

229
7-25-80
MMB

Lh. 1536

ELECTROLYSIS-BASED HYDROGEN STORAGE SYSTEMS

ANNUAL REPORT
JANUARY 1, 1978 TO DECEMBER 31, 1978

MASTER

APRIL 1979

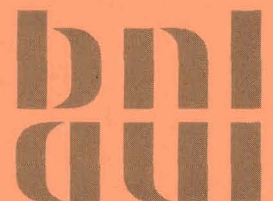
Work supported by the
DIVISION OF ENERGY STORAGE SYSTEMS
OFFICE OF CONSERVATION
UNITED STATES DEPARTMENT OF ENERGY

DEPARTMENT OF ENERGY AND ENVIRONMENT

BROOKHAVEN NATIONAL LABORATORY
ASSOCIATED UNIVERSITIES, INC.

UNDER CONTRACT NO. EY-76-C-02-0016 WITH THE

UNITED STATES DEPARTMENT OF ENERGY



DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ELECTROLYSIS-BASED HYDROGEN STORAGE SYSTEMS

ANNUAL REPORT
JANUARY 1, 1978 - DECEMBER 31, 1978

ALESSIO MEZZINA, Program Manager

Contributors:

A. Beaufrere	M. Rosso
M. Bonner	F. Salzano
J. Johnson	S. Srinivasan
G. Kissel	G. Strickland
P. Lu	R. Wiswall
S. Majeski	R. Yeo
J. Reilly	

APRIL 1979

DISCLAIMER
This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DEPARTMENT OF ENERGY AND ENVIRONMENT

BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy (DOE), nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

Price: Printed Copy \$6.00; Microfiche \$3.00

September 1979

340 copies

ABSTRACT

Contract management, technical monitoring and in-house research conducted by Brookhaven National Laboratory for the U.S. Department of Energy, Division of Energy Storage as described. The status of each project within four major areas of investigation is summarized. Activities deal with: (1) Electrolytic Production of Hydrogen; (2) Hydrogen Storage Systems; (3) Hydrogen Storage Materials; and (4) Systems Studies/End-Use Applications. The BNL programmatic responsibilities encompass the direction of 17 contractors and a \$3,200,000 budget.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

TABLE OF CONTENTS

	<u>Page</u>
EXECUTIVE SUMMARY.....	ix
1.0 INTRODUCTION.....	1
1.1 Program Description.....	1
1.2 Program Purpose and Objectives.....	2
1.3 Future Activities.....	3
2.0 ELECTROLYTIC HYDROGEN PRODUCTION.....	6
2.1 Solid Polymer Electrolyte (SPE) Water Electrolysis Technology Development.....	6
2.2 Development of Advanced Alkaline Water Electrolyzers.....	10
3.0 HYDROGEN STORAGE SYSTEMS.....	27
3.1 Underground Storage of Hydrogen.....	27
3.2 Automotive Storage Systems.....	30
3.3 Bulk Hydride-Hydrogen Storage.....	34
3.4 Hydrogen-Technology Advanced-Component Test System (HYTACTS).....	38
3.5 Heat-Transfer Modeling.....	40
References.....	46
4.0 HYDROGEN STORAGE MATERIALS.....	47
4.1 Hydrogen Storage Materials Development.....	48
4.2 Lightweight Metal Hydrides Development.....	52
4.3 Metal Hydride Studies of Hydrogen Storage Alloys.....	53
4.4 Brookhaven National Laboratory (BNL) In-House Research.....	55
References.....	61
5.0 SYSTEMS STUDIES AND END-USE APPLICATIONS.....	62
5.1 Feasibility Assessment of Falling Water Resources.....	62
5.2 Natural Gas Supplementation with Hydrogen.....	67
References.....	72
6.0 PROJECT MANAGEMENT.....	73
6.1 Project Planning and Liaison with Industry.....	73
6.2 Contract Management and Technical Monitoring.....	74

LIST OF TABLES

<u>Table No.</u>	<u>Title</u>	<u>Page</u>
2.1	Electrode Kinetic Parameters for Oxygen Evolution Reaction in TFMSA at 25°C.....	14
2.2	Electrode Kinetic Parameters for Oxygen Evolution Reaction on RuO _x , MnRuO _x From TFMSA at 25°C.....	15
3.1	Hydrogen Release Under Room Temperature Storage Conditions.....	32
3.2	Weight and Cost Summary for Reference Metal Hydride System (MHS) and Hybrid Microcavity System (MCS).....	33
3.3	Summary of Equations, n-Nodes.....	44
4.1	Low Temperature Activation Experiments for TiFe _x Mn _y Alloys.....	57
5.1	Principal Elements of the Natural Gas T&D Network.....	69

LIST OF FIGURES

<u>Figure No.</u>	<u>Caption</u>	<u>Page</u>
1.1	Hydrogen Project Budgetary Breakdown for FY 78.....	5
2.1	Single Cell Detail.....	15
2.2	Foil-Backed Molded Current Collector (Laboratory-Size).....	16
2.3	2 1/2 Ft ² Membrane and Electrode Assembly.....	16
2.4	Single Module S/N DOE-5 Testing.....	17
2.5	2 1/2 Ft ² Module assembled for leak test.....	17
2.6	Performance Comparison.....	18
2.7	Water Electrolysis Heat and Mass Computer Model Schematic.....	18
2.8	Proposed mechanism of performance degradation with time for oxygen evolution on RuO _x electrodes in SPE water electrolyzers.....	19
2.9	Tafel plots for oxygen evolution on RuO _x and MnRuO _x	19
2.10	Reflectivity of IrO ₂ in the range 0.5 - 4.5 eV for light polarized.....	20
2.11	Current-voltage curve obtained during a single triangular cycle at a scan rate of 1 V/min applied to virgin IrO ₂ single crystals with [111] (solid lines) and [110] (dashed lines) faces in a 1 N H ₂ SO ₄ solution at room temperature.....	21
2.12	Time dependence of the reflectivity of an Ir-metal electrode during oxide formation.....	21
2.13	ARIES Mechanical Schematic.....	22
2.14	Applied Research Industrial Electrolysis System (ARIES)...	23
2.15	Temperature-voltage behavior of time stabilized conventional components.....	24
2.16	Comparison of conventional and advanced cathodes.....	24
2.17	Efficiency loss for hydrogen production (voltage vs. time).....	25
2.18	Overvoltage changes for cell components (voltage vs. time).....	25
2.19	Performance characteristic comparison Nickel whisker vs. nickel screen.....	26
3.1	Aquifer Storage.....	43
3.2	Hydrogen release rate per ft ³ of MCS microsphere bed.....	43
3.3	Sectional view of fast-charge hydride-hydrogen storage vessel.....	44
3.4	Sketch of VPTU-2 constructed by Foster Wheeler Energy Corp.....	44
3.5	Comparison of predicted temperature profiles with experimental results.....	45

LIST OF FIGURES (cont'd.)

<u>Figure No.</u>	<u>Caption</u>	<u>Page</u>
4.1	Phase diagram for the $\text{TiCr}_{1.8}\text{-H}$ system derived from p-c-T and x-ray diffraction data.....	57
4.2	Pressure-composition desorption isotherms for the high temperature (Cl4) $\text{TiCr}_{1.9}\text{-H}$ system at various temperatures.....	58
4.3	Pressure-composition desorption isotherms for various $\text{Ti}_x\text{Cr}_{2-x}\text{Mn}$ alloys at -20°C	59
4.4	Pressure-composition desorption isotherms for FeTi alloys of various Mn contents at 40°C	60
4.5	A comparison of pressure-composition desorption isotherms for annealed and "as cast" $\text{TiFe}_{0.76}\text{Mn}_{0.13}$ at 40°C	60
5.1	Technical approach to hydrogen from falling-water concept.....	63
5.2	Hydrogen production cost estimates.....	65
6.1	Hydrogen Project Budgetary Breakdown.....	75
6.2	Contract Activities for Calendar Year 1978.....	76

ELECTROLYSIS-BASED HYDROGEN ENERGY STORAGE SYSTEMS
1978 ANNUAL REPORT (JANUARY 1, 1978 - DECEMBER 31, 1978)

EXECUTIVE SUMMARY

Brookhaven National Laboratory contract management, technical monitoring and in-house research and development activities for 1978 are described for the four major areas of investigation.

- (1) Electrolytic Hydrogen Production
- (2) Hydrogen Energy Storage Systems
- (3) Hydrogen Storage Materials
- (4) Systems Studies and End-Use Applications

The objectives of the Electrolysis-Based Hydrogen Energy Storage Systems Program are to:

- . Develop, test and deliver advanced water electrolysis systems capable of producing hydrogen at a competitive price in near-to-mid term chemical feedstock and fuels markets.
- . Identify and develop safe and cost-effective hydrogen storage and delivery systems.
- . Identify and develop storage materials comprising metal hydrides and other absorbers with properties permitting high capacity storage and long life.
- . Identify barriers and incentives for selected renewable resource (hydro-power, ocean thermal energy conversion, solar, etc.) conversion to hydrogen.

Contractor and BNL in-house research and development efforts are described as they relate to each of the major areas of investigation. Accomplishments during 1978 are:

Area 1 - Electrolytic Hydrogen Production

- . Reduction of catalyst loading on SPE electrolyzer electrodes was achieved by GE, from 4 gms/ft² to .25 gms/ft² thus reducing catalyst loading costs from \$22/ft² to \$1.75/ft².
- . GE completed a SPE electrolyzer 2.5 ft² electrode single-cell test and initiated a 50 kW cell module evaluation test.

. The mechanism of performance degradation of ruthenium (low cost) electro-catalysts was identified at BNL.

. An advanced alkaline electrolyzer 5-cell test rig (ARIES) was completed and 320 operational hours test time at 100°C was accumulated at Teledyne Energy Systems characterizing improved electrode and separator materials.

. The long term stabilities of materials for high temperature alkaline systems was carried out at Teledyne Energy Systems (TES), BNL and the University of Virginia.

Area 2 - Hydrogen Energy Storage Systems

. Feasibility and cost assessment of underground storage of hydrogen was initiated at the Institute of Gas Technology (IGT) based on current natural gas storage practices.

. Conceptual design and cost/performance analysis of microsphere/metal hydride hybrid storage system for automotive application was completed by R. J. Teitel Associates, projecting 50% weight and cost reductions compared to FeTi/Mg hydride hybrids.

. The experimental and analytical plan for heat/mass flow enhancement design evaluations was completed.

Area 3 - Hydrogen Storage Materials

. Continuous cycling absorption/desorption apparatus was fabricated at International Nickel Company (INCO) for the conduct of kinetic poisoning experiments.

. Equipment fabrication and alloy preparation was completed at Air Products & Chemicals, Inc. (APCI) and initial testing shows nickel powder to be an effective catalyst for certain Mg-based alloys.

. Hysteresis phenomena in alloy hydrogen absorption-desorption was explained and rationale developed at Denver Research Institute (DRI) associating molecular structure to hydriding capacity.

Area 4 - Systems Studies and End-Use Applications

. Falling water systems studies were completed by the Institute of Gas Technology and actions were initiated for activity in hydrogen production and marketing from small hydropower resources. These actions were based upon the identification of substantial small hydropower resources (especially in the Northeast) with potentially favorable cost for conversion to hydrogen production.

. The feasibility of hydrogen as a natural gas supplement in existing pipeline networks was established for moderate (up to 20%) mixtures.

Area 5 - Project Management

The project management activities encompassed directing the efforts of 17 contractors and a budget of \$3,200,000 including the BNL research and development work. One major competitive procurement was issued in the area of hydrogen production from small hydropower sites with two potential contractors selected, New York State Energy Research and Development Authority and Air Products and Chemicals, Inc. Other activities included coordinating the Annual Hydrogen Contractors' Review Meeting and conducting a workshop on metal hydride storage vessels.

ANNUAL REPORT
ELECTROLYSIS-BASED HYDROGEN ENERGY STORAGE SYSTEMS

1.0 INTRODUCTION

Brookhaven National Laboratory (BNL) has served as the focus for R&D in Hydrogen Energy Storage Systems for more than a decade based upon its pioneering in metal hydrides storage materials and systems. This has stimulated activities in other aspects of hydrogen technology that range from hydrogen production via water electrolysis to applications in mobile propulsion and urban energy systems as well as in chemical feedstock markets.

DOE/STOR assigned a major management role in Hydrogen Energy Systems development to BNL, aiming for greater interaction with the private sector and the academic community in order to accelerate the commercialization prospects for hydrogen technology. Early penetration of the energy infrastructure was seen as being brought about through utility load leveling applications as nuclear base-load capacity projections increased. The availability of low-cost, off-peak/spinning reserve electricity leads to the consideration of hydrogen production (and storage) as a supplement to natural gas and as the fuel for high efficiency fuel cells. These prospects have dimmed for the near term due to the virtual deferral of the nuclear option and marginal overall electric efficiencies of electrolyzer/fuel cell systems resulting in relatively high hydrogen production costs. The current program at BNL is structured about hydrogen production as an effective long term renewable resource conversion option, with chemical feedstock markets as the primary target-of-opportunity, closely followed by development and promotion of selected applications that promise near term, but modest impacts on the energy supply.

1.1 Program Description

Brookhaven National Laboratory's management and in-house research and development efforts address complementary areas of investigation in: Electrolytic Hydrogen Production; Hydrogen Storage Systems; Hydrogen Storage Materials; and, Systems Studies and End-Use Applications. The purpose of the investigations is to assess and promote hydrogen production and storage as a renewable resource conversion option for supplementing our chemical feedstock in the near term and

as a fuel supplement in the mid-to-long term. The technical approach establishes priorities for in-house research and subcontractor management activities that strike a balance with near-term prospects for technology commercialization. Emphasis is placed on Electrolytic Hydrogen Production via the development of low capital cost, high efficiency water electrolysis systems. These systems incorporate advances in solid polymer and alkaline electrolytes, electrocatalysts and separator/collector materials capable of operation in higher temperature and pressure regimes. Hydrogen Storage Systems and Hydrogen Materials investigations have shifted emphasis from stationary bulk storage applications to mobile, short-term storage. Systems Studies and End-Use Applications deal with analyses of barriers and incentives associated with renewable resource conversion and product marketing supplemented by demonstration tests to provide "hands-on" experience with near-term technology commercialization opportunities.

1.2 Program Purpose and Objectives

Programmatic guidelines and criteria derive from the recognition that hydrogen's entry into the energy infrastructure must consider the realities of the competitive marketplace for fuels. Therefore, in order to accelerate hydrogen's contribution to the U.S. energy stores, technology advances are pursued addressing cost-effective and safe production, storage and use of hydrogen. Technological advances aim toward the conversion, storage and distribution of dispersed renewable resources, in the form of hydrogen, identified as a flexible commodity with excellent energy carrying and storage characteristics.

Advanced water electrolysis systems development has been identified as the critical lead technology and retains the highest programmatic priority. Reduction in capital costs and high operating efficiencies are mandatory for attaining competitive prices per unit energy of electrolytic hydrogen product. Application of these systems as renewable resource conversion options will make hydrogen prices less susceptible to cost increases and inflationary pressures associated with current conventional fuels.

Hydrogen Storage Systems and Hydrogen Storage Materials utilizing metal hydrides and/or other absorbers provide safe and weight/volume effective storage and delivery of energy. Project priorities addressing systems development for

specific applications will be governed by cost effectiveness and market considerations.

Systems Studies and End-Use Applications investigations aim to provide the technical and economic basis for identifying targets-of-opportunity where economic and societal benefits can accrue followed by "hands-on" tests and demonstrations that can systematically introduce and transfer the technology to the private sector.

1.3 Future Activities

Future activities and accomplishments for FY 79 and beyond will depend largely on budget allocations and constraints. Expected accomplishments are delineated as follows:

Area 1 - Electrolytic Hydrogen Production

- . Fabrication and testing of 200 kW SPE electrolyzer system (60-cell; 2.5 ft² electrodes) at GE.

- . Design and development of 10 ft² electrode cells at GE.

- . Conduct of surface characterization of Ru, Ir and Ru-based alloys and mixed oxides at BNL as well as crystallographic-electrochemical properties correlation of IrO₂ and RuO₂ single crystals at BNL and Brooklyn College.

Area 2 - Hydrogen Storage Systems

- . IGT will identify underground storage sites and provide storage cost estimates.

- . Microsphere component of hybrid automotive storage system will be subjected to performance and cost verification tests (regarding capacity, attrition, time constraints, etc.) and R. J. Teitel Associates.

- . Heat transfer enhancement apparatus will be designed and tested and applied to performance evaluation of six candidate configurations at BNL.

- . HYTACTS testing of VPTU-2 will be conducted for one internal assembly option at BNL.

Area 3 - Hydrogen Storage Materials

- . Mechanisms of O₂, CO and water vapor poisoning of TiFe, manganese-substituted TiFe and LaNi₅ will be determined at INCO.

- . Evaluation of binary, ternary and quaternary Mg-based alloys as hydrogen storage media will be completed at Air Products and Chemicals, Inc.

. All thermal and capacity studies of AB₂, AB₅, Ti, and V-based solid solution alloys will be completed at Denver Research Institute.

. Cycling experiments with hydrogen/natural gas mixtures will be completed and kinetic measurements for gas separation will be started at BNL.

Area 4 - Systems Studies and End-Use Applications

. Contract award will be made to initiate investigations into hydrogen production from small hydropower resources to NYSERDA and APCI.

Successful implementation of projects formulated within the scope of DOE/STOR-BNL activities, will aim toward expansion of hydrogen's initial role as a chemical feedstock to encompass its use as a fuel supplement. Ultimately, the long-term potential of hydrogen as a generally useful fuel may be realized. Inexhaustible resources convertible to hydrogen production range from the modest contributions of small hydropower to the substantial potential available from undeveloped remote hydro in Canada and reallocable hydro in the U.S. Hydropower alone can provide up to 4 Quads/yr of mid-term cost-competitive fuel supplements. The future prospects for inexhaustible resource conversion only brighten the future energy horizons. Low-cost water electrolyzers and effective hydrogen storage and distribution systems can serve to ensure hydrogen's place in our energy stores and provide incentives for identification and capture of new energy markets.

Budgetary allocations to each of the major areas of technology as well as project management functions are shown in Figure 1.1.

