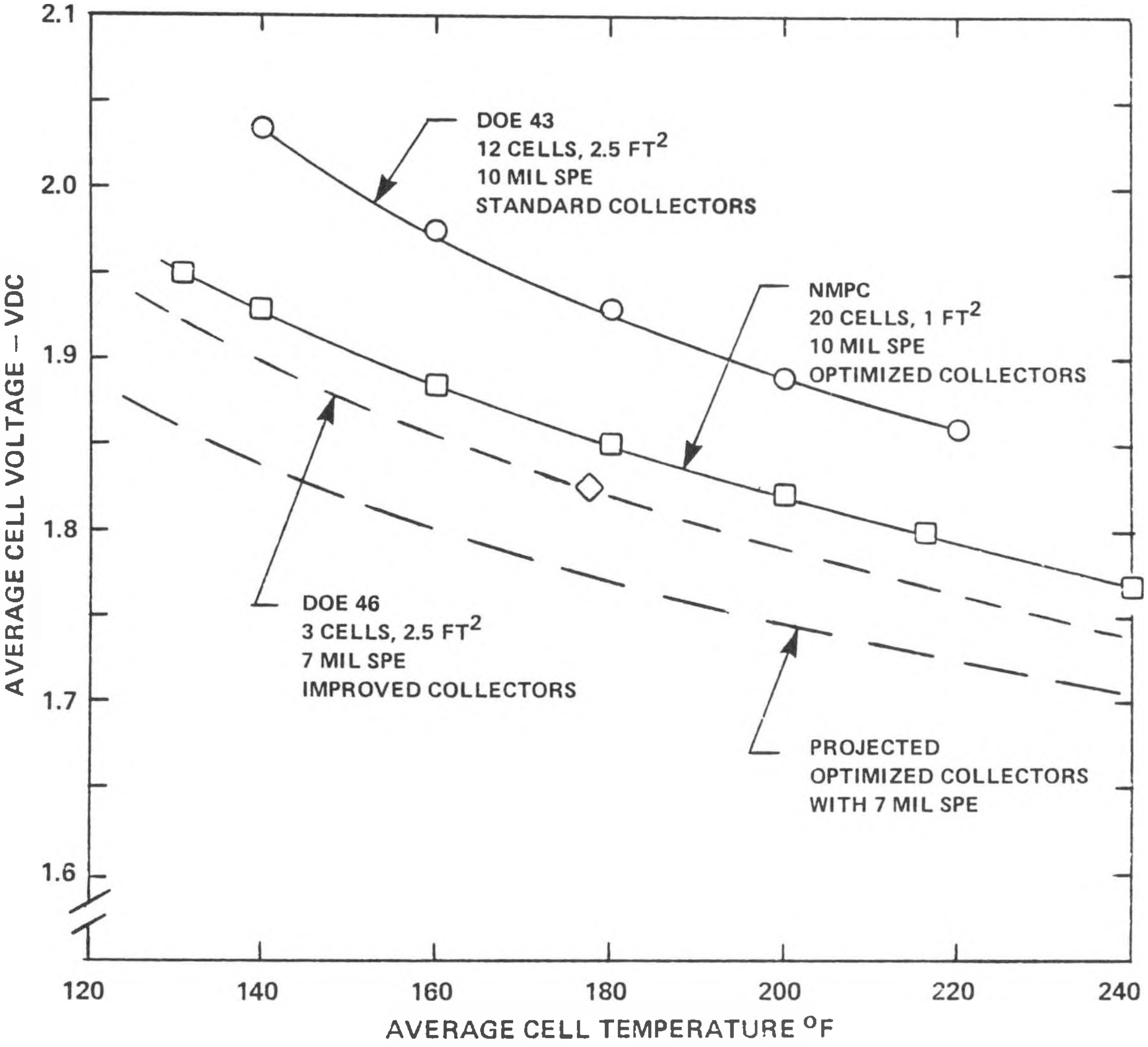


Figure 2.1 Cell Performance vs Temperature - 1000 ASF

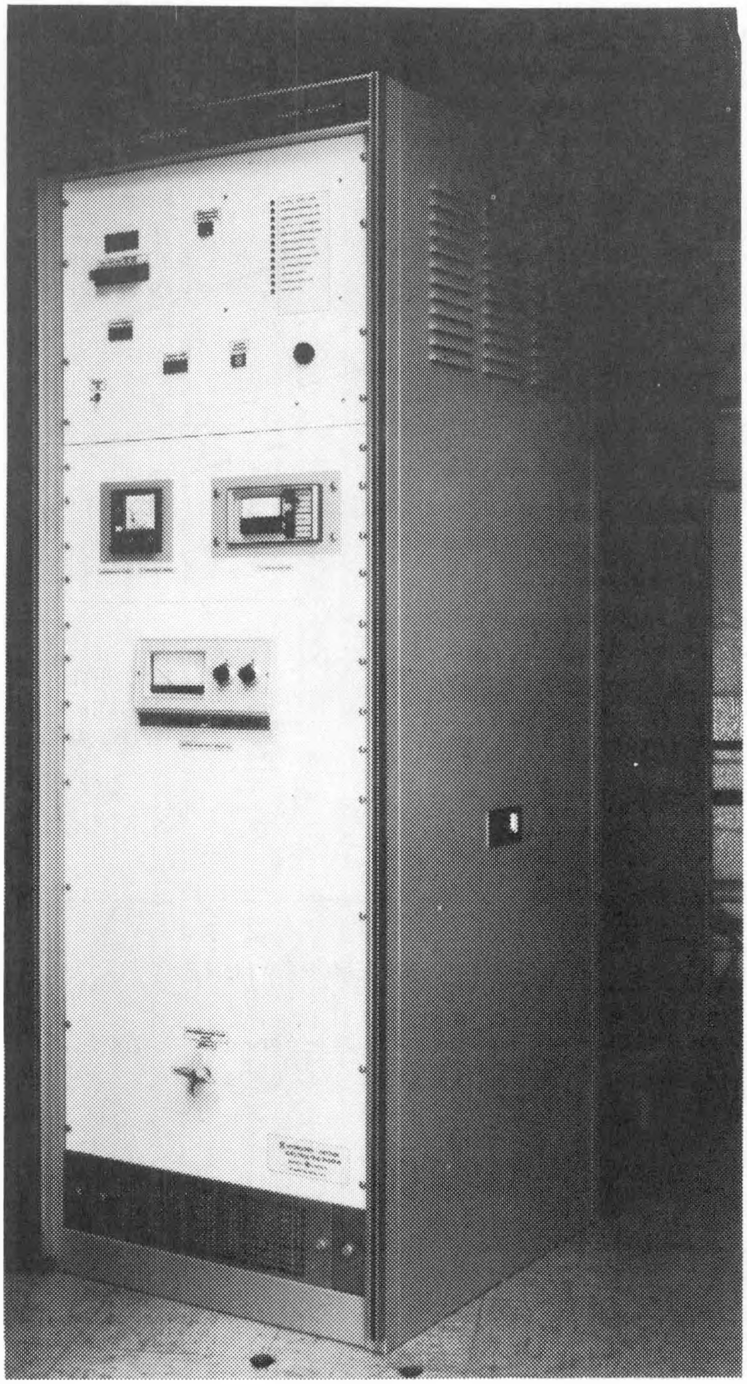


Figure 2.2 500 SCFH SPE Electrolysis System

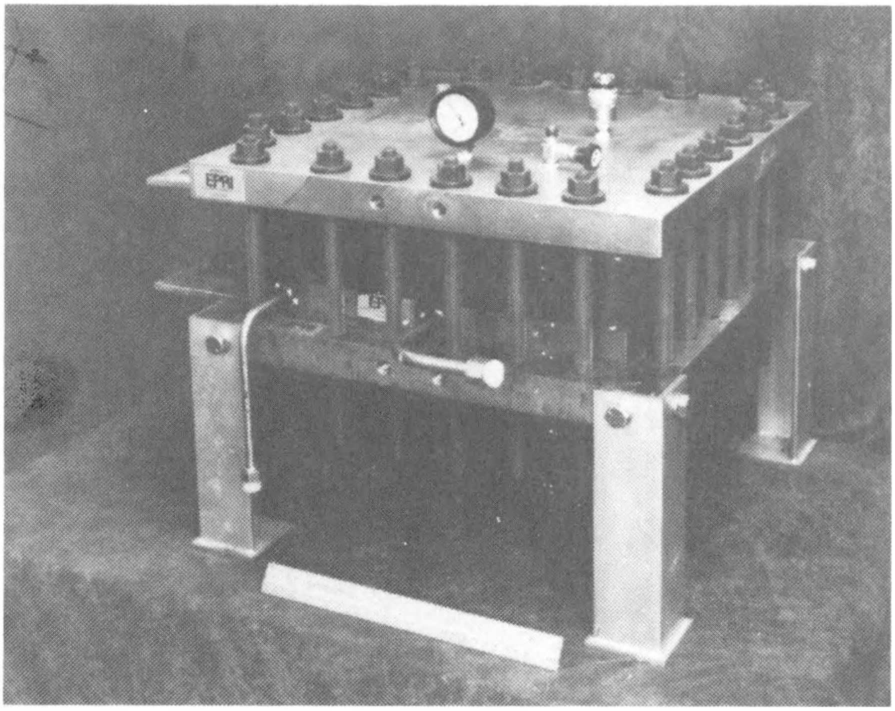


Figure 2.3 200 SCFH (1 ft^2) Water Electrolyzer

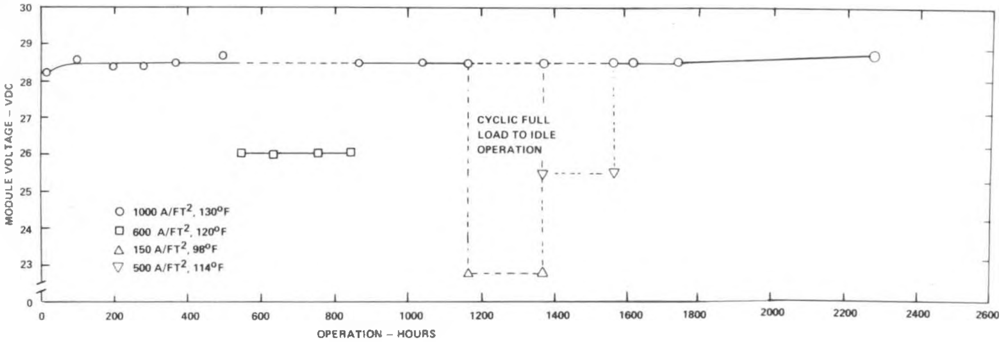


Figure 2.4 Performance vs Time - EPRI/PSE&G 200 SCFH Module Fourteen 1 ft^2 Cells

2.2 Advanced Alkaline Water Electrolyzer Development

Teledyne Energy Systems

Objective:

The overall goal of the program for advanced alkaline water electrolysis at Teledyne is to increase the efficiency of hydrogen production via electrochemical processing from the conventional state-of-the-art (60%) to approaching 100% at cell operating current density of at least 500 mA/cm^2.

During 1981 the objective was to continue investigations with improved electrolysis cell components with emphases on separator and anode technology for operation at 100^o to 125^oC.

Technical Progress:

The tasks are in part a continuation of the previous TES-BNL Contract BNL 507416-S. There, the C-AN cathode (H_2 evolving electrode) electrocatalyst was shown to be very effective in improving hydrogen production efficiency via the dc electrolysis of alkaline solutions. The next aspect to be pursued was the investigation of an improved electrode separator with continued but secondary emphasis placed on new anode (O_2-evolving electrode) structures. The two tasks of the new contract were the technology task and an International Energy Agency (IEA) participation task with respect to the Annex IV of the IEA H_2 research and development program.

The physical characterisitics of an electrode separator for use in the TES electrolysis cell designs are distinct from the separator requirements for other cell designs. The characteristics of major interest are those which affect the electrolyte resistance and therefore include the input electrolysis cell voltage, the gas retention pressure capability, and the mechanical strength in long-term operation at the desired operating temperatures up to 125°C.

During the contract period, a new satisfactory electrode separator has been developed and demonstrated to be comparable to the conventional asbestos electrode separator. Although the piece is not yet optimized, the use of 70 to 80 vol % potassium titanate (K_2TiO_3) fibers with 20 to 30 vol % polybenzimidazole (PBI) fibrid as a binding agent result in a mechanically strong porous board. The potassium hydroxide (KOH) wetted separator is considerably stronger than the equivalent asbestos piece, and the new separator was seen to allow approximately the same input voltage as the conventional asbestos separator while allowing quite high gas retention pressure. Ambient temperature stress relaxation testing showed the new composite to be slightly superior to the commercially available asbestos piece.

The experimental project has also demonstrated that "pure" porous PBI separators could be fabricated at a high density which allows a somewhat satisfactory stress relaxation capability. These high density pure PBI separators did, however, require higher input voltage such that equivalent performance could be projected if the PBI separator cell operation was at 125°C and the commercial asbestos cell operation was at 90°C. The addition of moderate amounts of K_2TiO_3 to the porous PBI separator did not significantly improve the test results relative to the "pure" PBI separator.

A significant experiment involving higher surface area experimental anodes prepared by the MPD Technology Corporation was performed. This experiment suggests the approach necessary for attaining greater than 100 mV input voltage savings. Anode test results show the positive benefits of the use of perovskite catalyst coatings placed on the conventional nickel wire screen anode. The perovskite coatings were prepared by Professor Giorgio Fiori of the University of Milan as a result of discussions following the IEA technical review meeting at Tokyo in June 1980.

The second task of the contract (considered the IEA documentation task) resulted in the preparation of two papers for the Water Electrolysis Workshop held in London on 27-29 May 1981. The two papers cover the TES/BNL contract status report as of approximately March 1981, and an outline on the economic factors involved in H_2 production; a workshop section lead-in paper requested by BNL. An IEA annual report draft was submitted to BNL at the end of September 1981 containing essentially the information presented in the DOE annual contractors' review summary paper.

With a PBI/K_2TiO_3 separator established that should survive the corrosive environment of 125°C, KOH electrolyte saturated with H_2 on one side of the separator and O_2 on the other side, all of the components for the advanced technology have been identified and individually demonstrated in the 50 cm^2 minicell hardware. Additional optimization efforts are required and should yield some limited but positive voltage gains. The next logical steps for development are (a) the wedding of these new technologies in the minicell.

with extended operation demonstrated up to 100°C (current minicell equipment limitation), (b) fabrication of a larger area advanced technology electrolysis module to be included within an advanced Industrial Test Bed (ITB) for testing at 100°C and above, and (c) two parallel design investigations which should lead to lower cost, more effective electrolysis modules and systems.

Publications:

Murray, J. N. Advanced alkaline water electrolysis. Proc. DOE Thermal and Chemical Storage Annual Contractors' Review Meeting, Tyson's Corner, Virginia, September 1981.

2.3 Development of Static Feed water Electrolysis for Large-Scale Hydrogen Production - Life Systems, Inc.

Objective:

The objective of this program is to investigate the applicability of the Static Feed water Electrolysis System (SFWES) to bulk hydrogen generation in large-size systems for industrial uses.

Specifically, this program is to demonstrate the inherent capability of the alkaline electrolyte-based SFWES to generate low cost hydrogen for chemical storage/industrial chemical applications.

Reductions in capital and operating costs will be addressed through operation at high current density (1000 mA/cm^2), cell area scale-up demonstrations and studies (1 to 5 ft^2), demonstration of low cell voltage operation, and testing with contaminated feed water (e.g., simulated seawater) to eliminate water treatment expendables and equipment.

Tasks:

Task 1. Conduct a series of experiments to demonstrate the upper current densities possible with the static feedwater concept.

Task 2. Conduct a series of experiments that will demonstrate the ability of the static feed water electrolysis cells to use contaminated water and, specifically, simulated seawater.

Task 3. Demonstrate the capability of the contractor's cell design to be scaled from 0.1-ft^2 area to 1.0-ft^2 area, or larger.

Task 4. Establish a sequence to be followed in future scale-up of electrode area and number of cells per module.

Technical Progress:

Task 1. Elevated Current Density Investigation: The first step was to determine if any limit in water vapor transport mechanisms would be encountered up to the goal of 1000 ASF. Two anodes, one an intermediate (WAB-1) and the other a high performance (WAB-6) type, were tested. The results for ambient pressure 180°F operation are shown in Figure 2.5. To determine the contribution of the individual electrodes (i.e., anode and cathode) to the overall cell voltage and to observe possible performance limits at either electrode, half-cell voltages vs the standard hydrogen electrode (SHE) were also measured. These data are shown in Figure 2.6. Again, no limits with respect to current density for the level investigated were observed.

Task 2. Operation with Contaminated Water: Operation with water requiring minimum pretreatment or operation with brackish or seawater directly would greatly reduce capital and operating costs. The static feed cell configuration has the potential for this mode of operation since the feed water is kept isolated from the electrodes, i.e., with only water in vapor form being transported to the electrolysis site.

As a first step to eliminate water purification, Life Systems had already demonstrated the ability of its static feed water electrolysis system to operate using deionized feed water (as opposed to an aqueous solution of potassium hydroxide) in the water feed compartment. The next step, was to replace the deionized water in the water feed compartment with tap water, brackish water, and/or simulated seawater.

Two cells were tested. One of the cells used a simulated seawater mix (used for salt water aquariums) as its water source; the other cell used untreated city tap water. The testing of the untreated city tap water was completed under a separate contract with NASA Ames Research Center, but the results were made available to BNL. The performance of these two cells was very nearly equal to the performance observed in baseline cells at similar operating conditions. A total of 1720 hours of operation were accumulated with the tap water cell and 1150 hours with the seawater cell. Performance levels versus time for the two cells are shown in Figures 2.7 and 2.8. Testing was halted to inspect the cells. No abnormalities were observed with the tap water cell. The cell using simulated seawater showed some small amount of corrosion on the nickel anode current collector and anode. The corrosion may have been caused by an accidental flooding (with salt water) of the cell 80 hours into the test. More testing has been recommended in this area.

Task 3. Cell Area Scale-Up: Sizing calculations for the SFWES style concept have been completed for 1.0-, 5.0-, and 10-ft^2 cells. In parallel, Life Systems fabricated actual scaled-up cell hardware having an active area ten times the present baseline, or 1.0 ft^2.

The 1.0-ft^2 cell design characteristics are:

- Active cell area - 1.0 ft^2
- Advanced electrodes (WAB-1 and WCB-2)
- Nominal current density - 400 ASF

- Operating temperature - 200°F
- Operating pressure - <550 psig

The fully assembled 1.0-ft^2 single cell is shown in Figure 2.9.

The test program for the 1.0-ft^2 single cell consisted of initial checkout testing, 300 hours of parametric testing at 100 to 400 ASF, 100 hours of endurance testing at a constant set of conditions, and 200 hours of exploratory testing at 400 to 800 ASF. The cell performance of the 1.0-ft^2 cell using the intermediate performance level anode (WAB-1) electrode is shown in Figure 2.10.

Figure 2.10 shows the cell scale-up activities have been successful in that the performance of the 1.0 ft^2 cell is comparable to the performance of a 0.1-ft^2 cell which uses advanced electrodes of the same style. The slope of the 1.0-ft^2 cell performance curve is slightly steeper which indicates a slightly higher IR voltage loss than encountered at the smaller cell area.

The results of the parametric and exploratory testing shown in Figure 2.11 indicate that the overall scale-up of the static feed concept, and cell configuration, with the "first generation" hardware has demonstrated that the static feed cell is capable of large-scale electrolysis of water at high current density. No major drawbacks or problems have been identified through current testing. Test experience with the 1.0-ft^2 single cell has uncovered some improvements needed which will be incorporated in second generation cell hardware to advance the static feed cell design toward a large-scale H_2 production application.

Task 4. In this task the future scale-up sequence to be followed for the static feedwater electrolysis concept was established. The goal was low development risk and minimum development cost. The results of this task were compiled into a single scale-up sequence report which discusses, in detail, various aspects of the scale-up process. Some of the factors discussed in the scale-up sequence report were:

1. Cost
    - The impact of electricity cost
    - The maximum allowable capital cost
    - The maximum allowable maintenance cost
2. Electrolyzer Stack
    - The ability to fabricate electrodes of larger sizes (e.g., up to 10 ft^2)

- The ability to prepare matrices similar in size to the electrodes
- The ability to stack a large number of cells in series
- The ability to to construct low resistance, low cost bipolar current collectors

3. System Level
   - The ability to scale up the peripheral system components
   - The ability to simplify the system
     - Component elimination
     - Low water quality
     - Low parasitic power

The projected overall scale-up sequence proposed for LSI's electrolyzer is shown in Figure 2.12. As shown in Figure 2.12 the work at the 0.1-ft^2 level would continue in the areas of contaminated water operation, high pressure and temperature operation, and high current density operation. Technology advancements in these areas in parallel with the scale-up will provide continuous information that will affect the economics of H_2 production. Table 2.1 summarizes the manufacturing capabilities/requirements for the electrolyzer cells.

Technical Problems:

There are no major problems with this work.

Publications:

Schubert, F.H. Static feed water electrolysis for large scale hydrogen generation. Proc. DOE Thermal and Chemical Storage Annual Contractors' Review Meeting, McLean, Virginia, October 1980.

Schubert, F.H. Static feed water electrolysis for large scale hydrogen generation. Proc. Chemical/Hydrogen Energy Systems Program Semiannual Contractors' Review Meeting, Arlington, Virginia, May 1981.

Schubert, F.H. and Burke, K.A. Static feed water electrolysis for large scale hydrogen generation. Proc. DOE Thermal and Chemical Storage Annual Contractors' Review Meeting, Tyson's Corner, Virginia, September 1981.

TABLE 2.1
ELECTROLYZER MANUFACTURING CAPABILITIES/REQUIREMENTS

	Cell Size, ft^2				Comments
	0.1	1.0	5.0	10.0	
Electrodes	x[a]	x	Added manufacturing facilities		All manufactured at LSI
Matrices	x	x	Added manufacturing facilities		Added large fixture for 5- and 10-ft^2 matrices
Current Collector	x	Fixtures needed Collectors in multicell modules[b]			Outside vendor
Insulation Plates	x	x	x	x	Outside vendor
Endplates	x	x	x	x	Outside vendor
O-rings	x	x	x	x	Outside vendor
Support Screens	x	x	x	x	Manufactured at LSI no additional capability needed
Cell Frame	x	3 Molds for cell frame (one for each cell size)[c]			

[a] x = capability already exists.
[b] Three welding fixtures needed for 1.0, 5.0, and 10 ft^2.
[c] Molds will be used toward the end of the development phase. Early development work will use machined parts.