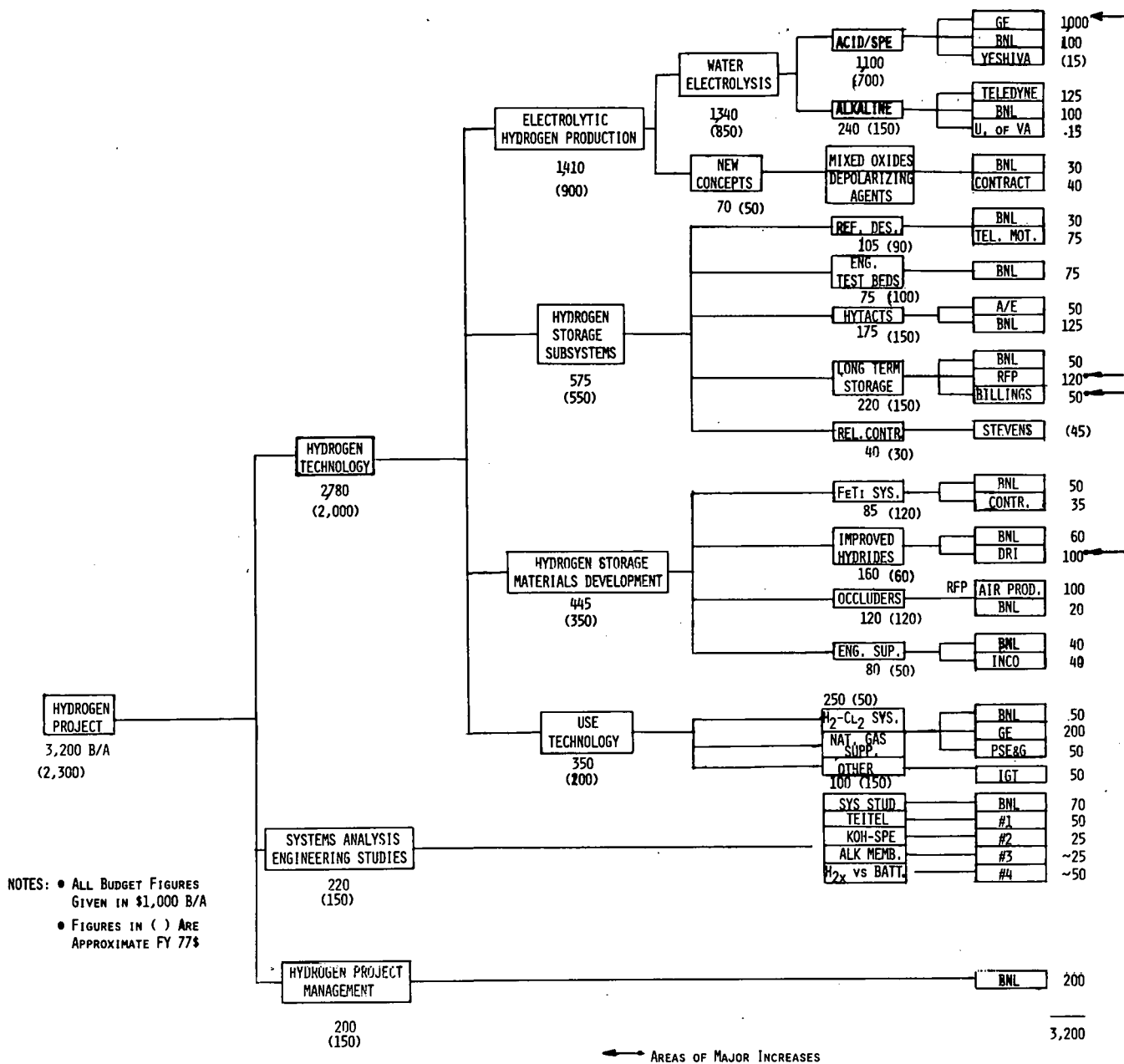


Figure 1.1. Hydrogen project budgetary breakdown for FY 78

2.0 ELECTROLYTIC HYDROGEN PRODUCTION

2.1 Solid Polymer Electrolyte (SPE) Water Electrolysis Technology Development

2.1.1 Design, Development, and Testing of 50 and 200 kW SPE Water Electrolyzers (General Electric Company)

Under the sponsorship of the Department of Energy, Niagara Mohawk Power Corp., Empire State Electric Energy Research Corp., New York State Energy Research and Development Authority and General Electric IR&D, General Electric is developing a highly efficient water electrolysis system using the solid polymer electrolyte technology. In this type of electrochemical cell, a solid sheet of perfluorinated sulfonic acid (Nafion) membrane serves as the electrolyte, and highly purified water is the only chemical feed into the cell. Because the cell environment is acidic and oxidative in the anodic compartment, noble-metal catalysts and corrosion resistant materials are required. Their high cost is largely offset by the very high current density ($\sim 1 \text{ amp cm}^{-2}$) and low cell potentials (1.85 V) for water electrolysis.

The aim of the program for 1978 was the design, fabrication and testing of a 50 kW (500 SCFH) system comprising 12 cells of the 2.5 ft² size. The design of the scaled-up cell (active area increased from 0.05 to 2.5 ft²) and module components was completed at the beginning of 1978. The effort centered largely on the membrane and electrode assembly, the molded carbon current collector, and the electrode supports. An isometric diagram of a portion of the 2.5 ft² module is presented in Figure 2.1.

Among various carbon/resin mixtures, the "wet" graphite/phenolic (80/20) mixture was selected for current collector material because it gave good adherence to metal foil (for anode oxidation protection) and adequate density and strength characteristics. Figure 2.2 shows a foil-backed molded carbon/resin collector.

The electrocatalysts are bonded on both sides of the membrane by a new improved rolling technique, in which the membrane is rolled onto a catalyst decal with minimal catalyst movements. A photograph of a membrane and electrode (M and E) assembly is shown in Figure 2.3.

A perforated titanium foil, produced by an acid etching technique, serves as the anode support while a commercially available carbon fiber paper is utilized as the cathode support.

A view of the test area is shown in Figure 2.4. Prior to assembly of an operational module, the end plates and pneumatic diaphragms were successfully proof-tested to 1000 psi using a manual water jack. The seal showed no signs of extrusion or failure and sealed dead tight at the high pressure. Subsequent tests using pneumatic pressures up to 300 psi showed very little gas leakage. Figure 2.5 shows a 2.5 ft² cell module installed in the test area.

The initial tests of the 2.5 ft² cell indicated poorer performance as compared to smaller cell (0.05 ft²), as shown in Figure 2.6. Upon disassembly of the cell, sections of the M and E assembly were cut out and tested in a 0.05 ft² cell. It was found that the M and E assembly performance was normal with only about 20 mV loss attributable to contamination, indicating that the performance loss was most probably due to high contact resistance, correctable by proper assembly and quality control.

Design studies initiated in 1978 for the 200 kW module will call for 60 cells with the active area of the electrodes of 2.5 ft². Figure 2.7 shows the schematic for the system. Heat and mass balance studies show that, at 300°F, some heat must be transferred from the cathode effluent water to the anode loop in order to eliminate the need for excessive stack cooling. A regenerative heat exchanger will, therefore, be necessary to accomplish steady state operation at 300°F. This heat exchanger, located in the feed water line, transfers heat from the cathode return water to the feed water supply, thereby preheating the feed water prior to delivery to the circulating water loop.

The 200 kW system was configured as a modular frame-mounted system, more representative of an industrial hydrogen generation installation than the 50 kW system. The removal of waste heat by an air coolant conditioner was chosen rather than water cooling due to its more universal acceptability. Six separate packages were planned as follows:

- (i) The 60-cell electrolysis module utilizing 2.5 ft² cells.
- (ii) The 7500 amp, 90 V dc power supply capable of driving the cells at 2000 amp/ft².
- (iii) The combination reverse osmosis-deionization water conditioner which processes municipal water to feed water.
- (iv) The waste heat management system which provides liquid cooling to the system and discharges waste heat to outside air.

- (v) The water and gas management subsystem which contains the pumps, separators, deionizers, and other fluid control elements.
- (vi) The control panel containing the fluid and electrical controls and instrumentation.

The achievements in the General Electric Program in 1978 may be summarized as follows:

- (i) Molded foil backed carbon 2.5 ft² collector developed.
- (ii) Membrane and electrode assembly successfully scaled up to 2.5 ft² active area.
- (iii) Electrode supports developed.
- (iv) Pneumatically loaded, 2.5 ft² module compression developed.
- (v) 50 kW (500 SCFH) test system completed.
- (vi) Operational testing of 2.5 ft² cells started.
- (vii) 200 kW (2200 SCFH) system defined.
- (viii) 200 kW (2200 SCFH) components ordered.
- (ix) Test facility for 200 kW (2200 SCFH) system started.

2.1.2 Electrochemical and Ellipsometric Studies on Anode Electrocatalyst (Brookhaven National Laboratory)

The oxygen evolution reaction is a highly irreversible reaction compared to the hydrogen evolution reaction, and is the predominant cause for efficiency losses in solid polymer electrolyte water electrolyzers. Iridium is one of the best electrocatalysts for the oxygen evolution reaction. However, it is the most expensive of the noble metals (Pt, Ru and Ir) and the least available. Ruthenium, about ten times less expensive and considerably more available than iridium, shows an initial electrocatalytic activity comparable to iridium; however, there are problems associated with its dissolution at anodic potentials and the loss in electrocatalytic activity with time. The latter phenomenon is observed on the other noble metals as well. Efforts are under way at the General Electric Company and Brookhaven National Laboratory to develop ruthenium-based catalysts. In order to do so, it is essential to elucidate the mechanisms of the degradation processes. The results of the electrochemical and ellipsometric methods, used for such investigations, are summarized as follows:

- (i) Optical analyses of ruthenium anodes reveal formation of Ru(OH)₃ films at 0.73 Volt versus the potential of the reversible hydrogen

electrode (RHE). The $\text{Ru}(\text{OH})_3$ film is further oxidized to $\text{RuO}_2 \cdot \text{YH}_2\text{O}$ at potentials above 0.94 V/RHE.

- (ii) The ellipsometric studies confirm that oxide films formed anodically can be reduced cathodically.
- (iii) The critical potential at which ruthenium corrodes rapidly in 25% trifluoromethane sulfonic acid is 1.45 Volts/RHE.
- (iv) The performance degradation for oxygen evolution on RuO_x catalyst is presumably due to the gradual accumulation of RuO_2 film on the surface of RuO_x particles by a dissolution-precipitation process (Figure 2.8).

Based upon the principles of solid solution and phase stability, a number of materials which appear promising as electrocatalysts for oxygen evolution were prepared. These electrocatalysts, including RuO_x , IrO_x , MnRuO_x , PbRuO_x , and SrRuO_x , were deposited by the thermal decomposition method on a titanium substrate. The electrodes were evaluated in 25% trifluoromethane sulfonic acid (TFMSA) at 25°C. The results are summarized in Table 2.1. IrO_x showed the best performance with respect to electrocatalytic activity and minimum time variation of performance. The performance of IrO_x in this study is comparable to that of the General Electric baseline catalyst (E50). The materials costs of the ruthenium-based catalysts will be about ten times less than the iridium-based ones. Of the Ru-based systems, MnRuO_x is most promising. SrRuO_x is unstable in the acidic environment. Figure 2.9 shows the Tafel plots for oxygen evolution on RuO_x and MnRuO_x in trifluoromethane sulfonic acid (TFMSA). Each type of electrode exhibited a two-section Tafel plot. The electrode kinetic parameters for the oxygen evolution reaction are listed in Table 2.2. It has been suggested that the change in the Tafel slope is due to the change in the mechanism of oxygen evolution.

2.1.3 Electrocatalytic and Optical Investigations on Single Crystal IrO_2 (Brooklyn College)

The fundamental electronic and vibrational properties of single crystals of IrO_2 as well as in situ electrochemical and combined electrochemical-optical measurements were investigated. The aim is to develop a general microscopic understanding of the nature of the electrocatalyst/electrolyte interface.

Single crystals of IrO_2 were grown by the chemical vapor transport method. The reflectivity of this single crystal at room temperature in the range 0.5-4.5 eV for light polarized parallel (\parallel) and perpendicular (\perp) to the c-axis

was measured utilizing a rotating light pipe reflectometer. These results are shown in Figure 2.10. It was observed that three independent t_{2g} subbands are present in the rutile IrO_2 suggesting that the Fermi surface topology will depend on the position of each subband relative to the Fermi level. As a result, one may expect the crystallographic dependence in the electrocatalytic activity of IrO_2 crystal.

Figure 2.11 shows a cyclic voltammogram for both [111] and [110] surfaces of freshly prepared IrO_2 in 1 N H_2SO_4 at a scan rate of 1 V/min. The voltage for oxygen evolution on both orientations is higher than that on polycrystalline Ir metal electrode. However, there is a significant difference in activity between the two orientations. Furthermore, there is no redox process at 0.93 V which has been reported for the Ir electrode. Both these features suggest that the IrO_2 single crystals are less electrocatalytically active than anodized Ir due to the stoichiometric composition of the former.

The potentiostatic method was used to measure current voltage curves on the Ir electrode sample and simultaneously the changes of reflectivity were recorded using the rotating light pipe reflectometer. Figure 2.12 shows the reflectivity, R, at 4000 Å of the polished Ir-metal electrode in 1.0 N H_2SO_4 as a function of time. The results indicate that there is a decrease of reflectivity with time at 1.22 V due to the formation of the oxide layer. On reducing the potential to zero, the reflectivity increases due to the reduction of the oxide.

2.2 Development of Advanced Alkaline Water Electrolyzers

2.2.1 Design, Construction, and Testing of Five Cell Water Electrolyzers (Teledyne Energy Systems)

The major task for 1978 was the construction and demonstration of the Applied Research Industrial Electrolysis System (ARIES). This system will be used for the long term evaluation of the most promising cell component materials, under commercial type electrolyzer conditions at temperatures up to 150°C. A photograph of the test rig and auxiliaries and a schematic of this system illustrating all subsystems are shown in Figures 2.13 and 2.14. Figure 2.15 shows the dependence of voltage on temperature at 450 mA/cm² in 25% KOH. However, the ultimate operating temperature is limited by the increased vapor pressure of the electrolyte, especially the dilute electrolyte. An overall module voltage

76% was observed at 125°C and 450 mA/cm². The DAUG Ni₂B and TES C-110 cathodes were tested in the cell module. The results are shown in Figure 2.16 along with those for conventional nickel wire screen cathode. Both types of novel cathodes exhibit improvement over the commercial cathodes.

A series of polymer samples were evaluated as potential candidates for separators. The major findings are:

- (i) Polyphenylene sulfide (PPS) is the most stable polymer studied thus far and has withstood, in fiber form, exposure to oxygenated KOH at 150°C for 500 h.
- (ii) Polysulfone (PS) is less stable than PPS, but withstood 125°C oxygenated KOH in similar tests.
- (iii) PPS and PS will require specialized fibre techniques and possible surface modification before they can be utilized as high temperature separators.
- (iv) Polybenzimidazole (PBI) was capable of withstanding 125°C oxygenated KOH and 150°C KOH in areas where the polymer was fully wetted. PBI is available in the required form for gas/liquid or interelectrode separator devices.
- (v) The major elastomer used in ARIES is ethylene-propylene terpolymer (EPT). It is rapidly degraded when fully exposed to oxygenated KOH at temperatures up to 125°C.

The 316 SS used in KOH-wetted portions of the system has shown a measurable corrosion rate. Scanning electron microscopy/energy dispersive x-ray (SEM/EDAX) analysis indicates no selective attack of the stainless steel components and showed a corroded layer of 5-10 μ thickness in 1000 h of exposure. There was a pitting-type corrosion seen in one anolyte/oxygen carrying tube section. The pits were associated with a form of titanium, one of the trace steel elements, but the mechanism of corrosion is unknown. The effects of a low steel corrosion rate were seen in a very high surface area component, a 316 SS sintered powder electrolyte filter. The filter lost a significant proportion of its original mass and proceeded to collapse under its own pressure difference. The corroding steel filter contributed a high concentration of cations to the electrolyte, most of which were effectively reduced at the cathode. No significant increase in electrode polarization was observed; however, a sintered Monel filter element has been substituted for evaluation.

2.2.2 Selection and Evaluation of Materials for Advanced Alkaline Water Electrolyzers (Brookhaven National Laboratory)

Over fifty organic and inorganic materials (porous, non-woven, polypropylene felts, ion exchange membranes, concretes, zeolites, etc.) have been tested as candidates for separators, first at below 100°C and the more promising ones up to 160°C. Only a small number of materials are suitable for separators in alkaline water electrolyzers operating at above 100°C. Nafion and potassium titanate are the most promising as confirmed by long-term evaluation (over 5000 hours) under water electrolysis operating conditions.

The performance of nickel cobalt oxide anodes and nickel boride cathodes were determined in single cells operating at 120°C and 150°C for periods over 2000 hours. The improvement in performance over nickel electrodes is very significant both from the point of view of higher electrocatalytic activity and minimal time variation of overpotential. Sintered nickel, impregnated with nickel hydroxide also shows promise as an oxygen evolution electrocatalyst.

The materials, screened for fabrication of cell containers, were polyarylether, polysulfone, Tefzel and polypropylene. Polysulfone proved to be the best. Teflon or Teflon-lined materials appear most satisfactory for seals in water electrolysis cells operating at temperatures in the region 100-150°C.

The following materials have been identified as the most attractive for advanced alkaline water electrolyzers operating at 120-150°C.

- (i) Anode Electrocatalysts - High Surface Area Nickel Cobalt Oxide
- (ii) Cathode Electrocatalyst - High Surface Area Nickel Boride
- (iii) Separator - Teflon Bonded Potassium Titanate or Nafion
- (iv) Cell Frame - Teflon or Teflon Based

The tests on barrier materials, electrodes, and cell components have so far been carried out on a static basis in a pressure vessel. In a joint BNL-TES-University of Virginia program, the most promising materials will be tested for performance and/or life in the Teledyne Energy Systems ARIES test rig.

Experimental data was accumulated for a six-month period on a 2-cell self-circulating electrolyzer with nickel electrodes and polymethyl methacrylate (PMMA) cell frames, deriving its energy from a wind-driven generator. This study demonstrated the feasibility of the concept of coupling electrolyzers with renewable energy sources (wind, solar). In addition, performance gains were apparent

with the highly intermittent electric energy pulses. During the year, a Hewlett-Packard Data Acquisition System was programmed for recording and plotting of cell performance data in the short and long-term water electrolysis experiments being carried out to screen and evaluate cell component materials. Previously acquired pertinent data are being processed and recorded in the Data Bank for future cross reference.

2.2.3 Selection and Evaluation of Materials for Advanced Alkaline Water Electrolyzers (University of Virginia)

The continuous efficiency loss for hydrogen production in alkaline electrolysis cell is attributed to the increasing cell voltage with time. Figure 2.17 shows the variation of voltage with time. The rate of change of cell voltage is higher for higher temperatures and higher current densities. Initial overvoltage changes are observed for both electrodes, however, the cathode is found to be the dominant factor in the cell voltage increases as illustrated in Figure 2.18. The nickel cathode changes to a blackish color during electrolysis except at low current density. Scanning Electron Microscopy investigation exhibited no major change in surface area as a result of electrolysis. Also, energy dispersive x-ray analysis of the black color indicated no heavy metal impurities and no gross change in composition. Preliminary studies suggest that the diffusion of hydrogen into the cathode accounts for the voltage increase.

Polycrystalline nickel whiskers were produced by chemical vapor deposition of nickel tetracarbonyl gas ($\text{Ni}(\text{CO})_4$) in an electromagnetic field. These whiskers were fabricated into a whisker electrode (network) by sintering at 800 to 1000°C under pressure in a reducing atmosphere, for approximately 1/2 hour. The resultant electrode is porous and fibrous. The true surface area to volume ratio is $10^4 \text{ cm}^2/\text{cm}^3$ and the true specific area is $5 \times 10^3 \text{ cm}^2/\text{g}$. The resulting high surface area obtained causes a decrease in electrode voltages. Overvoltage decreases of 60 to 100 mV were observed for the whisker electrode as compared to the screen electrode for both hydrogen and oxygen evolution, as illustrated in Figure 2.19. This comparison is made at equal total current. The corresponding apparent current densities range from 0.1 to 1 A/cm^2 . Incorporation of whiskers into electrode designs is a promising approach to minimize anodic and cathodic overpotentials.