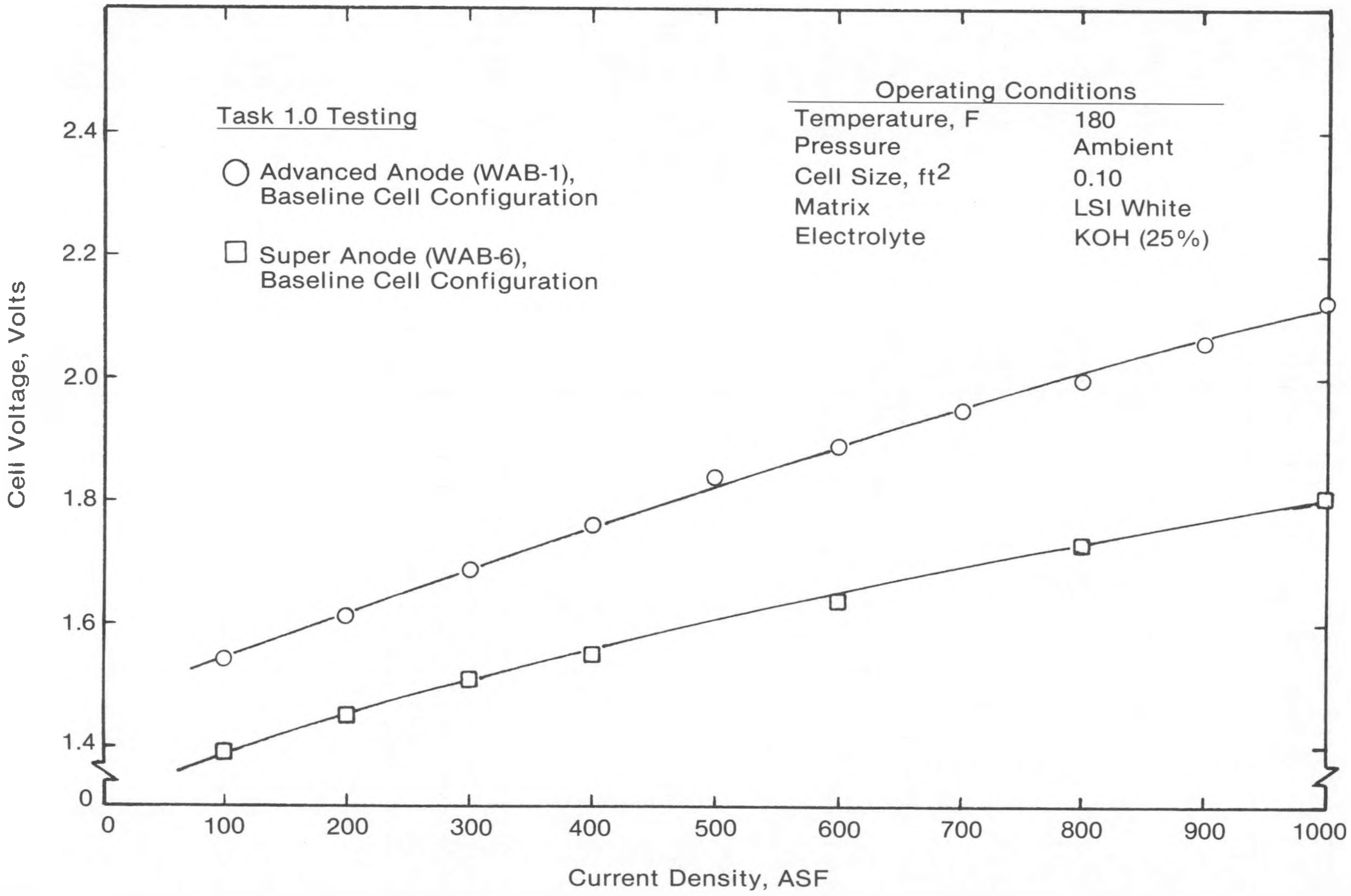


Figure 2.5 Cell Voltage vs Current Density

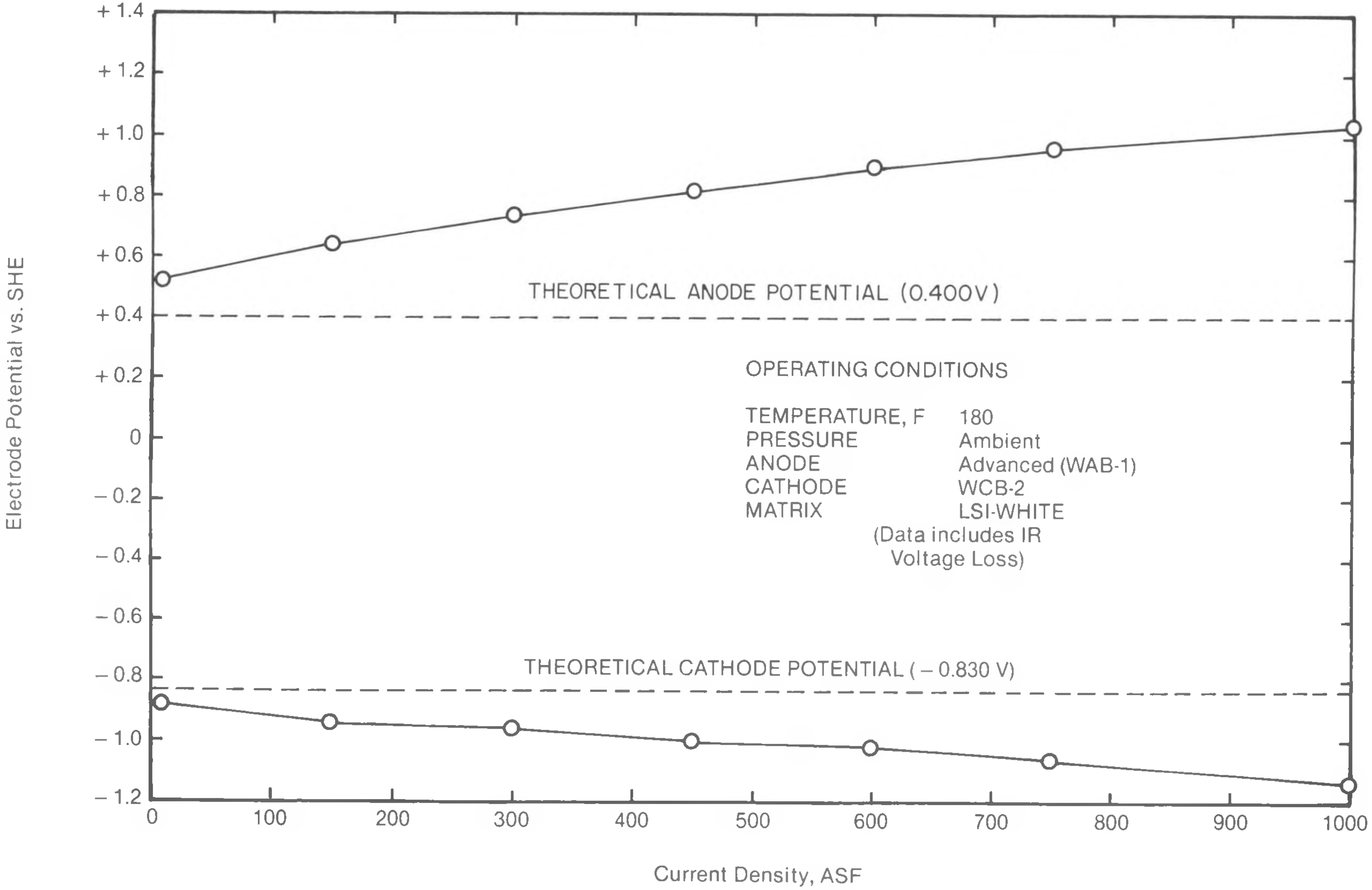


Figure 2.6 Half-Cell Potentials vs Current Density

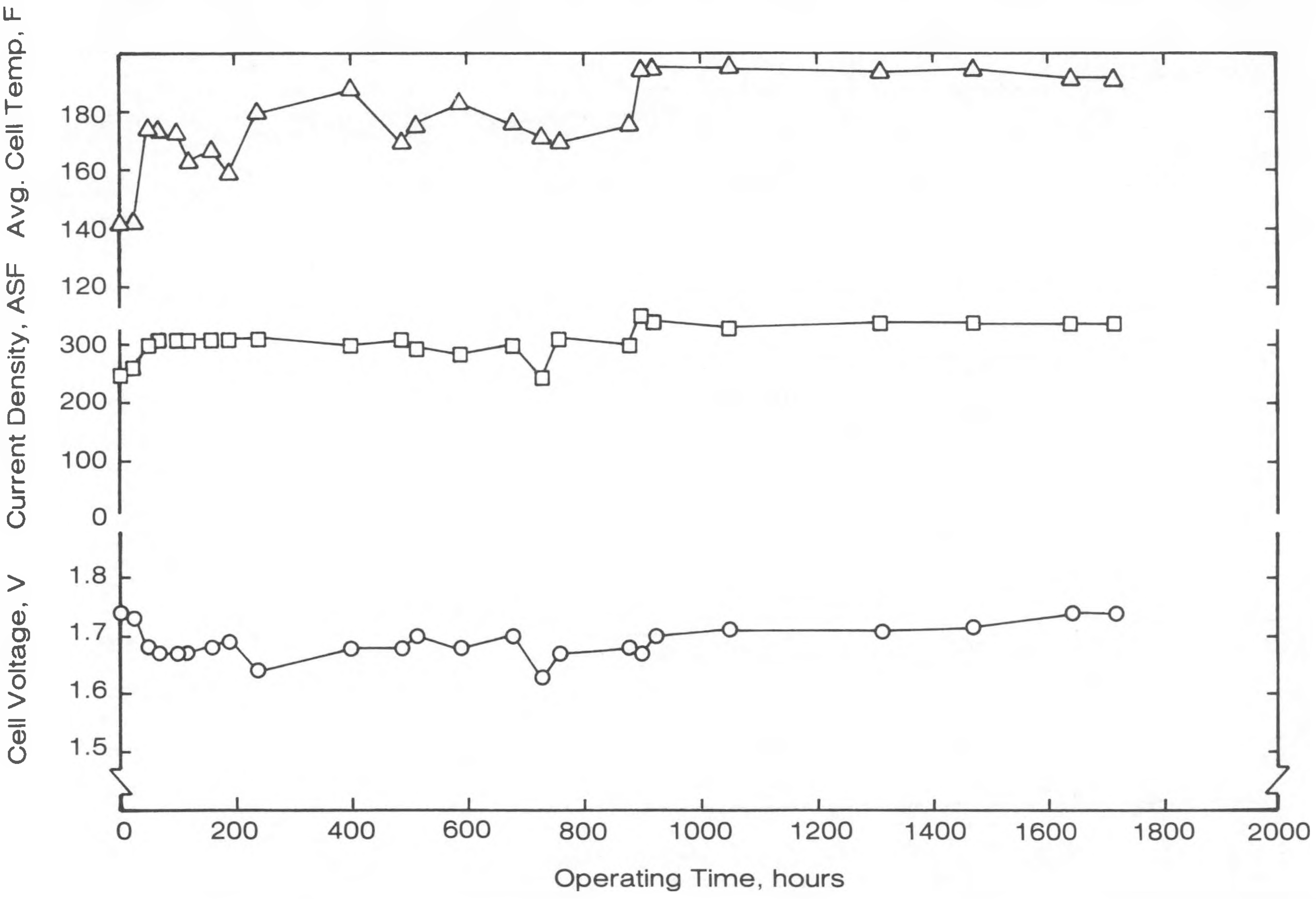


Figure 2.7 Cell Performance vs Time Using Tap Water Feed

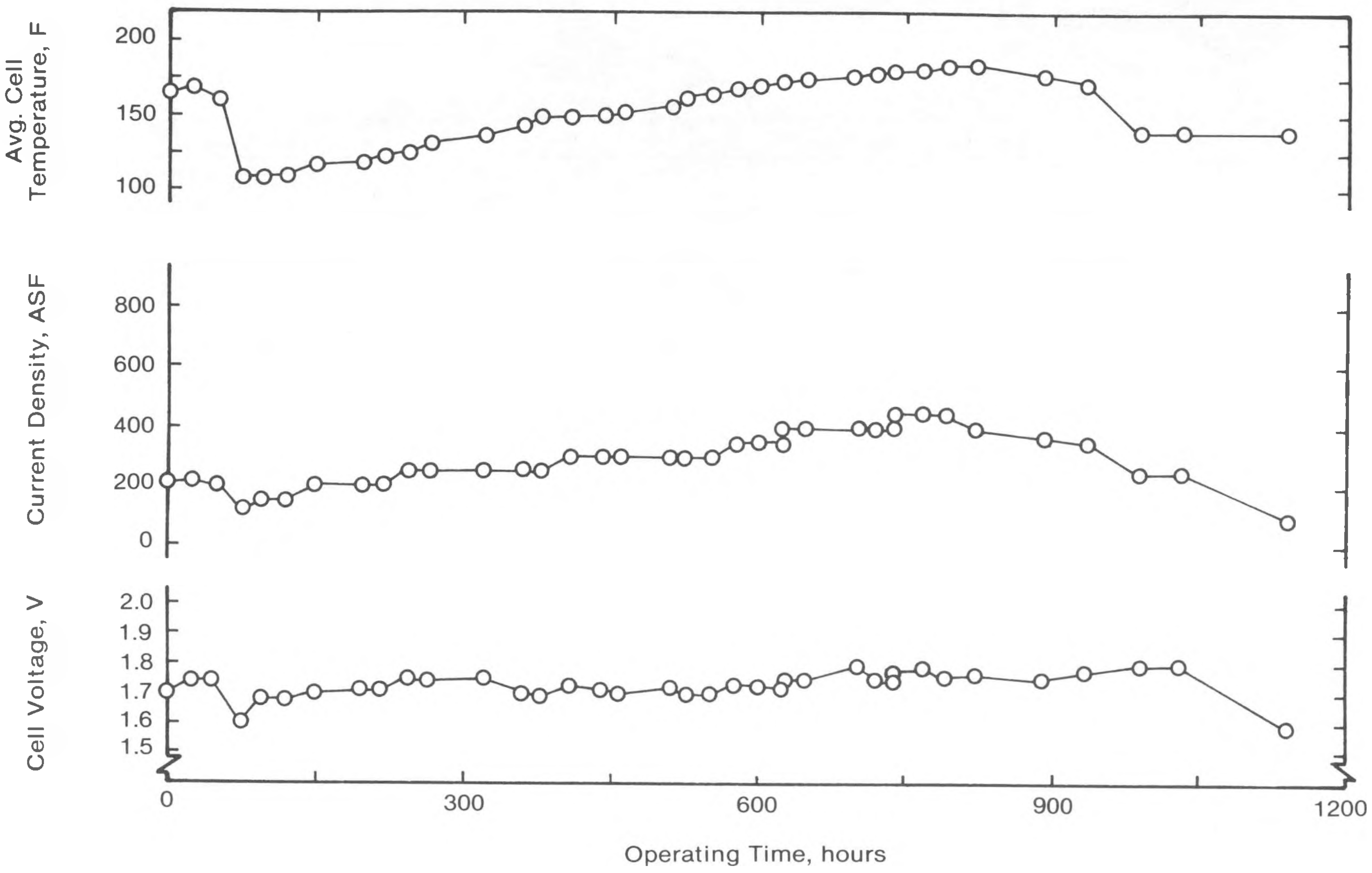


Figure 2.8 Cell Performance vs Time Using Simulated Sea Water Feed

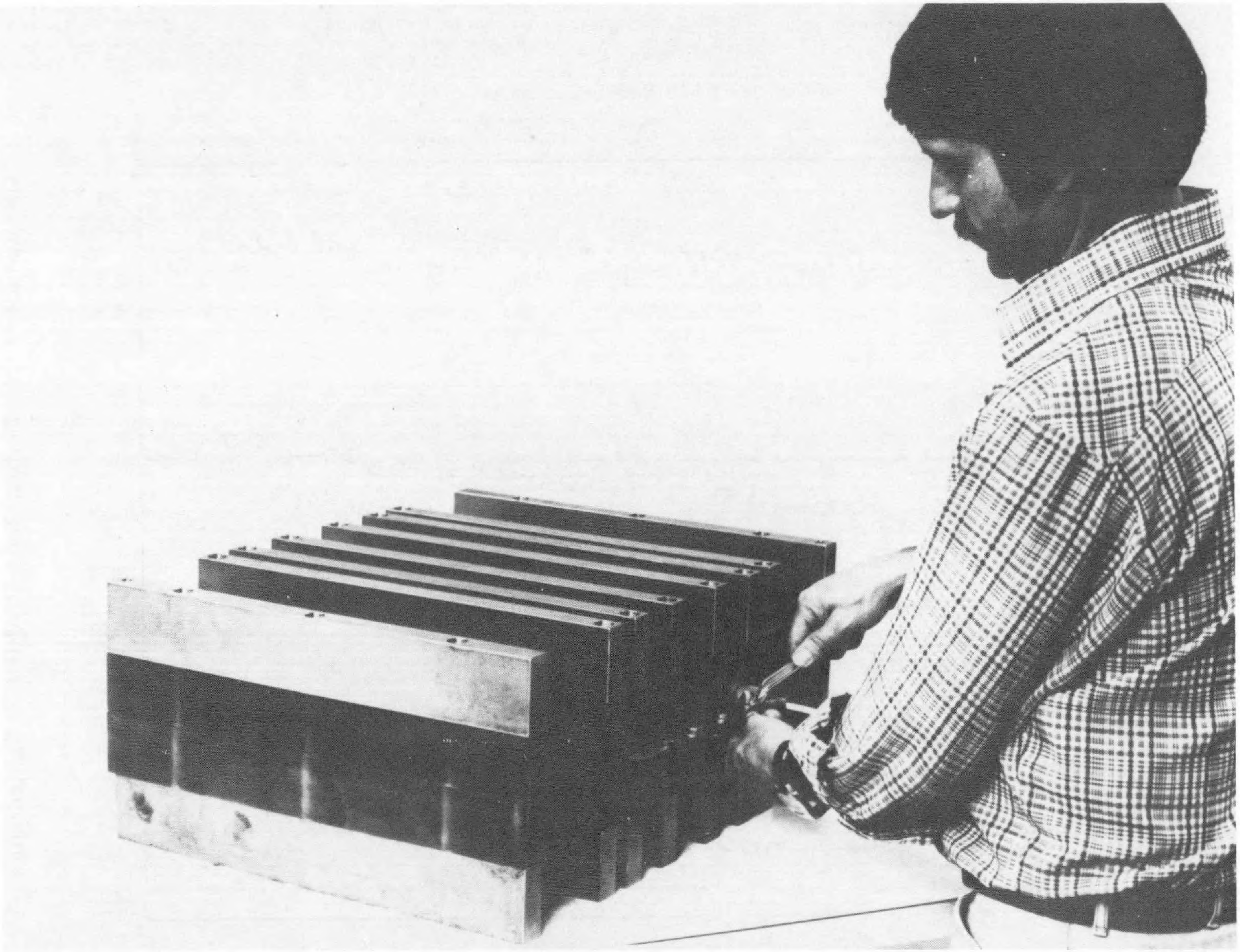


Figure 2.9 Assembled 1.0 ft^2 Single Cell

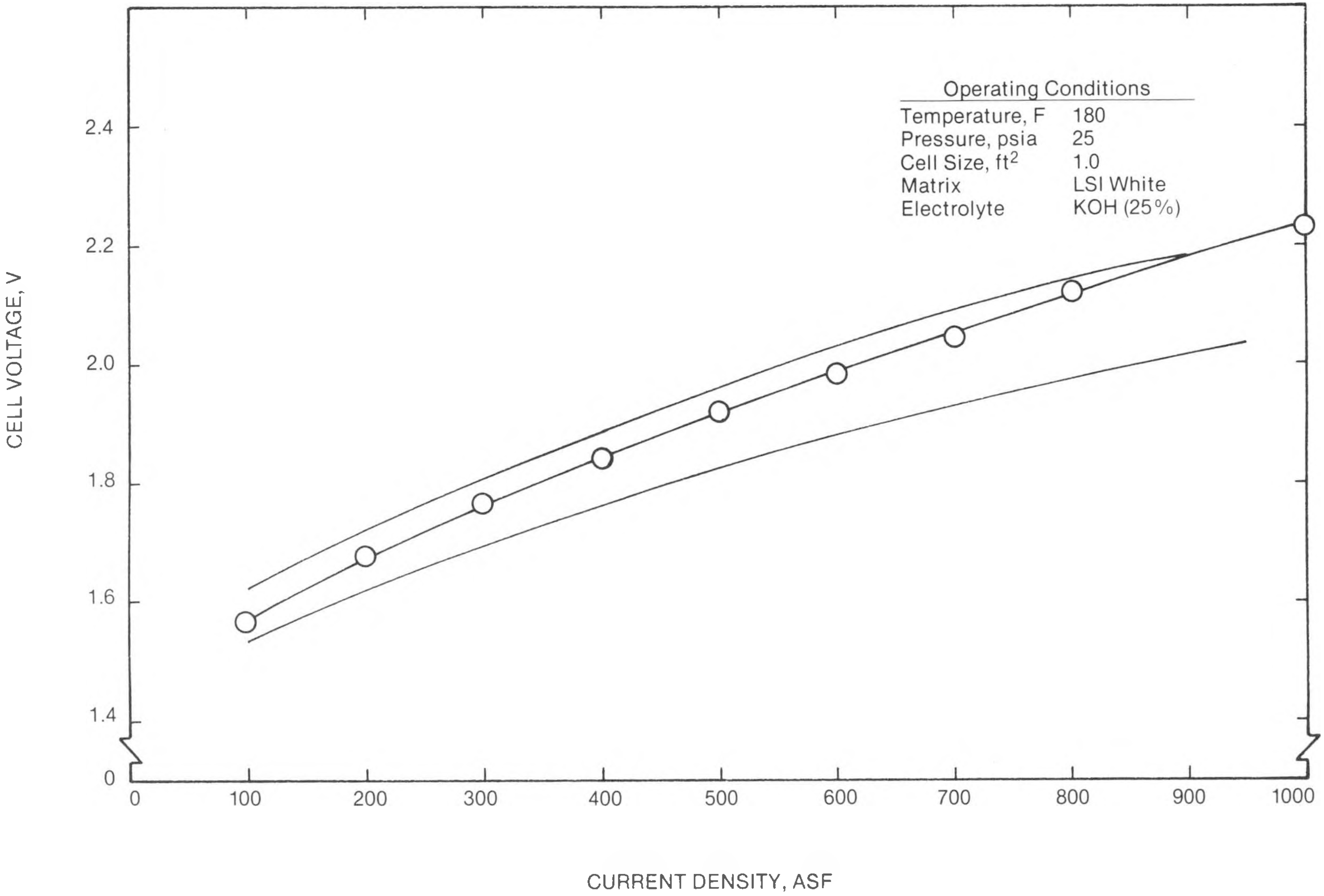


Figure 2.10 Cell Voltage vs Current Density - 1.0 ft^2 Single Cell

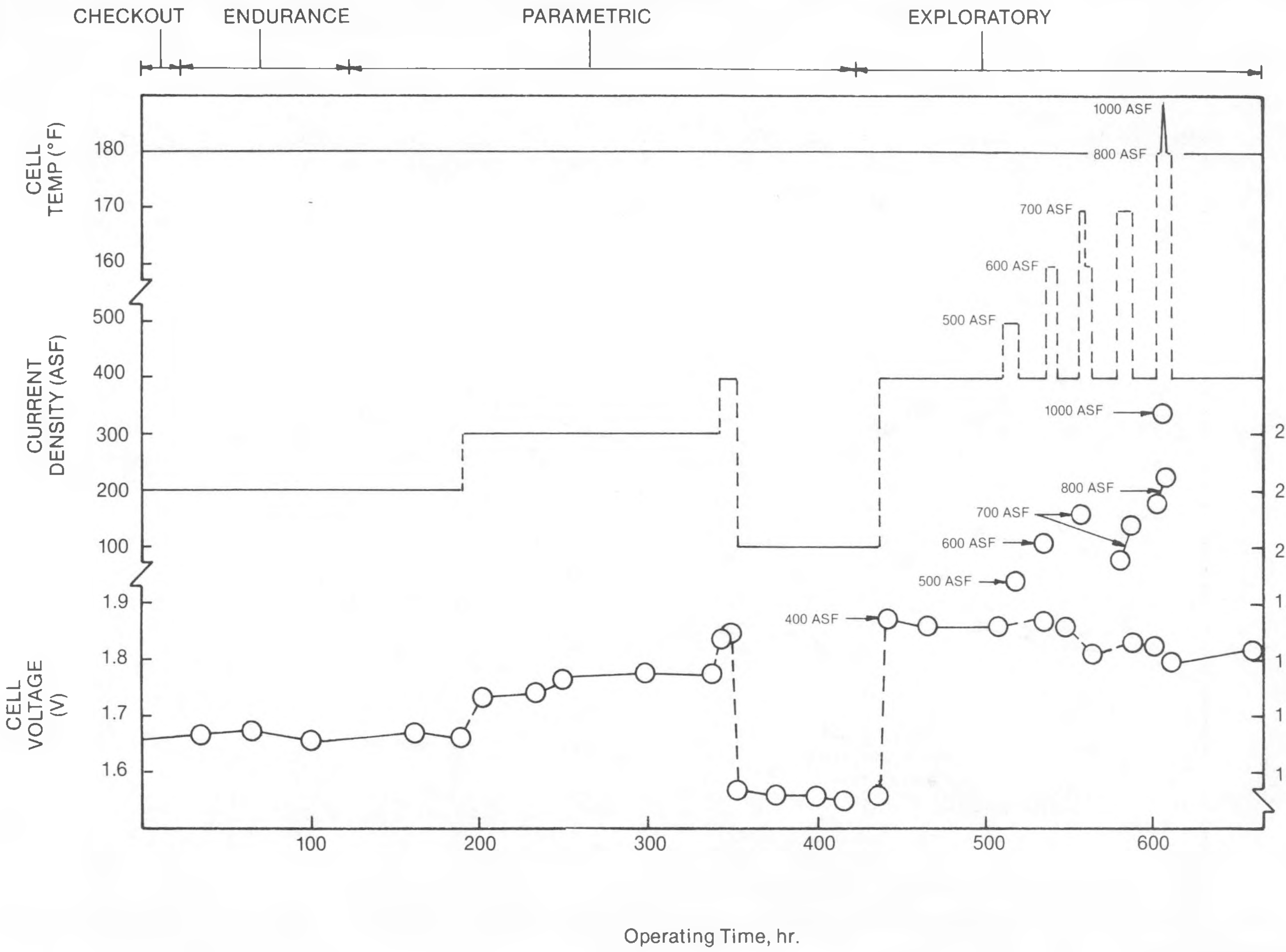


Figure 2.11 1.0 ft^2 Single-Cell Performance vs Time

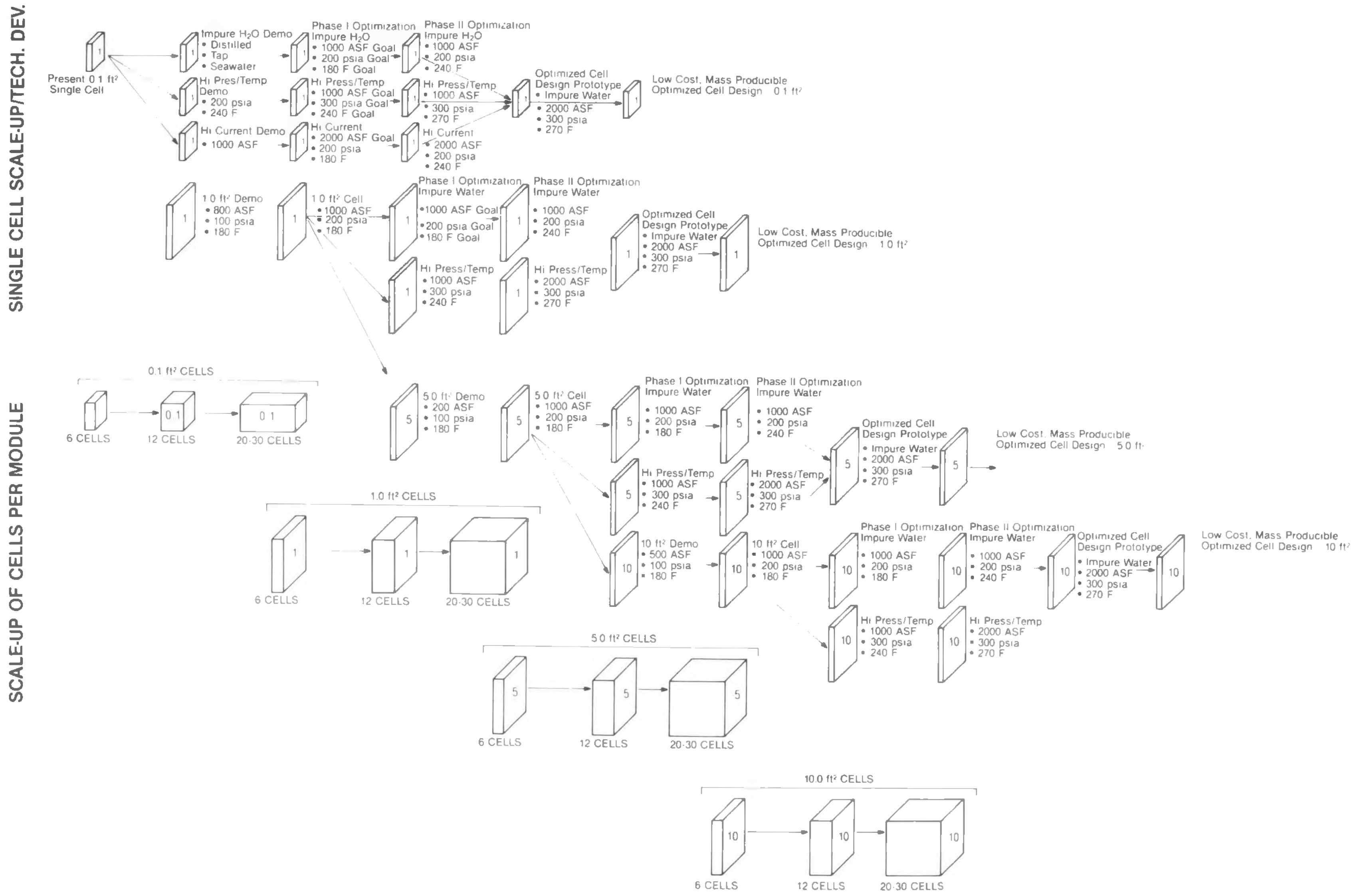


Figure 2.12 Static Feed Water Electrolysis Scale-Up Sequence

2.4 Electrochemical Evaluation of Nickel Whisker Electrodes

University of Virginia

Objective:

Previous research performed at the University of Virginia Electrochemistry Laboratory has indicated an improvement in the energy efficiency of the hydrogen evolution reaction for porous nickel whisker electrodes as compared to nickel 200 screens on an apparent area basis. It was not determined whether the energy efficiency gained by the use of sintered nickel whisker electrodes was due to their extremely high surface area or to some truly innate electrocatalytic property. The fundamental question of specific electrocatalytic behavior of nickel whisker electrodes, independent of their high surface area, is the principal objective of this research. As a result, standard quantitative comparative tests for electrocatalysis need to be developed and some basic questions concerning what determines an electrocatalyst are considered.

Tasks/Technical Progress:

Electrocatalytic behavior should be determined on the basis of true surface area. Therefore, if the electrocatalytic abilities of different electrodes are to be compared, a reproducible method for determining effective surface area is required. In this investigation, the electrocatalytic ability of the nickel whiskers was compared to that of conventional nickel 200. To measure electrochemical surface area, a low amplitude cyclic voltammetric surface area analysis was employed. This type of analysis was applied specifically for nickel in KOH; however, the technique is not necessarily limited to these conditions.

As an initial procedure, using cyclic voltammetry, the potential of the experimental electrode vs a calomel reference electrode was varied through a relatively large potential range, from hydrogen evolution to oxygen evolution, in a 30 wt % KOH electrolyte. The corresponding current passed during the potential sweep between the electrode, and the auxiliary counter electrode was monitored. This initial screening step was done in an effort to find a potential range where no reaction is occurring or where there is a minimum of faradaic current. On the current vs potential plot, this criterion corresponds to two parallel lines of low current value when swept in the cathodic and anodic directions, as shown in Figure 2.13.

Since nickel converts spontaneously to nickel hydroxide when immersed in KOH, it is difficult to obtain a non-faradaic region on a pure nickel surface in KOH. Even when the nickel is run at a potential cathodic to hydroxide formation in a region where thermodynamically no reaction should occur and nickel hydroxide should be reduced to pure nickel, some faradaic current is observed. Whether this current is due to impurities, unreduced hydroxide, absorbed hydrogen, or some other unknown reaction has not been determined. Nevertheless, the only apparent non-faradaic region observed for nickel in KOH is in the potential range of -450 to -400 mV vs SCE, which corresponds to a nickel hydroxide surface. This range was chosen for surface area calculations in the present work since it allowed a reproducible set of measurements with reasonable values on polished nickel 200 surfaces.

In a non-faradaic region, the current passed corresponds primarily to the charging and discharging of the electrode surface or double layer. In this region the current vs potential plot should be a perfect rectangle for a constant sweep rate. The shape of the plot is important because it indicates the presence of a true non-faradaic region in which the relation $C = I/(dv/dt)$ is valid. This allows measurement of the double layer capacitance (C) and is done by plotting the current vs potential sweep rate (dv/dt). The slope of this plot is the value of the capacitance, as seen in Figure 2.14. Once the capacitance of an electrode is found, it can be compared with the standard capacitance of the mercury electrode where no roughness is assumed. The capacitance value of the mercury electrode is taken as 20 $\mu F/cm^2$. Therefore, if a capacitance value of 40 μF results from a measurement, an active electrochemical surface area of 2 cm^2 is calculated by assuming a specific capacitance of 20 $\mu F/cm^2$. Dividing this area by the apparent geometric surface area gives an idea of the comparative roughness of the electrode surface. The sensitivity of this type of area measurement can be demonstrated by measurements performed on a .005-cm^2 apparent area electrode. Variations in measured surface area due to polishing with various grades of abrasive paper were determined and scanning electron micrographs were obtained.

Once the area of an electrode is known to an acceptable level of reproducibility, the electrocatalytic parameters can be determined by the generation of a Tafel plot. The slope of the log current vs potential voltage plot, and the exchange current density, are the important parameters in determining electrocatalysis. Tafel plots obtained for nickel 200, determined galvanostatically, are quite reproducible. With proper IR compensation, these plots are linear over six decades of current density as calculated using linear regression. A technique has been developed in this laboratory which allows a more precise IR compensation. A typical Tafel plot is shown in Figure 2.15. Table 2.2 shows that the average Tafel slope obtained for nickel 200 was 135 mV/decade and the average i_o was equal to 1.2×10^{-6} A/cm^2.

Now that surface area can be reproducibly measured and the electrocatalytic ability of conventional nickel 200 can be determined with reasonable precision, a comparison with polycrystalline nickel whiskers can be made. It was necessary to make a planar nickel whisker electrode which can be polished smooth and which has no gas masking problems due to porosity. This was accomplished by embedding the nickel whiskers in an epoxy resin and then polishing to a smooth planar surface.

Nickel Whisker electrodes of approximately 1-cm^2 true surface area were evaluated for electrocatalytic ability under identical experimental conditions as the conventional nickel 200. An average exchange current density of 8.2×10^{-7} A/cm^2 with an average Tafel slope of 133 mV/decade was obtained, as shown in Table 2.3. Therefore, no significant difference in electrocatalytic ability between the two types of nickel was observed. Annealed nickel 200, which has considerably larger grains and less strain energy than non-heat treated nickel 200 also exhibited essentially the same electrocatalytic properties as those already mentioned. From these evaluations of the electrocatalytic ability of extremely different types of nickel microstructure, it must be concluded that the increased energy of crystal imperfections does little to enhance the hydrogen evolving capabilities of nickel electrodes in KOH. Apparently, current-voltage improvements in alkaline electrolysis using nickel electrodes will be realized mainly by increases in electrode surface area.

Publications:

Cahen, G. L., Moran, P. J., Scribner, L. L., and Stoner, G. E. Investigation of nickel whisker networks for hydrogen and oxygen evolution. Accepted J. Electrochem. Soc. (September 1981).

TABLE 2.2
NICKEL 200 TAFEL PLOTS*

Date	Tafel Slope (mV/Decade)	Exchange Current Density (A/cm^2)	Linear Fit (0 - 1)	Experimental Conditions
4/8	150	2.1×10^{-6}	.9930	N_2 purge, Teflon airtight cell, low [Fe] KOH, 1/2-hr equilibrium time, 1-cm^2 electrode
4/9	139	1.4×10^{-6}	.9974	
4/10	132	1.1×10^{-6}	.9990	
4/12	135	1.3×10^{-6}	.9753	
4/13	133	1.0×10^{-6}	.9940	
5/29	138	1.2×10^{-6}	.9957	

*Experiments run April - May 1981

TABLE 2.3

NI WHISKER TAFEL PLOTS*

Date	Tafel Slope (mV/Decade)	Exchange Current Density (A/cm^2)	Linear Fit (0 - 1)	Experimental Conditions
Sintered Whiskers				
6/15	125	8.4×10^{-7}	.9945	N_2 purge, Teflon airtight
6/22	130	9.3×10^{-7}	.9963	cell, low [Fe] KOH, 1/2-hr
6/10	135	1.2×10^{-6}	.9921	equilibrium time, 1-cm^2
6/4	132	1.3×10^{-7}	.9955	electrode
Free Whiskers				
7/1	141	1.2×10^{-6}	.9932	" "
6/29	136	6.7×10^{-7}	.9954	

*Experiments run June - July 1981.

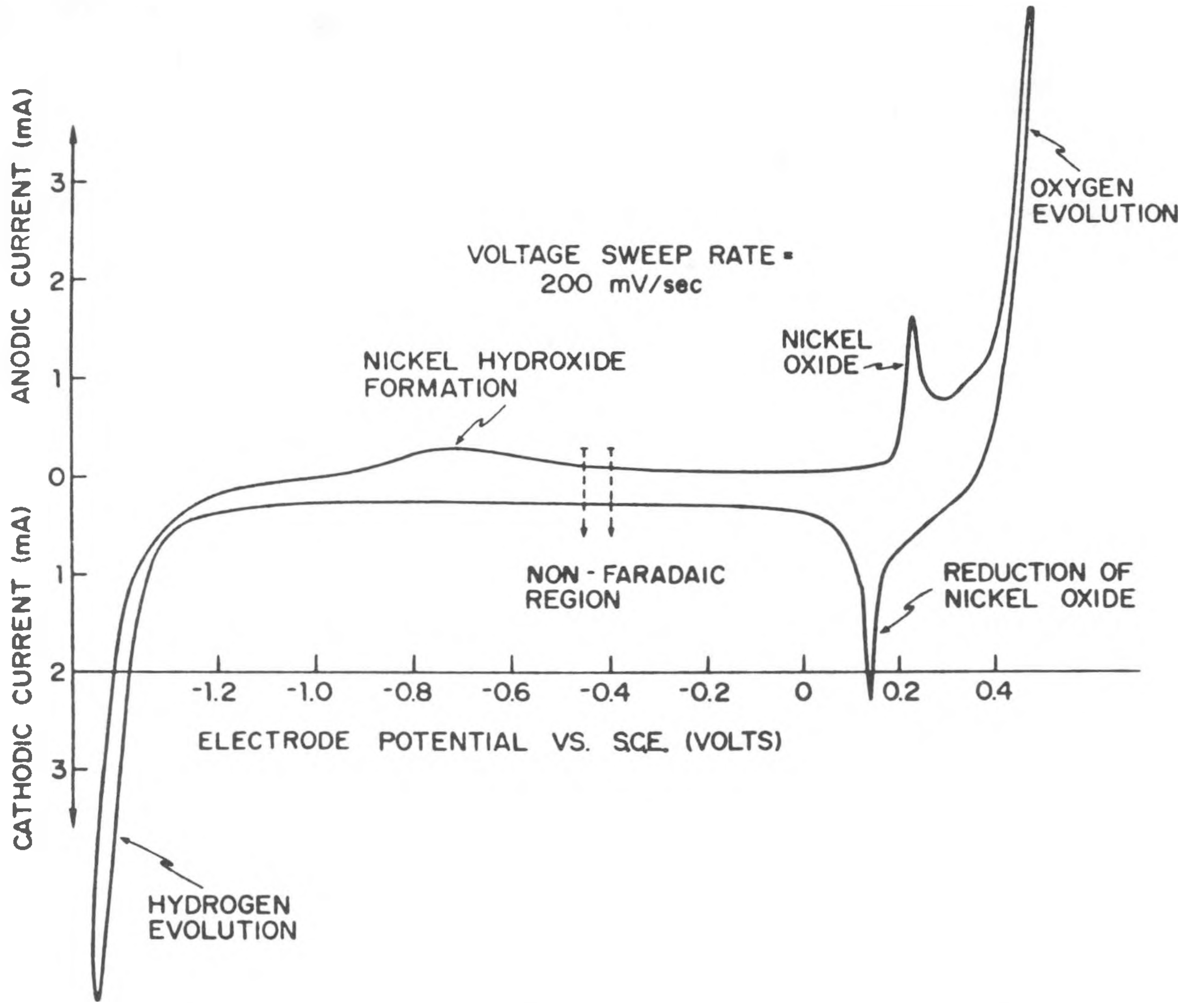


Figure 2.13 Cyclic Voltammogram Illustrating the Behavior of Nickel Electrodes in KOH

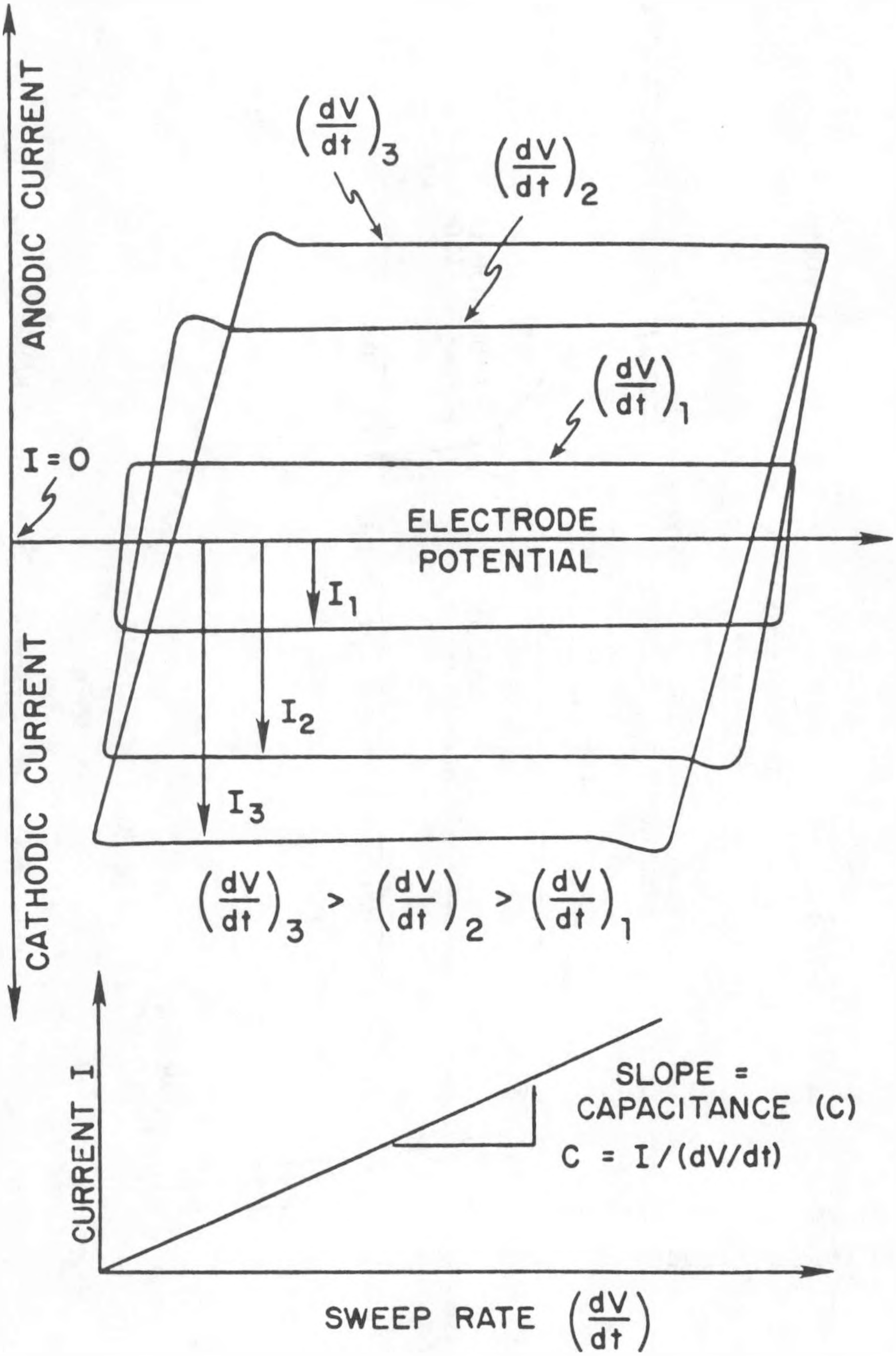


Figure 2.14 Cyclic Voltammetric Surface Area Measurements: Current vs Potential Plot in Non-Faradaic Region

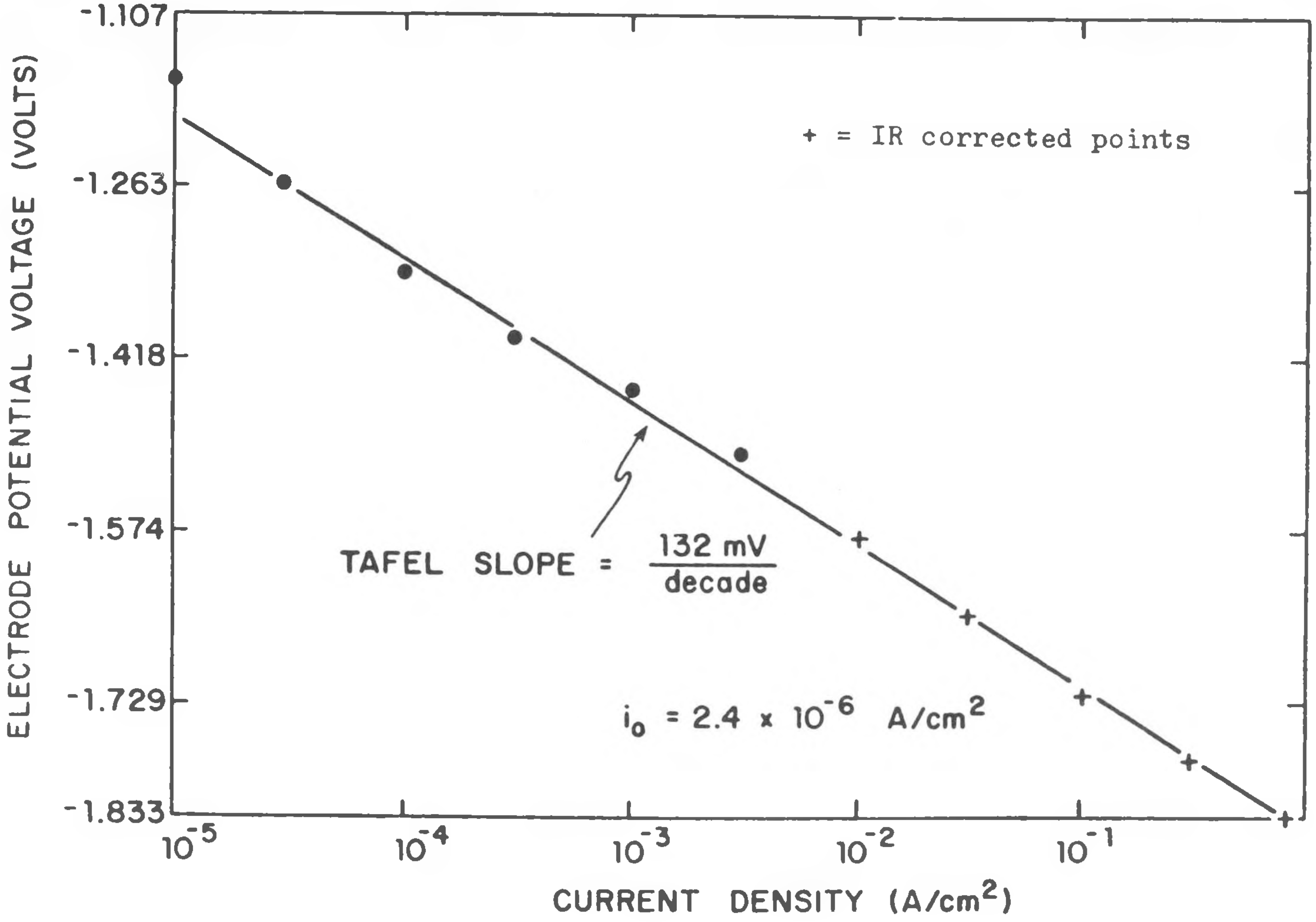


Figure 2.15 Tafel Plot for H_2 Evolution on Nickel 200 Electrode in KOH

2.5 Photoelectrochemical Characterization of Oxide Materials in Electrolyte Systems - Brookhaven National Laboratory and SUNY Stony Brook

Objectives:

Oxide materials are widely used in electrolytic systems, particularly in oxygen evolution electrodes. More recently it has been reported that many transition metal oxides can act as anodes in the photoassisted decomposition of water. Since most of these oxides are semiconductors, illumination can be used to generate electron-hole pairs, and a wide range of the fundamental properties of these materials can be elucidated from photoexcited phenomena. The objective of this project is to apply photoelectrochemical techniques to characterize transition metal oxides in an electrolyte environment, with the goal of developing better electrode materials. The emphasis is on determination of the electronic properties, charge transfer mechanisms, and the stability of these systems.

Tasks:

Task 1. The preparation and characterization of a TiO_2/Fe_2O_3 heterojunction electrode.

Task 2. The modification of TiO_2 electrodes with solid state electrochemical techniques.

Technical Progress:

Heterojunction electrodes have been prepared by chemical vapor deposition of a thin layer of TiO_2 film onto a thermally grown Fe_2O_3 substrate. This TiO_2/Fe_2O_3 electrode was examined with a scanning electron microscope (SEM) and showed a uniform, crack-free structure. The electrode was also analyzed with Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). The results confirmed that the surface of the electrode was only TiO_2 and no Fe_2O_3 or $FeTiO_3$ existed on the surface. Finally, the heterojunction electrode was characterized with transmission electron microscopy (TEM) and it was found that the electrode consisted of fine grain polycrystalline TiO_2 film coated on a coarse grain ($>5\,\mu m$) polycrystalline Fe_2O_3 substrate. The photoelectrochemical behavior of this heterojunction electrode is very promising. Shown in Figure 2.16 is the current-potential curve of the TiO_2/Fe_2O_3 electrode. The onset potential of the photocurrent curve 2 at -0.7 V (SCE) is very close to that of TiO_2. The change of slope and dramatic increase of photocurrent at 0.0 V (SCE) correspond to the onset potential of Fe_2O_3. This strongly suggests that hole injection was taking place. Therefore the feasibility of combining the best features of two semiconductor materials (good flatband potential and long-term stability of TiO_2, favorable bandgap energy of Fe_2O_3) was demonstrated.

A solid electrolyte cell based on fluorine ionic conductor BaF_2 has been used to modify the surfaces of several TiO_2 photoanodes. By properly controlling the potential, temperature, and operation time, the photoanodes were treated with different penetrations and concentrations of fluorine. It was found that the semiconductor bulk properties, surface structure, and photoelectrochemical behavior could be significantly varied in a controlled fashion. One particularly interesting treatment is shown in Figure 2.17. Curve 1 corresponds to the photoresponse of an untreated TiO_2 sample under illumination. Curve 2 corresponds to the photoresponse of the same sample with mild treatment of fluorine (penetration <1000 A, surface concentration $<10^{-5}$ atomic fraction). It can be seen that the treated sample shows a 30% increase of photocurrent at a given potential. Furthermore, the onset potential was shifted about 100 mV more favorably (in the cathodic direction). This demonstrates that solid electrochemical treatment is a valuable technique for modifying semiconductor properties.

Technical Problems:

At present there are no major technical problems.

Publications:

Yang, C. Y., Liou, F. T., Levine, S. N., and Srinivasan, S. Solid electrochemical modification of semiconductors. Submitted to Solid State Comm.

Liou, F. T., Yang, C. Y., and Levine, S. N. Photoelectrolysis at Fe_2O_3/TiO_2 heterojunction electrode. J. Electrochem. Soc., Feb, 1982 (in press).

Liou, F. T., Yang, C. Y., and Levine, S. N. Injection at Fe_2O_3/TiO_2 heterojunction electrode. Proc. Symposium on Photoelectrochemistry, Denver, Colorado, October 1981.

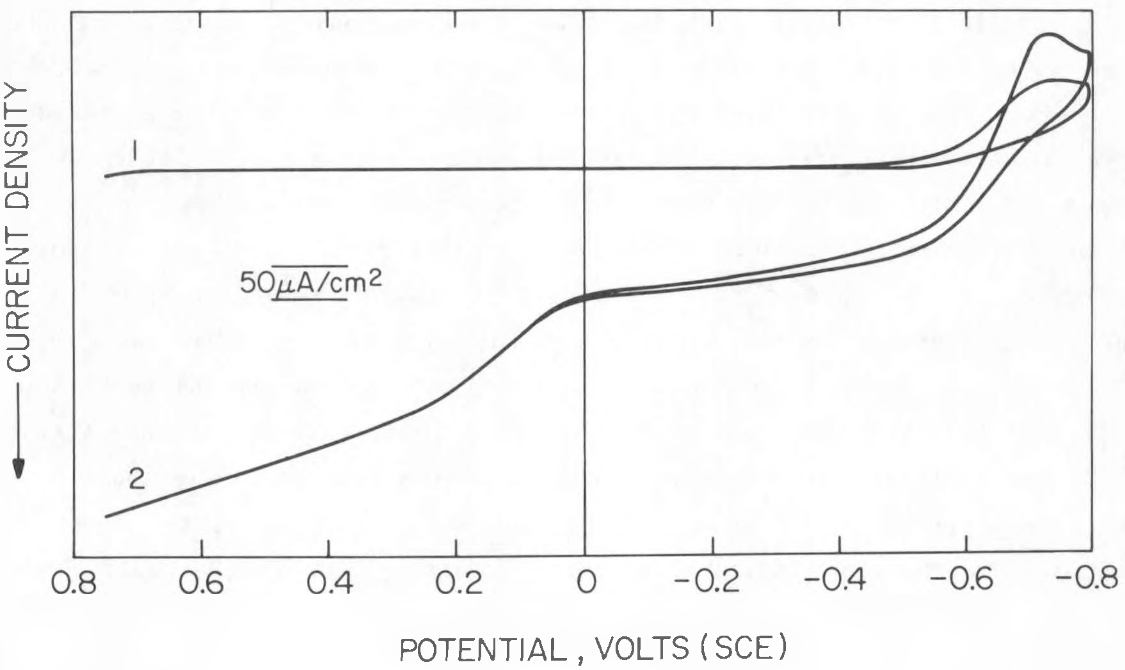


Figure 2.16 Current Potential Curve of the Heterojunction Electrode n-Fe_2O_3/TiO_2. Sweep Rate 20 mV Sec; Curve 1, Under Dark; Curve 2, Under Xenon Lamp Illumination of 0.2 W/cm^2.

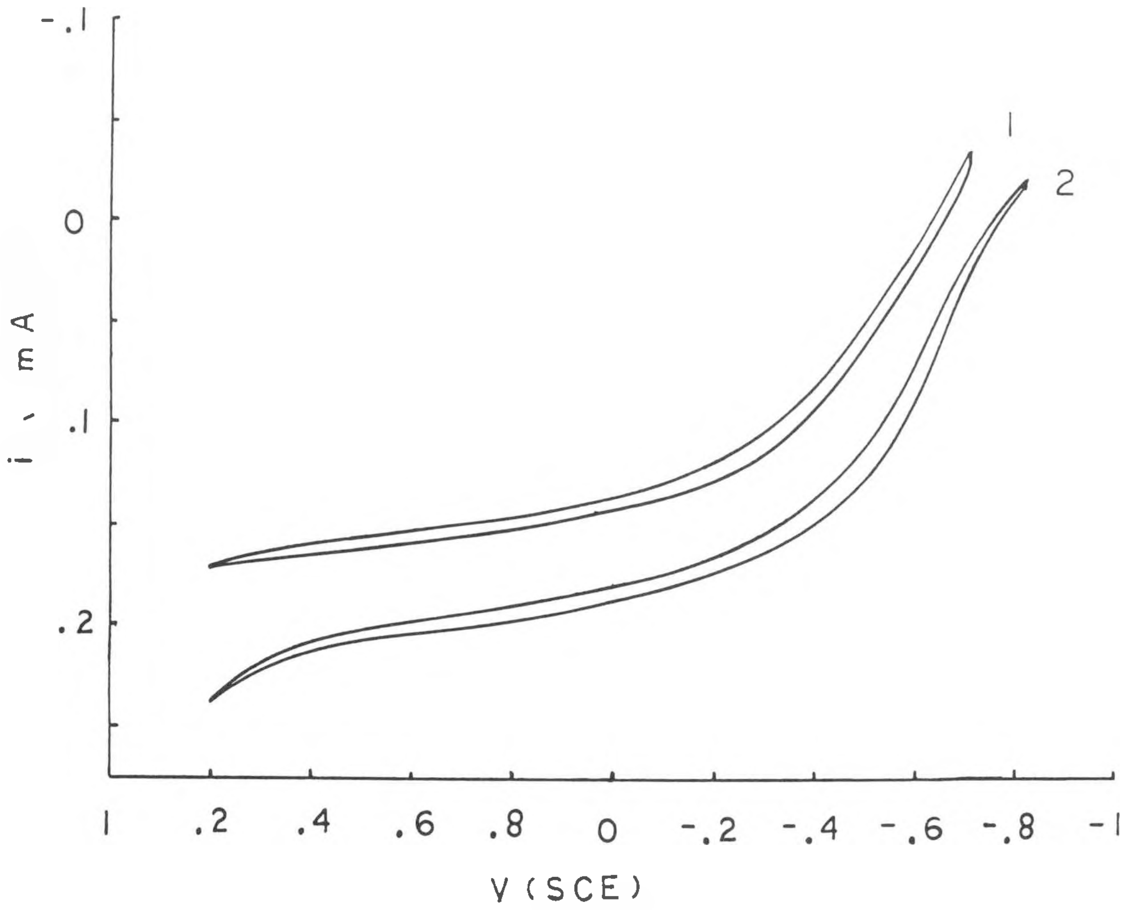


Figure 2.17 Photocurrent vs Applied Potential of a TiO_2 Anode in a Photoelectrolysis Cell. Curve 1 Before Fluorine Treatment; Curve 2 After Surface Modification With Fluorine. Xenon Lamp Illumination 0.1 W/cm^2. Potential Sweep Rate 40 mV/Sec. A Saturated Calomel Electrode (SCE) Was Used as Reference Electrode.

2.6 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 and Ru and their alloys as electrocatalysts for the oxygen evolution reaction has been found to be much superior to that of pure Pt. A major difficulty is the continuous decrease of current density with time. It has been suggested that this fundamental problem is related to the continuous growth of an 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. In order to gain more information about the nature of the electrocatalytic process, we have undertaken an investigation of the electrochemical activity on oriented single-crystal surfaces.

Tasks:

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

Technical Progress:

During the first year of this activity (1980), the method of chemical transport reaction in a flowing system to grow the largest reported single crystals of RuO_2 (~8 x 5 x 5 mm) was used. Several of these crystals are shown in Figure 2.18. In the presence of oxygen at 800° to 1500°C, gaseous oxides (RuO_3, IrO_3) exist. The reaction takes place by the mechanism:

$$\text{M (solid)} + \frac{3}{2}\, O_2 \longrightarrow MO_3\ \text{(gas)},$$

where M = Ru (or Ir). The volatile MO_3 gas dissociates to MO_2 in the cooler region. In our procedure, several grams of the Ru powder were contained in an alumina source boat. This boat was placed inside a Mullite tube at the center of the furnace which was raised to a temperature of 1400°C. Oxygen at atmospheric pressure was passed through the Mullite tube at a flow rate of about 15 cm^3/min. A second boat, which acted as a substrate, was placed

210 cm from the source boat in a cooler portion of the furnace (about 1000°C). After several days, crystals of dimensions up to 8 x 5 x 5 mm had formed in the substrate boat. A number of crystals were examined by X-ray diffraction and Laue backscattering and were found to be of relatively good quality.

We have performed a number of electrochemical investigations on virgin (100), (101), (001), and (110) surfaces of single crystals of RuO_2. The experiments include cyclic voltammetry in 1 N H_2SO_4 in the potential range 0 to 1.5 V vs RHE, as well as anodic and cathodic charging curves for each of the above orientations. Using these crystals (as well as previously obtained IrO_2) we have measured the near-normal incidence reflectivity for the electric-field vector, E, of the light parallel and perpendicular to the c-axis in the photon energy range 0.5 to 9.5 eV. Comparison of the optical constants with recent theoretical band structure and density-of-states calculations has enabled us to gain considerable insight into the nature of the metal d-electrons related to the electrocatalytic activity of these materials. Preliminary Raman spectroscopy studies have yielded information about the vibrational modes of the RuO_2. Significant differences between the different crystal surfaces have been observed. An attempt has been made to understand these differences on the basis of the various atomic compositions of the four planes. A cyclic voltammetry investigation has been carried out on (100), (101), (001), and (110) faces of single-crystal RuO_2. The differences in the results are correlated with the number of Ru and O atoms in the surface plane of the four different configurations. In addition, we have compared our results with those obtained by other workers for RuO_2 film as well as multicrystalline electrodes.

Technical Problems:

No technical problems were encountered.

Publications:

Goel, A. K., Skorinko, G., and Pollak, F. H. Polarization dependent reflectivity and optical constants of single crystal RuO_2 in the range 0.5 to 9.5 eV, Solid State Communications 39, 245 (1981).

Goel, A. K., Skorinko, G., and Pollak, F. H. Reflectivity and optical constants of single crystal RuO_2 and IrO_2 in the range 0.5 to 9.5 eV. To be published in The Physical Review.

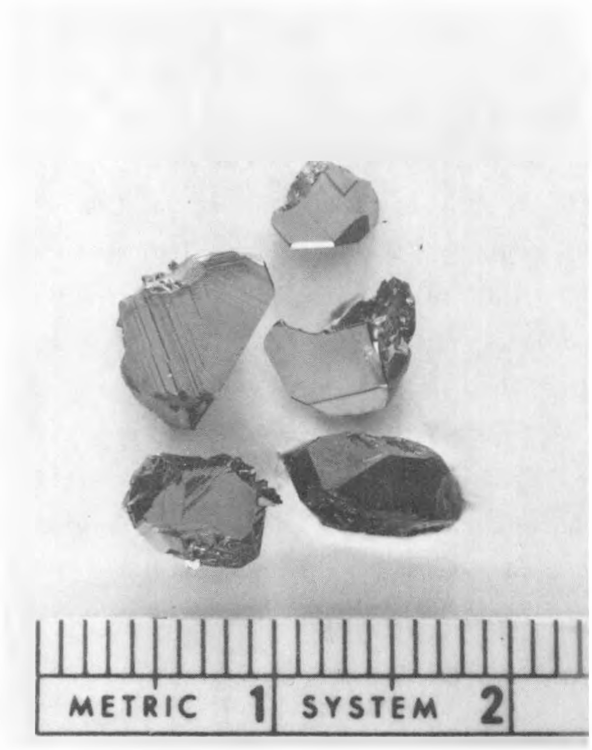


Figure 2.18 Several Large Single Crystals of RuO_2 Grown at Brooklyn College by the Chemical Vapor Transport Method

2.7 Selection and Evaluation of Materials for Solid Polymer Electrolyte Electrolyzers - Brookhaven National Laboratory

Objective:

The objective of this work was to elucidate the reactions occurring at the solid polymer electrolyte (SPE)/Catalyst interface using modern electrochemical techniques with the aim of defining factors that would limit low catalyst loading and also provide insight into membrane degradation mechanisms.

Tasks:

Task 1. Investigate the SPE/catalyst interface using electrode point contact techniques.

Technical Progress:

Figure 2.19 is a schematic drawing of one version of the cell used for electrochemical studies on the SPE-electrocatalyst interface. This particular cell consisted of a Nafion membrane, a platinum sheet counter electrode, a fused platinum ball contact working electrode, and a calomel reference electrode. Electrolytic contact between the reference electrode and the Nafion electrolyte was made via a Nafion strip "salt bridge." The calomel electrode was used as the reference electrode after other electrodes (e.g., Ag, Ag/Pd, and Pd) proved unstable. Apart from the fused platinum ball working electrodes, flat platinum electrodes of various areas were used. In the latter case, the electrode edges were masked with epoxy. The electrode-membrane assemblies were mounted in a machined polysulfone fixture. The fixture was enclosed in a beaker-type cell where the humidity and gas environment could be controlled. Typical measurements carried out were cyclic voltammetry, steady state measurements of hydrogen evolution, and investigations of the effect of ambient environment and electrode area on the SPE-electrocatalyst interface.

The cyclic voltammetry of a single-contact platinum electrode/Nafion interface is shown in Figure 2.20 for an area contact of 1.4×10^{-3} cm^2. The curves are similar to those obtained with aqueous sulfuric or trifluoromethanesulfonic acids. The maximum in the anodic currents around 0.73 V (SHE) resulted from the reduction of platinum oxide and showed little potential dependence on scan rate. The potential did depend on the maximum potential reached on cycling, and the decrease in the potential of the maximum indicated definite interaction with the sulfonic anions even though their mobility is restricted by the polymer chain to which they are bonded.

The current maxima and minima at potentials between 0 and 0.35 V result from the desorption and adsorption of hydrogen atoms in the platinum. The different peaks have been attributed to adsorption isotherm which depend on the crystallographic orientations of the polycrystalline platinum surface. The amount of charge associated with these adsorption processes has been considered as a measure of the degree of hydrogen coverage on the platinum. Taking a complete coverage as 210 C/cm^2 measurements of the charge was found to give areas a factor of 2 to 4 times that calculated from the geometric area.

These large areas may be associated with the diffusion of hydrogen atoms on the electrode surfaces not in direct contact with the electrolyte. Similar effects were noted on anodizing single contact titanium electrodes on Nafion where interference colors were seen on the surfaces adjacent to but not in contact with the Nafion. This may have important implications regarding current collector corrosion in the SPE electrolysis.

Publications:

Isaacs, H. S., Yang, C. Y., and McBreen, J. Research on advanced electrolytic hydrogen production. Proc. DOE Thermal and Chemical Storage Annual Contractors' Review Meeting, Tyson's Corner, Virginia, September 1981.