Table 2.1

ELECTRODE KINETIC PARAMETERS FOR OXYGEN
EVOLUTION REACTION IN TFMSA AT 25°C

Electrode (Fire Temp.)	Tafel Slope (mV/d)		Voltage at 10 mA(v)
	First Run	Second Run	
RuO _x (400°C)	50	56	1.532
(500°C)	48	50	1.551
(615°C)	64	72	1.600
(700°C)	68	76	1.634
IrO _x (400°C)	61	61	1.532
(500°C)	60	60	1.563
(615°C)	70	67	1.574
(700°C)	~134	--	1.696
MnRuO _x (400°C)	62	62	1.558
(500°C)	68	60	1.607
(615°C)	60/176	64/134	1.600
PbRuO _x (400°C)	51	52	1.568
(500°C)	56	58	1.568
(615°C)	40	70/140	1.583
SrRuO _x (400°C)	--	--	1.481
(500°C)	--	--	1.508
(615°C)	--	--	1.564

Table 2.2

ELECTRODE KINETIC PARAMETERS FOR OXYGEN
EVOLUTION REACTION ON RuO_x , MnRuO_x FROM TFMSA AT 25°C

Electrode	Tafel Slope (mV/d)		Exchange Current Density (A/cm^2)
	Low η	High η	
RuO_x	45	73	5.8×10^{-8}
MnRuO_x	38	65	2.3×10^{-8}

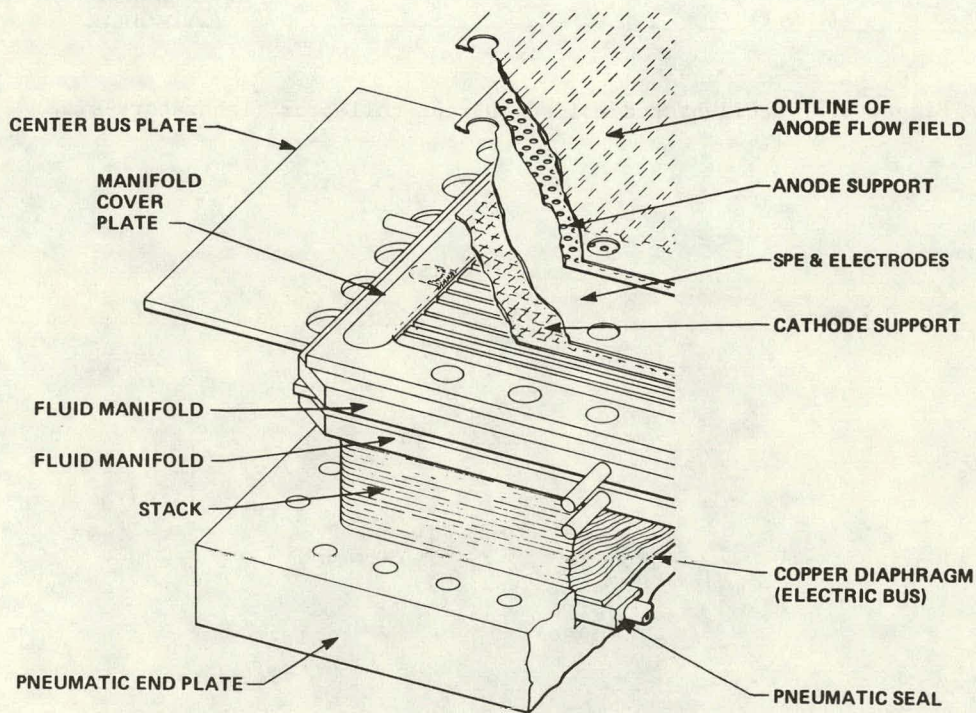
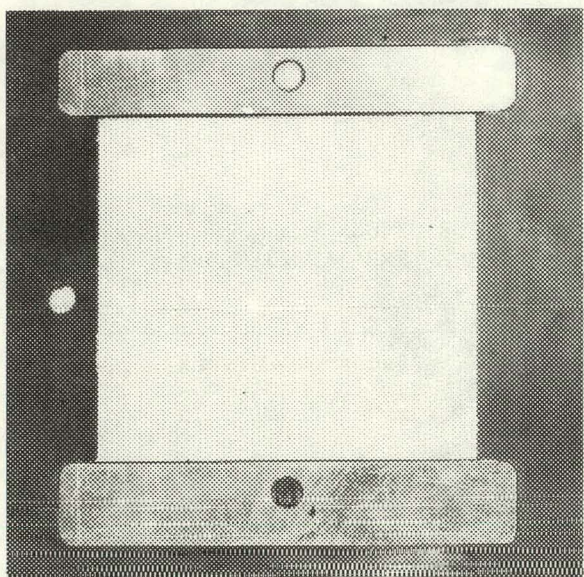
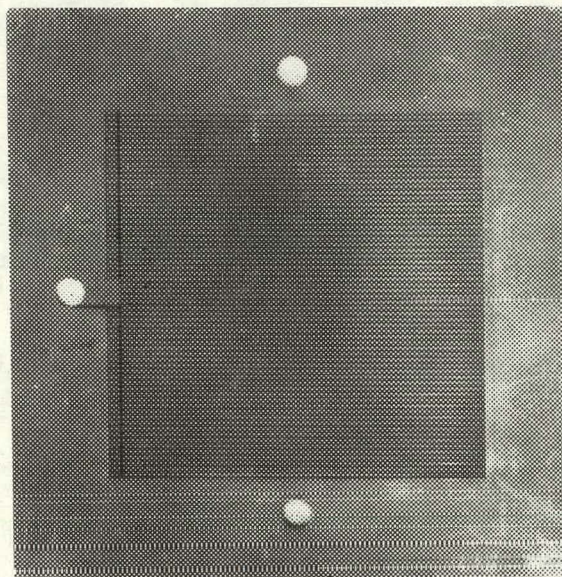


Figure 2.1. Single cell detail



OXYGEN SIDE
(ANODE)



HYDROGEN SIDE
(CATHODE)

Figure 2.2. Foil-backed molded current collector (laboratory-size)



Figure 2.3. 2-1/2 Ft² membrane and electrode assembly

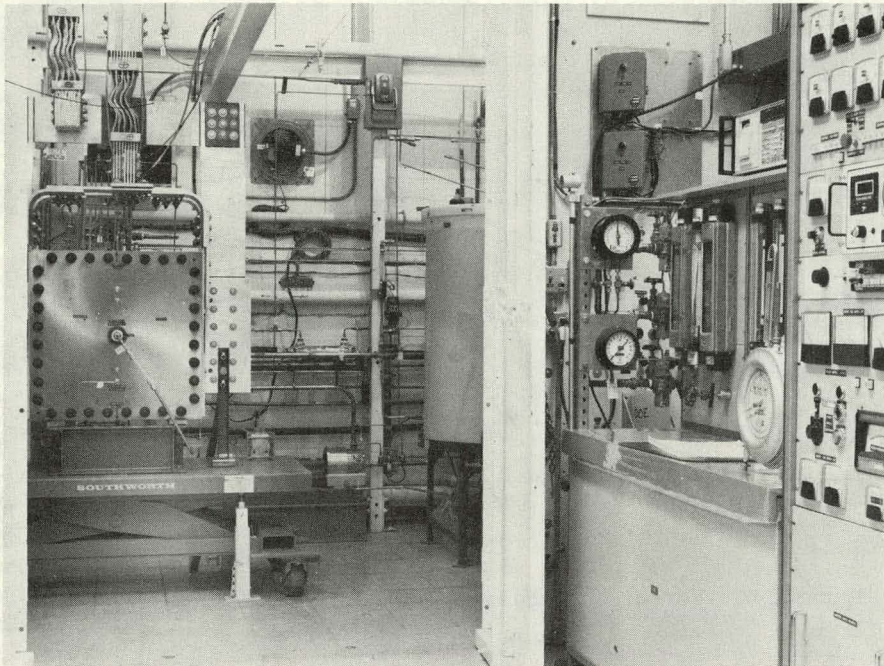


Figure 2.4. Single module
S/N DOE-5 testing

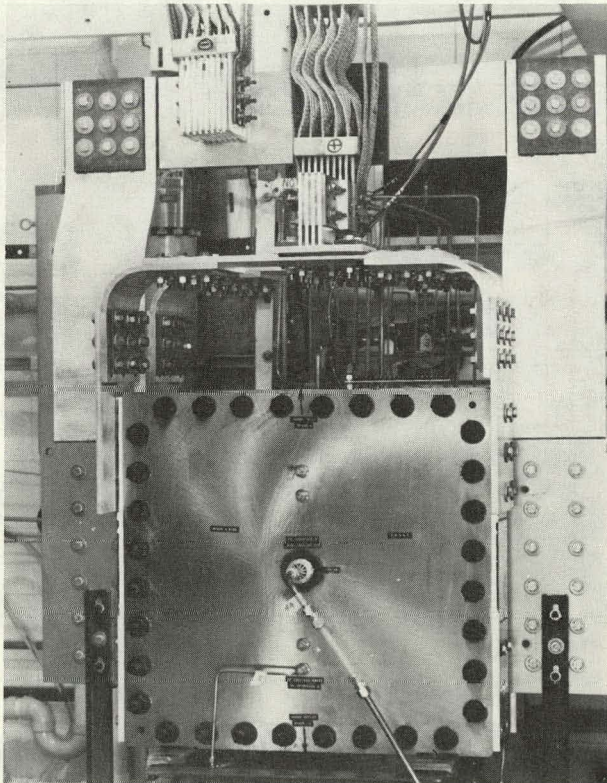


Figure 2.5. 2-1/2 Ft² module
assembled for leak test

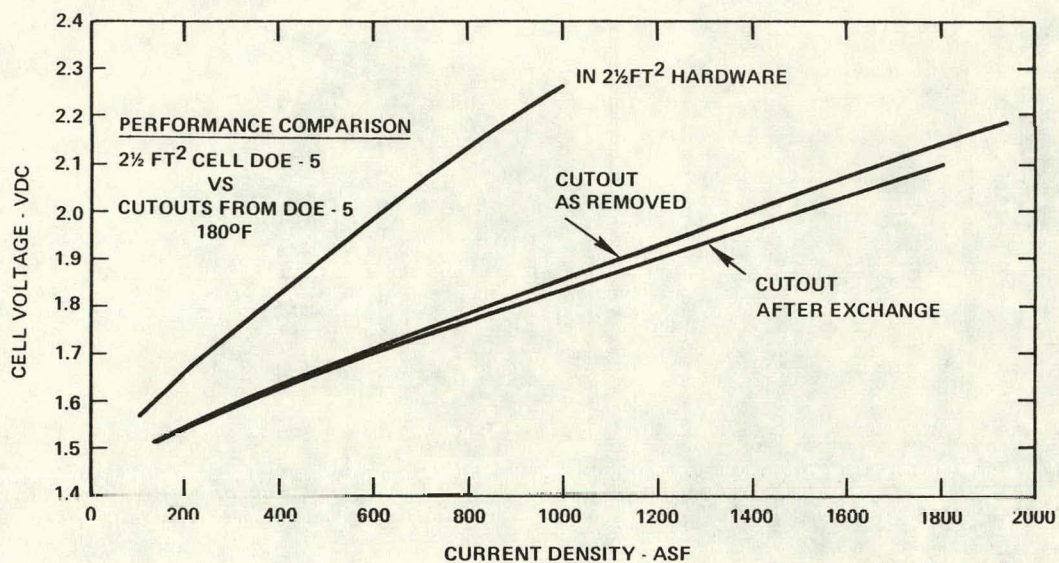


Figure 2.6. Performance comparison

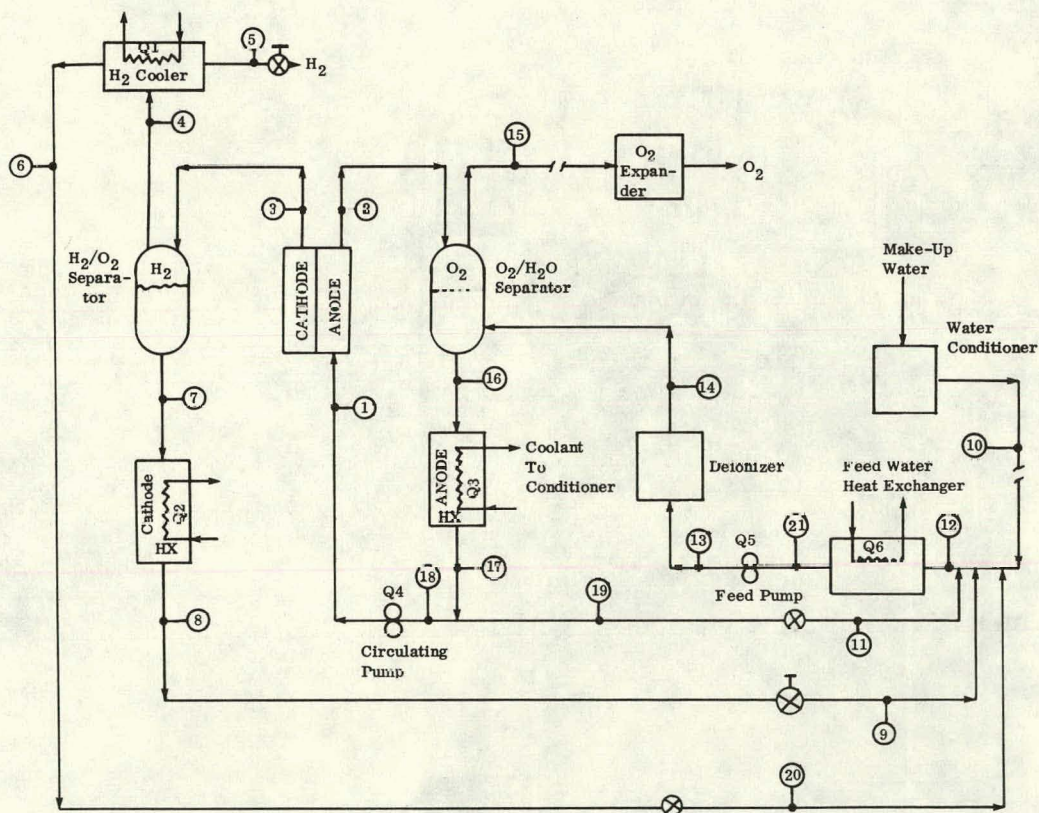


Figure 2.7. Water electrolysis heat and mass computer model schematic

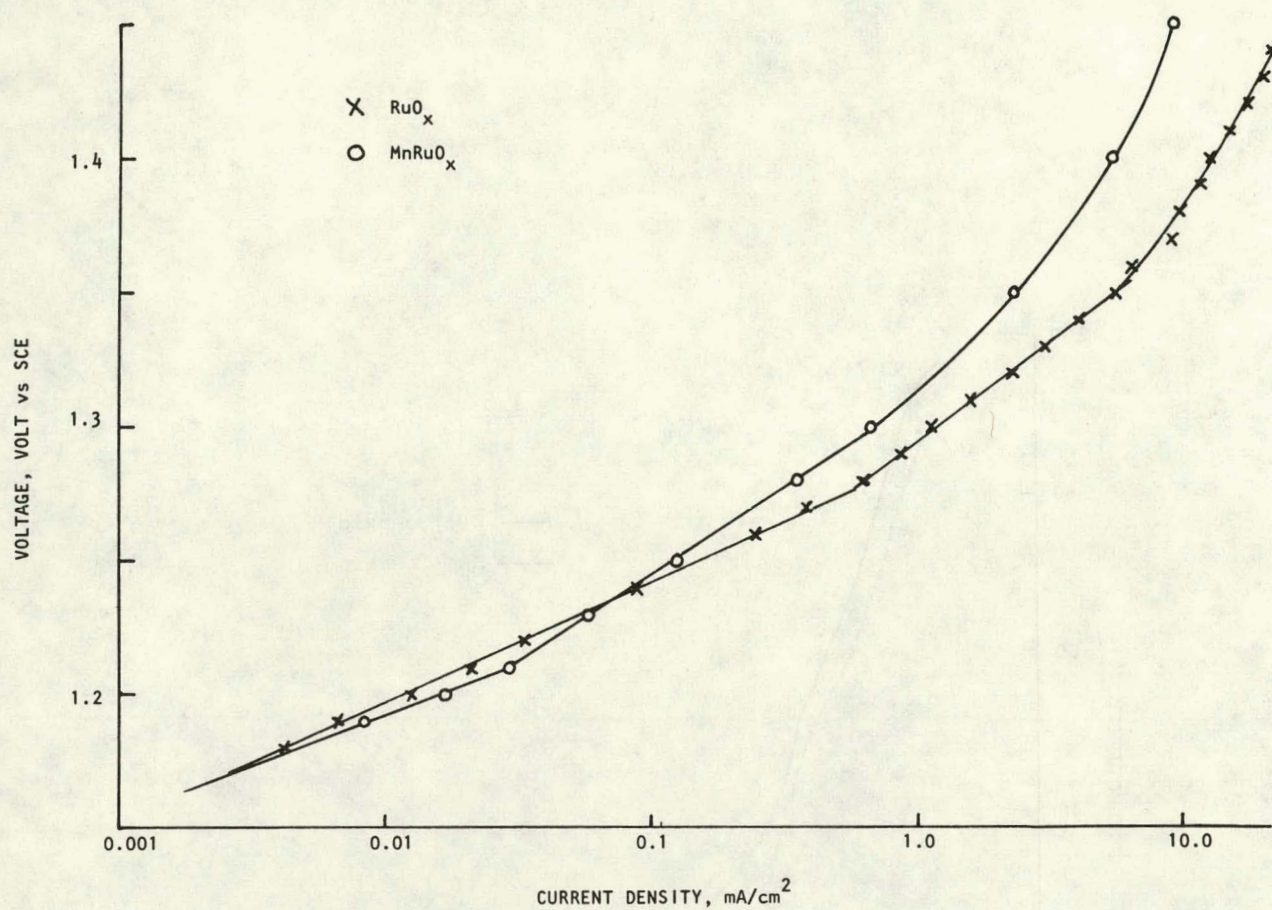


Figure 2.8. Proposed mechanism of performance degradation with time for oxygen evolution on RuO_x electrodes in SPE water electrolyzers

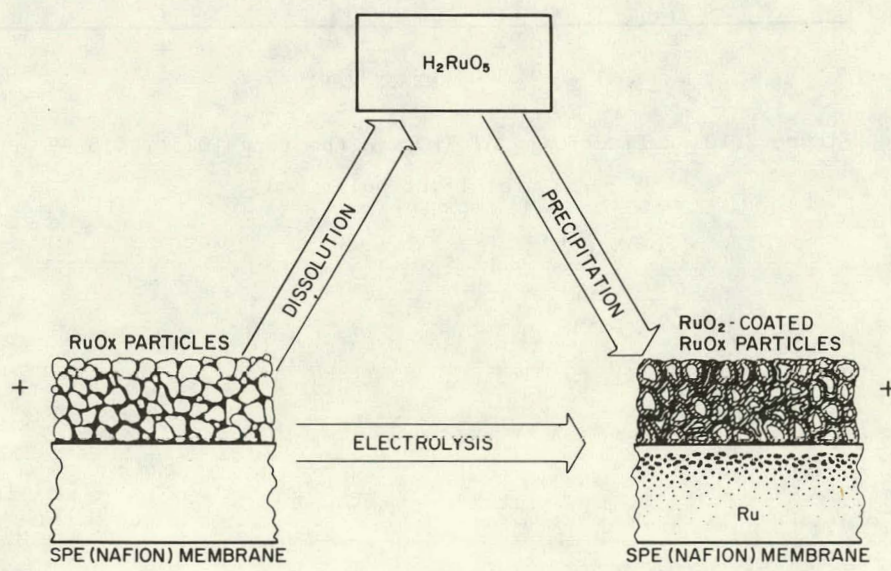


Figure 2.9. Tafel plots for oxygen evolution on RuO_x and MnRuO_x

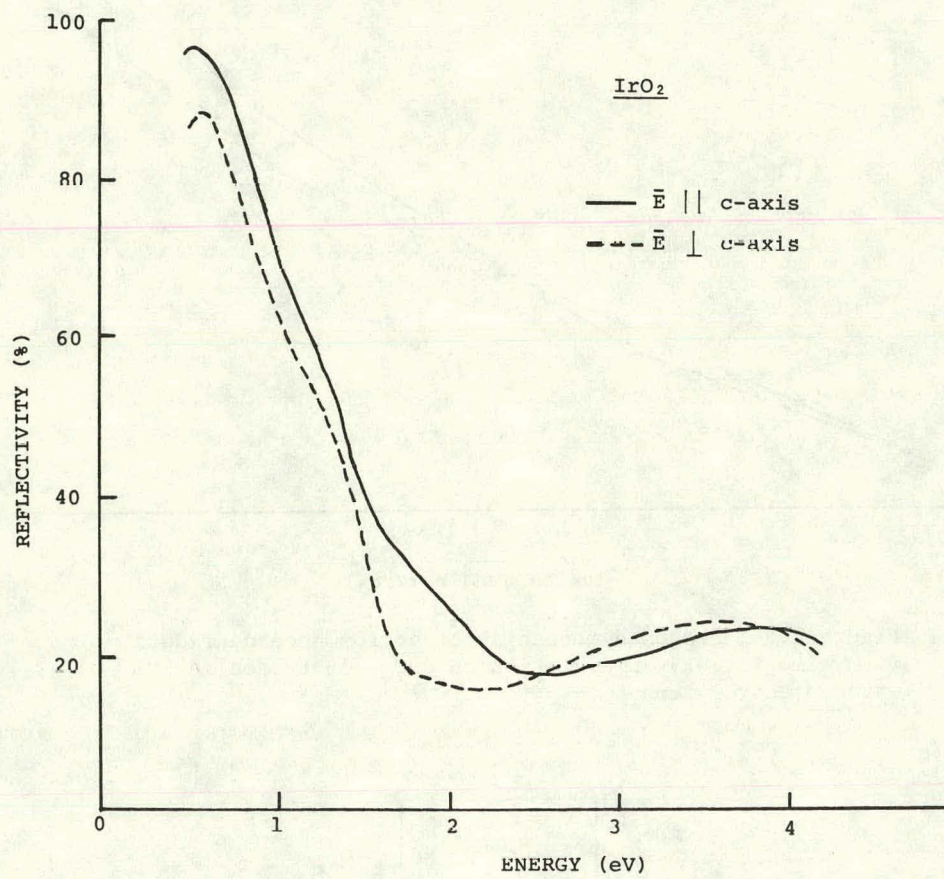


Figure 2.10 Reflectivity of IrO₂ in the range 0.5 - 4.5 eV
for light polarized

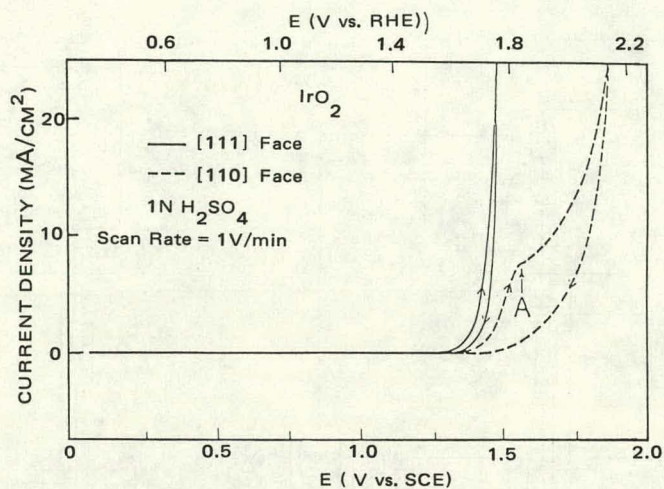


Figure 2.11. Current-voltage curve obtained during a single triangular cycle at a scan rate of 1 V/min applied to virgin IrO_2 single crystals with [111] (solid lines) and [110] (dashed lines) faces in a 1 N H_2SO_4 solution at room temperature

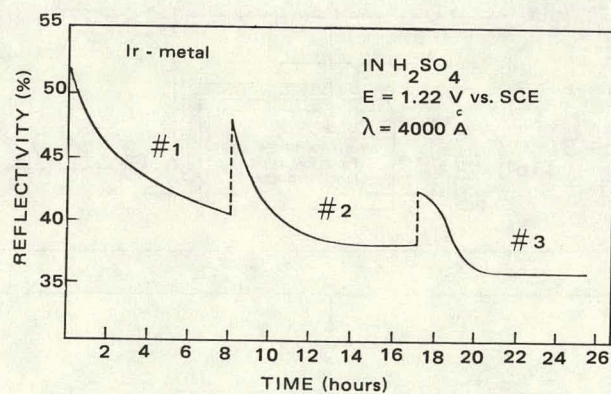


Figure 2.12. Time dependence of the reflectivity of an Ir-metal electrode during oxide formation

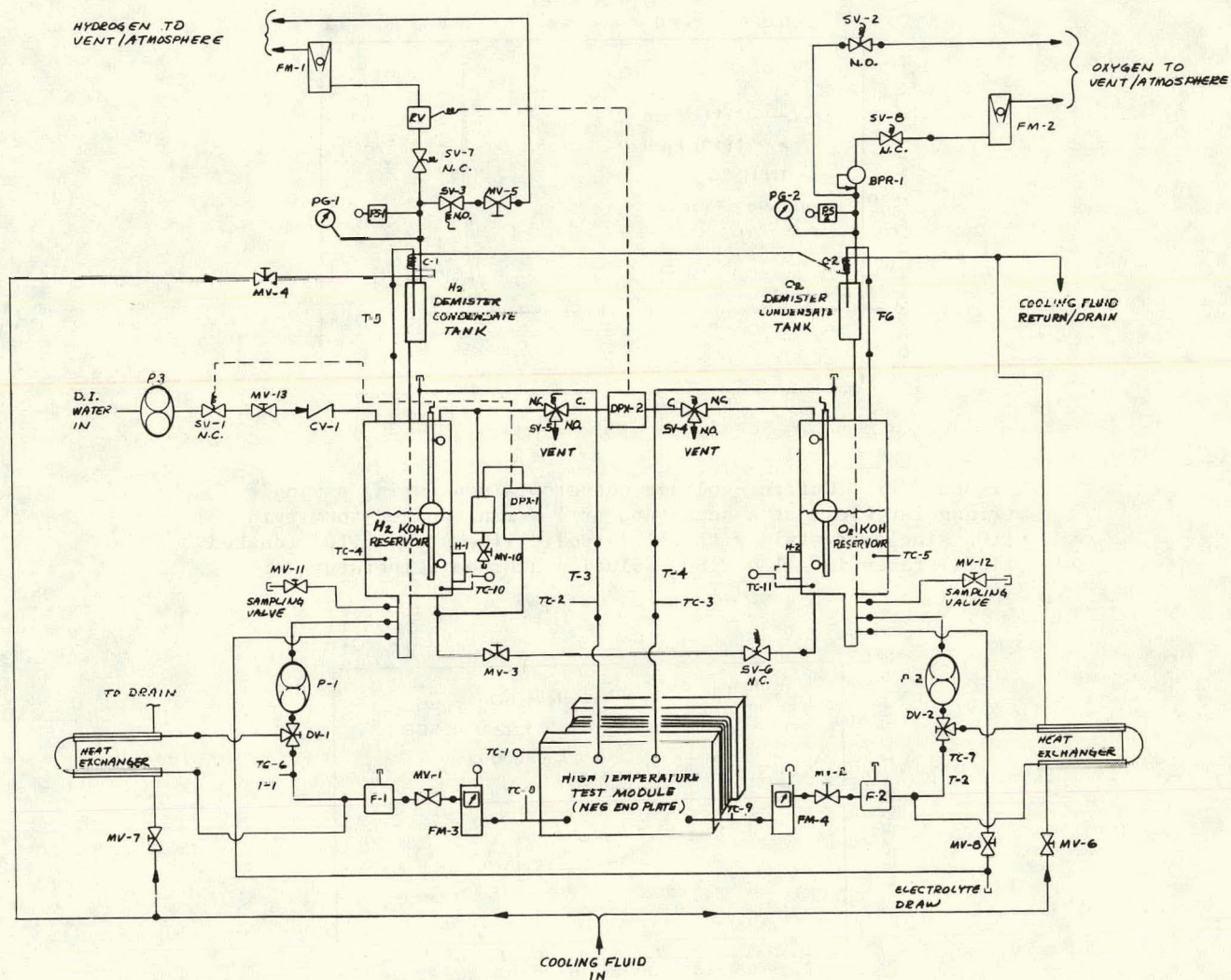


Figure 2.13. ARIES mechanical schematic

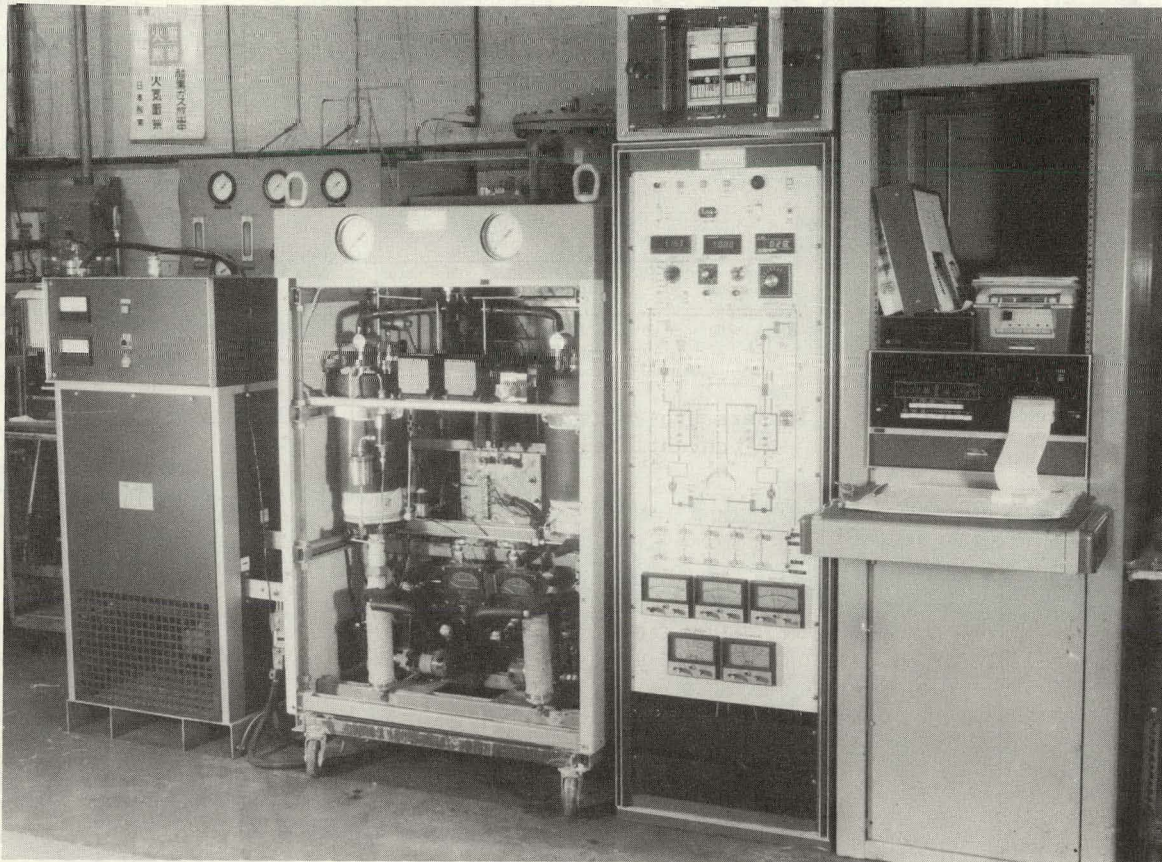


Figure 2.14. Applied research industrial electrolysis system (ARIES)

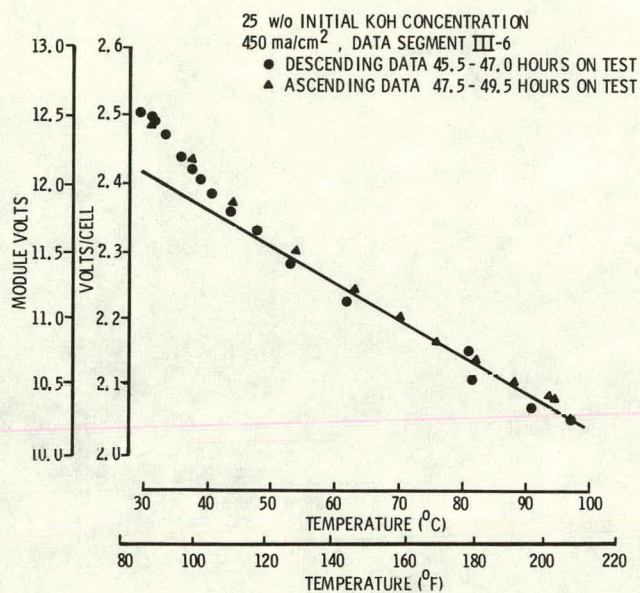


Figure 2.15. Temperature-voltage behavior of time stabilized conventional components

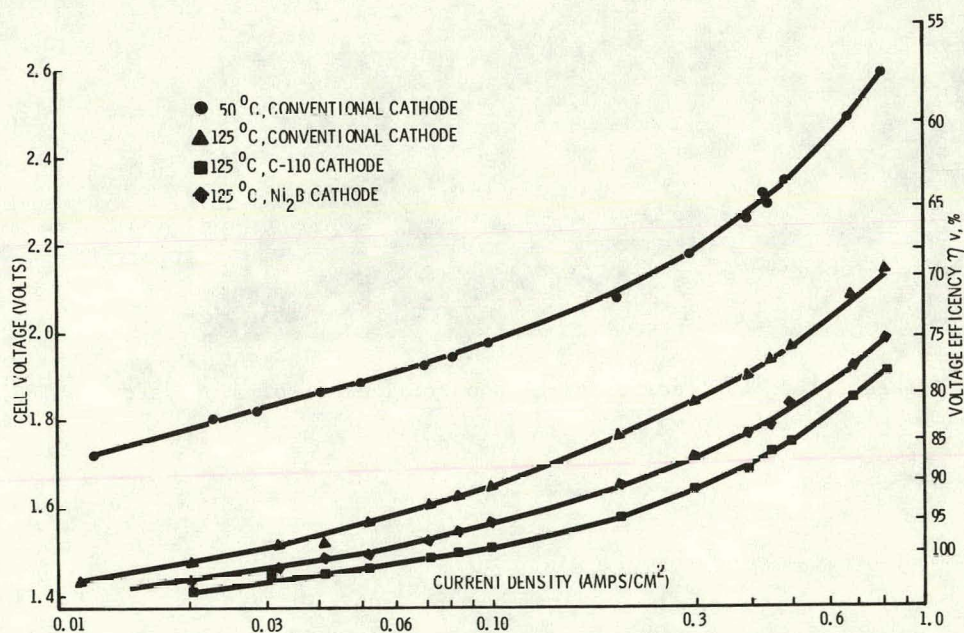


Figure 2.16. Comparison of conventional and advanced cathodes

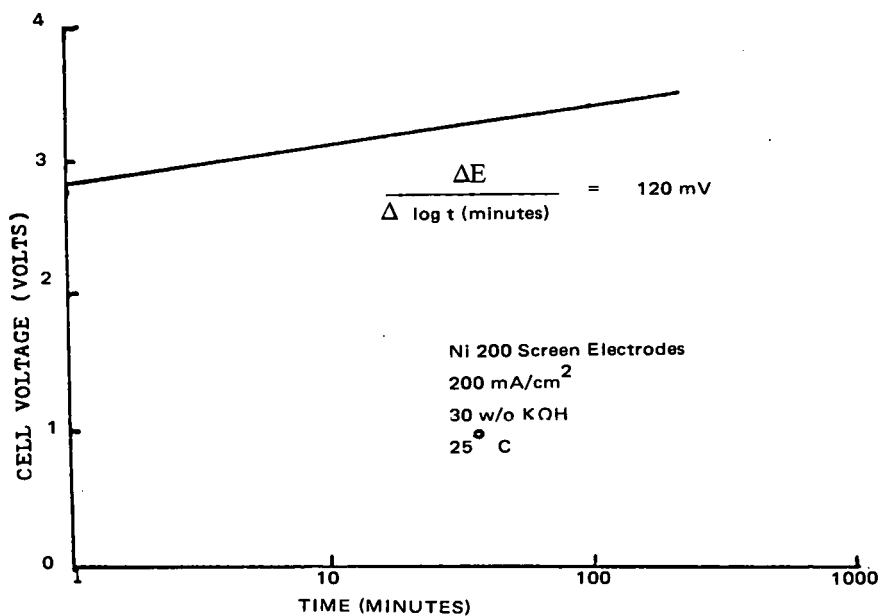


Figure 2.17. Efficiency loss for hydrogen production (voltage vs. time)

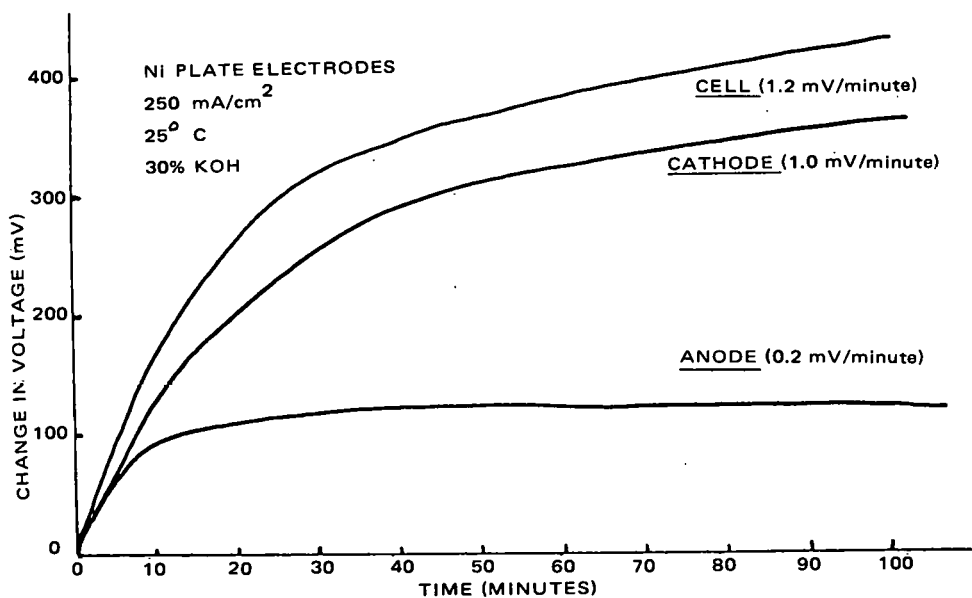


Figure 2.18. Overvoltage changes for cell components (voltage vs. time)

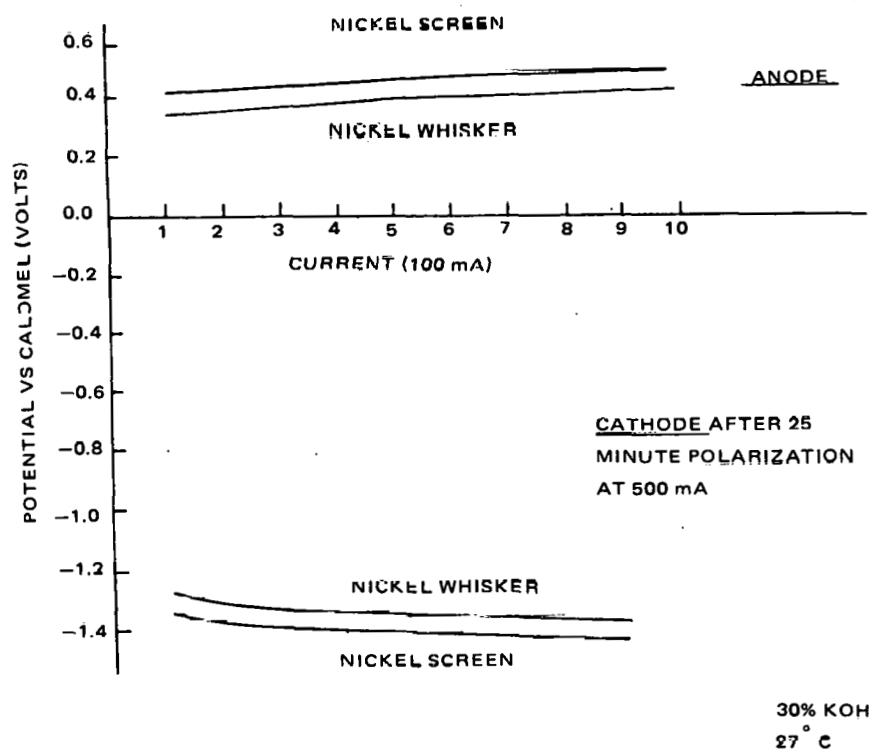


Figure 2.19. Performance characteristic comparison Nickel whisker vs. nickel screen

3.0 HYDROGEN STORAGE SYSTEMS

Brookhaven National Laboratory's management, technical monitoring and in-house research and development activities into hydrogen storage systems in 1978, have served to redirect programmatic emphasis from bulk hydride/hydrogen storage systems as conceived for utility load-leveling applications to stationary and mobile storage systems that would more closely relate to automotive requirements. Long-term storage needs as perceived for potentially large user demands, focus on systems analogous to those used for natural gas underground storage systems.