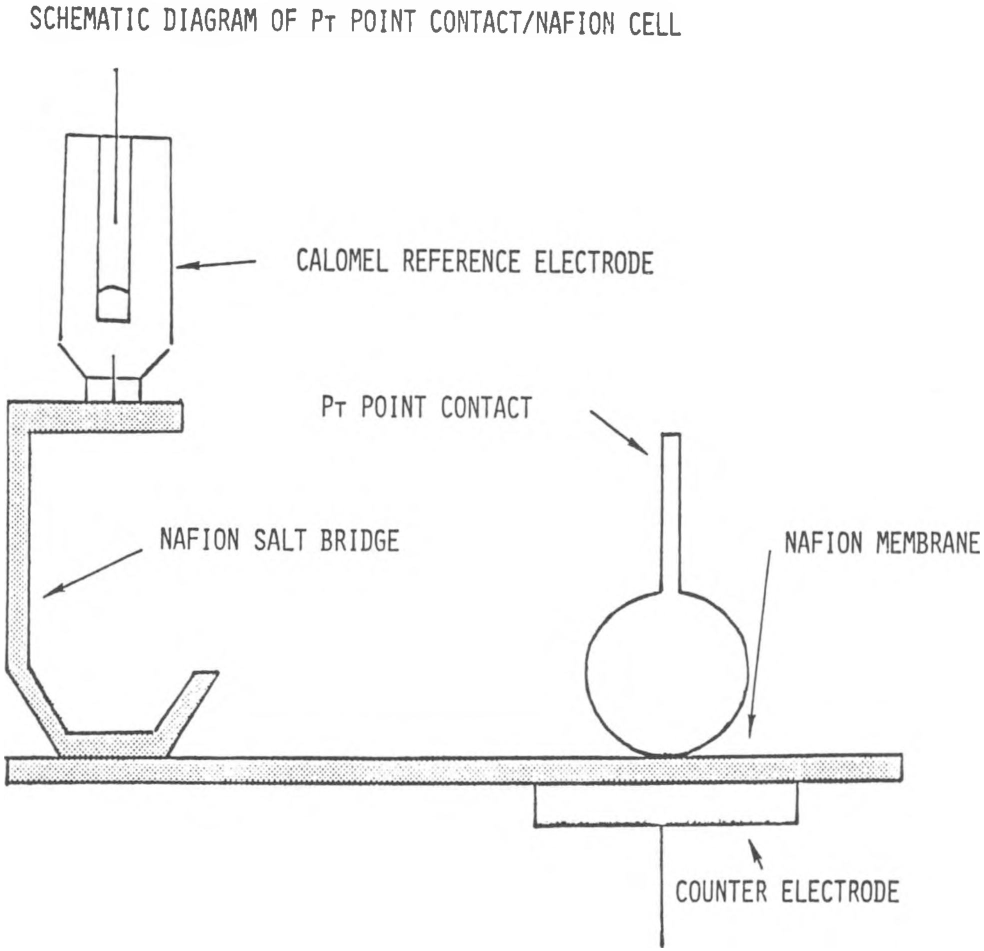


Figure 2.19 Schematic of Cell for SPE-Electrocatalyst Studies

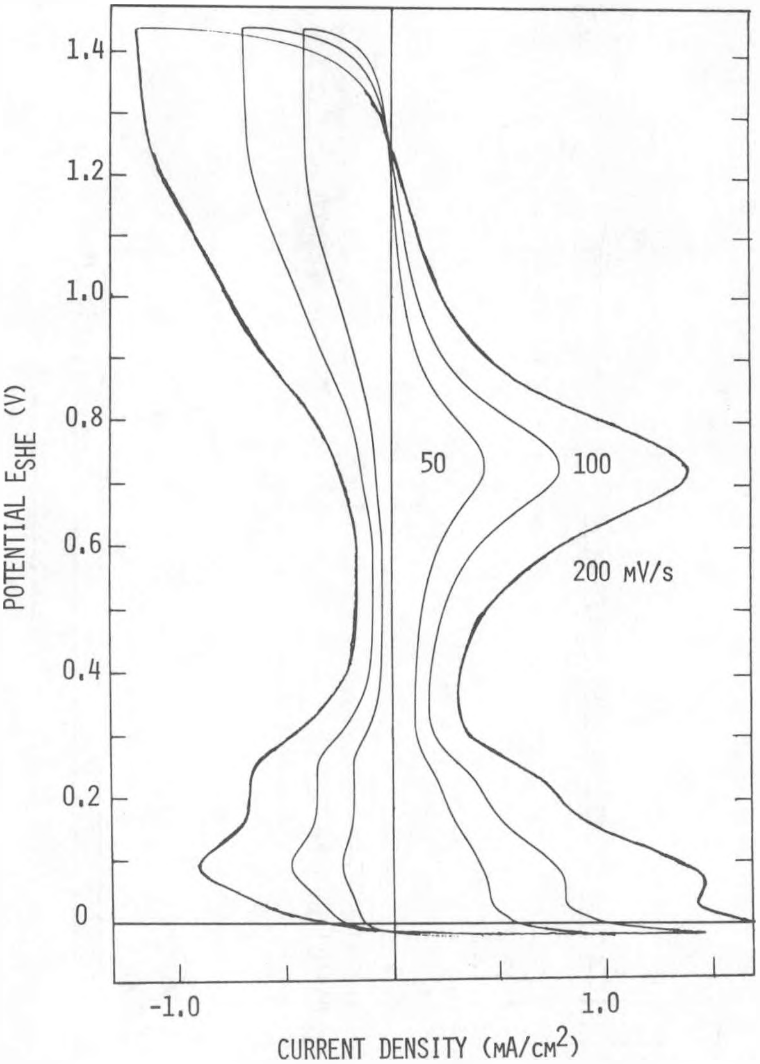


Figure 2.20 Cyclic Voltammograms on Pt Electrode in Contact with SPE Membrane

2.8 Technical and Economic Assessment of Water Electrolysis Technologies - Arthur D. Little, Inc.

Objective:

The project goals are to provide a technical-economic assessment of the solid polymer electrolyte (SPE) technology compared to other current and emerging water electrolysis technologies both in the United States and abroad.

Tasks:

Task I - Initial Assessment of SPE Technology

Task I consists of evaluating the present status of the SPE technology in terms of demonstrated performance and estimated costs, and the improvements that can be reasonably expected relative to published design goals. In addition, information will be gathered on competing current and emerging electrolyzer technologies including Teledyne and manufacturers in Canada and Europe. Capital and operating costs will be developed for the technologies, for a 2-MW system, and the relative strengths and prospects will be evaluated.

Task II - Detailed Comparison of GE and TES Technologies

This task, to be initiated only if warranted by the results of Task I, will be to make a detailed comparison between the GE SPE technology and the Teledyne advanced alkaline technology.

Technical Progress:

Detailed information on GE technology and costs has been assembled and is now undergoing detailed analysis and comparison. The methodology of cost analysis has been defined and the computer program for sensitivity analysis has been written and successfully run. Efforts are now directed to the Phase I Final Report.

At the time of publication of this report the findings of this study are incomplete. It is expected that the work will be completed in the first quarter of 1982 and the report will be published soon thereafter.

2.9 International Energy Agency (IEA) - Annex IV Working Group on Advanced Alkaline and Solid Polymer Electrolyte Water Electrolysis - Summary of Activities in 1981

The U.S. DOE, operating through Brookhaven National Laboratory, is responsible for coordinating the activities connected with the International Energy Agency cooperative effort on hydrogen production relating to advanced alkaline and solid polymer electrolyte water electrolysis (Annex IV). This is a brief summary of the technical highlights of work by the participating countries. The 1981 IEA Annual Report should be consulted for more detail.

The main goals of this cooperative program are: (1) to achieve efficiencies close to 100% and lower the capital costs of alkaline water electrolyzers by increasing the operating temperatures above those used in conventional systems (i.e., about 80°C) and to find improved materials for cell components, and (2) to develop the solid polymer electrolyte water electrolysis technology which shows promise of high efficiencies and low capital costs.

The Annex IV Working Group of the International Energy Agency serves as a forum for exchange of ideas and information on these technologies. It has also stimulated collaborations among the participating organizations by way of common approaches in attempts to solve the materials problems as well as to provide a supply of materials to be tested in different laboratories, with visits and regular communication between participating laboratories.

The progress made by each country in the two technological areas is briefly summarized below.

Belgium

The Belgian group has identified a new and novel membrane material, namely polyantimonic acid in a polysulfone binder. The membrane functions as a separator electrolyte material in a 15 wt % NaOH solution. This material has been tested in small hardware and found to give improved performance over conventional KOH asbestos systems. For example, cell systems exhibit 1.74 V at 1000 A/ft^2 and 120°C in laboratory tests of up to 8000 hours' duration with noble metal catalysts. Larger-scale hardware is under development to demonstrate the commercial applicability of this membrane system.

Canada

A long-term test facility for separator and electrocatalyst evaluations has been constructed at the Noranda Research Centre. Results are applicable to full-scale commercial electrolyzers. Electrocatalysts tested so far include NiB, $NiCO_2S_4$ (Teflon bonded) for the cathode, and $NiCo_2O_4$ for the anode. The NIB was supplied by Germany while the $NiCo_2S_4$ and $NiCo_2O_4$ were supplied by the U.K. under the IEA Annex IV agreement. Separator materials included the Japanese Teflon/potassium titanate and a polysulfone felt produced under the Canadian program. The generally negative results obtained (which are discussed in the referenced report) illustrate the absolute necessity of the long-term test program on commercial-scale equipment.

The work at the Atlantic Industrial Research Institute on perovskite and related oxide ceramic electrocatalysts for the oxygen evolution reaction has produced promising materials of the general formula $La_xSr_{1-x}AO_3$ where A is either Ni or Fe. Problems of adequately bonding these conducting ceramic powders onto suitable electrode substrates were encountered and remain to be solved.

The Canadian Annex IV program is focusing on the development of one or more Alkaline Solid Polymer Electrolytes (ASPE) suitable for either an advanced alkaline electrolyzer or fuel cell. Thus, the work at the National Research Council (NRC) has identified polysulfones as promising for these applications. Polyamides produced did not have the required chemical stability at elevated temperatures. A cooperative program involving Daychem Laboratories, McGill University, and the University of Calgary has succeeded in producing aromatic ionomer films on a small scale that show promise. These are alkoxycarbonyl-substituted phenylated polyphenylenes of differing equivalent weights. Optimization of the synthesis process itself, as well as of the final polymer, is in progress.

Commission of European Communities

In the French program at SRTI, the emphasis is on radiografting of specific chemical radicals which make wettable modifications of PTFE fabric that are stable in alkaline electrolysis cells at medium temperatures. The specific approach is the radiografting of vinyl-carboxylic or sulfonic acid radicals to PTFE fabric, with addition of cross-linking agents to improve stability. Three irradiation methods have been tested for radiografting:

γ irradiation, electron irradiation and electron pre-irradiation. Life tests performed in KOH at 200°C suggest it may be possible to achieve practical lifetimes for these materials under electrolysis conditions.

A ceramic diaphragm made of nickel titanate sintered on thin nickel net previously developed at the University of Darmstadt in Germany, was found to be unstable when exposed to cathodic hydrogen. Replacement of nickel titanate is being carried out with success. The sintering technology is being extended to a 30 x 30-cm-size diaphragm as was already successfully done with the nickel titanate material. Alternative diaphragm materials similar to sintered nickel are also being investigated. Some difficulties in duplicating the good laboratory results of previously reported anodic catalysts ($NiCo_2O_4$ and $La_{0.5}Sr_{0.5}CrO_3$) when scaled up at the 5-kW facility, have been experienced. Minor technological difficulties in the transfer to larger-scale systems are also being pinpointed and gradually eliminated in small-scale hardware testing.

At Panclor in Italy specific deposition techniques of metal electrocatalysts on SPE material have been successfully developed, by extending the Takenaka diffusion reduction method to nickel and/or cobalt and admixtures for use in alkaline electrolytes. Testing in prototype cells showed that acid corrosion of constitutive materials (due to the Nafion acidity) will be experienced where insufficient or no electrolyte renewal exists (e.g., near boundaries, under gaskets, etc.). Furthermore, though the catalyst stability on the membrane is excellent when electrolyte flow is sufficient, even a very short period of deficiency during electrolysis leads to destruction of the metallic electrocatalysts. However, as performance is limited by membrane conductivity this concept needs to be carefully reconsidered.

In further work at Panclor related to alkaline electrolysis, anodic catalysts were prepared from nickel and cobalt salts (either of inorganic or of organic acids) in the following range of compositions: 1 Ni/1 Co to 2 Ni/1 Co and 1 Ni/2 Co; 0.5 to 1 Zn was also added in specific cases. Cathodic catalysts were also prepared from benzoates of Ni + Mo or Ni + Mo + Zn or Ni + Mo + Al, without success. The best results were obtained with thiosulphate-treated nickel or iron, giving respectively -0.890 V (vs SHE) and -1.19 V (vs SHE) at 60°C and 1 A/cm^2. Further optimization is being carried out. In parallel with the above catalyst work, the experimental diaphragms produced by Politecnico of Milan have been tested. To date the best material is 0.7 mm asbestos cardboard reinforced with 10% of a copolymer 4 vinylpyridine-divinylbenzene. At 32°C it gives a surface specific resistivity of 0.25 cm^2 in KOH 4.8 N. This diaphragm, however, could be used only at temperatures lower than 120°C, but other choices are being developed and tested.

Japan

The work at Showa Denko in Japan is on component testing in a 1/5-scale electrolysis test plant prior to constructing the full-scale plant. Results of electrode and diaphragm testing are reported along with corrosion results. After 600 hours of operation, no significant change had occurred in the performance of the HSA electrode and PTFE diaphragm. The test plant will be operated for three months to test the durability of the electrodes and diaphragm. A pilot high pressure water electrolyzer plant with a production capacity of 20 m^3 hydrogen per hour will be constructed in 1982. The results of test plant operation, corrosion tests of metallic materials and a process dynamics study will be applied in the selection of electrode, diaphragm and construction materials as well as design of the pilot plant.

Additional work in Japan at GIRI is on test of a small SPE electrolyzer test plant completed in April 1981.

The construction materials of the electrolysis module are:

End plate	45 mm(t) steel plate
Bipolar collector	Titanium plate with channels
Support	Porous titanium foil and screen (coated with a thin Pt layer)
Isolator	PES resin
Gasket	FPM
Membrane-electrode composite	Ir alloy (anode)/Nafion 125/Pt (cathode)

Membrane-electrode composites were prepared by a special metal plating method developed at GIRI. During tests the average cell voltage at 1000 mA/cm^2, 130°C, and 8 mg/cm^2 is 1.70 V. The voltage is slightly higher (40 to 50 mV) than that expected from laboratory-size cells (50 cm^2), which is caused by a slight increase of internal resistance in the module. Differences in cell voltage between 10 cells were within 20 mV at the above conditions. Life testing is planned after reconstruction of a part of system line.

United Kingdom

The highlights of the United Kingdom program at City University, London, are as follows:

1. Li-doped Co_3O_4 anodes have been operated at 1 A/cm^2, 45% KOH, for over 6500 hours with only 20 mV increase in overvoltage, i.e., 1.52 V vs DHE to 1.54 V vs DHE (iR corrected).
2. $NiCo_2S_4$ cathodes have been operated for over 6000 hours at 1 A/cm^2, 45% KOH, at -100 mV vs DHE (iR corrected). Thereafter, it failed because of mechanical attrition.
3. Lithiation of the nickel screen current collection improved the corrosion resistance of the screen and conductivity of the protective nickel oxide film.
4. Two electrolysis cells (1 cm^2) have been tested continuously for 6000 hours at 1 A/cm^2, 1.85 V, 45% KOH, 85°C. The iR-corrected voltage was 1.60 V. Cell voltage increased by only 20 to 40 mV the first 6000 hours.

United States

The accomplishments of the United States program are described in Section 2.0 of this report.

Publications:

Task IV Advanced Alkaline and Solid Polymer Water Electrolysis Development - Annual Progress Report, IEA Programme of Research and Development on the Production of Hydrogen from Water, January 1982.

3.0 HYDROGEN STORAGE SYSTEMS, MATERIALS, END-USE TECHNOLOGY

Summary

This section includes the results of the systems study done at BNL which showed that ammonia, under certain conditions, can serve as a cost-effective hydrogen distribution and storage medium for small-scale users. The planning and conceptual design of the photovoltaic array/advanced electrolyzer interface project are also described. Background information and a description of the test approach are provided for the investigation of the hydrogen embrittlement effects on pipeline steels which has just gotten underway at Battelle Columbus Laboratories. And finally, the project for producing hydrogen using small hydropower, which was begun two years ago as a joint effort between DOE, NYSERDA, and the Village of Potsdam, is discussed. DOE and NYSERDA terminated their part in the project primarily because of high electric power reimbursement rates making the project economically unattractive at Potsdam. Details on the project are provided.

3.1 Ammonia as a Hydrogen Energy-Storage Medium

Brookhaven National Laboratory

Objective:

To assess the economic prospects for using purchased industrial NH_3 as a H_2 distribution and storage medium for small-scale users.

Tasks:

Task 1. Provide a rationale for the concept, and identify uses for the H_2 derived from NH_3 (H_2/NH_3).

Task 2. Compare the projected cost of H_2/NH_3 with H_2 obtained by other methods.

Task 3. Make recommendations for future work in pursuing the concept.

Technical Progress:

Task 1. The rationale was developed for choosing NH_3 as a practical H_2 carrier and is summarized as follows:

a) NH_3 is a liquid carrier of high H_2 content (17.8 wt %);

b) high-purity H_2 (up to 99.999%) can be readily obtained from NH_3 by conventional dissociation followed by purification as required;

c) technology for industrial-scale NH_3 production is highly developed and efficient;

d) there is a well-established infrastructure for NH_3 distribution;

e) safe handling techniques have been developed for current applications;

f) although NH_3 is now made from natural gas, and will be made from coal as the gas supply tapers off, it can be made from H_2O and air using an outside source of energy; and

g) no carbon oxides are involved; water is the main reaction product from heat engines and fuel cells (NO_x and residual NH_3 can be controlled).

Task 2. The current analysis was a sequel to the study made for OTEC NH_3 produced via ocean thermal energy conversion from air and H_2O. The favorable cost position for H_2/NH_3 in relation to electrolytic H_2 ($\underline{E}H_2$), H_2 produced from natural gas by steam reforming (H_2/NG), and liquid H_2 ($\underline{L}H_2$) led to the study of industrial NH_3.

In this second analysis, improved cost projections were made for various scenarios resulting in both cost increases and decreases, and the forecast costs of natural gas and electricity were expanded to include a second, and higher, set of energy prices. The lower set of prices was forecast by the Department of Energy for its 1980 Annual Report to Congress (ARC prices); and the second set was forecast by the National Center for the Analysis of Energy Systems at Brookhaven National Laboratory (BNL set of prices). The latter are based on parity pricing with oil. Prices and costs forecast for 1990 (in 1980 dollars) were used because it was expected that advanced-technology water electrolyzers would be in commercial use by then. Comparison with OTEC H_2/NH_3 was also then possible. The case of NH_3 produced from coal was also considered.

The range of plant sizes considered was increased to 33 to 300 million std ft^3 of H_2/yr (MSCFY), or 0.1 to 1.0 MSCFY, at a plant capacity factor of 0.9 (330 days' operation/year), in order to include the H_2 demand of a large semiconductor plant. Previously the size range was 10 to 100 MSCFY. Commercial dissociators that will satisfy the lower end of the range are readily available. In the current analysis a single scaled-up unit was specified in order to reduce the costs. The plant sizes selected were 33, 50, 100, 200, and 330 MSCFY. Purification of the H_2 by Polybed PSA (pressure-swing adsorption) was the method selected. For each source of H_2, the projections include all costs to the end user, except those which might be incurred for environmental reasons. Details of the costing methods used and on updated items are provided in the project report. Uses for the purified H_2 include chemicals, pharmaceuticals, fats and oils, metals, electronics, and float glass. The dissociator product can be used directly as a fuel for heat engines and H_2-air fuel cells. For heat-engine use, less than 20% of the NH_3 has to be dissociated.

The results of the cost analysis for H_2 obtained by various methods were generally the same as those found in the analysis, except that H_2/NH_3 was considerably less competitive with respect to electrolytic H_2 and H_2 from natural gas. Merchant liquid H_2 was by far the most costly. Its higher cost is due to the service performed; and its main advantages are convenience and suitability to discontinuous demands. Plots of the projected costs are shown for ARC energy prices in Figure 3.1 and for BNL energy prices in Figure 3.2 The greater spread for the latter H_2 costs is due to the wider range in energy prices. All of the H_2 costs decrease as the plant size increases, especially H_2 from natural gas. Hydrogen derived from NH_3 was competitive with H_2 from natural gas for plant sizes up to about 40 MSCFY for both sets of energy prices. Addition of the costs for increasing the purity of H_2 from natural gas above 98% (typical) will increase the competitive range of H_2/NH_3. Electrolytic H_2 was lower in cost than H_2/NH_3 for ARC energy prices, but there was some overlap above 120 MSCFY for BNL energy prices. A modest reduction in purification costs for H_2/NH_3 would considerably improve its competitive position. The dissociator product (N_2 + H_2/NH_3) was, unexpectedly, close in cost to electrolytic H_2. In the case of OTEC NH_3, the H_2 would be significantly lower in cost than H_2 from industrial NH_3.

Where natural gas is not available, and until electrolytic H_2 and OTEC H_2/NH_3 are available at the projected costs, H_2/NH_3 (industrial) would be the preferred H_2 source, provided the demand is fairly continuous. When NH_3 is mass-produced from coal in the future, the analysis showed that in order to be competitive with natural gas, the NH_3 production plant would have to be located at the mine mouth.

The general conclusion from this analysis is that NH_3 is a cost-effective H_2 distribution and storage medium for H_2 demands of up to 40 MSCFY. This range will be extended when purification costs are reduced, or if the projected costs for the alternative sources are not realized.

Task 3. The recommendations listed below apply to the use of H_2 as a commodity, and as a fuel. In order to better assess the future role of NH_3 as a H_2 carrier, these factors should be examined.

- Low-cost purification
- H_2 purity vs cost
- Dissociation by other methods
- Expansion of the infrastructure
- Shipping and distribution costs
- Safety and handling
- Environmental regulations

The additional development needs for the use of NH_3 in fuel applications are listed below. Safety and environmental factors are more critical for vehicular use because of closer contact and increased vulnerability compared with stationary application.

- Safety and handling
- Environmental regulations
- Dissociator size reduction
- Low-temperature dissociation
- Fundamental combustion studies
- Reduction of NO_x in exhaust gas
- Use of $N_2 + H_2/NH_3$ in fuel cells
- Direct use of NH_3 in fuel cells

Technical Problems:

The main technical problem to be solved before H_2/NH_3 is used as a commodity is development of a cost-effective method for separating N_2 and H_2. For the use of H_2/NH_3 in vehicles, development of a compact moderate-temperature dissociator is essential. Successful development of a fuel cell which could use NH_3 directly would constitute a major advance in energy conversion.

Publications:

Strickland, G. Small-scale uses and costs of hydrogen derived from OTEC ammonia. Proc. 16th Intersociety Energy Conversion Engineering Conference, Atlanta, Georgia, August 1981. BNL 29667.

Strickland, G. Small-Scale Costs of Hydrogen Derived from Ammonia. BNL 51487, November 1981. To be presented at World Hydrogen Energy Conference IV, Pasadena, California, June 1982.

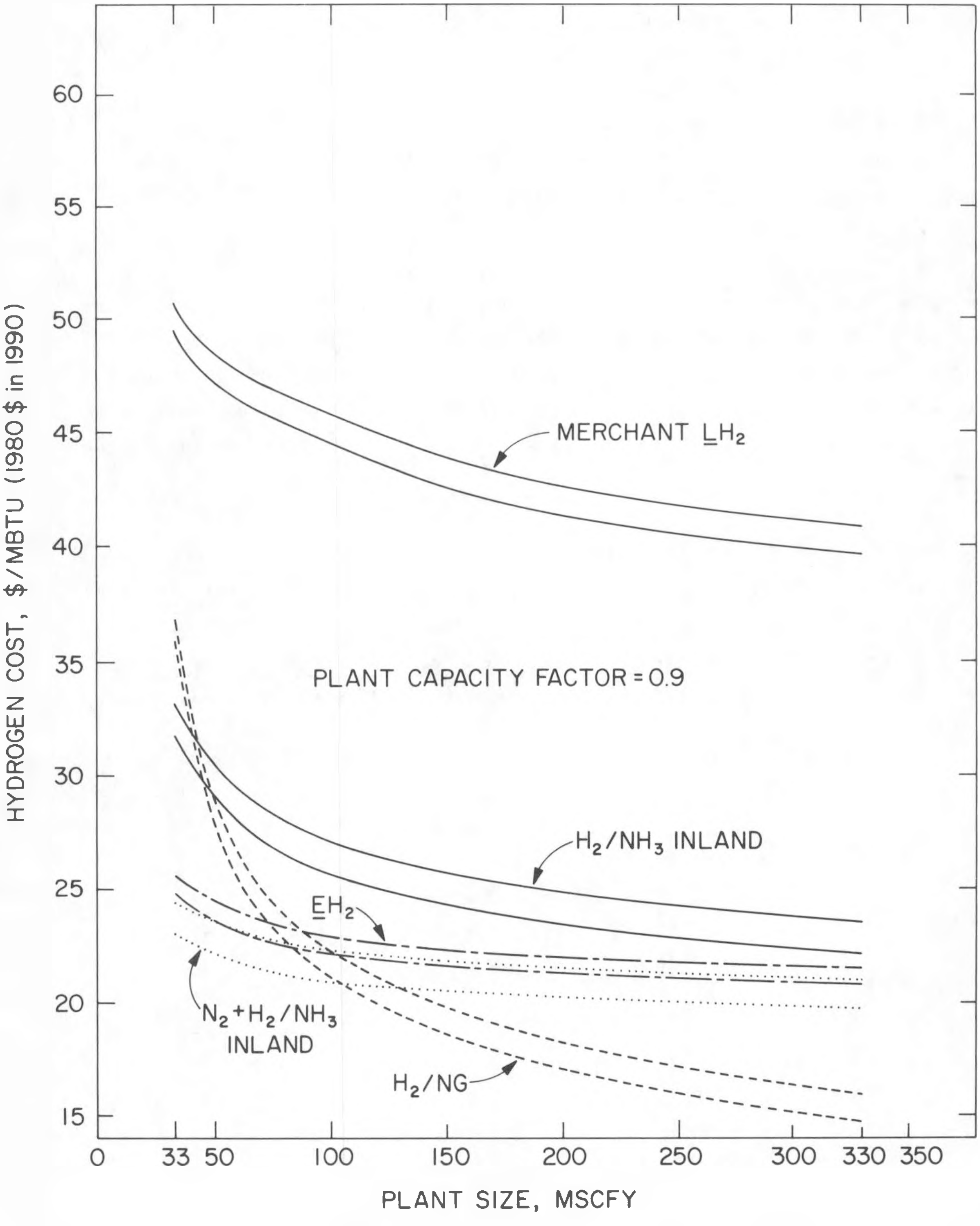


Figure 3.1 Projected Costs of Hydrogen Using ARC Prices For Natural Gas and Electricity

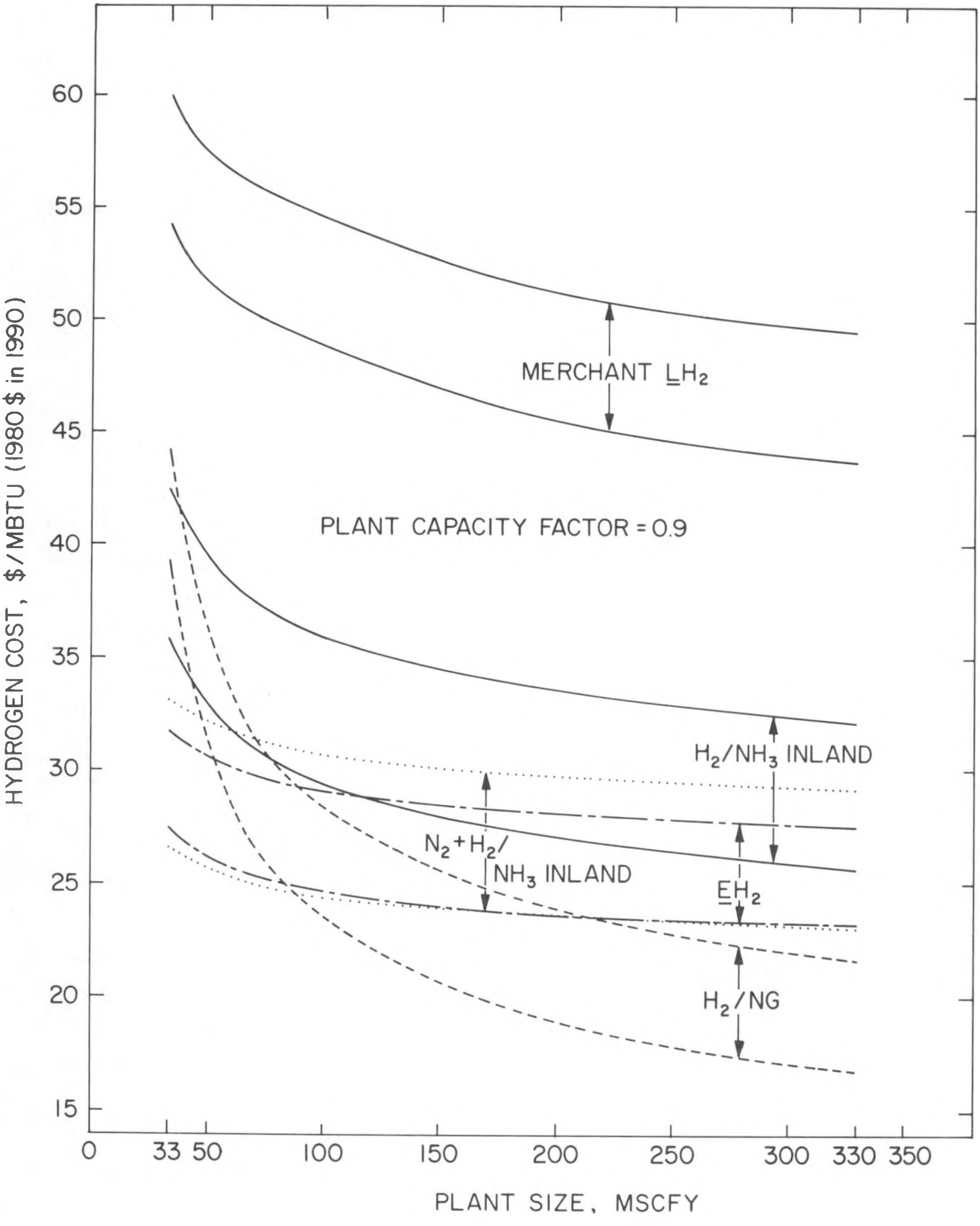


Figure 3.2 Projected Costs of Hydrogen Using BNL Prices For Natural Gas and Electricity

3.2 Photovoltaic Array/Advanced-Technology Electrolyzer Testing

Brookhaven National Laboratory

Objective:

The purpose of the program is to test and illustrate the interface technology of state-of-the-art photovoltaic array (PVA) and an advanced-technology electrolyzer for H_2 production. Subsequently the objective may be expanded to include testing of an end-use device such as a H_2-air fuel cell, or a small vehicle fueled by H_2.

Tasks:

Task 1. Prepare a multiyear program plan and a site plan, and initiate system design.

Technical Progress:

Task 1. A 3-year program plan was prepared for the project after it was initiated in October. Additional items to be included in the first year, pending DOE guidance, are completion of system design, preparation of equipment specifications, procurement, and completion of a safety review. Construction and installation are scheduled for the second year so that the test program can be completed in the third year. At an appropriate time battery storage will be provided so that a stand-alone system can be tested.

A preliminary plot plan was prepared for installation of the PVA-electrolyzer as part of the HYTACTS (Hydrogen-Technology Advanced-Component Test System). The electrolyzer was sized at 20-kW output (200 SCFH H_2) and the PVA rating was limited to 5 kW (peak) in order to minimize the capital investment and local environmental impact. Thus the bulk of the power will be provided by the ac line. The power conditioner will be designed to combine both sources in order to simulate 100% solar input; and it will also be able to supply all of the power for initial baseline testing. Under solar simulation conditions, the system response to transient insolation will be studied. The effect of battery energy storage can be simulated by reducing the ac line component vs time during a given test. Subsequently, battery storage will be added so the stand-alone system can be tested. Consideration will be given to integration of a wind turbine at a later date.

Preliminary technical specifications were prepared for the advanced technology electrolyzer so that vendors manufacturing electrolyzers of differing technologies can provide quotations on a comparable basis.

Consideration is being given to the purchase of the power conditioner and PVA as a system rather than design and fabricate the power conditioning equipment at BNL and seek a decommissioned photovoltaics array.

Technical Problems:

The main technical problem is interfacing the photovoltaics array and the electrolyzer, which will be addressed with the design of the power conditioner. A custom design is necessary since there are no standard units having the required characteristics.

Publications:

None.

3.3 The Effects of Hydrogen on Low-Cycle-Fatigue Life and Slow Crack Growth in Pipeline Steels - Battelle Columbus Laboratories

Objectives:

To investigate the enhancement of fatigue-crack-growth rate by hydrogen gas in representative line-pipe steels as a function of hydrogen pressure, cyclic frequency, and cyclic load magnitude. To establish whether sustained-load slow-crack growth is likely to occur in weld areas of steel pipelines transporting hydrogen.

Introduction

This project was started in midyear 1981 with the initial efforts devoted to selection of materials and assembly and checkout of the test systems. Testing began at the end of the calendar year without any results that can be reported at this time. Plans for a test program and the results of the characterization of metallographic and mechanical properties of the X42 line-pipe steel that will be used for the bulk of the tests on this program will be described.

Characterization of Test Materials

The 40-foot-long section of 12-inch-diameter, 0.375-inch wall API5LX42 pipe purchased in September represents the primary experimental material for the program. Fatigue-crack-growth tests and sustained-load slow-crack-growth tests in hydrogen and argon will be performed on 0.25-inch thick compact tension specimens that are being machined from the pipe wall. For comparison, compact tension specimens also are being machined from A516 Grade 70 and X60 steel plate obtained from Sandia Laboratories. Both cyclic and sustained-load crack-growth tests are planned for the A516 steel whereas, only sustained-load crack-growth tests are planned for the X60 steel. Fatigue-crack-growth experiments will be performed on internally flawed end-capped sections of the X42 pipe as well as on sections of 4-inch-diameter, 0.375-inch wall, A106 Grade B pipe obtained from Sandia. The fatigue loading of the pipe sections will be accomplished with internal pressurization with hydrogen or argon.

The characterization of the mechanical properties and metallography of the X42 line-pipe steel has been completed. Chemical compositions of the X42 and the three other steels to be tested on this program are given in Table 3.1. The compositions of all four steels are within the ranges specified by API for X42 and X60 and by ASTM for A516-70 and A106B. The X42 steel is representative of a great deal of the line pipe currently in underground service; its chemical composition is significantly different from the modern high-strength,low-alloy, line-pipe steel, such as X60, that is expected to constitute the bulk of underground pipelines to be constructed in the future.

The tensile properties of the four steels measured in air are given in Table 3.2. All four materials meet the minimum requirements for tensile properties specified by API (X42 and X60) and ASTM (A516-70 and A106B). Sandia Laboratories has tested the tensile properties of A516-70 and A106B in 1000-psi hydrogen and reported reductions in area of 38 and 14%, respectively, but essentially no change in yield or ultimate strength for either alloy. Comparable data for X42 and X60 will be obtained on the present program.

Figure 3.3 shows the base metal microstructure of the X42 steel. The banded microstructure consisting of ferrite and pearlite shown in that figure is typical of conventional hot-rolled line-pipe steels. The hardness of the base metal is 81 Rockwell B. A fairly accurate correlation exists between hardness and ultimate tensile strength (UTS) for steels. If that conversion is applied to the X42 base metal hardness, an UTS of 74 ksi is obtained. That value of strength is in good agreement with the measured UTS of 71 ksi for the X42 as reported in Table 3.2.

The seam weld on the X42 pipe purchased for this program was produced by the ERW (electric resistance weld) process. This type of seam weld is used on practically all line pipe with diameters of 12 inches or less. Sandia has observed subcritical crack growth in 1000-psi hydrogen in the heat-affected zone (HAZ) of welded X60 plate. Those welds were not from actual line pipe and were fusion-type submerged arc welds (SAW). That type of weld is characteristic of the seam welds on the newer large-diameter line pipe. During the current program, additional specimens from the same welds studied by Sandia (SAW) and the X42 seam weld (ERW) will be evaluated for subcritical-crack-growth in 1000-psi hydrogen gas.

Figure 3.4 shows the structure of the X42 seam weld at low magnification. Figure 3.5 is a higher magnification photomicrograph of the weld bondline taken near midthickness. Table 3.3 gives data for hardness at selected distances from the bondlines of weld near midthickness and approximate UTS by conversion. Those data indicate that the seam weld is considerably harder than the X42 base metal. However, such variations in hardness probably are typical of many ERW seam welds in pipe that currently is in use.

Tests With Compact Tension Specimens

The fatigue-crack-growth tests using compact tension specimens have not begun because of delays in the delivery of specimens from a subcontracting machine shop and in the delivery of the stainless steel load cell for use inside the test chamber. Except for the load cell, all aspects of the test apparatus have been completed and testing can begin upon delivery of the specimens and the load cell. Testing is expected to start in late December or early January.

Pipe-Section Tests

The pipe-section tests have been started and initial tests have been conducted on the 4-inch A106B pipe section without any operational problems. Results will be reported when the data analysis is completed.

Publications:

Holbrook, J. H., Cialone, H. J., and Mayfield, M. E. Hydrogen compatibility of steels. Proc. Thermal and Chemical Storage Annual Contractors' Review Meeting, Tyson's Corner, Virginia, September 1981.

TABLE 3.1
CHEMICAL COMPOSITION OF ALLOYS (WEIGHT PERCENT)

	Alloy			
Element	X42	X60	A516-70	A106B
C	0.26	0.12	0.22	0.26
Mn	0.82	1.29	1.10	0.57
P	0.020	0.014	0.009	0.007
S	0.028	0.016	0.023	0.016
Cu	0.02	0.03	--	0.01
Ni	0.02	0.01	--	0.01
Al	0.00	--	--	0.02
Si	0.01	0.25	0.21	0.15
V	0.00	0.03	--	0.00
Cb	0.00	0.01	--	0.00
Cr	0.04	0.02	--	0.01

TABLE 3.2
TENSILE PROPERTIES OF ALLOYS

	Alloy			
Property	X42	X60	A516-70	A106B
0.2 Percent YS (ksi)	45	69	54	67
UTS (ksi)	71	98	78	81
Percent elong. (1 in.)	21	24	17	14
Percent RA	52	62	70	58

TABLE 3.3
X42 HARDNESS/DISTANCE FROM ERW BONDLINE

Distance, in.	Hardness, R_B[a]	TS, ksi[b]
0.000	99	112
0.030	95	101
0.095	93	96
0.220	88	85
1.000 (base metal)	81	74

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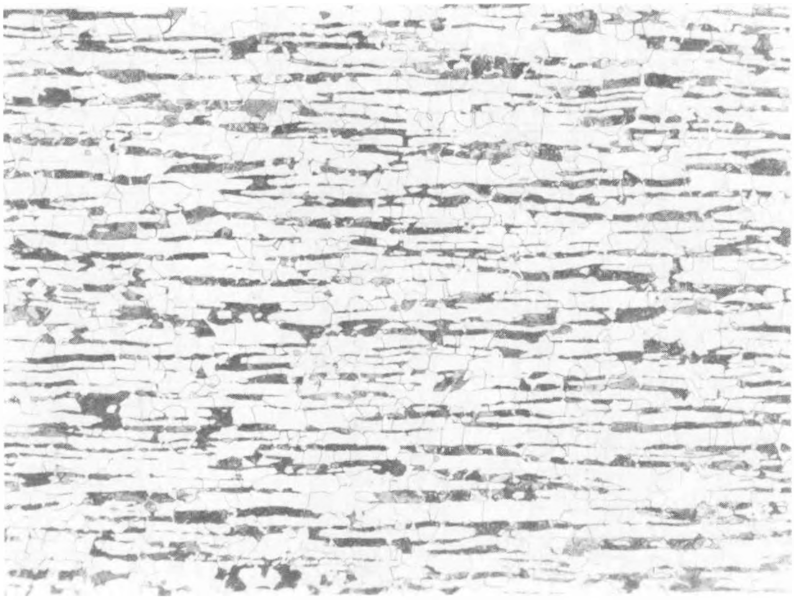
[a] Converted from KNOOP microhardness values.

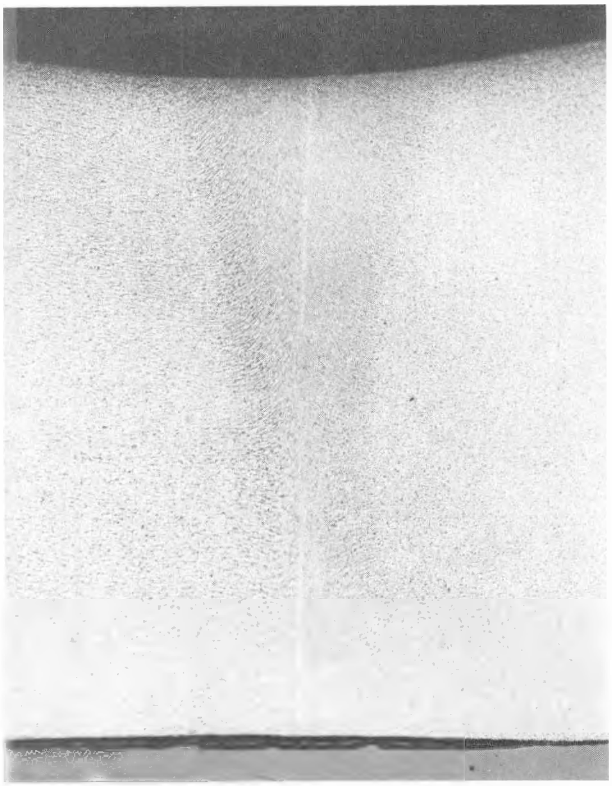
[b] Converted from hardness values.



100X Nital Etch 6K135

Figure 3.3 Microstructure of X42 Base Metal

The microstructure is banded and consists of ferrite and pearlite.



10X Nital Etch 6K126

Figure 3.4 Microstructure of Seam Weld in X42 Pipe

100X Nital Etch 6K127

Figure 3.5 Microstructure of X42 Seam Weld Near Mid-Thickness of Pipe Wall

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

Objective:

The purpose of this project was to verify the commercial prospects for merchant hydrogen production from a small hydropower site which would have led to a field demonstration in Potsdam, New York. This project was to be jointly funded by DOE and NYSERDA, with the Village of Potsdam contributing an equal share if the project were taken through construction and operation. NYSERDA was the implementing contractor assisted by Rist-Frost Associates Consulting Engineers from Glens Falls, N.Y. In 1981, the decision was made by DOE and, independently, by NYSERDA, not to proceed to the construction phase of the project for reasons indicated below. The Village of Potsdam subsequently decided to continue the redevelopment of the hydropower site for electric power generation under its own funding and the work is currently in progress.

Tasks:

Phase I	Planning and Analysis	Completed 1980
Phase IIa	Site Selection	Completed 1980
Phase IIb	Site Engineering	Completed 1981
	Decision not to proceed	June 1981
Phases III & IV	Construction & Operations	Not Applicable

Technical Progress:

Background

The goals of the demonstration project at Potsdam, New York, were twofold. First, an existing low head hydropower site, typical of many throughout the State of New York, was to be redeveloped. Second, a determination would be made of the economic viability of a hydrogen electrolyzer facility in conjunction with the hydropower redevelopment.

The economic viability of the hydrogen electrolyzer was determined by an engineering evaluation of current electrolyzer technology, followed by final design and costing of a facility. Concurrently, a market survey and economic analysis of the project were done to define potential customers and price levels at which the product hydrogen would be competitive with commercial hydrogen.

Low-head hydropower represents an energy resource which has been neglected to a large degree in recent years. Many existing sites were abandoned during the mid-twentieth century because of the availability of cheap petroleum. Still other sites remain undeveloped because of the high capital cost of generating facilities.

A further disincentive to low-head, small hydropower has been the low price utilities have been willing to pay for "dump" power. Hydrogen generation by electrolysis would overcome this disadvantage by allowing energy storage. The hydrogen would be used as supplemental fuel in fossil-fuel peaking power generation or shipped for use in the commercial hydrogen market. Either use of hydrogen would provide more revenue than the sale of electricity at dump power rates (historically in the 5 to 6-mil range) and in some cases would eliminate the need for interconnection with the utility grid.

The Village of Potsdam was selected in 1978 as the site for the hydrogen from hydropower demonstration project because it had an existing, but unused, low-head site available on the Raquette River. This run-of-river facility had 10 ft of head, typical of many sites which have not been economically feasible to redevelop. The Village had previously supported hydropower redevelopment with a feasibility study performed by Rist-Frost, Associates in 1976. One other indication of Potsdam's willingness to support the project was the fact that the space for the electrolyzer facility was made available at the sewage treatment plant.

Project Accomplishments:

An engineering evaluation was made of the characteristics of the Potsdam hydro site. An 800-kW vertical semi-Kaplan turbine installation in the existing powerhouse was selected as capable of providing the highest output at the least capital cost per installed kilowatt capacity. Final plans and specifications were prepared for a facility which would wheel power over the utility lines to the electrolyzer, and also provide standby power to the Village water treatment plant. A license exemption was secured from the Federal Energy Regulatory Commission (FERC), along with state and federal permits.

Nine electrolyzer manufacturers were contacted to determine their capability and interest in providing a demonstration unit at Potsdam. Five were eliminated because of excessive cost, outdated technology, or lack of interest. The remaining four - General Electric, Norsk Hydro, Teledyne Energy Systems, and The Electrolyzer Corporation, Ltd. - were studied further. Detailed technical data were obtained and a system design was developed for each manufacturer's product to provide realistic capital and operating costs. A life cycle economic analysis then narrowed the field to the General Electric 250 Solid Polymer Electrolyte (SPE) unit (see Table 3.4). Construction plans and specifications were prepared for a 2500 standard cubic feet per hour (SCF) facility with gas purification and compression.

A market survey was conducted to determine:

a) What price users of hydrogen would be willing to pay for electrolytic, high-purity gaseous hydrogen.

b) The characteristics of the commercial hydrogen market in the Potsdam region (see Figure 3.6).

Distributors, producers and consumers were contacted and market constraints were identified (see Figure 3.7). A life cycle analysis of the integrated hydro and hydrogen facility determined the revenue at which the electrolyzer facility (capital, operating, and maintenance costs) represented a breakeven investment.

Conclusions of Study:

The demonstration project was continued through the preliminary and detailed design, and economic analysis stages. The conclusion is that the solid polymer electrolytic facility is technically sound, but will not be economically viable in the context of a small hydro project such as Potsdam.

The hydro facility can be economically self-sustaining at first year revenues of \$.045/kWh. At that cost of power, the GE 250 electrolyzer requires a sale price of \$0.70/HCF (or about \$30/MBtu) at the site in the first year of operation to be economically viable. Because of both the high cost of transportation and the lack of demand for high-purity gaseous hydrogen, such a sale price is not likely to be attained in Potsdam. Gaseous hydrogen is noncompetitive with liquid hydrogen both in transport costs and in product purity. The conclusion must be drawn that a small electrolytic hydrogen facility is unlikely to be competitive with commercial producers unless a consumer can be located on site or within a short pipeline distance.

Figure 3.6

HYDROGEN PRICE STRUCTURE (POTSDAM AREA)

INDUSTRY	RETAIL PRICE	ANNUAL CONSUMPTION	SOURCE	COMMENTS
Electric Utility	Sliding Scale: \$4.90/HCF First 20,000 ft^3 \$1.95/HCF Next 80,000 ft^3 \$1.15/HCF Over 100,000 ft^3 Plus: \$0.08/25 mi/HCF haul fee	Not Available	Gaseous - Tube Trailer	Prices at Production Plant
Metal Heat Treating	\$.85/HCF	4.2 million SCF	Liquid Tank Trailer	Price Delivered
Semiconductor Manufacture	\$.78/HCF plus \$1100/mo. Facility Fee	4.8-6.0 million SCF	Liquid Tank Trailer	Price Delivered
Metallizing	\$1.71/HCF Plus \$500/mo. Trailer Rental	4 million SCF	Gaseous - Tube Trailer	Price Delivered Canadian Dollars
Generator Manufacture	\$.68/HCF plus \$2000/mo. Facility Fee	12 million SCF	Liquid Tank Trailer	Price Delivered
Semiconductor Manufacture	Not Available	6.6 million SCF	Liquid Tank Trailer	
Semiconductor Manufacture	\$4.80/HCF plus \$600/mo. Trailer Rental	0.18 million SCF	Gaseous - Tube Trailer	

Figure 3.7

RESULTS OF MARKET SURVEY (POTSDAM VICINITY)

Potential Customers: Merchant H_2 Firms, Industries, Utilities

Product Offered: Electrolytic Hydrogen, Grade E, 1983 Price $.70-.80/HCF at Potsdam

Customer Response: Generally negative - possible interest if cost of natural gas escalates significantly

Contributing Factors	Reasons Given
1. Unattractive Price	Present cost \$.19 to .38/HCF from steam reformed natural gas.
2. Market Distance/Transport Cost	No customers within 50 mile radius. Gaseous H_2 too expensive to ship. Liquid H_2 is cheaper at \$1.50/mile.
3. Product Handling Restrictions	Most customers prefer liquid H_2 (cryogenic) delivery. Conversion to gas presents problems.
4. Contract Constraints	Most customers have multi-year contracts with penalties for nondelivery. Reliability of the small hydro supply was an issue.
5. Purity	For many manufacturing operations higher purity liquid H_2 is required.

TABLE 3.4
SUMMARY OF COSTS[1]
Potsdam Hydrogen Electrolyzer Selection
(Costs in $1,000)

		TELEDYNE		GE			NORSK		GE
MANUFACTURER		I	II	Proto-type	Production	ELECT. LTD.	I	II	250
Capital Costs+	Bldg.	25	25	25	25	58	63	63	55
	Other	371	410	491	381	359	524	439	426
Annual Operating Costs (1983 $)	Electricity (4.5¢/kWh)	100	81	61	61	82	107	79	126
	Other	18	18	11	11	19	12	12	10
Major Overhaul	Cost	10	10	100	100	20	18	18	34 52
	Period (yr.)	3	3	5	5	12	3	3	5 10
Electrolyzer Output (SCF)		1272	1272	1000	1000	1270	1865	1400	2500
Annual Income @ $2.00/100 SCF		216	216	175	175	217	327	245	394
Life Expectancy of Equipment		20	20	20	20	30	25	25	20

+Capital costs in current dollars.

++$1.50 Present value inflated @ 15%/yr for 2 years to first year of operation.

*Costs presented for GE 250 are projections based on development goals for this electrolyzer. (1983)

[1] These comparative costs were developed and adjusted for the particular unit required at Potsdam. The costs and relative merits of the systems could vary considerably for different-sized systems or design conditions, i.e., extrapolation or generalizations regarding the above data may not be valid.

[2] Two design options were presented by both Teledyne and Norsk Hydro.

4.0 CHEMICAL ENERGY STORAGE/RECOVERY SYSTEMS

Summary

This section describes the efforts of three investigators to recover hydrogen from existing or waste gas streams, which are summarized as follows.

- Several waste streams having a potential hydrogen recovery of 2 x 10^9 SCFD were identified, and hydride behavior tests with individual impurities were completed. The results have been used to improve the predictive model for damage caused by individual impurities, leaving the effect of multiple impurities to be determined. A cost comparison showed that the hydride process has no general economic advantage over steam reforming of the selected streams.
- Bench-scale tests on bubbling hydrogen sulfide through molten copper showed that the copper could be recycled, leaving sulfur dioxide as a by-product. Since the market for sulfur dioxide (or sulfuric acid) will not support the process economically, the commercial prospects for the process are poor.
- Metal-hydride (La-Ni-Al) processing was selected as a cost-effective method of hydrogen recovery. Laboratory-scale tests showed that 80% of the hydrogen in transmission-line natural gas (no odorant), supplemented with 20% hydrogen, could be recovered provided the carbon dioxide is removed first. The estimated hydrogen cost was $1.40/MBtu at a scale of 1 x 10^6 SCFD.

BNL through its National Center for the Analysis of Energy Systems conducted separate techno-economic assessments of the above processes and the conclusions are incorporated in the above summary and described separately herein.

4.1 Development of a Commercial Metal Hydride Process for Hydrogen Recovery

Ergenics Division of MPD Technology, Air Products & Chemicals, Inc., and INCO Research & Development Center

Objective:

The proposed program, which has as its primary objective the commercialization of a hydrogen recovery process based on metal hydride technology, is to be accomplished in three program phases. Phase I, Process Identification, is currently being funded and will, subsequent to BNL/DOE decision, be followed by Phase II, Engineering, and Phase III, Pilot Plant Demonstration.

Tasks:

The Phase I program consists of seven principal tasks. The experimental effort is conducted by both APCI and IRDC personnel at their respective R&D centers.

Task 1. Select Sites and Streams: Identify the types and availability within the United States of process streams from chemical and refining industries now being discarded or flared. Select several candidate streams and sites and recommend impurities and impurity combinations for studies in Tasks 2 and 3.

Task 2. Quantify Poisoning by Key Contaminants: Subject the alloys FeTi, (Fe,Mn)Ti, $LaNi_5$, Mg_2Ni, and Mg_2Cu to mixtures of hydrogen containing gaseous impurities such as CO, O_2, H_2S, C_2H_4, NH_3, SO_2, and CH_4, under conditions of temperature and concentration not heretofore studied. Quantify the loss of absorption/desorption kinetics and hydrogen capacity.

Task 3. Evaluate Pretreatment Options: Develop cost and performance data for gas pretreatments amenable to the treatments of the poisons identified in Tasks 1 and 2.

Task 4. Develop Regeneration Procedures: Evaluate purge, evacuation, and/or thermal treatments in an effort to restore the kinetics and capacity of the alloys poisoned in Task 2. Determine minimum requirements for *in situ* regeneration.

Task 5. Integrate Process Options: Specify process conditions for a metal hydride - hydrogen recovery system based on results from Tasks 1 to 4. Test process on a simulated stream.

Task 6. Preliminary Process Economics: Prepare process flowsheets, capital and operating costs, and sensitivity analyses for process(es) identified in Task 5.

Task 7. Phase I, Phase II, and Phase III Plans: Prepare a detailed plan and cost estimate for the work proposed for Phases II and III.

Technical Progress:

Task 1. The stream survey has identified 2.1×10^9 SCFD of hydrogen potentially available for recovery. Streams in the petroleum refining and Olefin industries were recommended as candidates. (Topical Report G.)

Task 2. Screening tests were done with 7 alloys and 12 binary gas mixtures at several temperatures. A qualitative summary of results is given in Table 4.1. Detailed information about each test is given in Topical Reports A, C, E, H, and I. CO poisoning is dramatically lessened by selecting a working temperature above 100°C where operation with CO concentrations in excess of 0.1% has been demonstrated. Sulfur-containing species, H_2S and COS, have been found to be poisons at both low and intermediate temperatures. Detailed interaction studies (Topical Reports B, D, and J) have led to the formulation of a predictive model for the damage caused by impurities.

Task 3. Stream pretreatment options were identified from the literature, and capital and operating costs were generated for cases in which a single gaseous impurity is to be reduced. (Topical Report L.)

Task 4. Regeneration procedures were evaluated in parallel with the poison studies of Task 2. Cycling in pure H_2 restores capacity lost by site blocking but not for alloy consumption (oxidation). (Topical Reports F and K now in preparation.)

Tasks 5 and 6. Preliminary separation costs have been estimated for the purge gas from a petroleum refinery hydroprocessing unit. Costs are based on 3 hydride beds in parallel to provide continuous H_2 production (300 psig, 99% purity, and 90% recovery). For a 5-MMSCFD H_2 recovery plant, the estimated capital cost is $\$2.8 \times 10^6$. Production costs are estimated at \$1.85/MSCF which includes stream fuel value, one hydride bed change-out, and excludes pretreatment costs. Current costs of H_2 made by the steam reforming of methane are estimated to be \$2.20 to 2.75/MSCF in quantities exceeding 50 MMSCFD. (Topical Report M.) The deregulation of natural gas pricing will further improve the economics of H_2 recovery as compared to steam reforming when the feedstock is natural gas.

Technical Problems:

All experimental work planned for Phase I has been completed. Two Topical Reports (F and K) remain to be completed (target January 15, 1982). Delivery of the Phase II Plan and the Final Report is targeted on February 15, 1982.

Although the Phase I results indicate that hydride technology can be applied to industrial off-gas streams, no testing has been done on either a synthetic or an actual stream containing multiple impurities. Until bench-scale tests and pilot demonstration data have been obtained on existing off-gas streams, no commercial assessment can be made. The work proposed for Phases II and III will address these issues.

The streams proposed for hydrogen recovery by the hydride process can themselves be steam reformed. Thus the hydride process should also be compared with steam reforming of the selected gas streams rather than just steam reforming of natural gas. When such a comparison is made there appears to be no economic advantage, in the general case, for hydride separation over steam reforming of the same gas. This appears to be true with assumed hydride alloy lives in excess of lives demonstrated to date.

Publications:

A status report was prepared for the Thermal and Chemical Storage Annual Contractors' Review Meeting, Washington, D.C., September 14-16, 1981. Four papers are currently in preparation for the June 1982 International Symposium on the Properties and Applications of Metal Hydrides - II. Proposed titles are: Hydrogen Separation from Mixed Gas Streams Using Reversible Metal Hydrides; Hydrogen Separation from Gas Mixtures Using $LaNi_5$ Pellets; Cyclic Response of Reversible Hydriding Alloys in Hydrogen Containing Carbon Monoxide; Cyclic Hydriding Response of $LaNi_5$ in Hydrogen Containing Oxygen as a Minor Impurity.

TABLE 4.1[a]
SUMMARY OF SCREENING TESTS FOR ALLOY-IMPURITY INTERACTIONS

Alloy	Temp (°C)	CO	O_2	H_2O	CO_2	H_2S	NH_3	N_2	CH_4	C_2CH_4	MOH	COS	Amine
					Impurity Concentrations 1 to 3%								
Mg Ni	300	I-H	-	I	H-C	I-H	P	-	H	H	H	P	-
$LaNi_4Al$	150	H	-	-	I	P	I	-	-	-	-	-	-
	115	H	-	-	-	-	-	-	-	-	-	-	-
					Impurity Concentrations 0 to 1%								
$LaNi_5$	115	H-C	C	-	-	-	-	-	-	-	-	-	-
	85	P	C	-	H	-	I-H	I	I	I	-	-	-
	25	P	C	I-H	H	(P-C)	(I-H)	-	(I)	(I)	(H)	-	(I)
(Fe,Mn)Ti	115	H	-	-	-	-	-	-	-	-	-	-	-
	85	P	H-C	-	H	-	-	-	-	-	-	-	-
(Fe,Ni)Ti	115	H	-	-	-	-	-	-	-	-	-	-	-
	85	P	H-C	-	-	-	-	-	-	-	-	-	-
	25	P	H	-	-	-	-	-	-	-	-	-	-
FeTi	115	H	-	-	-	-	-	-	-	-	-	-	-
	85	P	H-C	-	-	-	-	-	-	-	-	-	-
	25	P	P	P	-	-	-	-	-	-	-	-	-

[a] Symbol Key: I = Inert
H = Inhibits absorption kinetics
C = Capacity gradually reduced
P = Poison by surface occlusion

4.2 Recovery of Hydrogen from Hydrogen Sulfide

SRI International

Objective:

Investigate a proposed process using liquid copper for the recovery of hydrogen from the large quantities of hydrogen sulfide currently being produced in the desulfurization of sour crude oil and sour natural gas. (See Section 4.4 for a technical/economic assessment of this concept.)