3.1 Underground Storage of Hydrogen

The Institute of Gas Technology was awarded a contract on August 14, 1978, as a result of evaluations of submissions by four major organizations in response to BNL RFP HYD-77-1. The objectives of the project are to:

- . Establish the engineering feasibility of using geologic or engineered underground sites for hydrogen storage.
- . Identify the research and development needs aimed toward cost reduction and safety considerations.
- . Identify possible sites for hydrogen storage.
- . Provide realistic cost estimates for the restoration or development of underground hydrogen storage systems.

The project team comprises a mix of technical disciplines and project-related experience consistent with project needs, as follows:

- . Institute of Gas Technology
- . Dames & Moore
- . Texas Gas Transmission Company
- . Northern Illinois Gas Company
- . Transcontinental Gas Pipeline Corporation
- . Southern California Gas Company

3.1.1 Characterization of Underground Storage Facilities

The initial investigations seek to evaluate current practices and associated cost/economics of natural gas underground storage systems. These evaluations will serve to define the key elements to be considered as they impact

cost-of-service and safety factors pertinent to the conversion, restoration or newly engineered hydrogen storage and delivery systems.

Aquifer Storage

Figure 3.1 illustrates the concept of aquifer storage. The geological requirement is existence of an anticline (concave downward hump) in a water-saturated porous formation that is overlain by a highly impermeable caprock. Storage is accomplished by pumping gas into the top of the anticline to displace the original water. The injection pressure, and therefore the rate, must be limited so that the capillary forces that provide the caprock seal are never exceeded. Withdrawal rate from storage must be low enough that the pressure sink at a withdrawal well does not result in upward coning of underlying water which would block gas production. A practical effect of these considerations is that several years are required to reach the full storage capacity of an anticline. Also, even with multiple wells, the maximum practicable withdrawal rate is less than 1% of stored gas per day.

In the case of hydrogen storage, "base" gas and "nonrecoverable" gas are critically important considerations. Base gas is the fraction of total injected gas that is not normally withdrawn during cycles of storage operation. For aquifers, this is roughly two-thirds of the total gas inventory. The cost of hydrogen base gas will probably be several times greater than all other costs of the storage facility. Nonrecoverable gas is the portion of gas that can never be recovered due to economic considerations, or because it will be bypassed by water and trapped in place. Estimating nonrecoverable gas and defining the economic implications are the key elements of the study to be performed.

Depleted Fields

Depleted natural gas fields are widely used for natural gas storage. The geological environment is similar to that shown in Figure 3.1 for aquifer storage. The major differences are--

- . A substantial amount of natural gas remains when operating costs exceed the value of production from a gas field. This remaining natural gas will mix with hydrogen during use for hydrogen storage.
- . Permeability of the rock formation is generally lower than for aquifers so so that pressure drop in the vicinity of each well, rather than water coning, limits withdrawal rate.

- . Many depleted fields involve substantially greater depths and storage pressures than the aquifers that have been used for storage to date.

Washed Salt Caverns

In contrast to aquifer and depleted field storage, a cavern washed in salt is literally a large hole. Injection and withdrawal rates are not controlled by geological characteristics such as permeability or water movement. With available technology, production of up to one-third of the total gas in storage in a single day is straightforward.

The optimum depth for salt cavern storage is less than about 5000 feet. This is because salt is a plastic material that creeps under stress. A deep cavern would require a large investment in base gas to avoid closure at the end of the withdrawal cycle.

Mined Caverns

With the exception of one unique, abandoned coal mine, mined caverns are not in use for natural gas storage in the United States at the present time. However, underground storage of a variety of liquid products, including propane, in mined caverns in Europe and the United States have proved technologies that are believed applicable to storage of gases. Such storage of hydrogen will be evaluated in this study because--

- . The local geology precludes the other types of storage in many geographical areas, such as New England.
- . Base gas and nonrecoverable gas will be much less than for aquifers or depleted fields. Therefore, the high cost of hydrogen may provide strong motivation to pursue mined caverns.

3.1.2 Project Status

Specific examples of the three types of storage widely used by the gas industry are being subjected to case studies. These include:

- 1) Media Storage Field in Henderson County, Illinois--an aquifer storage facility.
- 2) Hanson Storage Field in Hopkins County, Kentucky--a depleted gas reservoir.

3) Eminence Salt Dome in Covington County, Mississippi--a salt cavern. Preliminary cost evaluations will be performed for converting these facilities as well as mined caverns to hydrogen service. Key elements of cost considerations

pertain to the lower Btu value of hydrogen per unit volume (~ 3 -fold less than natural gas), hydrogen embrittlement, safety and base gas requirements--especially in view of the comparative high cost of hydrogen versus natural gas.

A mathematical model is being developed that will permit the conduct of cost-of-service sensitivity analyses over a wide range of storage/delivery and system design scenarios. Findings to date give cause for optimism regarding the technical and economic viability of underground storage of hydrogen.

3.2 Automotive Storage Systems

3.2.1 Metal-Hydride Storage

The requirements of metal-hydride storage systems suitable for automobile propulsion differ from those for bulk hydrogen storage in that much higher hydrogen transfer rates are required and that there is a practical limitation on the system weight. For bulk storage, hydrogen charging and discharging times are typically 5-10 hours; whereas for automobiles times of less than 15 minutes are essential. This requirement is based on the short refueling time of gasoline-fueled vehicles as well as upon a high load condition such as the flow surge required for more than a brief acceleration. Associated with the flow of hydrogen is the transfer of heat in order to sustain the flow; heat must be removed from the hydride bed during charging, and it must be supplied during discharging. Thus the main design change required for the automotive application is to greatly increase the rate of heat transfer; the overall heat-transfer coefficient must be increased at least 20-fold. Furthermore, the storage system weight is much higher than it is for gasoline; hence there must be a trade-off between vehicle range and system weight. The objective of this program is to develop a cost-effective hydrogen storage system suitable for automotive propulsion.

The factor having the greatest effect on heat-exchanger design for a hydride particle bed is the low thermal conductivity of the hydride. Reducing the bed thickness and enhancing heat transfer in the bed will increase the conductivity. Canning the hydride in small-diameter tubes and incorporating a material of high thermal conductivity in the bed are expected to achieve the desired improvement. Aluminum or copper in the form of metal foam, knitted wire mesh, short fibers, and powder are the candidate items to be tested. The various configurations will

be evaluated on a relative basis by observing the rate of axial temperature rise in the hydride bed. Formal design and construction of the test vessel will be completed in the first quarter of 1979. A copper container (2- to 3-in. diam.) will be used in order to minimize the wall resistance to heat flow.

The procedure planned consists of immersing the test vessel in a water bath at 30°C, to stabilize its temperature, and then rapidly relocating the vessel in another bath at 80°C. For each configuration, tests will be made at various hydrogen pressures (0-200 psia) and degrees of bed compactness. Deactivated TiFeH_x will be used, rather than TiFe alloy, in order to include the effect of particle fragmentation which is characteristic of the hydride. No thermal effects related to a reaction with hydrogen are expected because the hydride will not be reactivated.

The results of these tests will be used in specifying the design of a single heat-transfer cell suitable for obtaining absolute heat- and mass-transfer rates. Subsequently a full-size storage vessel will be designed, constructed, and tested using hot water to simulate the engine coolant. Work with Mg-based hydrides is expected to follow.

3.2.2 Microcavity Storage

A study of a new concept for storing hydrogen at high pressure in hollow glass microspheres was completed by Robert J. Teitel Associates of San Diego, California.¹ Microcavity storage (MCS), as it is called, is based on the high permeation rate of hydrogen through certain glasses at temperatures near 200°C (392°F), and very low release rates at ambient temperatures. The projected storage density is about 11 wt % hydrogen for microspheres of 25-85 μm diameter (0.8-1.5 μm wall) and an internal pressure of 400 atm, at room temperature. In this study MCS was coupled with TiFe-based metal-hydride storage (MHS) to provide a system superior to either alone. The latter MHS, furnishes hydrogen for cold starting and minimizes losses by absorbing hydrogen after shutdown; whereas MCS supplies hydrogen for most of the driving range.

As shown in Figure 3.2, the permeability of hydrogen through glass is highly temperature dependent; it is also a strong function of the glass composition and the percentage of "non-network formers" in the glass. Their effect on release rate room temperature is shown in Table 3.1. The numbers in parentheses represent the weight of metal hydride (lb) required to absorb leakage from the MCS.

For MCS only sensible heat is involved in adjusting the system temperature; whereas MHS involves much higher heats of reaction. In the conceptual design studied, the MHS system is initially charged (and cooled) by an external source at 500 psi and is subsequently partially recharged upon shutdown; periodic external recharging will probably be required. For the MCS system, the microspheres must be replaced, the spent supply being collected for recycling to the filling plant which would probably be located at the hydrogen production site. Details of the filling procedure remain to be fully developed.

The utility of the hybrid MCH system was evaluated by comparing it with a reference MHS design based on the dual-hydride system: $\text{TiFe}_{0.85}\text{Mn}_{0.15}\text{H}_x$ and MgH_x catalyzed with 10 wt % Ni (2:1 wt ratio). The reference design is for a 4-passenger car rated at 0.02 HP/lb, based on a gross vehicle weight of 3300 lb, and a range of 150 miles; its hydrogen content is 17 lb. In Table 3.2, the MHS and MCS systems are compared on the basis of equal weights of stored hydrogen. The projection shows that the MCH system weighs half as much, has twice the volume, and is expected to cost half that of the MHS system. Thus the MCH system warrants further examination.

In calendar year 1979, further contract work is planned in order to obtain experimental data on the behavior of glass microspheres and further evaluate the feasibility of this new concept.

TABLE 3.1
HYDROGEN RELEASE UNDER ROOM TEMPERATURE STORAGE CONDITIONS

Hydrogen released, % of stored hydrogen (weight of hydride, lb)*			
Time	M**=0	M**=5	M**=10
1 hr	2 (1.5)	.12 (.09)	7×10^{-3} (.005)
1 da	37 (28)	2.8 (2.1)	.16 (.12)
1 wk	94 (71)	18 (14)	1.2 (.90)
2 wk	98 (78)	33	2.3 (1.7)

*Weight of the metal hydride $\text{TiFe}_{0.85}\text{Mn}_{0.15}\text{H}_x$ per lb of hydrogen initially stored on microsphere bed. Weight % hydrogen for $\text{TiFe}_{0.85}\text{Mn}_{0.15}$ assumed as 1.333.
M** denotes mole percent of non-network forming constituents.

TABLE 3.2

WEIGHT AND COST SUMMARY FOR REFERENCE METAL HYDRIDE SYSTEM (MHS)
AND HYBRID MICROCAVITY SYSTEM (MCS)

	MHS	MCS
Weight of Stored Hydrogen (lb)	17	17
Total Weight of Storage System (lb)	1016	569
Weight of H ₂ /Weight of System	.017	.030
Volume of Storage System (ft ³)	6.9	15
Cost of Storage System (1975\$)	1684	827

3.2.3 Energy Storage System Study

Lawrence Livermore Laboratory (LLL) is conducting a study on energy storage systems for the automobile, in cooperation with Argonne National Laboratory for battery systems and Brookhaven National Laboratory for hydrogen systems.² The major Brookhaven effort in 1978 was preparation of the preliminary design for a dual-hydride system, and estimates of its performance. A similar system had been developed and tested by Daimler-Benz AG of West Germany.³ Featured in the design is a storage vessel capable of being charged with hydrogen in about 10 minutes. A sketch of the vessel is shown in Figure 3.3. The hydride is contained in 1-in.-diam. tubes, and foamed-metal inserts enhance heat transfer. A thin wrap of knitted wire mesh is used to maintain contact with the container wall. Each tube has an end filter and connects to the hydrogen plenum.

The complementary properties of the Ti-based and Mg-based hydrides used in the system provide performance superior to either alone. Cold-starting capability is provided by $\text{TiFe}_{0.9}\text{Mn}_{0.1}\text{H}_x$, and range extension is provided by MgH_x catalyzed with 10 wt % nickel; they are used in a 2:1 weight ratio in aluminum alloy (6061-T6) and stainless steel (Type 304) vessels, respectively. The design

is linearly scaled by changing the number and/or length of the tubes. Data on the projected weight, energy density and power density of the storage systems is provided in the LLL report.² Projections were also made for a liquid-hydrogen storage system. In both cases, the projections were higher and more realistic than they were in 1977.

The various types of energy-storage vehicles modeled at LLL were evaluated at four performance (HP/lb) categories and four weight (range) categories. Vehicle weights and initial costs were calculated along with their life-cycle costs (\$/mile) based on the amount of energy expended in traversing a standard drive cycle. All values were calculated at two confidence levels, 50% C.L. representing the most likely value, and 10% C.L. representing an optimistic or upper-limit value. The conclusions derived from the work on hydrogen storage systems are as follows.

- . Although liquid hydrogen can provide high-performance, low-cost vehicles, safety considerations may exclude this system from widespread vehicle use.
- . A dual-hydride hydrogen storage system is comparable to advanced battery systems in specific energy and is considerably better in specific power. The present high cost of producing and distributing hydrogen for automobile use is an obstacle to be overcome.

3.3 Bulk Hydride-Hydrogen Storage

3.3.1 BNL Program

The bulk storage of hydrogen was originally conceived for electric-utility load leveling using off-peak power to produce electrolytic hydrogen for storage as a decomposable metal hydride; subsequent conversion to electricity was to be accomplished in a hydrogen-air fuel cell. Sizing of the system would be a function of the amount of stored energy needed, the basic characteristic of the system being that hydrogen charging and discharging times are 5-10 hours. A 12.5-kW system of this type was tested at Public Service Electric & Gas Company of New Jersey, using a 13-lb hydrogen storage vessel designed and constructed at BNL.^{4, 5, 6}

Subsequently this shell-and-tube design was scaled up to a 50-kW, 500-kWh storage vessel that was designed and constructed by Foster Wheeler Energy

under contract to BNL. As shown in Figure 3.4, the vessel is fabricated from 26-in. diam. carbon-steel pipe (A-106 Grade B) and is 10-ft long. It has a flanged head for installation of the U-tube heat exchanger and has a pressure rating of 500 psig. The 33 tubes, made of Type 304 stainless steel (0.75 in. O.D. x 0.065-in. wall), are located on a 2.25-in. square pitch. Because plans called for testing several heat exchanger configurations, the vessel was named Variable-Parameter Test Unit-2 (VPTU-2), VPTU-1 being a smaller unit (24-in. diam. x 3-ft long) built at BNL for related tests.

Featured in the VPTU-2 design are two devices, described below, that accommodate hydride expansion, which can result in excessive strain of the vessel if the hydride bed becomes compacted. The results of a specific test, and experience with other storage vessels, have demonstrated that gradual settling of the hydride bed occurs and restricts vertical expansion of the hydride during hydrogen charging. At this point the hydride expands the vessel laterally, and in a few cycles excessive strain can occur.⁷ There is no constraint in a hydride bed less than about 6 in. deep, provided the diameter is at least 1 in., because the interparticle friction is not great enough to prevent upward expansion. The primary means of avoiding vessel strain in VPTU-2 consists of fluidizing the bed for a few seconds prior to hydrogen charging. A group of six tubes, located along the vessel bottom and having porous-metal segments on their upper surface, is used for hydrogen distribution.

The VPTU-2 test program will be limited to testing the U-tube heat-exchanger option in the Hydrogen-Technology Advanced-Component Test System (HYTACTS). Details of this system are provided in Section 3.4. Heat- and mass-transfer rates will be determined, and the ability of the bed-loosening system to avoid vessel strain will be evaluated. Upon delivery to BNL, VPTU-2 will be checked out, loaded with 3000 lb of $\text{TiFe}_{0.9}\text{Mn}_{0.1}$ alloy, and then moved to its outdoor location for connection to the HYTACTS piping. The alloy is being produced by MPD Technology Corp., a subsidiary of International Nickel Company.

On a smaller scale, two limited-bed-depth options for dealing with hydride expansion are planned; both have hydride beds only 3-4 in. deep. In the first concept the hydride is to be contained in a stack of conical trays made of embossed heat-transfer panels. It is intended that both the top and bottom tray

surfaces be used for heating and cooling of the hydride. A 4-1/4-in. deep tray (17-1/4 in. x 28 in.) made of carbon steel is being constructed for testing the concept in VPTU-1. There is provision for tilting the tray 13° in order to simulate behavior of the hydride in a conical tray. Hydrogen transfer rates will be determined for both positions (0° and 13° inclination). In the second concept, the hydride is contained in 4-in.-diam. tubes which are arranged horizontally in a water tank, each tube being a pressure vessel. This concept will be tested using a single tube provided with a removable water jacket. The construction material is carbon steel, and the unit is being fabricated by Foster Wheeler Energy Corp. for testing at BNL. Hydrogen transfer rates will be measured and the tube diameter will be monitored for expansion.

3.3.2 BEC Storage Vessel

Billings Energy Corp. constructed a hydride/hydrogen storage system, under contract to BNL, for use with their Hydrogen HomesLead which was built to demonstrate and evaluate the use of hydrogen for domestic applications.⁸ Hydrogen, produced by the BEC-developed water electrolyzer at the rate of 2 lb/day, is stored in a Ti-Fe-Mn hydride. The main objective of the project was to determine the storage vessel performance. The tasks were to:

- . design the storage system and carbon-steel vessel;
- . select and obtain the hydride;
- . obtain and install all equipment and instrumentation;
- . operate the system to obtain data on hydrogen transfer rates;
- . determine the useful storage capacity of the hydride; and
- . monitor the vessel for strain due to hydride expansion.

Rather than design and construct a vessel matched to the job, BEC elected to use a surplus, but unused, carbon-steel vessel that had been built for 850-psi service as a pressure accumulator. The suitability of the particular carbon steel for this service was verified with the assistance of Sandia Laboratories (Albuquerque).⁹ The vessel consists of two hemispherical shells welded to a short cylindrical section (10-in. high). Pertinent information on the vessel is as follows:

- . Analysis of carbon steel (wt %): 0.15% C, 1.1% Mn, 0.09% Cr, 0.005% N
- . Vessel size: 38.3-in. diam. x 48.5-in. height x 0.937-in. wall

- . Internal volume: 21.08 ft³
- . Pressures: original design, 850 psig; test, 1000 psig H₂
- . Heat exchanger: four turns of copper tubing bonded to the cylindrical section; heat-transport fluid is water
- . Operating conditions: 1-500 psig, 55°C (131°F) at heat exchanger.

Inside the bottom of the vessel a cylindrical hydrogen distributor is provided for use in loosening the bed if hydride expansion causes vessel strain. Thermistors, pressure sensors and girth measuring devices are provided for monitoring vessel conditions. The storage vessel, electrolyzer, hot-water tanks, and the computer monitoring system are located in a detached garage at the rear of the Homestead.

The following data pertains to the alloy that BEC obtained and tested in the storage vessel during the first discharge cycle:

- . Composition of alloy: TiFe_{0.863}Mn_{0.098} (Ti₅₁Fe₄₄Mn₅).
- . Useful weight of H₂: 55.2 lb (1.4 wt %).
- . Sustained flow rate and time: 12 lb max/day for 76 min when fully charged.
- . Expected daily rate: 3-6 lb max.

Details on temperature, pressure and other flow rate measurements are provided in the final report which is being reviewed.¹⁰ BEC observed no girth changes due to hydride expansion in the first cycle of operation.

Also provided in the final report, but not part of the contract effort, were the results of a hydride expansion test made with a pair of their commercial cylinders (AHT-5) containing the same hydride. Hydrogen was cycled between the tanks by alternately heating and cooling each tank. The hydride bed dimensions were 4-in. diam. x 20.2 in. deep at the conclusion of the test. No increases in cylinder diameter were observed, other than $2-3 \times 10^{-3}$ in. of corrosion product, after 825 cycles of testing, including 358 cycles with one tank periodically vibrated. The absence of vessel expansion was attributed to activation of the hydride in another container, and use of a storage vessel that is strong enough to resist the expansive force. It might also be attributed to the fact that the change in hydride composition was restricted by conditions of the experiment.

BEC concluded that the hydride/hydrogen storage system is technologically feasible. A proposal for continued cycling of the system and several improvements is being reviewed. Another task requiring attention is completion of a safety review; BEC conducted an internal review of the Hydrogen Homestead and storage system, and listed the items required. Release of a formal report, reevaluation of the needs, and installation of the remaining equipment need to be done.

3.4 Hydrogen-Technology Advanced-Component Test System (HYTACTS)

An engineering-scale system for testing components of a hydrogen storage system has been completed and is ready to begin operation. It consists mainly of a piping loop in which hydrogen, at pressures of 15-600 psi, can be transferred at carefully measured and controlled flow rates. The system is comprised of three major components: the hydrogen metering loop, the thermal transport loop, and the control panel and data acquisition section. Initially the HYTACTS will be used for testing VPTU-2, the 50-kW, 500-kWh storage vessel. Subsequently it will be used for testing hydrogen storage devices for automobiles, or for other applications using devices fabricated by BNL or others.

3.4.1 Hydrogen Metering Loop

Hydrogen, at 1000 psia, is admitted from the storage tanks to a dome-loaded regulator where the pressure is reduced to 500 psi. The gas is then metered and controlled by two MICON digitally-controlled valves (range 0-300 CFM) which have been preprogrammed to provide the appropriate flow rate for a particular charging run. The valves may be used individually or in parallel for flow rates up to 600 CFM. A third digital valve (range 0-6000 CFM) is also available for the higher charging flow rates which are anticipated for fluidizing the hydride bed of the VPTU-2 bulk-storage vessel. The VPTU-2 will be the first component tested in the HYTACTS. By manipulation of the appropriate valves, the hydrogen discharge rate can be metered and controlled, by the same digital valves, venting to the atmosphere. All other normal operating valves are pneumatically operated remotely from a control room in which all the control instrumentation and data acquisition equipment are housed. Sensors, appropriately positioned in the piping, monitor hydrogen temperatures, pressures, water vapor content (down to -80°F (-62°C) dew point) and oxygen content (1-10 ppm).

3.4.2 Thermal Transport Loop

The heat released when the hydrogen is chemically combined with the alloy must be removed so that additional hydrogen can be absorbed. And, conversely, heat must be supplied to the bed when liberating the hydrogen that is stored in the hydride. The thermal transport loop, which is a closed heating and cooling system, is designed to perform that function for the storage vessel tests. The fluid (50% water - 50% ethylene glycol) flow rate is metered and controlled by a digitally-controlled valve having a range of 1-100 gallons/minute. The heat for dehydriding is supplied to the fluid by a 120-kW electric heating unit and the cooling is provided by a 7.5-ton Dunham-Bush air-cooled chiller. The thermal transfer for the cooling system takes place in a shell-and-tube counter-flow heat exchanger, the shell side of which forms a closed system with the chiller, the fluid being circulated by one of two 50-GPM centrifugal pumps. The desired fluid temperature is adjusted by blending the hot fluid, which flows through the heater, and the cold fluid, which flows through the tube side of the heat exchanger, in a Koch stationary mixer. The system is constructed of 2-inch schedule-10 pipe and is rated for 150 psi so that temperatures above 100°C can be reached. As in the hydrogen metering system, all temperatures and pressures are monitored by the data acquisition system, and all valves, whether motorized or pneumatically actuated, are remotely operated at the control panel.

3.4.3 Data Acquisition Section

The major components of the data acquisition system include include a Model 240 Doric Digitrend Data Scanner and a Model 4051 Tektronix Graphics Computer.

The data scanner has the capability of monitoring 140 data points at the rate of 10 per second. Each point is provided with 2 low and 2 high set-point alarms. The function to be read and the alarm points are set by software instructions either at the instrument face or from the computer acting as an I/O terminal. Priorities for each point can be set so the critical points can be monitored more frequently than once each 14 seconds. To allow for transient signals, the scanner can be made to ignore up to 9 out-of-range indications before activating the appropriate alarm signal. Each alarm, when tripped, energizes a reed delay which can take corrective action by opening or closing the appropriate valve.

The Tektronix 4051 Graphics Computer is equipped with a number of peripheral units which greatly expand the capability of the data acquisition system. More than one million bits of data can be taken from the scanner and stored on magnetic tape or on floppy discs. The data can then be used by the computer to do number crunching, and data analysis, by utilizing previously prepared programs. A hard copy of the results can be tabulated on the line printer and graphs output on the plotter. With the addition of a communications link, the Tektronix can act as an input/output terminal and communicate directly with the large CDC 7600 computer, which is time shared via the BNL FOCUS system.

3.5 Heat-Transfer Modeling

A model is being developed at Oak Ridge National Laboratory to predict the behavior of metal-hydride beds used for hydrogen storage. The model assumes that hydrogen is always in equilibrium with the metal hydride, and that no pressure drop occurs in the bed. Under such conditions, heat transfer controls performance.

The model is being tested by comparing the results obtained for it with data reported by Strickland and Yu¹¹ from a cylindrical bed containing 84 lb of iron-titanium alloy. Hydrogen was introduced and withdrawn at the center line of the vessel through a porous metal tube, and heat was transferred to and from the system by water flowing in an annular shell around the test bed. Each run consisted of a period during which the hydrogen feed (or withdrawal) rate was held constant at some value between 10 and 40 std liters/min. Data for axial and radial temperature profiles show that heat transfer occurred primarily in the radial direction, and no significant temperature difference was detected between the entering and the exiting cooling water.

This model assumes, as was measured in the experimental results, that heat transfer occurs only in the radial direction. In the initial phase of the modeling work only the charging portion of the cycle was considered. Before each run, the bed was brought to equilibrium at 30°C and 16 psia. The boundary conditions were taken to be: BC/1) $\frac{\partial T}{\partial r} = 0$, $r = 0$; BC/2) $T_w = 30^\circ\text{C}$ and BC/3) $F = F_L$, $t \leq t$ ($P = 500$ psia), $P_L = 500$ psia, $t > t_{500}$.

The initial conditions were $T_0 = 30^\circ\text{C}$ and $P_0 \sim 16$ psia. The first boundary condition assumes no heat transfer across the center of the bed. The last two boundary conditions correspond to experimental values for the water temperature

T_W , and the flow rate F_L or the bed pressure P_L was maintained constant during the first portion of the run. Heat transport and thermodynamic properties (equilibrium pressure, thermal conductivity, heat of reaction, etc.) are represented in the model as functions of temperature, pressure and composition whenever possible.

In the first test of the model, a hypothetical 6-in.-diameter bed was subdivided into 20 nodes located on equal radial increments, Δr . The first node was situated at the outside edge of the porous-metal tube, and the last node was positioned at the inside edge of the vessel wall. The nodal energy balance equations are summarized in Table 3.3. $T_{1,i}$ and $T_{2,i}$ designate the temperature of node i before and after a timestep of Δt ; $C_{1,i}$ and $C_{2,i}$ refer to composition. Only one of the boundary conditions, BC3, is used, depending on whether the experiment is in the constant flow or the constant pressure regime. The equations are solved simultaneously by using two nested Newton-Raphson (N-R) procedures for the constant flow condition; the solution for constant pressure is simpler, only one N-R procedure is required.

A preliminary set of predicted temperature profiles is illustrated in Figure 3.5. The results show the same trend as the experimental data. They agree quite well, qualitatively, although the calculated temperatures are lower than the experimental values. These results are encouraging since the model contains no empirically derived parameters. As more of the physical property data become available, improvement in the quantitative agreement is expected.

TABLE 3.3

SUMMARY OF EQUATIONS, n-Nodes

INTERNAL NODES:

$$T_{2,i} + \beta C_{2,i} = \beta C_{1,i} + \frac{\alpha \Delta t}{\Delta r} \left[T_{1,i-1} \left(1 - \frac{\Delta r}{2r_i} \right) + T_{1,i+1} \left(1 + \frac{\Delta r}{2r_i} \right) - 2T_{1,i} \right] + T_{1,i}$$

EquationsUnknown

n-2

2(n-2)

NODE-1, BC1

$$T_{2,1} = T_{2,2}, \quad C_{2,1} = C_{2,2}$$

2

2

NODE-n, BC2

$$T_{2,n} + \beta C_{2,n} = \beta C_{1,n} + \frac{\alpha \Delta t}{r_n \Delta r} \left[T_{1,n-1} \left(\frac{2r_n}{\Delta r} - 1 \right) + \gamma T_w \right]$$

1

2

EQUILIBRIUM

$$P = f(T_{2,i}, C_{2,i})$$

n-1

1

$$\text{BC3: } \begin{cases} F_U \text{ or } L = \Pi \Delta z L \left[(C_{2,1} - C_{1,1}) + (C_{2,n} - C_{1,n}) r_n + \sum_{i=2}^n 2(C_{2,i} - C_{1,i}) r_i \right] \\ P = P_U \text{ or } L \end{cases}$$

1

WHERE

2n+1

2n+1

$$\beta = \frac{\Delta H_R}{\rho C_p}; \quad \alpha = \frac{k}{\rho C_p}; \quad \gamma = \frac{2k_{ss} h r_{ss}}{k[k_{ss} - h r_{ss} \ln(r_n/r_{ss})]}; \quad \Delta t = \frac{r_n \Delta r^2}{\alpha[2r_n + \Delta r(\gamma - 1)]}$$

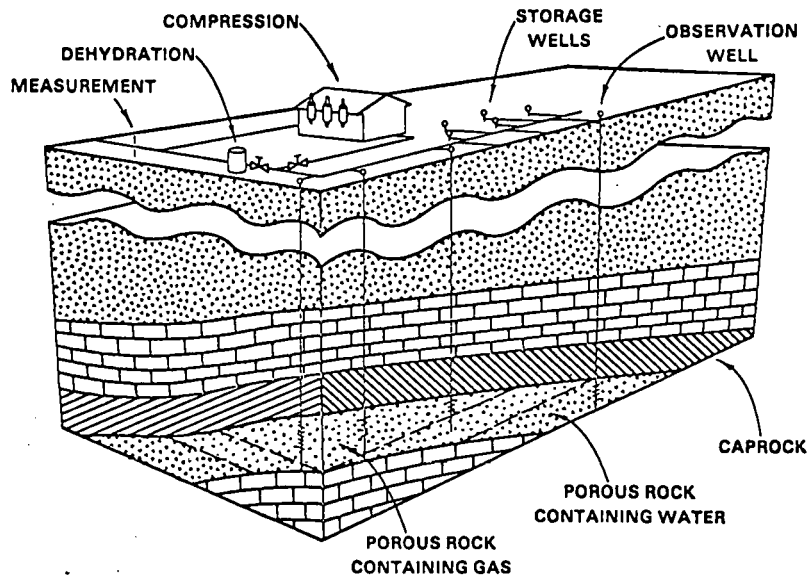


Figure 3.1. Aquifer storage

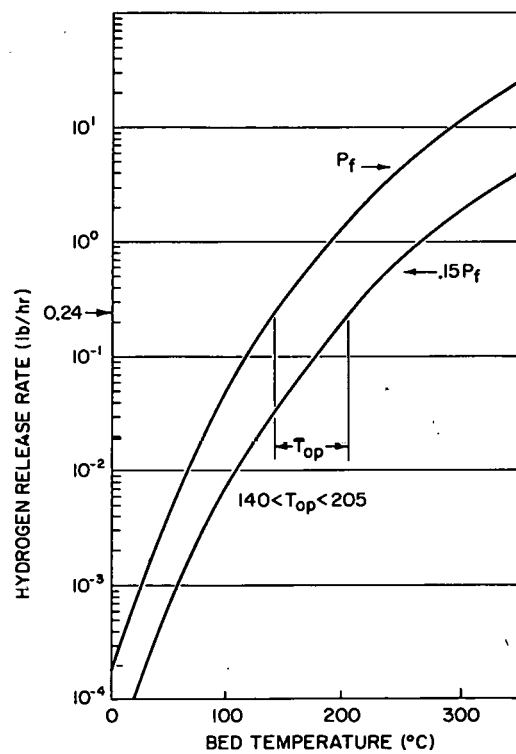


Figure 3.2. Hydrogen release rate per ft^3 of MCS microsphere bed

CONSTRUCTION: ALL WELDED
 A. 6061-T6 ALUMINUM FOR TiFe-
 BASED, LOW-TEMPERATURE HYDRIDE.
 B. 304 STAINLESS STEEL FOR Mg-
 BASED, HIGH-TEMPERATURE
 HYDRIDE.

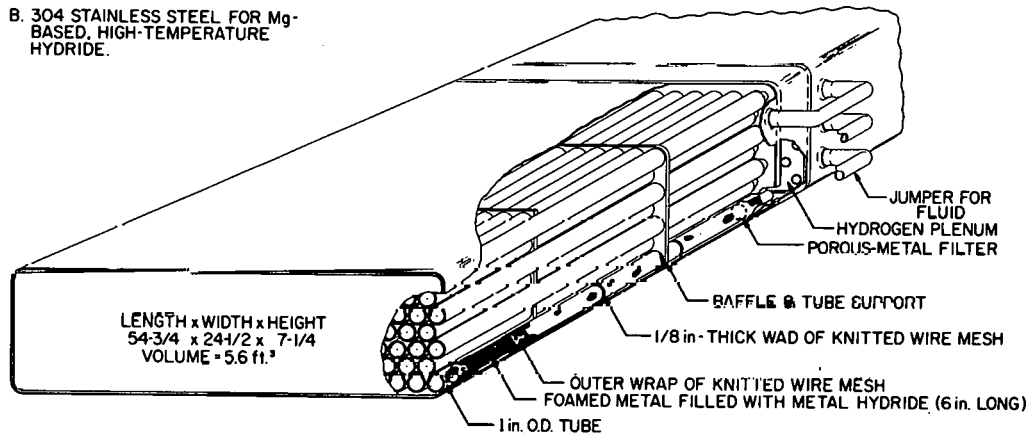


Figure 3.3. Sectional view of fast-charge hydride-hydrogen storage vessel

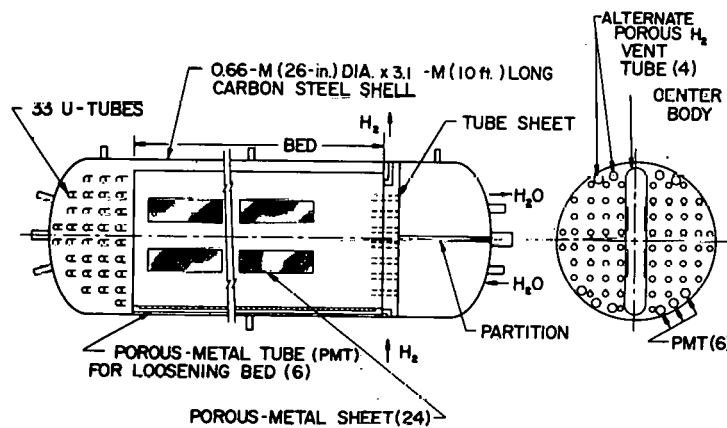


Figure 3.4. Sketch of VPTU-2 constructed by Foster Wheeler Energy Corp.

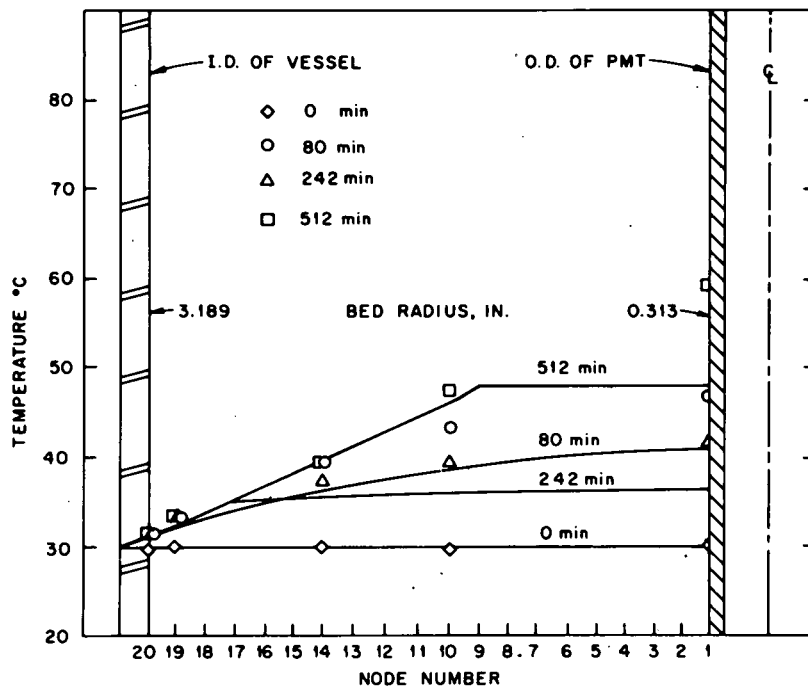


Figure 3.5. Comparison of predicted temperature profiles with experimental results

REFERENCES
3.0 HYDROGEN ENERGY SYSTEMS

1. Teitel, R.J., Henderson, T.M., Luderer, J.E., and Powers, J. Microcavity Systems for Automotive Applications, Final Progress Report, RJTA Report No. 780001006U-R2, R.J. Teitel Associates, San Diego, California, November 1978.
2. Behrin, E., Anderson, C.J., Bomelburg, H., Farahat, M., Forsberg, H.C., Hudson, C.L., Kullman, B.C., O'Connell, L.G., Strickland, G., and Walsh, W.J. Energy Storage Systems for Automobile Propulsion: 1978 Study, Volume 1: Overview and Findings, Volume 2: Detailed Report, UCRL 52553, prepared for Division of Energy Storage Systems, U.S. Department of Energy, in press.
3. Buchner, Helmut and Saufferer, H. The hydrogen/hydride energy concept. Presented at the Second World Hydrogen Energy Conference, Zurich, Switzerland, August 1978.
4. Strickland, G., Reilly, J.J., Wiswall, R.H., Jr. An engineering-scale energy storage reservoir of iron titanium hydride, Hydrogen Energy, Part A, pp 611-620, T. Nejat Veziroglu, Ed., Plenum Press, (1975).
5. Strickland, G., Reilly, J.J. Operating Manual for the PSE&G Hydrogen Reservoir Containing Iron Titanium Hydride, BNL 50421, February 1974.
6. Burger, J.M., Lewis, P.A., Isler, R.J., Salzano, F.J. Energy storage for utilities via hydrogen systems. Presented at the 9th Intersociety Energy Conversion Engineering Conference, San Francisco, California, August 1974.
7. Strickland, G. Some Observations on the Effects of the Volumetric Expansion of Iron Titanium Hydride on Vessels Built at BNL, Informal Report, BNL 23130, August 1977.
8. Billings, R.E. Hydrogen homestead. Proc. of the 2nd World Hydrogen Energy Conference, Zurich, Switzerland, Volume 4, pp. 1709-1729, Pergamon Press, Oxford, England.
9. Robinson, S.L. Analysis of the Suitability of Hydride Containment Vessel Alloy for Service in the Billings Energy Corporation Hydrogen Homestead, SAND77-8293.
10. Billings Energy Corporation, First Year Performance Report Large Diameter TiFeMn Hydrogen Storage Vessel, November 1978. (Draft)
11. Strickland, G. and Yu, Wen-Shi. Some Rate and Modeling Studies on the Use of Iron-Titanium Hydride as an Energy Storage Medium for Electric Utility Companies, BNL 50667, April 1977.

4.0 HYDROGEN STORAGE MATERIALS

Metal hydrides offer a convenient, safe and attractive alternative to the conventional methods of hydrogen (energy) storage as a compressed gas or cryogenic liquid. Hydrogen is absorbed by a metal or alloy with the release of heat and may be stored for short or indefinite periods of time and recovered (desorbed) by providing the necessary decomposition energy. The resulting solid hydride compounds, in general, are similar in appearance to the starting metals or alloys and those of practical importance are easily reversible or rechargeable.