Tasks:

Task 1. Construct an experimental bench-scale reactor to study the rate of reaction.

Task 2. Measure the rate of reaction of hydrogen sulfide with liquid copper as a function of gas flow rate, nozzle orifice size, temperature, gas residence time, etc.

Task 3. Incorporate the experimental results into a mathematical model and elucidate the rate-controlling step.

Technical Progress:

Task 1. A schematic diagram of the apparatus assembled for the rate measurements is shown in Figure 4.1. The reactor is an alumina or mullite tube surrounded by an electrically heated muffle furnace. The furnace can be heated to 1300°C, and can maintain a constant temperature zone of 10 cm at 1200°C. The copper melt is contained in an alumina or quartz crucible inside the reactor. Hydrogen sulfide is metered through a mass flowmeter and is introduced into the copper melt by means of alumina, quartz, or mullite nozzles. The product gases exit the reactor near the top and are analyzed for hydrogen, hydrogen sulfide, and other gaseous reaction products by gas chromatography. Two gas chromatographs are used in parallel, one for measurement of hydrogen, and the other for measurement of hydrogen sulfide and other gases. Provisions are made for evacuating the reactor, for purging with an inert gas, and for introducing gaseous impurities such as methane or carbon dioxide. The hydrogen sulfide stream can be replaced with oxygen or air for the purpose of oxidizing cuprous sulfide back to copper. A Pt-(Pt 10 to Rh) thermocouple is used to measure the temperature of the melt. Oxygen-free high-conductivity copper and technical-grade gases were used as reactants.

Two reactors were assembled: (1) an alumina reactor, 3.6 cm i.d., and (2) a mullite/quartz reactor, 10 cm i.d. The small alumina reactor can accommodate up to 400 g of copper; and up to 3 std liters per minute of hydrogen sulfide can be passed through it. A higher capacity of 6 kg and a flow rate of 20 std liters per minute can be achieved in the 10-cm reactor. The results shown under Task 2 were obtained in the small reactor.

Task 2. At 1200°C the rate of reaction of hydrogen sulfide with liquid copper was rapid and the conversion to hydrogen was found to be near the equilibrium level. Figure 4.2 illustrates the composition of reactor exit gas as a function of time when hydrogen sulfide was used as the reactant gas. The calculated conversion of copper to cuprous sulfide is also shown. It is seen that the rate of reaction remains constant until nearly all the copper is converted into cuprous sulfide. This is because (1) copper and cuprous sulfide are immiscible liquids at the reaction temperature; (2) cuprous sulfide is less dense than copper; and (3) the reaction rate is rapid. The immiscibility and the difference in density assures the movement of cuprous sulfide product away from the reaction interface leaving fresh copper for further reaction. Because of the rapid reaction rate, the residence time of the gas can be relatively short.

The steady state conversion of hydrogen sulfide to hydrogen was studied as a function of flow rate and orifice diameter. Flow rates ranging from 25 to 2370 SCCM (standard cubic centimeters per minute), and orifice diameters ranging from 0.07 to 0.9 cm were used. Under these conditions the conversion of hydrogen sulfide to hydrogen remained above 99%. Even at the highest flow rates used, 3000 SCCM, the conversion remained at (99.7 ± 0.03%) until nearly all the copper was converted to cuprous sulfide. It is estimated that a gas residence time less than one hundred milliseconds is sufficient for the completion of the reaction.

A few experiments concerning the recovery of copper by the oxidation of cuprous sulfide were also carried out. This reaction step has been well studied and is practiced commercially. Under laboratory conditions copper sulfide can be converted to copper by bubbling air or oxygen through the melt. The test results in Figure 4.3 show a high degree of conversion.

Carbon dioxide and hydrocarbons such as methane are potential impurities in hydrogen sulfide streams. Hence hydrogen sulfide containing 10%

CH_4 or 10% CO_2 was allowed to react with liquid copper at 1200°C. The presence of these impurities did not affect the hydrogen sulfide conversion rate. Methane decomposed to produce hydrogen and a carbon deposit inside the reactor. Carbon dioxide was transformed into carbon monoxide by reverse water-gas shift reaction as follows

$$2Cu + H_2S \quad Cu_2S + H_2, \tag{1}$$

$$CO_2 + H_2 \quad CO + H_2O. \tag{2}$$

Task 3. The interface reaction and liquid-phase diffusion were eliminated as possible rate-controlling steps, because of the high temperature and the formation of an immiscible, less dense cuprous sulfide reaction product. Thus diffusion of hydrogen, or hydrogen sulfide in the gas bubble to or from the gas-liquid interface, is likely to be the rate-controlling step. Using an unsteady-state diffusion model, the time required for complete depletion of hydrogen sulfide in bubble sizes ranging from 0.2 to 2 cm i.d. were calculated. The required residence time was found to vary from 5 msec for a 0.2-cm-diameter bubble, to 30 msec for a 1-cm-diameter bubble, to 120 msec for a 2-cm-diameter bubble. The verification of this model requires data from the larger reactor which are currently being obtained.

Technical Problems:

At present there are no major technical problems; however (see Section 4.4), disposition of reaction product SO_2 converted to sulfuric acid, which is in excess on the current market, makes the concept economically unattractive at this time.

Publications:

Krishnan, G. and D. L. Hildenbrand. Recovery of hydrogen from hydrogen sulfide. Proc. of the Thermal and Chemical Storage Annual Contractors' Review Meeting, Tyson's Corner, Virginia, September 1981.

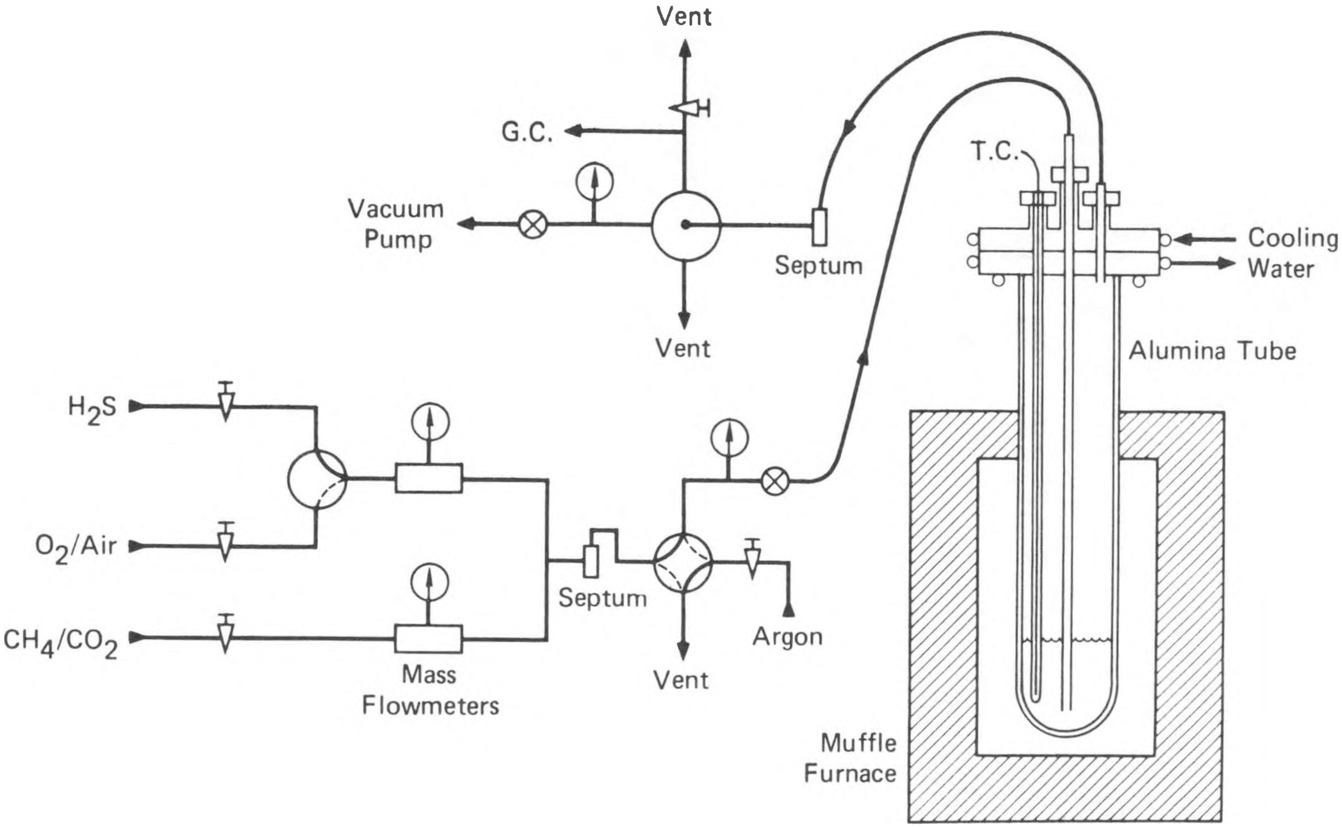


Figure 4.1 Schematic Diagram of the Bench Scale Reactor

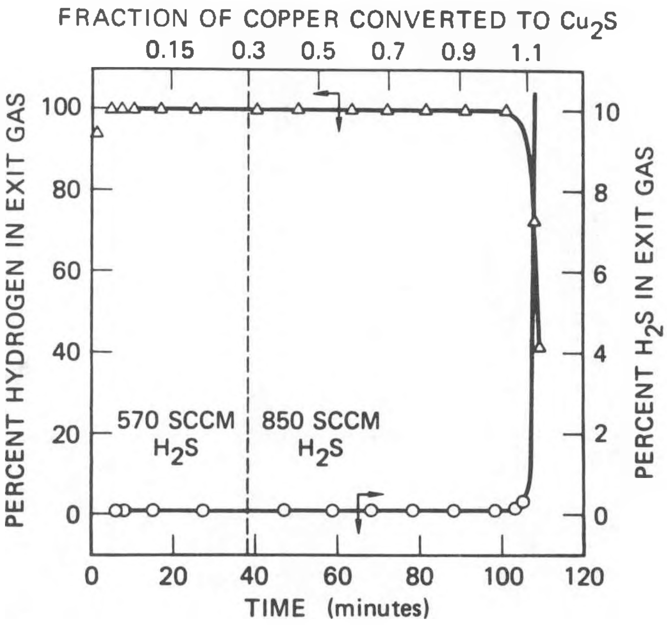


Figure 4.2 Composition of Reactor Exit Gas as a Function of Reaction Time; Initial Melt Height = 3.5 cm; Nozzle Diameter = 0.9 cm

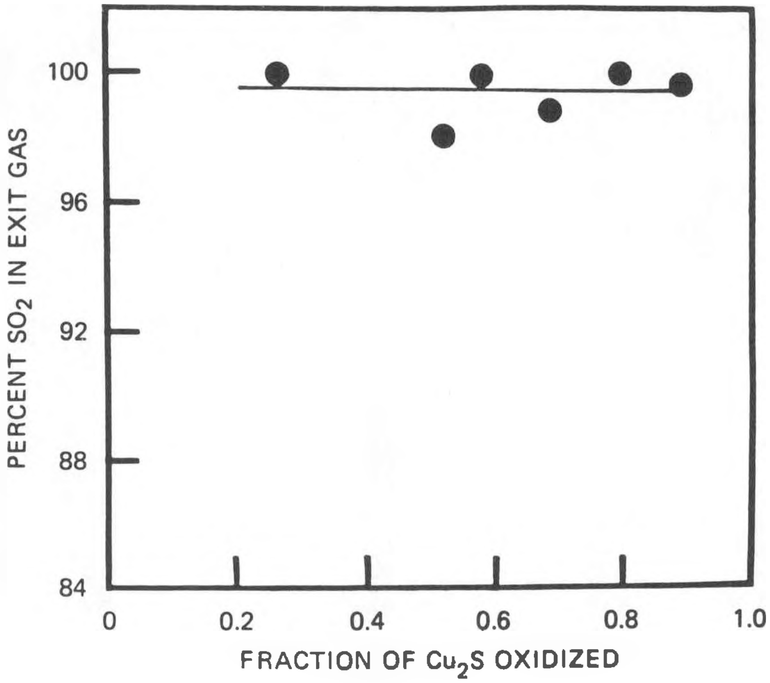


Figure 4.3 Percent of SO_2 in the Reactor Exit Gas as a Function of Fraction of Cu_2S Oxidized When Pure O_2 was Bubbled Through Cu_2S Melt at 1200°C; Nozzle Size = 0.9 cm; O_2 Flow Rate = 47 SCCM

4.3 Hydrogen Recovery from Natural Gas - Brookhaven National Laboratory

Objective:

The idea of extending natural gas supplies by addition of hydrogen has attracted considerable interest recently. Blends of natural gas with up to 25% hydrogen, so-called "supplemented natural gas," would be tolerated by existing transmission and distribution systems and would require little or no change in end-use devices. The objective of this project is to develop cost-effective processes for the recovery of hydrogen from supplemented natural gas using metal hydrides or other sorbents. This program complements the MPD-APCI program on hydrogen recovery from industrial process waste streams.

As a result of a review of existing separation processes, the hydrogen recovery process selected for detailed study was based on the use of metal hydrides. These materials selectively absorb hydrogen from mixtures with other gases and subsequently desorb the hydrogen in substantially pure form as the pressure is decreased or temperature increased. They are particularly effective in recovery of hydrogen at the low partial pressures existing in supplemented natural gas since metals or alloys can be found with very low hydride dissociation pressures. Recovery by alternative means, such as pressure swing adsorption or membrane processes, is favored by higher hydrogen partial pressures in the feed stream.

Tasks:

Task 1. Process Feed Stream Identification

Task 2. Selection of Separation Process and Sorbents

Task 3. Study of Alloy-Gas Interactions

Technical Progress:

The project work was completed during 1981 and the results are as follows:

Task 1. Process Feed Stream Identification - The feed stream is taken to be a blend of 20% hydrogen with natural gas leading to the composition shown in Table 4.2. The odorants, as will be mentioned below, severely poison the alloy to be used. It is thus desirable to take the feed from the transmission line before its juncture with the distribution system where the odorants are added. The minimum pressure at such a takeoff point is typically 400 psia. This pressure will be taken as the recovery process feed pressure. Hydrogen production rates of interest range from 1 to 100 x 10^6 SCFD.

Task 2. Selection of Separation Process and Sorbents - In the present work $LaNi_{4.7}Al_{0.3}$ was chosen as the process alloy since it has adsorption pressures which are small compared to a feed partial pressure of, say, 5 atm, at convenient, near-ambient temperatures. Pressure-composition isotherms for this alloy were measured at 25°, 50°, and 100°C. The results are shown in Figure 4.4. From the Van't Hoff relation, the heat of absorption was found to be 8.1 kcal/g-mole H_2 in agreement with the values given by Huston and Sandrock.[1] The difference between the absorption and desorption pressures is greater in the present work than that reported by Huston and Sandrock.

Task 3. Gas-Alloy Interactions - The interaction between gas mixture components and the hydriding alloy was studied to determine the nature of the interaction and to determine parameters of the interaction important for process design. Tests were conducted involving exposures of pure nonhydrogen components to the alloy and of mixtures of these components with hydrogen.

Pure Component Tests. In these tests, the adsorption of pure nonhydrogen components on the alloy surface was measured. Also the effect on the hydrogen absorption rate of exposure of the alloy surface to such components was measured. For those gases which poisoned the alloy, reactivation was sought by raising the alloy temperature in the presence of hydrogen. Experimental procedures and results are reported in detail in Reference 2. The results important for present purposes are as follows. The alkanes generally do not diminish the hydrogen absorption rate, CO_2 acts as an inhibitor, and the mercaptans are poisons. Regeneration of alloy surfaces poisoned by mercaptans requires exposure to UHP hydrogen at temperatures in the range 260^o to 500°C.

Mixture Tests. A schematic diagram of the apparatus for these tests is shown on Figure 4.5. Two forms of alloy were used: powder and pellets. The powder was INCO HY-STOR 207 with a nominal formula of $LaNi_{4.7}Al_{0.3}$ and heat #T-84405-2. The pellets which were also made of $LaNi_{4.7}AlAl_{0.3}$ are proprietary materials developed by an MPD Technology - Air Products joint venture. The reactors were made of stainless steel and contained 2.5 grams of active alloy each.

The temperature of the reactor was maintained constant to within ±0.1°C by means of a constant temperature oil bath. The experimental procedure was as follows:

1. Activate the alloy sample, and then cycle several times with H_2 (Matheson UPH grade with a minimum purity of 99.999% H_2) at the chosen temperature until a steady absorption rate was obtained. This is defined as the baseline or original absorption rate.
2. Cycle with hydrogen-impurity mixtures until a steady absorption rate was obtained.
3. Cycle with hydrogen at the same temperature to investigate the extent of recovery of the original absorption rate.

The ratio of the absorption time immediately following activation to that following subsequent operations was defined as the relative absorption rate.

Three types of experiments were performed: batch, constant pressure and flow-through. The batch and constant pressure experiments were carried out using dead-end reactors. In the batch operations, absorption involved a fixed volume of H_2 in a closed system. Constant-pressure operation involved the same system connected to a live H_2 source maintained at constant pressure. Flow-through experiments were operated at a constant H_2 flow rate and a fixed pressure level.

H_2-CO_2 Mixtures. Batch contacting experiments on interactions between H_2-CO_2 mixtures and $LaNi_{4.7}Al_{0.3}$ were carried out with repeated cycles of exposure and evacuation at several temperature levels. The relative rate decreased with number of cycles to a steady value usually after about 5 to 10 cycles, a typical result being shown in Figure 4.6. Following attainment of a steady value, restoration of the original absorption rate was attempted by repeated cycles of exposure to H_2 and evacuation. As shown in Figure 4.6 an increase in relative rate was obtained which leveled off after about 3 to 4 cycles. Results of a series of such experiments are shown in Table 4.3, where "ultimate evacuation pressure" means the final equilibrium pressure in the evacuation part of the cycle. Only batch experiments were conducted. Both alloy powder and pellets were tested.

One striking point as seen from Table 4.3 is that the original rate for the alloy powder was completely recovered when a 16-psia ultimate evacuation pressure was used, whereas only partial recovery was effected at 0.1 Torr

(1.9×10^{-3}-psia vacuum). However, for alloy pellets, the original rate was not fully recovered with the 16-psia ultimate evacuation pressure at 50°C but was completely recovered with 0.1 Torr at 100°C. It seems that the ultimate evacuation pressure has a stronger effect on the alloy powder than on the pellets and the temperature has just the opposite effect. In all cases, a higher temperature, a higher evacuation pressure, and a lower CO_2 concentration increase the hydrogen absorption rate.

It is also seen from Table 4.3 that much higher absorption rates were obtained with pellets than with powder either with H_2 or with mixtures. This is consistent with the principles underlying the design of the pellets.

H_2-CH_4 Mixtures. The results for these tests are presented in Table 4.4 for alloy powder and in Table 4.5 for pellets. In batch experiments with powder, it is seen from Table 4.4 that the steady relative rate is strongly affected by the CH_4 concentration. Since CH_4 does not interact with the alloy, the reduction in absorption rate should be due to mass transfer resistances. To confirm this, experiments were carried out with pellets under batch, constant pressure, and flow-through conditions as described before. As shown in Table 4.5, the hydrogen absorption rate increases from batch to flow-through conditions not only with H_2 but also with the mixtures. With H_2, the change was small because any diffusion limitation or mass transfer resistance is small. However, the improvement of the hydrogen absorption rate was dramatic with H_2-CH_4 mixtures, especially at higher CH_4 concentrations. Under flow-through conditions, the absorption rates with mixtures were about the same as with H_2, indicating that mass transfer resistance or diffusion limitation was almost completely eliminated.

As seen in Table 4.5, most of the equilibrium capacity was reached in the first minute of absorption under flow-through conditions. This suggests that a short absorption cycle time may be employed.

Process Design and Economics

On the basis of the experimental work described above, a preliminary process design was prepared. The principal process components consist of a pretreatment section and a hydrogen recovery section as shown in Figure 4.7. Pretreatment is definitely required if mercaptans are present. If mercaptans are absent, pretreatment may be required to reduce the CO_2 concentration prior to hydrogen absorption. Alternatively, larger absorption needs may be used to overcome the reduced rates brought about by the presence of 0.6% CO_2. The choice of one approach or the other will depend upon cost estimates yet to be made. It is likely that the pretreatment option will be less expensive.

The pretreatment scheme shown is for removal of either mercaptan or CO_2 and would entail adsorption with an adsorbent appropriate for the species of interest. A two-bed system is shown. One bed is on line while the other is being regenerated.

The hydrogen recovery section consists of two beds of $LaNi_{4.7}Al_{0.3}$ pellets, one absorbing and the other desorbing. A third bed may be necessary if further work discloses that a long desorption time is required.

Cost estimates for hydrogen recovery were prepared using the Lang factor method (References 3 and 4) and assuming an alloy cost of $10/lb, 80% hydrogen recovery, 70% utilization of the alloy capacity, and carbon steel as the material of absorber construction. The cost of any required regeneration is not included.

Results of the cost estimation work are given in Table 4.6. While the base case cost of $\$1.40/10^6$ Btu appears to be at least competitive with the costs of other hydrogen recovery methods, including membrane processes and pressure swing adsorption processes, the final cost is expected to be higher. Hence it is too soon to pass judge the process on the basis of cost consideration.

Cost sensitivities are shown in the lower half of Table 4.6. The cost is highly sensitive to the concentration of hydrogen in the feed and to the presence of odorants. It is only weakly sensitive to production rate and feed pressure.

Conclusion

Experimental studies of interactions of the components of supplemented natural gas with $LaNi_{4.7}Al_{0.3}$ have shown the following.

(a) Alkanes were physisorbed by the alloy and did not detrimentally modify surface behavior. An external mass transfer resistance was evident in the absorption of hydrogen from H_2-CH_4 mixtures. This resistance was greatly reduced in a flow system.

Publications:

Huang, D. T.-J., Reidinger, F., and Hill, F. B. Hydrogen recovery from supplemented natural gas by metal hydrides. Proc. DOE Thermal and Chemical Storage Annual Contractors' Review Meeting, Tyson's Corner, Virginia, September 1981.

References:

1. Huston, E. L. and Sandrock, G. D. Engineering properties of metal hydrides. J. of Less Common Metals, No. 74, p. 435 (1980).

2. Reidinger, F. and Hill, F. B. Development of a metal hydride process for hydrogen recovery from supplemented natural gas. Proc. Second World Congress of Chemical Engineering, Montreal, October 1981.

3. Lang, H. J. Simplified approach to preliminary cost estimates. Chemical Engineering, pp 112-113 (June 1948).

4. Guthrie, K. M. Capital cost estimating. Chemical Engineering, pp 114-142 (March 1969).

TABLE 4.2
COMPOSITION OF PIPELINE NATURAL GAS AND OF SUPPLEMENTED NATURAL GAS

Compound	Composition, percent by volume Pipeline Gas	 Pipeline Gas + 20 percent H_2
H_2	0.0	20.0
CH_4	96.3	77.0
C_2H_6	2.1	1.7
C_3H_8	0.4	0.3
i-C_4H_{10}	0.2	0.1
n-C_4H_{10}	0.1	0.1
i-C_5H_{12}	0.1	0.1
n-C_5H_{12}	0.1	0.1
CO_2	0.7	0.6
Odorant[a]	4 ppm	3 ppm

[a] Primarily mercaptans, principally t-butyl mercaptan.

TABLE 4.3
EFFECT OF CO_2 ON H_2 ABSORPTION RATE---BATCH EXPERIMENTS

A. UHP H_2 absorption for freshly activated alloy

T,°C	Initial H_2 partial pressure, psia	Absorption rate (r_o), Δ(H/M)min[a]	
		powder	pellets
1. Ultimate evacuation pressure (P_{eV}) <0.1 Torr			
25	89	0.405/0.27	---
50	89	0.405/0.78	0.663/0.11
100	180	0.095/0.43	0.316/0.98
2. P_{eV} = 16 psia			
50	90 (powder),80 (pellets)	0.429/1.08	0.66/0.6
75	142	0.406/1.4	0.58/0.58
100	180	---	0.28/0.55

B. Absorption of H_2 from H_2-CO_2 mixtures (y_{CO_2}=0.6%, except as noted)

T,°C	H_2-CO_2 mixture		UHP H_2	
	No. of cycles for steady rate	r/ro	No. of cycles for steady rate	r/ro
1. P_{eV} <0.1 Torr				
powder				
25	13	0.075	4	0.41
50	11	0.132	5	0.566
100	5	0.41[b]	3	0.57
100	7	0.18	5	0.57
pellets				
50	14	0.207	10	0.63
100	16	0.59	5	1.00
2. P_{eV} = 16 psia				
powder				
50	4	0.20	6	1.00
75	8	0.32	5	1.00
pellets				
50	15	0.217	14	0.63
75	6	0.65	7	0.93
100	5	0.67	3	1.00

---

[a] Actual absorption

[b] y_{CO_2} = 0.2%.

TABLE 4.4
EFFECT OF METHANE ON H_2 ABSORPTION RATE---ALLOY POWDER

Batch experiments

Ultimate evacuation pressure = 16 psia
Initial H_2 partial pressure = 144 psia

T,°C	y_{CH_4},%	UHP H_2	H_2-CH_4 mixture
		r_o, (H/M)min[a]	r/r_o
60	10	0.265/0.123	0.013
60	50	0.265/0.127	0.00015
75	0.6	0.406/1.03	0.954
75	10	0.265/0.38	0.0122

---

[a] Actual absorption time.

TABLE 4.5
EFFECT OF METHANE ON H_2 ABSORPTION RATE---ALLOY PELLETS

Ultimate evacuation pressure < 0.1 Torr

Batch (Initial H_2 partial pressure = 80 psia, except as noted)

T,°C	Y_{CH_4},%	H_2 absorption rate,Δ(H/M)min[a]	
		UHP H_2	H_2-CH_4 mixture
50	10	0.71/0.5	0.486/0.5
50	--	0.74	---
75	10	0.526/0.07[b]	0.526/0.38[b]
75	10	0.27	0.197
75	50	0.27	0.062

Constant pressure (Feed H_2 partial pressure = 80 psia)

50	10	0.762/0.5	0.586/0.5
75	10	0.47	0.234
75	50	0.47	0.084

Flow-through (H_2 partial pressure = 80 psia, flow rate = 300 SCCM)

50	10	0.762/0.5	0.753/0.5
50	--	0.77/30	---
75	10	0.47	0.44[c]
75	50	0.47	0.475[c]

---

[a] Actual absorption time: one minute, or as shown.

[b] Initial H_2 partial pressure = 138 psia.

[c] Slightly different operating conditions.