The evaluation of a hydride system for an energy storage application, whether mobile or stationary in nature, involves consideration of: (1) wt % hydrogen stored; (2) volumetric hydrogen density; (3) pressure-composition-temperature properties; (4) thermodynamics of absorption-desorption reactions; (5) raw alloy materials cost; (6) reaction kinetics; and (7) physical and chemical stability. When one considers these criteria, the rather large number of available hydride systems is reduced to four general classes of alloy-hydrogen systems suitable for storage (long-term or short-term) applications. These systems are: (1) ferrotitanium alloy hydrides; (2) lanthanum pentanickel (or AB₅) type alloy-hydrogen systems; (3) magnesium and some of its alloy hydrides; and (4) vanadium hydride. This list will expand as new insights are gained by investigators in the field of hydrogen storage materials development.

A major effort in 1978 was devoted to identifying and characterizing alloys capable of storing >3 wt % hydrogen while increased attention in the candidate alloy selection process was also given to decreased raw materials cost (leading to a reduction in the dollars/lb stored hydrogen) and good thermal (thermodynamic) properties at or near ambient temperatures.

Two new programs were initiated in the hydrogen storage materials area in 1978. The first was a contracted program with the International Nickel Company (INCO) to investigate the mechanisms of surface poisoning in metal hydrides. The second program was a BNL in-house effort directed at the separation or removal of hydrogen from mixed gas streams. The two new programs are closely related since, in the process of hydrogen removal from gas mixtures, contaminant gases such as O₂, H₂O(v), CO and H₂S will likely be present to some degree. The removal of

hydrogen from gas mixtures (streams) utilizing metal hydrides places these materials in a new role where emphasis is not on storage (long- or short-term) but as media for rapid absorption-desorption of hydrogen. The inventory of metal hydride can be reduced in this application and would be directly related to the kinetics of the absorption-desorption process.

4.1 Hydrogen Storage Materials Development

The objective of the Denver Research Institute (DRI) research conducted during 1978 was to expand the number of materials with storage capabilities and to increase their storage capacity. The ultimate goal of the DRI program was to develop hydrides with more than 3 wt % hydrogen storage by utilizing a DRI developed predictive technique. This hypothesis relates the free energy of hydride formation (ΔG_f) to the starting alloy unit cell volume of interstitial holes. Simply stated the larger the unit cell volume or interstitial holes in a starting alloy or metal, the more thermally stable will be the hydride formed from such material. Additionally, predictive criteria developed in other laboratories, such as the "rule of reversed stability"^{1,2} formulated in the Philips Research Center and a general set of reaction rules developed at BNL,³ were also used in the materials selection process.

Research at DRI during 1978, was carried out in four major areas. These areas of research were: (1) studies of the hydriding characteristics of AB_2 (A and B = transition metals) Laves phases; (2) studies of hydriding properties of titanium-base β -solid solution alloys; (3) studies of the hydriding properties of rare earth-base quaternary alloys; and (4) investigations of the relationship between intermetallic compound structure and hydride formation. The Laves phase AB_2 alloys were chosen for investigation since they represent rather open structures (structures with a large volume available for hydrogen occupancy) with a high theoretical maximum for H/M ($H/M_{\max} = 5.67$ or AB_2H_{17}). Many such alloys exist. The Ti-based β -solid solution alloys were of interest since titanium is rather cheap and abundant in comparison to other transition metals, the low atomic weight of titanium enhances chances for increased hydrogen storage capacity and β -titanium exists in many combinations of binary alloys whose hydride stability can be varied by adjusting the content of the second transition metal component or by the substitution of a third metal, smaller in atomic size than

the metal it is replacing. The rare earth-base quaternary alloy-hydrogen systems research was undertaken to explore the potential of substituting less expensive elements such as Mn, Fe or Cu for the B elements in AB_5 alloys (B = Ni, Co etc.) and mischmetal for La in the AB_5 compound (A = La, Sm etc.). Finally, the structural work was undertaken to study and rationalize, if possible, those factors that limit total hydrogen absorption from a geometric point of view. It was hoped that this information, in turn, would optimize the success of the alloy selection process (an additional tool for more rational selection of candidate alloys to be investigated).

The Laves phase hydriding investigations at DRI centered on the AB_2 systems $ZrFe_2$, $TiFe_2$ and the pseudo-binary system $TiCr_2$ - $TiMn_2$. None of the above parent systems will absorb much hydrogen at room temperature with high pressure hydrogen because of unfavorable thermodynamics. This is, also, as predicted by the DRI hole size versus free energy hypothesis. Substituted alloys such as $(Zr_{1-x}Y_x)_2$, Fe_2 , $Zr(Fe_{1-x}M_x)_2$ and $Ti(Fe_{1-x}M_x)_2$ where M = Mn or V plus $Ti(Cr_{1-x}V_x)$. Mn, however, should have more favorable hydriding thermodynamics. This results from the fact that a larger metal atom (Mn, V or Y) is replacing a smaller one (Zr, Fe or Cr) and therefore the substituted alloy will have a larger volume than the parent intermetallic giving rise to more stable hydrides. Several series of substituted alloys with the general formulas noted above were prepared and their hydriding (storage) properties investigated. The alloys exhibiting the best hydriding properties were found to be: $Zr(Fe_{0.85}V_{0.15})_2$, $Zr(Fe_{0.7}Mn_{0.3})_2$ and $Ti(V_{0.2}Cr_{0.8})Mn$. Their respective storage capacities are 1.6, 1.3 and 1.7 wt % hydrogen. Although these hydrides do not reach the goal of 3 wt % storage, they do supplement the rather limited list of metal-hydrogen systems available for practical applications. Additionally, they all have good thermal and kinetic properties at room temperature.

Considerable time and effort was also expended by DRI on hydriding investigations of β -titanium based $TiMo$ alloys and substituted AB_5 ($LaNi_5$) alloys. The DRI size-stability correlation was utilized in selecting alloys for investigation; however, in no case was an alloy identified that had better thermal and storage properties than the parent systems. $Ti_{0.7}Mo_{0.3}$, which stores ~2.9 wt % hydrogen but is very stable, was the starting alloy for the substituted β -titanium stabilized solid solution-hydrogen systems investigated whereas $LaNi_5$ served as the prototype for the substituted rare earth AB_5 systems.

A low level of effort was directed toward rationalizing hydride capacities (maximum achievable H/M ratios) in terms of starting intermetallic structure. The size, number and relative positions of the various types of tetrahedral interstitial holes in AB₅ (CaCu₅) hexagonal structure) and AB₂ (C15 cubic and C14 hexagonal) phases have been tabulated. Maximum H/M values were then calculated based on occupancy of the largest interstitial holes taking into account that hydrogen-hydrogen distances should not be smaller than ~ 2.8 Å. Comparison between the theoretical maximum H/M values and those observed experimentally have been good.

One of the main areas of in-house BNL work in the hydrogen storage materials development portion of the applied hydrogen production and storage program has also dealt with investigations of the physio-chemical properties of AB₂ Laves phases. This resulted partly from literature reports^{4,6} on such systems indicating these materials were capable of absorbing large amounts of hydrogen (see above) and also from qualitative screening investigations performed at BNL several years ago verifying this fact. Of particular interest to BNL was the AB₂ system TiCr₂. This intermetallic exists as two temperature dependent allotropes. The low temperature form is of cubic symmetry whereas the high temperature phase is hexagonal. Both forms will react with hydrogen to form hydride phases which contain an appreciable amount of hydrogen.^{7,8} The maximum hydrogen capacity for the cubic phase, to date, has been 2.5 wt %. That for the high temperature hexagonal phase is 2.4 wt %.

BNL has reported some of the properties of the cubic (C15) TiCr₂-H discussing the pressure-composition characteristics including hysteresis effects, thermodynamic considerations, and the method of preparation of the starting intermetallic. The most important points were that two hydride phases exist in the system at -78°C (195°K), hysteresis is virtually absent, and the hydrides are very unstable having dissociation pressures of 2.2 atm and ~ 50 atm at the above temperature. In order to more fully characterize this system, extensive x-ray diffraction investigations on hydrides of varying composition were carried out. From this data and the isotherm information, a phase diagram for this alloy-hydrogen system has been constructed. Figure 4.1 shows this result. A paper was published on the low temperature-hydrogen system.⁷

Work has been initiated on the high temperature hexagonal TiCr₂-H system. To date, BNL has been successful in preparing metallurgically single-phase

amples and has found that this alloy also forms two hydride phases. Starting with the hydrogen saturated solid, the two reactions taking place at -78°C may be written as follows:

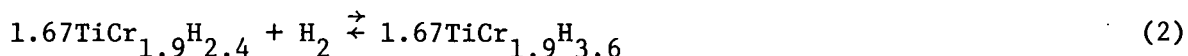
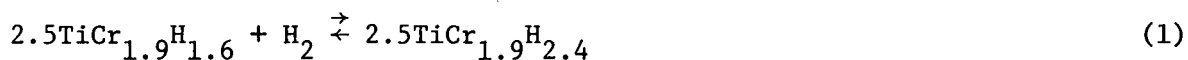


Figure 4.2 illustrates p-c-T isotherms for the hexagonal $\text{TiCr}_{1.9}$ -hydrogen system. The thermodynamic stability of these hydride phases is considerably higher than for those formed in the corresponding cubic TiCr_2 -hydrogen system. This is apparent from the plateau dissociation pressures for the hydrides, which are ~ 2 and 50 atm in the (C15) cubic system and 0.2 and 30 atm for the (C14) hexagonal system.

Whereas the "rule of reversed stability" would predict the formation of stable hydrides from the low and high temperature forms of TiCr_2 they are, in fact, very unstable, even to the point of limited utility for practical applications. However, as we have seen previously for substituted ferrotitanium alloys (8-10) and a variety of other intermetallics it should be possible to modify their properties by compositional changes. To this end, investigations of manganese and titanium substituted TiCr_2 hydrides have been undertaken. The alloy systems which have been investigated are of the general formulas $\text{Ti}_x\text{Cr}_{2-x}\text{Mn}$ and $\text{TiCr}_{2-x}\text{Mn}_x$. Most emphasis, to date, has been directed toward the alloy-hydrogen systems of composition $\text{Ti}_x\text{Cr}_{2-x}\text{Mn-H}_y$. Figure 4.3 demonstrates the variation in pressure-composition properties of these hydrides as a function of titanium content at -20°C . The notable features here are an increase in stability and decrease in usable hydrogen with increasing titanium content. Additionally, we have investigated hysteresis for a few such systems and found it to be small as in the present system.

Alloy systems of general composition $\text{TiCr}_{2-x}\text{Mn}_x$ appear more promising than the $\text{Ti}_x\text{Cr}_{2-x}\text{Mn}$ -hydrogen materials. Preliminary investigations performed on the hydride system $\text{TiCr}_{0.75}\text{Mn}_{1.25}\text{-H}_x$ indicate that its hydrogen storage capacity (usable hydrogen content) is significantly greater than the corresponding

Ti_{1.25}Cr_{0.75}Mn-hydrogen system, while it is only slightly less stable. Plateau pressures at -20°C being 3 atm for the TiCr_{0.75}Mn_{1.25}-H_x system. At this time, it appears that for the TiCr_{2-x}Mn_x alloys a hydrogen storage capacity greater than 2.5 wt % may be achievable with good thermal properties (good dissociation pressures at ambient temperature). Significant alloy cost reductions over the parent TiCr₂ and substituted Ti_xCr_{2-x}Mn systems is also gained by utilizing the TiCr_{2-x}Mn_x alloys (manganese is considerably cheaper than chromium or titanium; manganese = \$0.50/lb). Work is therefore continuing on the manganese-substituted alloy-hydrogen systems.

4.2 Lightweight Metal Hydrides Development

Air Products & Chemicals, Inc. of Allentown, Pennsylvania, was granted a contract in February of 1978, in response to RFP from BNL for the development of new hydrogen storage systems for automotive hydrogen fuel storage. The ultimate goal of this program is to identify and characterize alloy-hydrogen systems having two properties of primary importance. These properties are: (1) a hydrogen storage capacity of 3 wt % or greater; and (2) a dissociation pressure of at least 1 atm at a temperature of 175°C. Other properties such as kinetics of the hydrogen absorption-desorption reaction, cost of alloy materials, etc., must also be considered. The alloys of prime importance to APCI are Mg-based materials and the research performed during this period of time rests on two basic hypotheses. The first hypothesis is that the stability of magnesium alloy hydrides is affected by the element(s) alloyed with the Mg. The lower the stability of the hydride formed by the second metal, the lower will be the stability of the overall alloy hydride (compared to MgH₂). This is the chemical stability effect. The second hypothesis is that the stability of magnesium hydride may be decreased by alloying a second metal which contracts the magnesium lattice. This is equivalent to the size-stability hypothesis put forward by the investigators at DRI¹¹ and the "rule of reversed stability." This is strictly a geometric effect.

The major contributions made by APCI are summarized as follows: (1) several new Sievert-type apparatuses (p-c-T setups) were designed and put in use, including systems with the capabilities of simultaneously activating a multiple number of alloys, automatically and continuously generating a detailed isotherm for a given sample at a specific temperature, and automatically screening an alloy to

obtain an approximate p-c-T plot; (2) the size-stability (geometric effect) developed by Lundin et al, at DRI¹¹ was found to agree qualitatively but not quantitatively, for magnesium based alloy hydrides. As the unit cell volume of the starting magnesium alloy decreased, the stability of the resulting hydride decreased but always by considerably less than would quantitatively have been predicted; (3) nickel powder mixed with certain magnesium alloys acts as a catalyst in the activation process and in subsequent hydriding-dehydriding cycles (the nickel speeds up the reaction rates); (4) second metals which form hydrides less stable than magnesium lead to hydrides which are less stable than the parent system (chemical effect); and (5) smaller magnesium alloy particle sizes give rise to faster kinetics of hydriding. These results were obtained by investigations of the physio-chemical properties of a large number of magnesium solid solution and intermetallic-hydrogen systems. The alloy identified as most promising is Mg_2Al_3 with 1 wt % nickel added as a catalyst to the melt. It will store 2.3 wt % hydrogen and has a dissociation pressure of 1 atm at 230°C. Improvements in other potentially attractive magnesium alloy systems such as Mg_4Al_5 and $MgAl$, which are known to have 1 atm dissociation pressures at 210 and 230°C, will result by improving reaction kinetics through the development of good catalysts for the hydriding-dehydriding reactions. Each of these alloys could have maximum storage capabilities in excess of 3 wt % with reasonable dissociation pressures if reaction kinetics can be improved.

4.3 Metallurgical Studies of Hydrogen Storage Alloys

International Nickel Company (INCO) was awarded a contract in July, 1978, to investigate the mechanisms of surface poisoning of metal hydrides. The successful application of rechargeable hydrides for hydrogen storage or gas separation applications depends on a number of interrelated technical and economic factors. In previous DOE contract efforts,^{12,13} INCO concentrated on the metallurgy and production economics of FeTi, presently the lowest cost, room temperature hydrogen storage alloy. The cost and basic thermodynamic properties of the alloy, however, do not constitute sufficient information to quantify the cost of the hydrogen storage system. Other properties, such as hydride powder particle dynamics, thermal conductivity, and surface poisoning response must be known. Of these, surface poisoning is probably the least understood phenomenon.

Virtually all the experimental work done, to date, on rechargeable hydrides has used high purity hydrogen. A sample properly activated in high purity hydrogen exhibits an extremely fast charging period that is for all practical purposes as fast as the heat of reaction can be removed. However, as the sample is cycled in impure hydrogen a reduction in performance is observed. Initially, there is a loss in kinetics but given enough time, 100% capacity is reached. With additional cycling in impure hydrogen, a point is reached where there is a loss in ultimate capacity in addition to a continued loss in kinetics and the sample will become deactivated or totally poisoned. In many cases, the sample may be reactivated. For example, oxygen poisoned FeTi can be heated to 300-400°C in high purity hydrogen to achieve substantial recovery of original capacity and kinetics.¹⁴

This contract will systematically study the poisoning problem for the first time.

The main objective is to gain an understanding of the basic mechanisms of surface poisoning leading to the development of improved (more resistant) alloy hydrides. Three common storage alloys will be studied. These are FeTi, $\text{TiFe}_{0.9}\text{Mn}_{0.1}$ and LaNi_5 . Each of these alloys is known to activate differently⁸ and the LaNi_5 intermetallic is reputed to be much less sensitive to poisoning than either FeTi or the manganese-substituted ferrotitanium alloy.

A major portion of contract effort will be devoted to generating quantitative poisoning data in which plots of percent hydriding reaction versus time for varying numbers of absorption-desorption cycles will be measured. Experiments will be performed in the presence of varying levels of O_2 , $\text{H}_2\text{O}(\text{v})$ and CO . Reactivation also will be quantified in order to obtain information about the type of surface contamination. This will be accomplished by carrying out heating cycles at room temperature and 350°C as well as hydrogen treatment at 350°C. Additionally, surface contamination reactions will be studied using a variety of surface analytical techniques. The objective of this work will be to study the kinetics of film formation, independent of the hydriding reaction.

Major contract accomplishments attained in 1978 include: (1) a continuous cycling absorption-desorption apparatus was constructed. This unit is an automated Sievert's apparatus which can operate in a constant pressure or constant mass flow mode. Kinetic hydriding or dehydriding plots in the presence of gas impurities will be obtained utilizing this instrumentation; (2) a special thin layer specimen holder has been developed to better isolate true kinetics

from thermal effects; (3) all alloy samples have been prepared for poisoning and kinetic studies; (4) baseline kinetic data for pure hydrogen absorption has been measured for TiFe, $\text{TiFe}_{0.9}\text{Mn}_{0.1}$ and LaNi_5 ; and (5) the kinetics of oxygen film growth on TiFe and $\text{TiFe}_{0.9}\text{Mn}_{0.1}$ have been measured and the data is being analyzed. It should also be pointed out that in the generation of kinetic poisoning data by INCO, information will result which is of a more immediate practical engineering nature. This information, which is a natural offshoot of the more fundamental work, will set practical limits on the levels of gaseous impurities which are tolerable for storage alloys of current interest.

4.4 Brookhaven National Laboratory (BNL) In-House Research

In addition to the research described on Laves phase and substituted Laves phase compounds, BNL has also been involved in work on manganese-substituted ferrotitanium alloys and the use of alloy hydrides as media for hydrogen separation from gas mixtures. The substituted ferrotitanium alloy research was completed in the first half of 1978 whereas the hydrogen separation work was initiated in October. Completion of the research on manganese-substituted iron titanium alloys has resulted in a more complete understanding of such systems; including: (1) substitution of manganese for iron in FeTi results in alloy hydrides of increased thermodynamic stability with increasing manganese content; (2) heat treatment of substituted alloys can drastically affect the characteristic pressure-composition properties for such alloy-hydrogen systems; and (3) activation (hydriding for the first time) may be accomplished much more easily for the substituted alloys than for the parent FeTi intermetallic. The effect of manganese substitution on the hydriding properties of FeTi is illustrated in Figure 4.4 which shows that by addition of manganese one can "tailor make," to a high degree, an alloy-hydrogen system with properties appropriate for a particular application, at no loss of hydrogen storage capacity, up to an alloy composition of $\text{TiFe}_{0.7}\text{Mn}_{0.3}$. The effect of heat treatment on the p-c-T properties of the alloy $\text{TiFe}_{0.76}\text{Mn}_{0.13}$ at 40°C is illustrated in Figure 4.5. Generally, sloping plateaus as encountered in the "as cast" sample are replaced by flat plateaus as a result of annealing. This phenomenon, however, is composition dependent. Ease of initial activation results are shown in Table 4.1. The "% reaction" column is a measure of hydrogen content actually attained versus the maximum possible for a

totally activated sample under the conditions specified. As can be seen, all manganese-substituted samples activated much more easily than FeTi and many needed no heating whatsoever. This is an important advantage for the substituted alloys.