TABLE 4.6
PRELIMINARY ESTIMATES OF COST OF HYDROGEN RECOVERY

Base case

H_2 concentration in feed	20%
Feed pressure	400 psia
H_2 recovery rate	1×10^6 SCFD
Mercaptan concentration in feed	0 ppm

Factor	Change in Base Case Cost, %
H_2 Concentration in feed = 10%	+120
Feed pressure = 1000 psia	-3
H_2 recovery rate = 10×10^6 SCFD	-12
Mercaptan concentration in feed = 1 ppm	+ 64

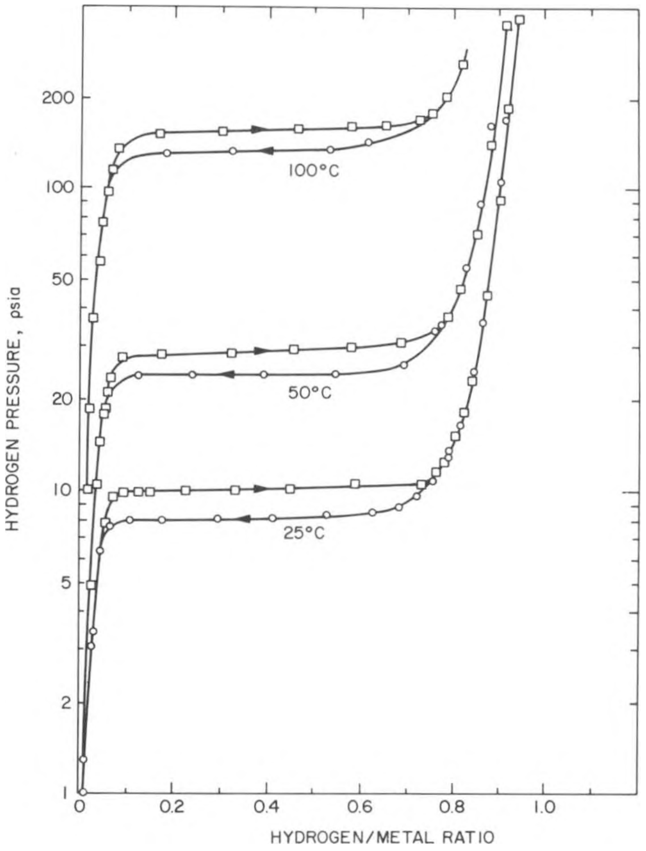


Figure 4.4 Hydrogen Absorption/Desorption Isotherms for INCO HY-STOR 207, $LaNi_{4.7}Al_{0.3}$ (Heat No. T-84405-2)

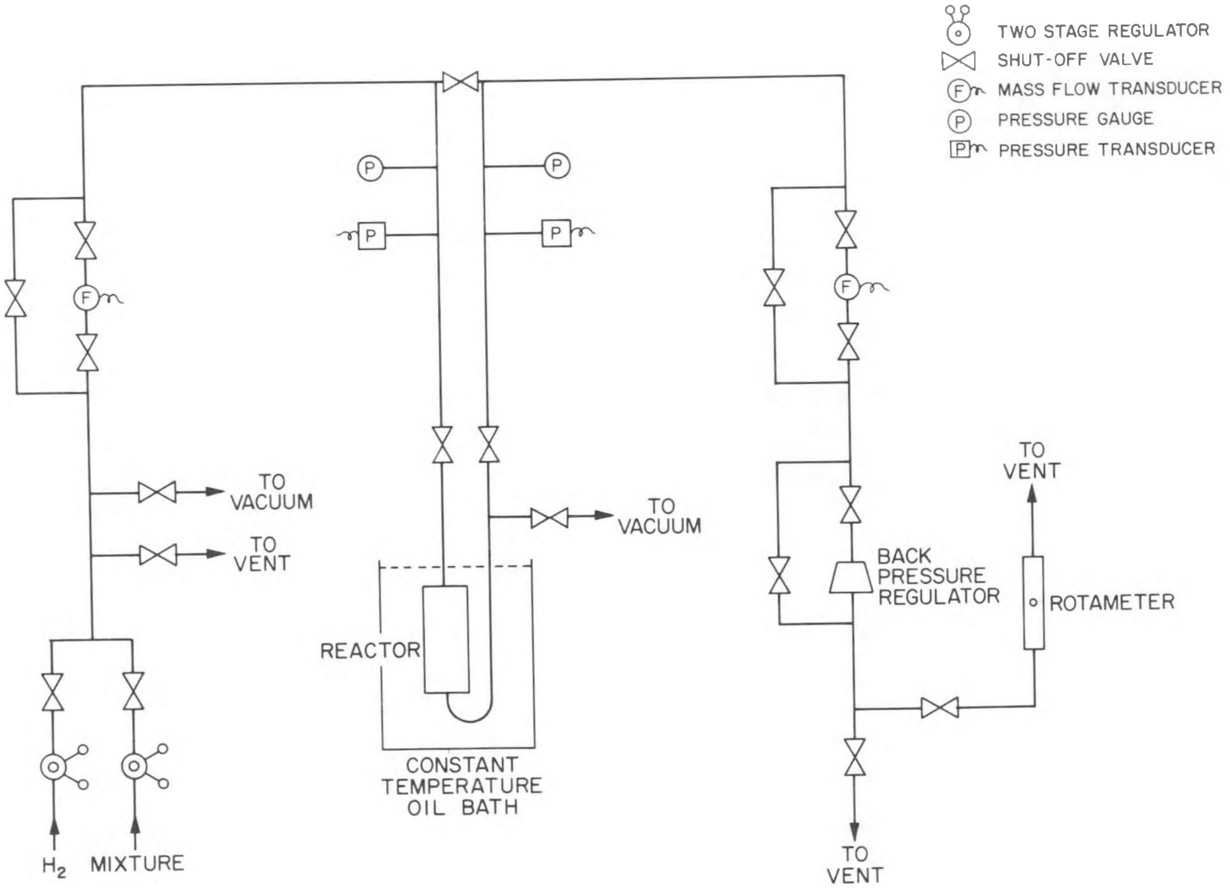


Figure 4.5 Schematic Diagram of Experimental Apparatus

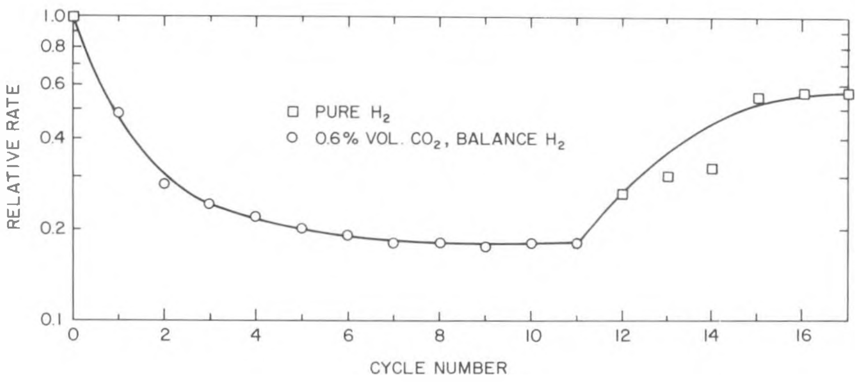


Figure 4.6 Cyclic Test of $LaNi_{4.7}Al_{0.3}$ Powder at 100°C

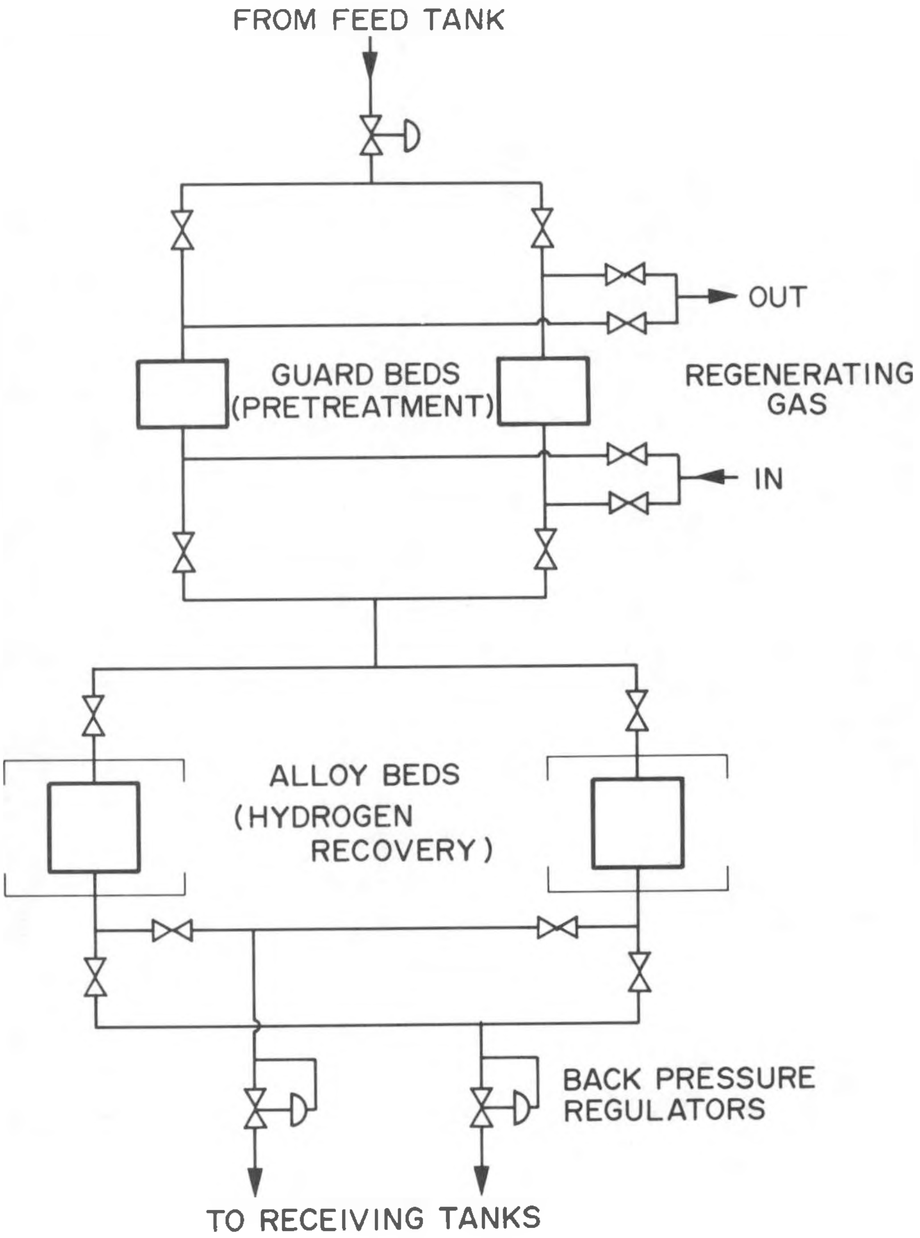


Figure 4.7 Process Flowsheet (Conceptual Design)

4.4 Systems Analysis Activities - Brookhaven National Laboratory (National Center for Analysis of Energy Systems)

Objective:

Provide quantitative assessment of technical/economic issues associated with specific technological options for the Chemical/Hydrogen Energy Systems activities.

Tasks:

Task 1. Analysis of Hydrogen/Natural Gas Supplementation and Separation.

Task 2. Evaluation of the SRI Hydrogen Recovery Process from hydrogen sulfide.

Task 3. Study of the use of metal hydrides for hydrogen purification.

Technical Progress:

Task 1. The hydrogen/natural gas supplementation option study was designed to assess barriers and incentives for the concept. The study included the selection of a specific site for the concept, an analysis of supply and demand relationships for the region, and an estimate of the potential for hydrogen by the various consuming sectors. Upon completion of this phase of the program, a workshop of representatives from industry, utilities, and goverment was convened to discuss the problems and benefits associated with the concept. On the basis of the workshop results, barriers and incentives were delineated. A 1977 Ad Hoc Committee report on hydrogen supplementation of natural gas was reevaluated in the light of current economics. A brief economic analysis of the concept was conducted and the findings are summarized in Figure 4.8. This shows that when natural gas is deregulated, hydrogen derived from coal gasification can compete with hydrogen from natural gas reforming in the year 2000 time frame, and that subsequently hydrogen from water electrolysis may become attractive. In summary, the hydrogen supplementation option has some attractive features which fit well with the existing energy system. However, hydrogen must compete economically with natural gas to provide large-scale penetration into the industrial sector.

Task 2. An SRI concept to recover hydrogen from hydrogen sulfide (H_2S) waste streams was analyzed. The process employs a molten copper bath to decompose H_2S into hydrogen and sulfur dioxide (SO_2). Current practices for eliminating H_2S rely on converting it to sulfur and water. The analysis studied existing markets for sulfur, hydrogen, and SO_2. On the basis of the market study, it was concluded that the SO_2, an environmental pollutant, required subsequent conversion to sulfuric acid, which is in excess supply. The sulfur produced by existing processes has a ready market. In summary, the study indicates that little, if any, advantage is gained by employing the SRI process. It recommended that H_2S decomposition work should focus on production of both sulfur and hydrogen.

Task 3. The use of metal hydride systems to separate hydrogen from chemical process streams was analyzed from both a process and an economic standpoint. The study was completed, and it was concluded that the process cost of the hydride system is crucially dependent upon the alloy lifetime. The hydride process for hydrogen separation competes against hydrogen costs from other sources. If hydrides in this type of service can demonstrate lifetimes of at least one year when used in these systems, then the hydride system might be competitive with natural gas-derived hydrogen at natural gas prices of about $6.00/MMBtu or greater.

Technical Problems:

None

Publications:

D'Acierno, J. and Beller, M. Analysis of the use of hydrogen as a supplement to natural gas, BNL 51442, September 1981; also presented at the 2nd World Congress of Chemical Engineers, Montreal, Canada, Sept. 1981.

Hermelee, A., Beller, M., and D'Acierno, J. Systems analysis of hydrogen supplementation in natural gas pipelines, BNL 30440, Nov. 1981; also presented at the 4th Miami International Conference on Alternative Energy Sources, Dec. 1981.

Beller, M. and D'Acierno, J. Assessment of SRI H_2S Technology, BNL 30022, Sept. 1981.

Beller, M. and Skaperdas, G. Assessment of Metal Hydride Process for Separation of Hydrogen from Waste Streams, draft, Nov. 1981.

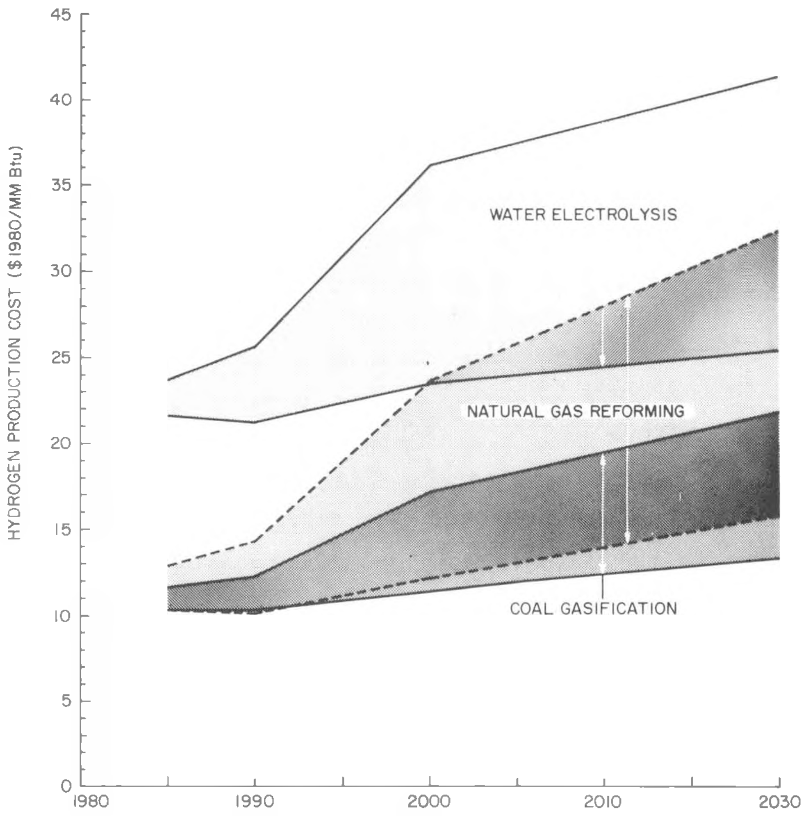


Figure 4.8 Forecasts of Hydrogen Production Costs Based on Natural Gas Price Parity with Residual Fuel Oil and Coal Prices Related to World Oil Prices

4.5 Microcavity Hydrogen Storage - R. J. Teitel Associates

Objective:

The objective of this project was to evaluate commercially available grades of glass microspheres for hydrogen storage and their performance in large beds (1 to 2 ft^3 in volume).

Tasks:

Task 1. Program Plan - A program plan was prepared to include test criteria, goals, and acceptable values for storage capacity, permeability rate, cost and attrition for several example applications.

Task 2. Microsphere Bed Preparation - Three 1-ft^3 microsphere beds were acquired. Two 1-ft^3 beds were filled to the highest attainable pressure, on a best effort basis, and all three cubic feet of microspheres were shipped to BNL for dispensing tests.

Task 3. Screen Tests - Screening tests included crush tests, total storage capacity tests, microsphere dimensional analyses, and chemical analyses. Standardized test procedures were developed. A minimum of eight grades of commercially available microspheres were tested. Two grades having the most promising performance properties for the microcavity storage system were selected for further study.

Additional tasks covering microsphere optimization tests, storage cost estimates, and cyclic tests were deleted midway through the program.

Technical Progress:

The bulk of this work was completed during 1980 and is described in the BNL Annual Report for 1980. The final report for the project was issued during 1981 with the following conclusions and problem areas:

Conclusions

The most significant conclusions drawn from this experimental study are:

- Two cubic feet of hydrogen-filled microsphere beds have been produced with reasonable reproducibility. They were handled, packaged, and shipped to BNL without appreciable loss of hydrogen.
- None of the commercially available "off-the-shelf" microspheres can be used under fill-dispense cycles for 400-atm room-temperature hydrogen storage without breakage on the first fill-dispense cycle. "Customized" microspheres might yield better performance.

- Although the microsphere strength requirement may be met, the dispension characteristics of candidate grades for automotive applications will need improvement by adjusting the glass composition.
- A new source of high strength microspheres with high hydrogen permeability was found in the Emerson & Cuming grades HAS and HASY.
- The crush strength of microspheres depends upon the chemistry of the atmosphere. Microspheres appear to be stronger in hydrogen than in either helium or nitrogen.
- Although the commercial "off-the-shelf" grades of microspheres are not satisfactory, some of the microspheres were filled and dispensed to a storage pressure of 400 atm, thus establishing that the microsphere storage concept is feasible.

Problem Areas:

The use of commercial-grade hollow-glass microspheres for high pressure hydrogen storage has been shown to be not cost effective. The major factors affecting storage costs are: the initial material cost, the breakage due to fill/release cycling, the hydrogen storage density, the recoverable hydrogen fraction, and the energy intensiveness of the filling and release process.

- The material cost, originally estimated to be on the order of 10¢ per pound, has been quoted by two manufacturers to be between $1.00 and $1.75 per pound.
- Microspheres are fragile and breakage as a result of filling and dispensing hydrogen can be appreciable. High differential pressures across the thin glass wall, whether internal or external, tend to break the microsphere. Loss or breakage as low as 1% per cycle is not cost effective.
- The results of the experimental effort show that commercially available microspheres can usefully store less than 5% hydrogen by weight instead of the original estimate of 10%.
- Commercial-grade microspheres are not suitable for hydrogen storage, although material customized for that application may fare better.

5.0 CHEMICAL HEAT PUMPS

Summary

This section describes the activities on two chemical heat pump (CHP) programs using different reaction systems, and also the results of an assessment of CHP's as compared with the competing technologies. Rocket Research completed its test program on the verification test unit demonstrating the capabilities of the sulfuric acid/water system. In the industrial waste heat upgrade mode, temperature amplification of 113°F was achieved in going from an input of 195°F to a process outlet temperature of 308°F. Problems encountered during the test program involving bed retention led to design changes including the use of Carpenter 20 steel for the reaction trays. In the program conducted by SOCAL/Solar Turbines to develop a metal hydride chemical heat pump, a conceptual design and preliminary market survey were completed. A hydride pair was selected, $LaNi_5/LaNi_{4.5}Al_{.5}$, and the thermal/mechanical design of a test unit was initiated. The market survey indicated that the industrial waste heat upgrade application was most promising with potential applications in the food, textile, paper and pulp, and chemical industries.

A cost-effectiveness evaluation of CHP technologies was completed by TRW, Inc. The study indicated that in industrial applications CHP's were more cost effective than conventional vapor recompression equipment. The only commercially available heat pump, the Westinghouse Templifier, is limited to temperatures below 230°F which is below the range of CHP's. In residential HVAC applications only the solar-driven systems appeared to be competitive, while because of the cooling load, commercial HVAC applications were very unfavorable.

Argonne National Laboratory provided engineering analysis support to the program in assessing the thermal design of the metal hydride CHP.

5.1 H_2SO_4/H_2O Chemical Heat Pump/Thermal Energy Storage - Rocket Research Company

Objective:

The objectives of this project are to produce an H_2SO_4/H_2O chemical heat pump verification test unit (VTU) which incorporates commercial design features and materials where possible, provides engineering scale-up data, and determines economic feasibility.

Tasks (1981):

The tasks conducted in 1981 were:

Task 3. VTU Fabrication and Assembly: This task consists of the procurement and construction of components, site preparation, and installation and assembly of the VTU including system instrumentation.

Task 4. VTU Testing: The VTU test program consisted of vacuum leak checks, system shakedown testing using both water and acid (including a low temperature 150°F checkout), establishing acid fill and drain procedures, and conducting performance testing with the unit operating in the industrial waste heat upgrade mode.

Technical Progress:

Task 3. The fabrication and installation of the VTU along with the necessary peripheral equipment such as the waste heat simulator have been completed. Figure 5.1 presents a photograph of the completed VTU without the simulated heat source sinks attached. The VTU was designed with both horizontally integrated combined generator/condenser and absorber/evaporator reaction components. The horizontally integrated design is both compact and adaptable to scaling. The reactors are fashioned from 18-inch-diameter pipe closed at one end by a welded elliptical end cap, and closed at the access end with an ASME-rated flange. The interior of the pipe and end cap are completely lined with vitreous porcelain enamel. The lower half of the reactor contains a Carpenter-20 reaction tray. Both the generator section and the condenser assembly, as well as the evaporator/absorber, are removable for inspection or component change or replacement, and are designed to interface with standard acid and water plumbing.

Acid service heat exchangers were designed by RRC in response to requirements imposed by the VTU which exceed design limits of existing commercial units. Low-cost readily available hardware and common materials of construction were used throughout to create a heat exchanger with higher performance limits and lower costs than competing brands. Each heat exchanger contains 60 square feet of surface area with 31 Pyrex glass tubes, Carpenter-20 Cb-3 tube sheets, and Kalrez O-rings on the acid side.

Acid and water storage tanks were designed for the VTU. Each tank is ASME pressure rated and each is fully vacuum capable. The acid tank is located low on the support frame to allow gravity drainage from the rest of the system components.

The acid plumbing for the VTU has been configured in Teflon-lined pipe and clamp valves; water plumbing is black iron pipe. A natural gas-fired water heater was selected to simulate the waste heat source. A combination flash and hot-water storage tank was added, as the water heater has no storage.

Raw material procurement and subcontractor selection was completed with few problems. The larger components, in particular the reactors, reaction trays, acid tank, and main frame were fabricated by local contractors. The porcelain lining was also applied by a local firm. Parts were made to print, and deliveries were on schedule.

Task 4. The VTU test program was completed in December 1981. The closed loop temperature amplification capability of the VTU was successfully demonstrated with measured data correlating well with performance predictions. With a simulated source input of 195°F, a maximum process outlet temperature of 308°F (amplification equal to 113°F) was measured. An acid temperature of 324°F was produced in the absorber. This represents the limit of the sulfuric acid system operating with a single waste heat source of 195°F. During the performance testing, electrical coefficients of performance were monitored and found to range between 9 and 11.

Performance predictions for a system operating with two reject heat sources of different temperature were analyzed during the current year. The results indicated that temperatures of 350° to 420°F can be achieved for industrial process purpose.

A significant start-up requirement for chemical heat pumps and all similar devices was identified as a result of the test program. The absorber and process heat exchanger thermal mass temperatures must be increased by an external heat source to the desired amplification temperature before the cycle is started. Otherwise, significant working fluid dilution occurs and the process temperature, CHP output, will be lower than desired. This external heat input is required only during the start-up transient and was simulated during the test program by starting with higher acid concentrations than desired, thereby using the heat of dilution and absorption for warmup during the start-up transient. This requirement is not expected to result in a major system cost impact.

Technical Problems:

Early in the Task 4 VTU test program, two equipment problems were observed during shakedown testing: retention of the column packing in both the generator and absorber, and collapse of the Teflon liner in the 4-inch-diameter acid plumbing. System acid flow was reduced and liquid holdup was produced in the generator and absorber. The loss of this liquid in the system plumbing caused cross-pressurization between the generator and absorber, therefore eliminating continuous cycling. The 4-inch Teflon-lined pipe fittings were returned to the manufacturer and replaced without additional cost with new units having special vacuum ports for balancing pressure across the lining. The bed retention problem was solved by changing the design of the reaction trays and making new units, using welded Carpenter-20 Cb-3. The system was reassembled and the testing was successfully completed as described previously.

Publications:

Clark, E. C. and Morgan, O. M., Chemical heat pumps for industry. Proc. 16th Annual Intersociety Energy Conversion and Engineering Conference, Atlanta, Georgia, August 1981.

Clark, E. C. Sulfuric acid/water chemical heat pump. Presented at the DOE Heat Pump Integration Task Force Meeting, McLean, Virginia, June 1981.

Clark, E. C. The sulfuric acid/water chemical heat pump/thermal energy storage program. Proc. DOE Thermal and Chemical Storage Annual Contractors Review Meeting, Tyson's Corner, Virginia, September 1981.

Clark, E. C. Chemical heat pumps with seasonal energy storage. Proc. International Conference on Seasonal, Thermal, Compressed Air Storage, Seattle, Washington, October 1981.

5.2 Metal Hydride/Chemical Heat Pump Development Project - Southern California Gas Company (SOCAL)

Objective:

The objective of the project is research and development aimed at the design, development, and demonstration of a cost-effective metal hydride heat pump (MHHP) for residential, commercial, or industrial application.

Tasks:

The development effort is planned as a three-phase program. The first phase was directed toward establishing the conceptual design. This was followed by a national market survey and commercial feasibility study to identify the most promising applications and markets. An engineering development test unit (EDTU) is being designed for the target market application.

In Phase II, the EDTU will be fabricated, tested, rebuilt as necessary, and retested. This will lead to the detailed design of an engineering evaluation test unit (EETU). Additionally, on the basis of the technical results obtained in this phase, a more in-depth commercial feasibility analysis will be performed. During Phase III, the EETU will be fabricated and tested.

Technical Progress:

The contractor is currently under contract for Phase I of the program which is nearing completion. Funding for Phases II and III has not yet been obligated.

Conceptual Design. The metal hydride heat pump (MHHP) consists of two different metal alloys that absorb and desorb hydrogen. Heat is generated on H_2 absorption while H_2 desorption is endothermic. The two metals are maintained in separate parts (see Figure 5.2) of the same container. The hydrogen is thermally driven from hydride 1 to hydride 2 and back. No hydrogen is consumed. Because the cooling processes are intermittent, two or more containers are used in an out-of-phase manner to achieve continuous cooling or temperature upgrading. Heat amplification is nearly continuous.

The charge and refrigeration side of the heat pump cycle are shown in Figure 5.2, which shows hydrogen driven from the warm side alloy to the cold side alloy. Heat generated in the cold side alloy by H_2 absorption is rejected by the nearly ambient temperature water, T_c. Once the tube is charged (all the hydrogen is on the cold side), the outside temperatures are changed reversing the pressure differential inside the tube. The hydrogen then returns to the warm side hydride. To provide the heat of dissociation, the cold side alloy extracts heat from the cooling fluid at T_E. Ambient temperature water is sufficient to maintain the warm side hydride at a temperature low enough to remove the heat of formation while it reabsorbs the H_2. Once all the hydrogen is on the warm side hydride, recharging must occur. Heating and temperature upgrading work in similar fashions but extract useful heat at different temperatures. Since this cycle can operate from very low temperature sources, the economic value of the input energy can be very low. The MHHP, which is almost silent in operation, could prove to be extremely efficient and economic for small-scale units (0.5 to 10.0 tons of refrigeration). Another application is for vehicle air conditioning. Those units would be driven by the thermal energy in the cooling fluid and require no shaft horsepower.

Market Survey. An extensive market survey was undertaken as part of this effort. This task involved characterization of the marketplace for HVAC equipment, definition of configurations for the MHHP in the market, selection of screening criteria, and, finally, selection of a target application for this effort. A preliminary commercialization plan is being developed.

The results of this survey show that the most promising MHHP configuration is the industrial waste-heat-driven temperature upgrade cycle, which uses an intermediate temperature heat source and provides a higher temperature process stream. One of the critical factors in this decision was the large amount of waste heat that is available in industrial processes. Applications in the food, textile, pulp and paper, and chemical industries appear very promising.

Thermal/Mechanical Design. Hydride materials comminute and expand about 25% by volume upon hydriding. These characteristics make heat transfer and physical containment difficult. A primary goal of the program is to design containment vessels with low mass and high heat transfer. In addition, a separator (filter) must be designed into the container to separate the metal powders from the hydrogen gas. These separators cannot operate like conventional filters by capturing particles, or they will soon cause high pressure drops and stop the MHHP. The separated powders must be quickly removed from the flow field. High thermal transfer rates are difficult with powders but essential if the MHHP is to achieve cost goals. The higher the transfer rate, the less powder is required per ton of refrigeration.

Computer analysis was used to study the heat transfer and thermal transient problems of various MHHP heat exchanger configurations. Tubular approaches and other geometries, such as an externally finned tube hydride heat exchanger, were studied to determine concept feasibility and optimum design geometry.

Test rigs to study the actual heat transfer characteristics of computer-selected heat exchanger structures were built. These rigs were used to verify and support the results of the computer studies. An optimum configuration will be chosen and designed in detail on the basis of the computer and test-rig results.

Materials. The hydride materials selected for use in the MHHP, in addition to possessing proper pressure/temperature characteristics, should have low hysteresis losses. An alloy pair has been selected as applicable to a temperature upgrade MHHP application - $LaNi_5/LaNi_{4.5}Al_{0.5}$. This alloy pair will operate in the temperature ranges of T_E (low temperature) -1° to 45°C (30° to 110°F), T_c (midtemperature) 70° to 100°C (160° to 230°F) and T_G (high temperature) 140-190°C (280-375°F). The heat pump would therefore upgrade heat from T_c to T_G.

Controls. Controls for the MHHP will be very simple once the timing cycles are well documented and the strategies developed. For the Phase II unit now under development, the control unit must allow for control strategy flexibility and provide for extensive data acquisition.

The hardware prototype control unit will be built utilizing the Intel "Multi Bus" and catalog circuits compatible to that bus system. Little or no hardware development is anticipated. For Phase III the control will be accomplished with a single-chip microcomputer.

Technical Problems:

None

Publications:

None

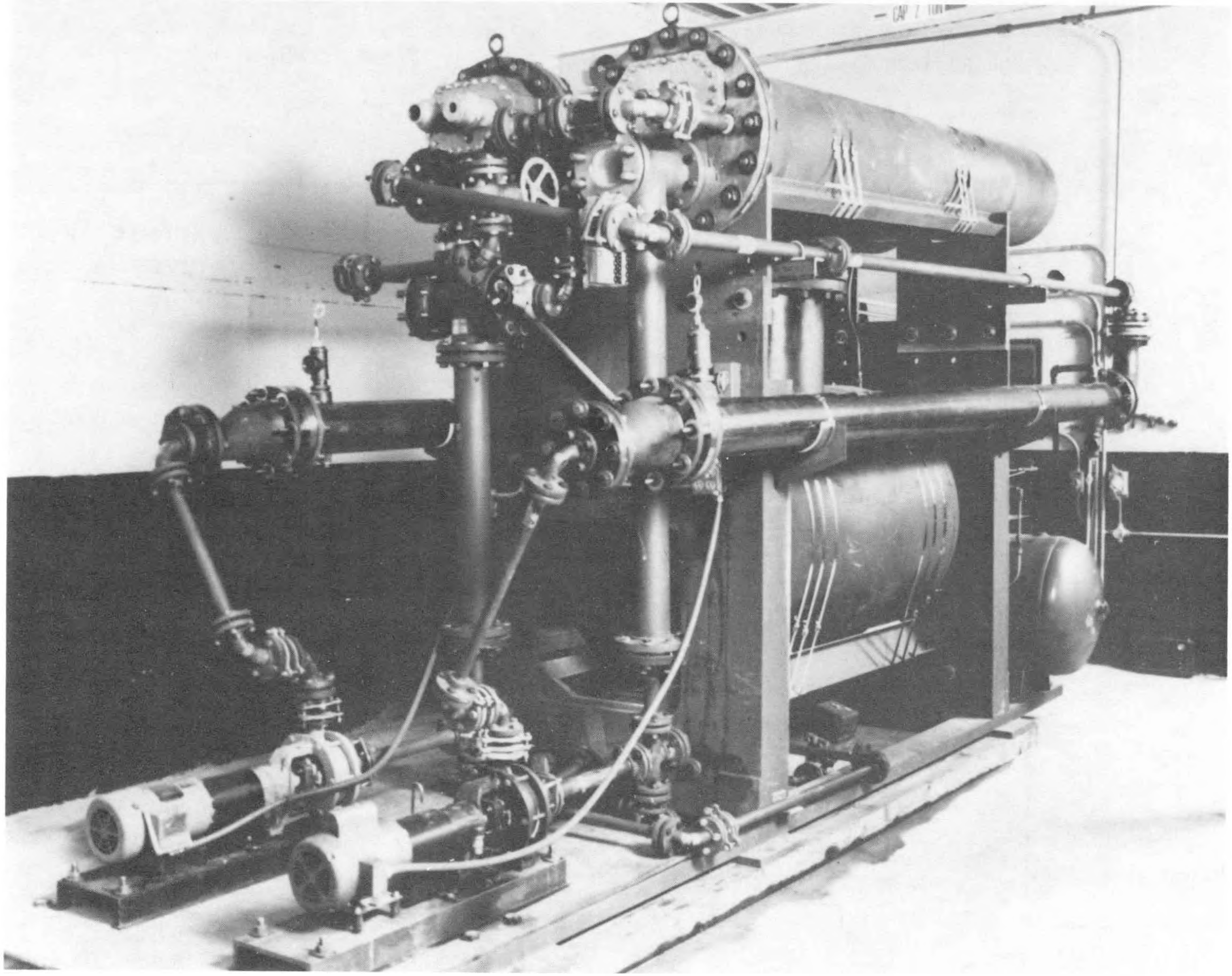
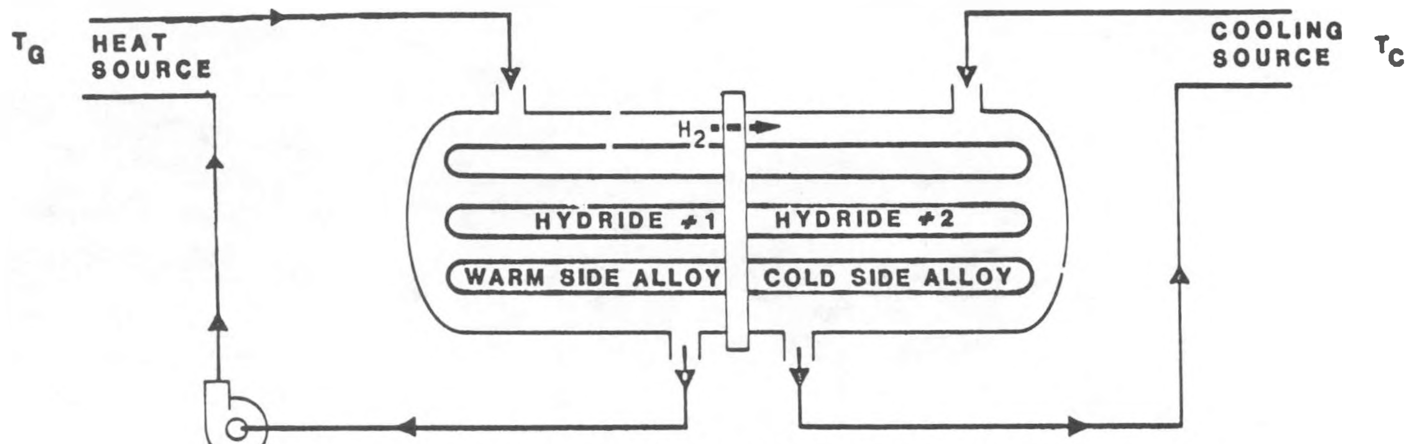
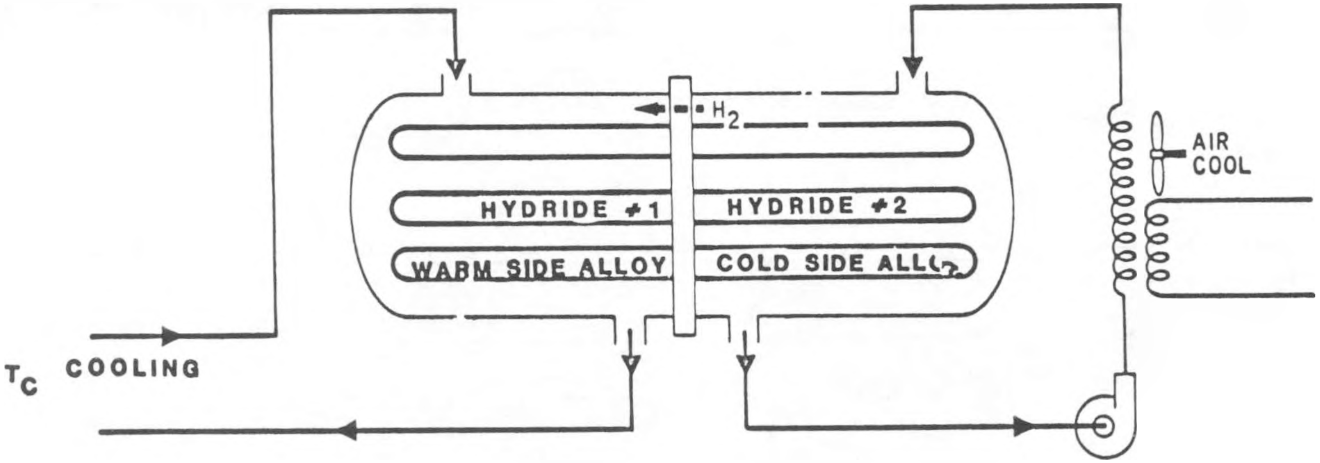


Figure 5.1 Verification Test Unit (VTU)



CHARGE CYCLE (HIGH PRESSURE)



T_G = 180°F OR HIGHER; T_C = 80-100°F; T_E = 35°F OR LOWER

Figure 5.2 Heat Pump Conceptual Design

5.3 Metal Hydride/Chemical Heat Pump Technical Support Program - Argonne National Laboratory

Objective:

The major objective of this program is to provide technical assistance to Brookhaven National Laboratory (BNL) in support of the metal hydride/chemical heat pump development project.

Tasks:

Task 1. Analytical Work - Metal Hydride Heat Pump Performance Analysis

Task 2. Technical Support - Evaluation of Contractor's Metal Hydride Heat Pump Analysis and Design

Technical Progress:

Task 1. Analytical expressions for the coefficient of performance (COP) of a multitube metal hydride heat pump design employing regenerative heat exchange have been developed for the heating and cooling modes. An examination of system design and operating parameters and determination of the sensitivity of thermal performance to variations in these parameters has been made to identify and seek methods of improving the COP. Limits have been established on the maximum theoretical Carnot COP, which is governed by the unit design temperatures. To minimize hydride material requirements, and thus capital cost and unit size, the plateau widths for selected hydride pairs should be as large as possible. The analytical results indicate that the best available COP corresponds to, among other things, the case of reducing the unit thermal mass to as small a value as possible by careful design and improving the fluid-to-hydride bed heat transfer as well as employing regenerative heat exchange.

Task 2. Periodic progress reports from the contractor (Southern California Gas Company) have been reviewed and evaluated. Criteria for the selection of the engineering development test unit have been developed. An optimum finned tube hydride heat exchanger based on minimizing the thermal mass outside the hydride materials has been proposed. Tests to verify the heat transfer analysis and measure the hydride utilization factor have also been designed. The sensitivity of the calculated COP's to changes in the design and operating parameters needs to be studied. As yet, no attempt has been made to apply regeneration to improve the thermal performance.

5.4 Cost-Effectiveness Evaluation of Chemical Heat Pump

TRW Energy Systems

Objective:

The objective of this study is to evaluate the cost effectiveness of specific chemical heat pump technologies compared to a set of baseline and emerging technologies. The CHP's are evaluated in HVAC applications for both residential and commercial buildings in the Northeast (Boston) and Southwest (Albuquerque). They are also evaluated in an application for industrial waste heat recovery.

Tasks:

Task 1. Project Plan and Methodology
Task 2. Baseline Technologies
Task 3. Emerging Technologies
Task 4. Chemical Heat Pump Technologies
Task 5. Comparison and Final Report

Technical Progress:

Task 1 - Task 3. Completed during 1980.

Task 4. CHP Technologies: The chemical heat pump systems were evaluated in residential and commercial HVAC applications and in applications for industrial waste heat recovery and upgrading.

Task 5. Comparison and Final Report: The final report for this project was completed and approved by BNL, and has been submitted for publication through NTIS.

In residential HVAC aplications, the role of CHP's in energy conservation is best served through solar-driven applications, the economics of which are somewhat better than those of either baseline or emerging systems. Direct-fired CHP's are less expensive to own and operate, but are not a good approach to energy conservation. Given the increased complexity of the sulfuric acid system and the barriers to commercialization (safety, institutional, and customer-psychological), the methanolated salt system would probably be the most attractive CHP technology for residential use.

Because of the dominance of the air conditioning load, use of either CHP for heating and cooling a commercial office building would be very expensive, competitive only with the most expensive emerging systems. Since this use of CHP's is also not very attractive from an energy standpoint, there appears to be little incentive for CHP's in HVAC applications in commercial buildings.

The industrial CHP's were found to be more cost effective to own and operate than a conventional electrically driven vapor recompression system because of the high energy cost for electricity. CHP's were more cost effective than the self-driven vapor recompression system because of the high capital cost of the power-recovery turbine capable of exhausting to very low pressure. The only commercially available industrial heat pump, the Westinghouse Templifier, is constrained to temperature levels below 230°F, and is not considered to be a serious competitor for process heat applications in the temperature range of interest to BNL.

These comparisons are illustrated in the accompanying Figures 5.3, 5.4, and 5.5.

Publications:

Standley, W. R., Gornman, R., and Moritz, P. S. Chemical Heat Pump Cost Effectiveness Evaluation, Final Report to BNL under Contract No. 519403-5, May 1981 (to be published through NTIS).

Moritz, P. A. and Gorman, R. Comparative economics and energy consumption of chemical heat pumps and competitive systems, Proc. 16th Intersociety Energy Conversion Engineering Conference, Atlanta, Georgia, August 1981. (Paper No. 819401)

Standley, W. R. CHP cost effectiveness evaluation. Proc. of the DOE Thermal and Chemical Storage Annual Contractors' Review Meeting, Tyson's Corner, Virginia, September 1981.

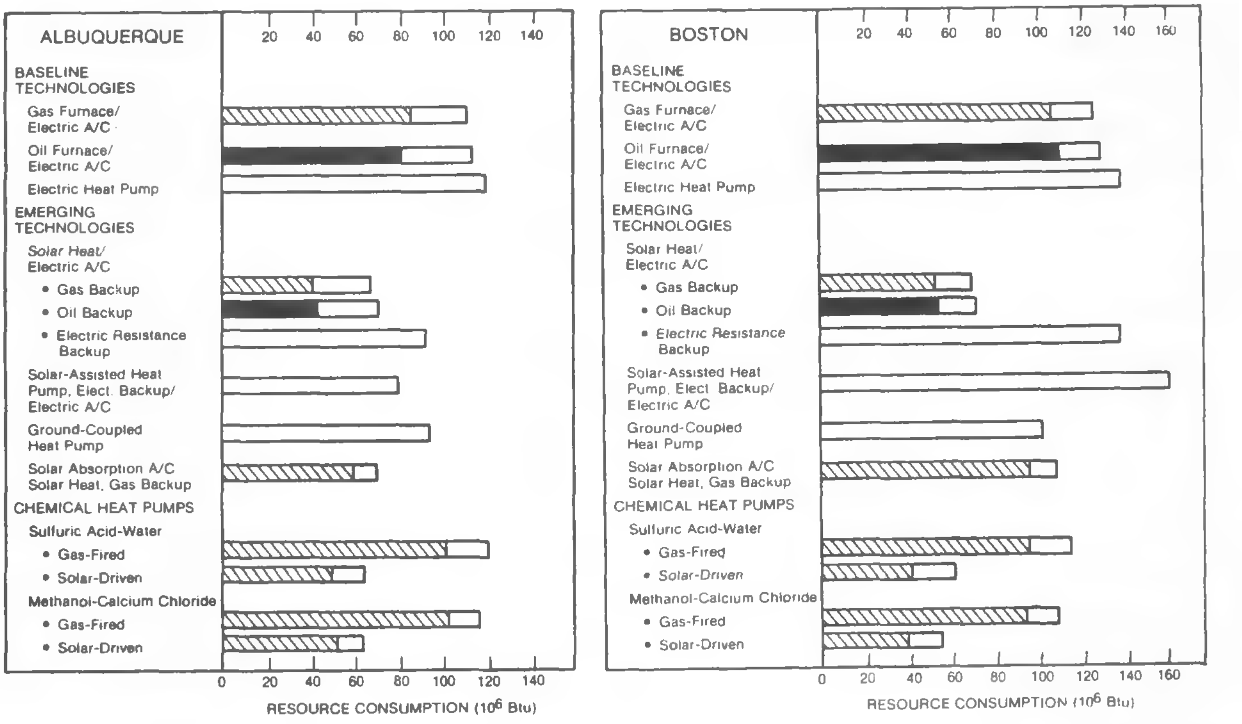


Figure 5.3 Annual Energy Resource Use Summary: Residential Building

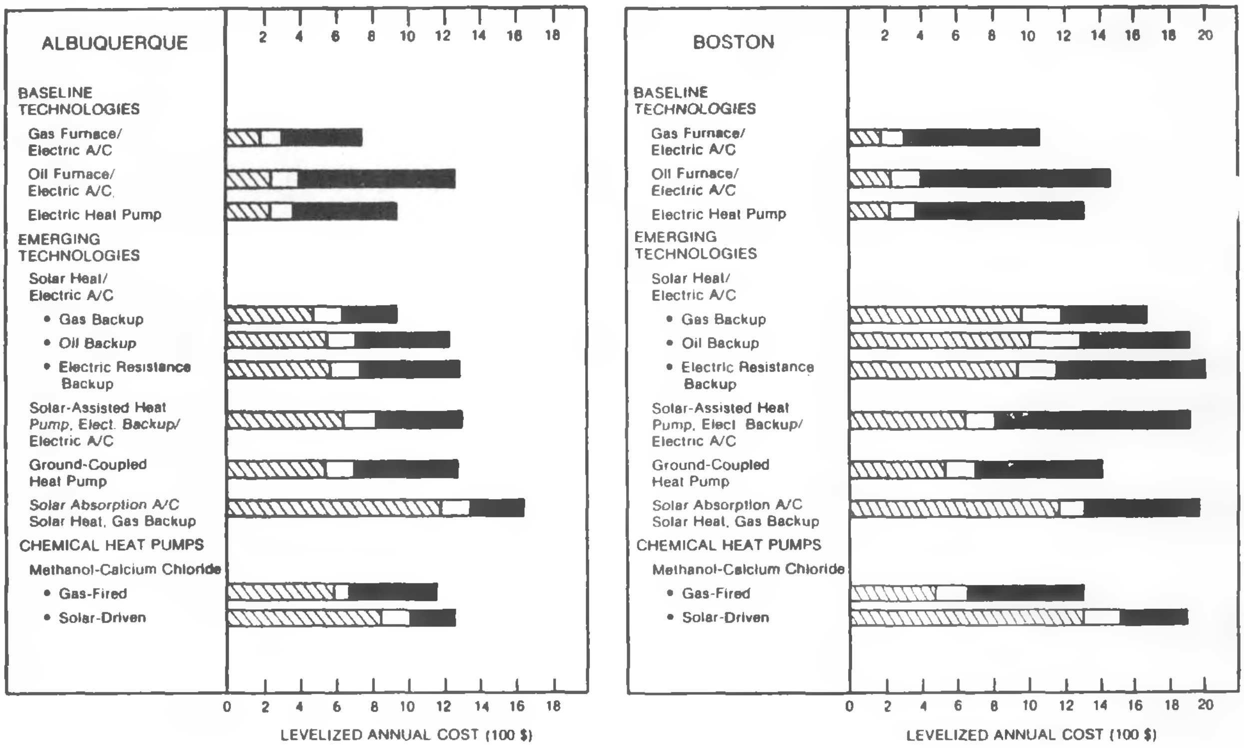


Figure 5.4 Levelized Annual Cost Summary: Residential Building

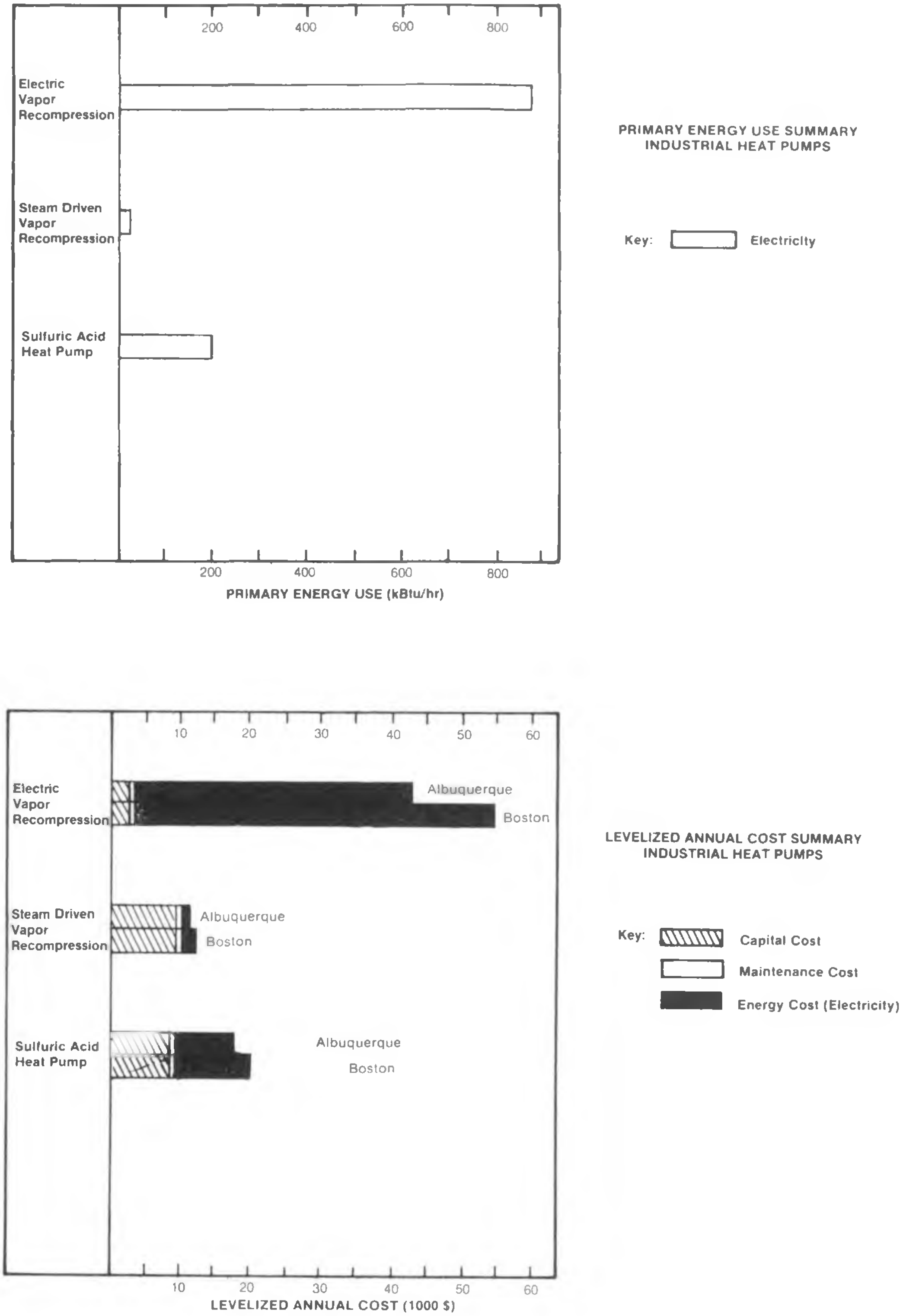


Figure 5.5 Industrial Heat Pump Summary: Process Steam Application

6.0 THERMOCHEMICAL HYDROGEN PRODUCTION

Summary

This section describes the work on the three remaining projects concerned with the the thermochemical production of hydrogen. These projects are expected to be completed by mid-1982, essentially phasing out the effort supported by DOE's Division of Energy Storage Systems.

General Atomics is completing the engineering studies of the sulfuric acid/iodine cycle, with emphasis on improving the chemistry aspects of the process. The main problem addressed was an energy-intensive step for decomposition of the hydrogen iodide in which liquid phase homogeneous catalysis has replaced the high temperature vapor phase decomposition. Cost estimate and process flow sheets were prepared for both solar- and fusion-driven systems.

The work at Jet Propulsion Laboratory has been aimed at evaluating the key process problems with thermochemical cycles. Critical process parameters for the decomposition of sulfuric acid were defined. Some preliminary work was done on the production of hydrogen by reacting coal with sulfuric acid in the presence of catalysts. The interface requirements of thermochemical cycles with solar heat sources were also explored.

The work at Los Alamos National Laboratory has been concerned with identifying candidate thermochemical reaction systems and investigating alternative process steps for existing cycles. During 1981, two different bismuth sulfate cycles were investigated as intermediate steps in the formation of sulfuric acid. A cobalt oxide cycle to operate at temperatures attainable in a solar tower was also investigated.

6.1 The Sulfur-Iodine Thermochemical Water-Splitting Process - General Atomic Company

Objective:

To demonstrate the viability of the sulfur/iodine thermochemical water-splitting cycle and evaluate its technical performance.

Tasks:

Complete installation and testing of bench-scale unit operations. Improve chemistry of critical operations of process. Develop conceptual engineering flowsheet and carry out preliminary cost estimate of process.

Technical Progress:

Bench Scale

The equipment of the Section for the Purification and Decomposition of Hydrogen Iodide (HI), which had been previously installed, was operated successfully. A major part of the effort was expended in modifying the equipment to improve operability, in increasing throughput, and in gathering process data during operation.

The HI separation column and H_3PO_4 concentration columns were modified to increase boilup rate and thus throughput. High throughput rates of viscous H_3PO_4 resulted in flooding of the columns. The separation efficiency decreased when the flooding was eliminated through the use of larger size packing in the columns. Plate-type columns have been ordered, which will eliminate this problem.

The hydrogen iodide cracker was operated with no major problems. A conversion ($2HI \rightarrow H_2 + I_2$) of 22% per pass has been routinely obtained. The predicted equilibrium conversion at the measured reactor outlet temperature is 16%. This discrepancy has not been fully explained yet, but the observed conversion is characteristic of a higher temperature than actually measured in the catalyst bed. Efficient iodine removal from the product stream was achieved by increasing the heat transfer area of the iodine trap and by lowering the temperature. Glass HI traps were replaced with stainless steel pressure vessels allowing longer run times and better control of the recycle HI flow.

The iodine knockout portion of Section III has been moved closer to the Section I prime reactor to allow a faster return of the separated iodine. In the new location, the equipment is placed in a "hot box" for improved temperature control. In addition, better use of fluid density differences to obtain self-automation of process flows was made.

Engineering

The flowsheets for Sections I, III, and IV were revised. These revisions are the basis for a hydrogen production cost estimate which is now being completed at General Atomic (GA). Preliminary indications are that the cost of hydrogen from the GA thermochemical water-splitting process using solar heat as the energy source is in the range of \$12 to \$20 per MBTU depending on the cost of solar heat.

PRELIMINARY COST CAPITAL ESTIMATE FOR GA
PROCESS 650 MW(th) SOLAR PLANT

SECTION	M$
I. Main Solution Reaction	16
II. H_2SO_4 Decomposition	160
III. HI Purification	98
IV. HI Decomposition	13
V. Power Generation, Heat Transfer, and Energy Storage	Not done yet

Process Chemistry

The processing of the lower-phase HI solution, high in iodine and containing significant amounts of H_2O, is a critical step in the GA sulfur-iodine water-splitting cycle because of its potentially high cost. At present, HI is recovered by adding concentrated H_2PO_4 such that the final H_3PO_4-H_2O solution exceeds 85% H_3PO_4. In doing so, two things happen:

1. Much of the excess I_2 separates as a second liquid phase.
2. The HI is increased in chemical activity while the H_2O activity is decreased and the HI can be distilled out of this mixture and recovered as a dry liquid.

While H_3PO_4 accomplishes the necessary steps, it requires a considerable H_3PO_4 recycle flow; also, the energetics for removing the H_2O from the H_3PO_4 are demanding. At present, this is done quite efficiently by the use of compressive work, but the equipment in the form of heat exchangers and vapor recompression turbines is quite expensive.

of compressive work, but the equipment in the form of heat exchangers and vapor recompression turbines is quite expensive.

Research has been carried out to investigate other methods of processing the HI_x product solutions. We were successful in identifying two very promising processes which can perform the necessary separations. The advantage of one of these concepts is that no phosphoric acid treatment is required and the amount of water needing to be evaporated is only a fraction of the old flowsheet value. The other process, while it boils the water, requires considerably less equipment. Patent protection is being sought for these new process improvements. However, a number of process details still need to be investigated before either system can be adopted as an alternative for HI_x product solution purification.

Liquid Hydrogen Iodine Catalyst Studies

During the past years, General Atomic has studied the advanced concept of decomposing HI in the liquid phase. Theoretical calculations have indicated that high conversions were possible. Measured conversion values compared well with the high values predicted theoretically, and reaction rate data, extrapolated to higher process temperatures, indicated that application of the system to the GA cycle would result in a viable process.

Two major conclusions can be drawn from the work performed to date. First, noble metal catalysts provide the highest rates of decomposition, and, second, there is significant attrition of noble metal into the liquid HI environment. The cost of using noble metal catalysts for this process was not found to be excessive. Also, catalyst recovery is common in the chemical industry. Therefore, catalyst attrition is not expected to be a problem.

We also pursued a new, very attractive homogeneous catalysis scheme which includes catalyst recycle and does not require catalyst regeneration. Results of this work are very encouraging, indicating a possible improvement over the present system.

6.2 Thermochemical Processes for Hydrogen Production

Los Alamos National Laboratory

Objective:

The objective of this project is to address basic chemistry problems of thermochemical cycles for the production of hydrogen from water.

Tasks:

- Investigation of the technical and economic nature of thermochemical cycles.
- Investigation of the engineering principles involved in interfacing individual thermochemical cycles with heat sources including solar, fusion and fission devices.
- Continuing research on the use of sulfates, oxides and other compounds as the basis for improved cycles, especially with very high temperature heat sources.
- Interfacing with international organizations conducting thermochemical research via IEA Annex I.

Technical Progress:

Basic thermochemistry studies have been completed for two different steps in the decomposition of bismuth sulfate. Two different bismuth sulfate cycles have been defined, depending on the acid strength. The eventual 'best' cycle will depend on the energy required to form sulfuric acid at different concentrations.

A rotary kiln has been used in experiments to decompose bismuth, lanthanum, and zinc sulfates as well as a higher cobalt oxide, Co_3O_4. Over 90% decomposition of all but the lanthanum salt was obtained at temperatures below 1285°K with a residence time of 60 seconds. This temperature is in the range of solar furnaces.

The successful decomposition of the cobalt oxide at temperatures attainable in a solar tower may lead to an oxide cycle capable of operating in an open, fludized-bed receiver. The lower oxide can be oxidized using iodine-iodate chemistry, with hydrogen produced by decomposition of the resulting hydrogen iodide.

The heat requirements for decomposing sulfuric acid and bismuth sulfate were compared and evaluated relative to the heat delivery characteristics of a gas-cooled reactor. While sulfuric acid is well suited for a gas-cooled reactor, bismuth sulfate is better suited to an isothermal heat source such as a solar furnace.

Publications:

Hollabaugh, C. M. and Bowman, M.G. Alternate thermochemical cycles. Proc. DOE Thermal and Chemical Storage Annual Contractors' Review Meeting, Tyson's Corner, Virginia, September 1981.

6.3 Advanced Hydrogen Production Concepts and Processes

Jet Propulsion Laboratory

Objective:

The purpose of this work is to assess current problems in thermochemical production of hydrogen and related technology.

Tasks:

To investigate advanced methods of hydrogen production including water splitting, new methods using fossil energy, and methods which recover energy in the form of hydrogen. To examine process conditions for thermochemical cycles relative to advancement of the cycles to pilot operation.

Project Status:

Studies on interfacing thermochemical cycles with solar heat sources were conducted to determine the characteristics of the interface. Concentration ratios on the order of 1500 suns will be required for efficient utilization of heat at 800° to 900°C. As a result, the optical quality of the solar source must be excellent. Overall conversion efficiencies at this concentration ratio will probably be less than 60% on the basis of the combined efficiencies of the heat source and second law effects.

Continuing experiments on the production of hydrogen from coal by reaction with sulfuric acid indicated that the dissolution of coal was enhanced by the presence of catalysts. This result was expected from examination of the literature on the Kjeldahl procedure for analysis of organic nitrogen. A good material balance is not yet available because of the difficulty in containing the initial decomposition reaction. Some interest has been generated in industry to produce carbon dioxide from coal by this method.

Analysis of the sulfuric acid decomposition step in thermochemical cycles indicated the need to keep the decomposition gases above the dew point of sulfur trioxide. Failure to do so will create a stable mist of sulfuric acid which will cause unacceptable corrosion of downstream equipment. To prevent the mist, concentrated sulfuric acid must be used as the absorption medium. Production of concentrated sulfuric acid by re-oxidation of a portion of the sulfur dioxide produced is proposed.

The solubility of sulfur dioxide in sulfuric acid was measured to determine the temperature and pressure under which electrolyzers for sulfur dioxide could operate. Sulfur dioxide has a limited solubility in 50%

sulfuric acid, leveling off to 10% at about 60°C, corresponding to a pressure of 150 psi. Electrolyzers for sulfur dioxide should be operated at this condition.

Publications:

Chang, K. K., Compton, L. E., and Lawson D. D. Solubility of sulfur dioxide in sulfuric acid. Proc. DOE Thermal and Chemical Storage Annual Contractors' Review Meeting, Tyson's Corner, Virginia, September 1981.