The work performed at BNL dealing with the problem of hydrogen separation from gas mixtures (streams), utilizing metal hydrides, during the last three months of 1978 consisted of conducting a literature search to determine the most attractive alloys to initially investigate. This search was completed and the AB₅ alloys were chosen (i.e., LaNi₅ and copper-substituted materials of the general formula LaNi_{5-x}Cu_x).

Table 4.1

LOW TEMPERATURE ACTIVATION EXPERIMENTS FOR
TiFe_xMn_y ALLOYS

Alloy Composition	Maximum Outgassing Temperature (°C)	Time at 500 psia(hr)	Final H/Ti	Reaction
TiFe	200	72	0.0	0
TiFe _{0.9} Mn _{0.1}	25	27	0.48	25
TiFe _{0.9} Mn _{0.096} (INCO)	25	19	1.72	96
TiFe _{0.85} Mn _{0.15}	25	6	1.94	100
TiFe _{0.8} Mn _{0.2}	25	45	1.16	60
TiFe _{0.7} Mn _{0.2}	50	3.5	1.79	94
TiFe _{0.77} Mn _{0.09}	25	27.5	1.79	100
TiFe _{0.73} Mn _{0.13}	25	19	1.82	100

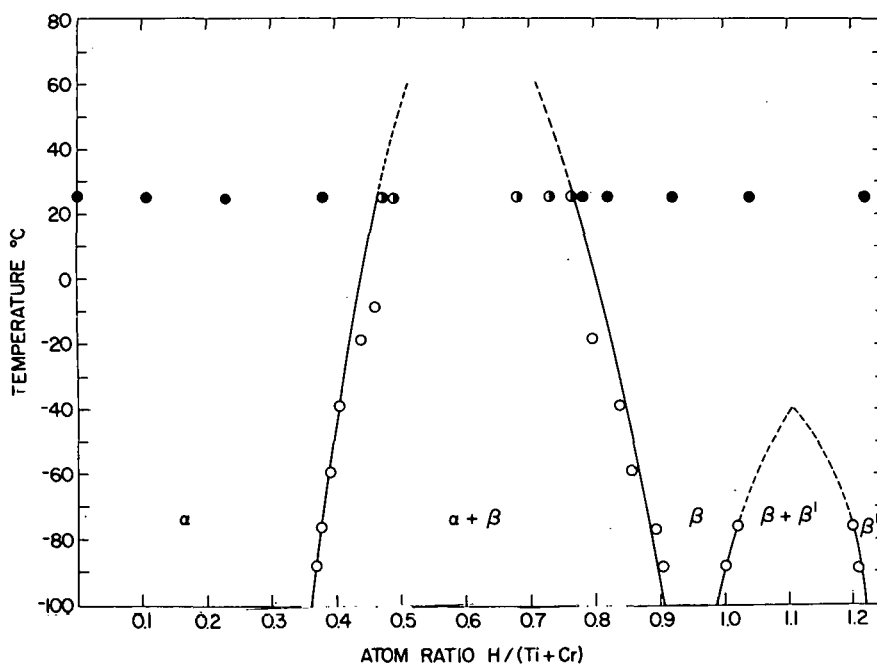


Figure 4.1. Phase diagram for the TiCr_{1.8}-H system derived from p-c-T and x-ray diffraction data

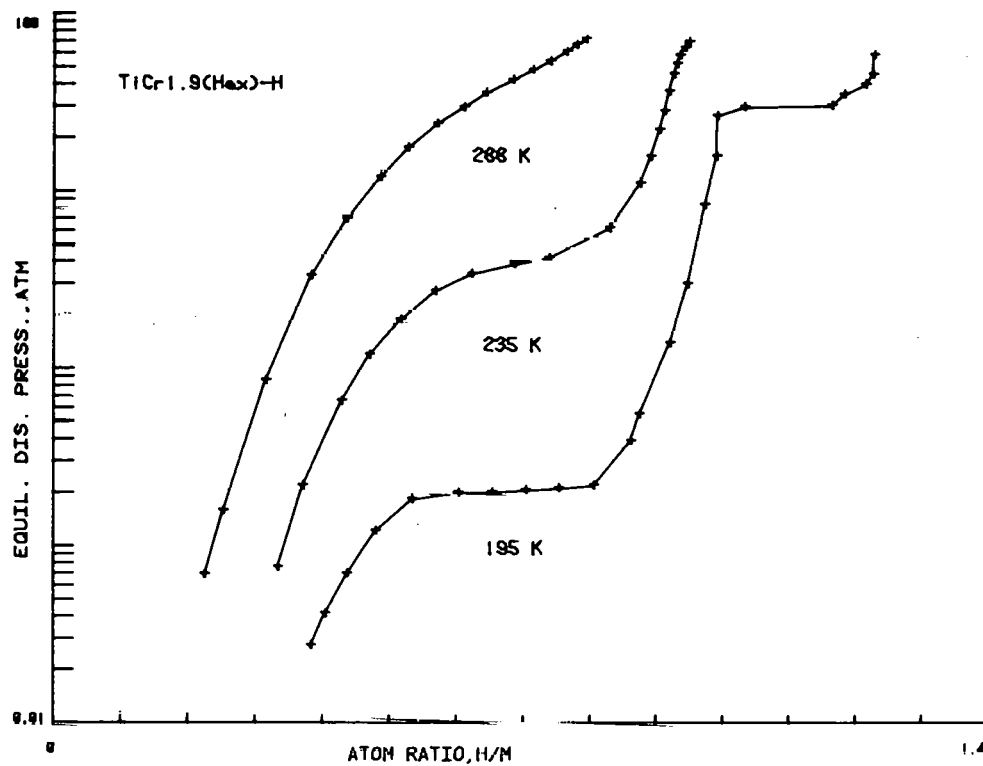


Figure 4.2. Pressure-composition desorption isotherms for the high temperature (Cl4) $\text{TiCr}_{1.9}\text{-H}$ system at various temperatures

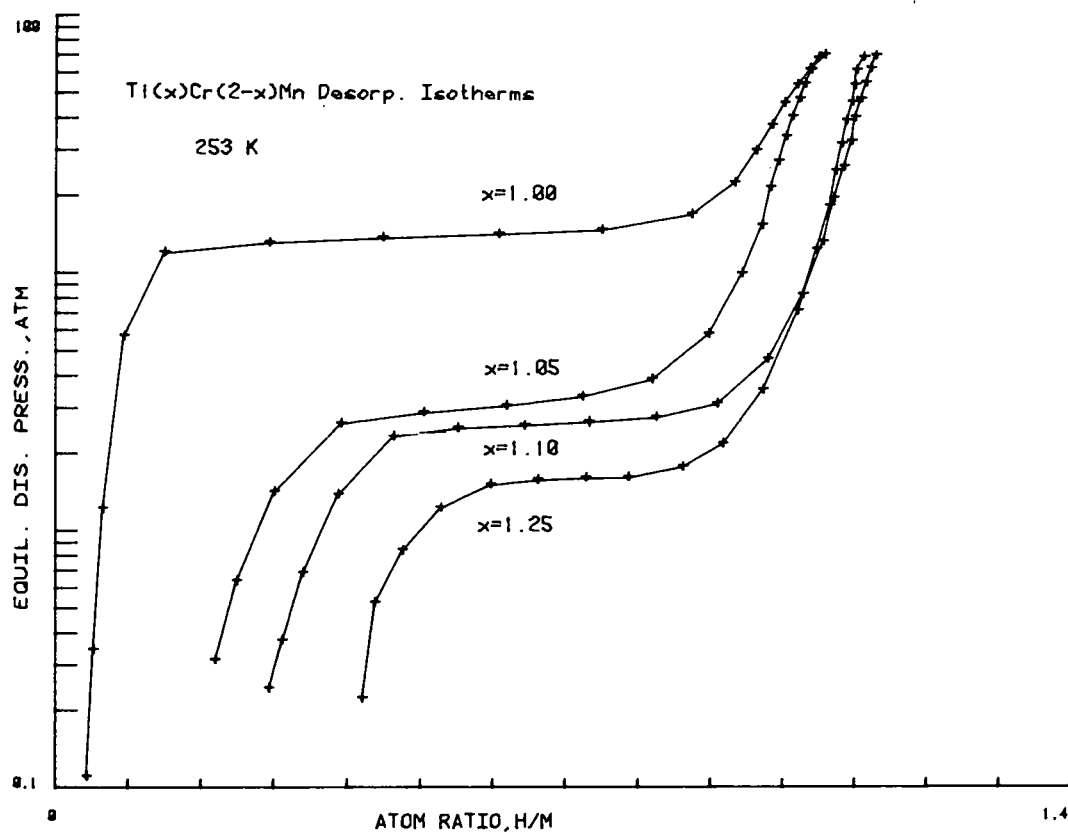


Figure 4.3. Pressure-composition desorption isotherms for various $\text{Ti}_x\text{Cr}_{2-x}\text{Mn}$ alloys at -20°C

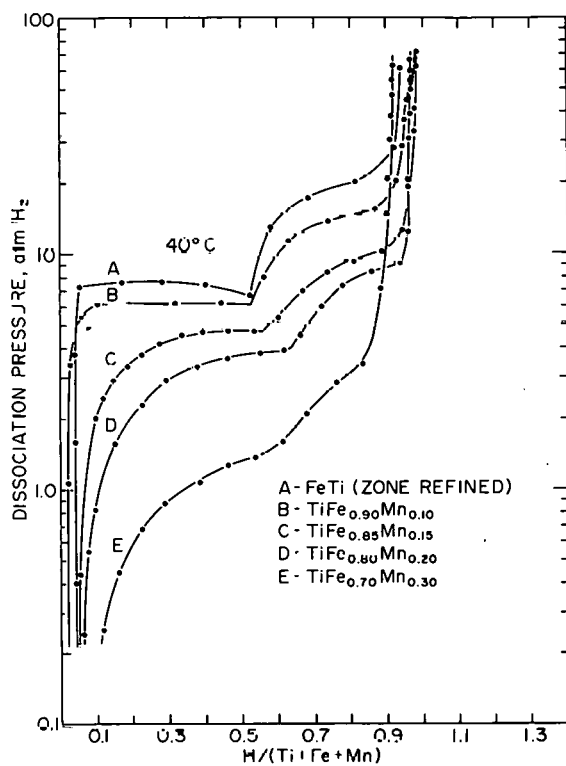


Figure 4.4. Pressure-composition desorption isotherms for FeTi alloys of various Mn contents at 40°C

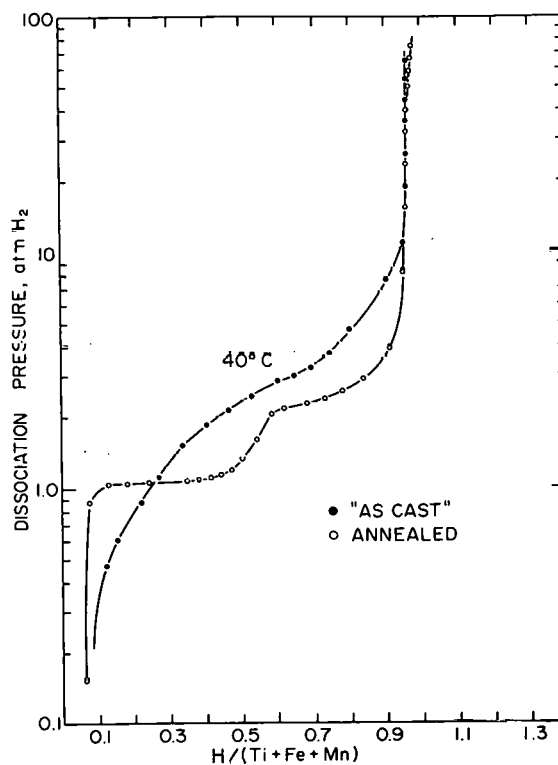


Figure 4.5. A comparison of pressure-composition desorption isotherms for annealed and "as cast" TiFe_{0.76}Mn_{0.13} at 40°C

REFERENCES
4.0 HYDROGEN STORAGE MATERIALS

1. van Mal, H.H., Bushow, K.H.J., and Miedema, A.R. J. Less-Common Metals 35, 65 (1974).
2. Miedema, A.R., Boo, R., and DeBoer, F.R. J. Less-Common Metals 41, 283, (1975).
3. Reilly, J.J. Hydrides for Energy Storage, A.F. Andresen and A.J. Maeland, Editors, p. 301, Pergamon Press, New York, 1978.
4. Pebler, A., and Gulbransen, E.A. Electrochemical Technology, 4(5-6), 211, (1966).
5. Pebler, A., and Gulbransen, E.A. Trans. Metall. Soc. AIME 239, 117, (1977).
6. Shaltiel, D., Jacob, I., and Dabidov, D. J. Less-Common Metals 53, 117 (1977).
7. Johnson, J.R., and Reilly, J.J. Inorg. Chem. 17, 3130 (1978).
8. Johnson, J.R., and Reilly, J.J. The metal hydride research and development program at Brookhaven National Laboratory. Proc. of the DOE Chemical/Hydrogen Contract Review Meeting, Washington, D.C., November 1978.
9. Reilly, J.J., and Johnson, J.R. Titanium alloy hydrides; their properties and applications. Proc. 1st World Hydrogen Energy Conference, Miami Beach, Florida, March 1976.
10. Johnson, J.R., and Reilly, J.J. The use of manganese substituted ferro-titanium alloys for energy storage. Proc. of the International Conference on Alternative Energy Sources, Miami Beach, Florida, December 1977.
11. Lundin, C.E., Lynch, F.E., and Magee, C.B. J. Less-Common Metals 56, 19 (1977).
12. Sandroock, G.D. The Interrelations Among Composition, Microstructure, and Hydriding Behavior for Alloys Based on the Intermetallic Compound FeTi, Final Report, International Nickel Company, Suffern, New York, June 1976.
13. Trozzi, C.J., and Sandroock, G.D. A thermodynamic and economic study of various techniques for the large scale production of hydriding grade FeTi. Proc. DOE Chemical Energy Storage and Hydrogen Energy Systems Contract Review Meeting, Hunt Valley, Maryland, November 1977. JPL Publication 78-1.
14. Reilly, J.J., and Johnson, J.R. Metal hydride materials program at BNL current status and future plans. Proc. of the ERDA Contractors' Review Meeting on Chemical Energy Storage and Hydrogen Energy Systems, Airlie, Virginia, November 1976.

5.0 SYSTEMS STUDIES AND END-USE APPLICATIONS

Hydrogen has been identified as an effective energy carrier and energy storage medium. It is a commodity that offers the flexibility of satisfying portions of the current chemical feedstock markets as well as for supplementing future fuel needs as the cost/availability constraints of conventional fuels become increasingly apparent. BNL has contracted for services addressing key factors that would enhance the probability of hydrogen's early penetration of the energy infrastructure. The intermittent nature of our solar, wind and hydropower resources strongly points to hydrogen production, storage and use as a renewable resource recovery option. Although the initial uses of hydrogen will find their place within the chemical industries, opportunities present themselves for the near-to-mid term potential of hydrogen's application as a natural gas supplement.

5.1 Feasibility Assessment of Falling Water Resources

The prospect of delivering hydrogen energy from small capacity hydropower sites using water electrolysis was evaluated in a 5-month study¹ (supported by the U.S. Department of Energy (DOE) and administered by Brookhaven National Laboratory) by a team consisting of the Institute of Gas Technology (IGT) and the Pennsylvania Gas and Water Company (PG&W). The premise of the study was that the combination of rising fossil fuel prices and expected near term (approximately 1980) developments in electrolyzer technology, resulting in increased efficiencies and decreased capital costs, can result in competitively priced hydrogen from small capacity hydropower facilities. Such sites are referred to as "falling-water hydrogen" facilities to distinguish the concept from hydroelectric power. With hydrogen, rather than electricity, as the final product, the dispersed small capacity falling-water resource could be more readily integrated into the national "energy grid." Depending on regional rainfall patterns, terrain, and water requirements, local areas may have constructed many small dams or a few large dams for municipal water usage, recreation, flood control, irrigation, or other nonhydropower uses. In addition, there are dams that were designed for and equipped with hydroelectric facilities that have since been decommissioned and/or dismantled due to economic considerations. These facilities are of various vintages and in varying states of repair. Specific sites may require limited to extensive excavation and other modifications/additions to the civil

works. Many are equipped with piping and valving for reservoir level control, which may be readily adapted to energy extraction.

Magnitude of the Resource as Hydrogen Energy

The basic concept for adapting small existing dams to hydrogen production is presented in Figure 5.1. As can be seen, the concept entails three energy conversion steps:

- 1) hydropower-to-shaftpower via a hydraulic turbine,
- 2) shaftpower-to-electrical power via a generator, and
- 3) electrical-power-to-hydrogen (and oxygen) via a water electrolyzer

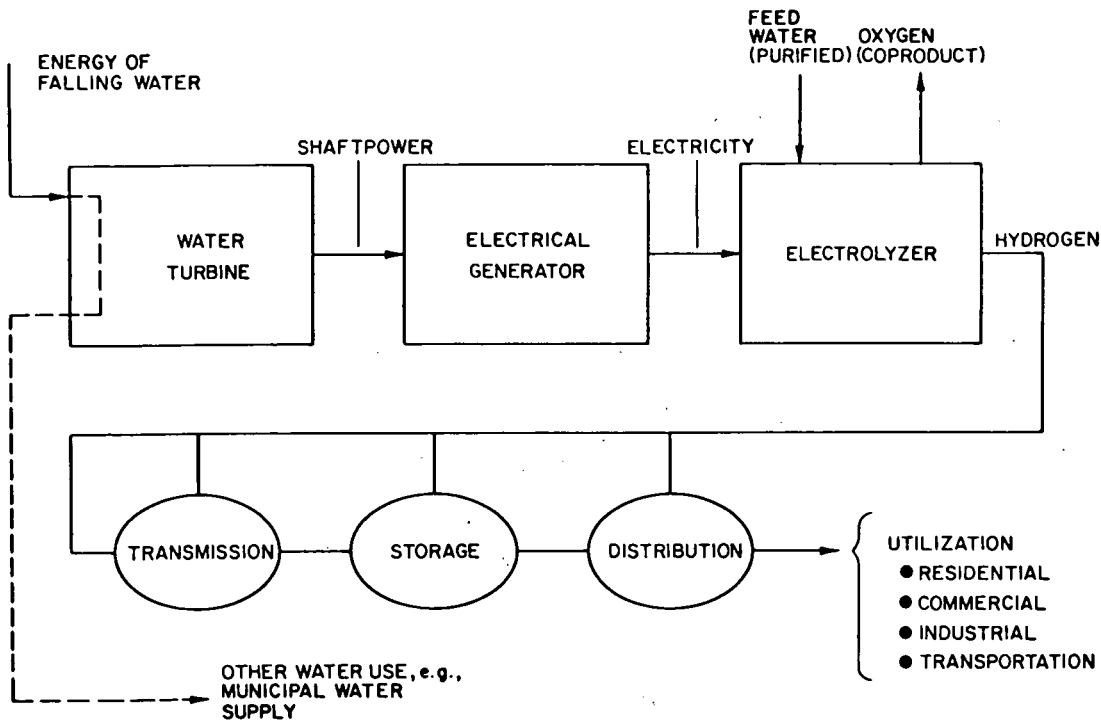


Figure 5.1. Technical approach to hydrogen from falling-water concept

One main task for the study was to quantify the undeveloped small capacity (less than 500 kW) falling-water hydrogen resource base for the United States, with an emphasis on the Northeastern United States. The results of three separate surveys--1) a special state-by-state survey of nine Northeastern states

(Maine, Massachusetts, Vermont, Rhode Island, Connecticut, Pennsylvania, New York, New Hampshire, and New Jersey) by PG&W; 2) a New York Polytechnic survey² of the same nine states; and 3) a U.S. Corps of Engineers survey³ for the entire United States (separated into regions)--were utilized for estimating the resource base.

The hydrogen energy available from the small capacity falling-water sites in the Northeast was estimated at 0.05-0.75 Quads. This energy output represents about one-third of the output from this category of sites for the entire nation. Also, almost two-thirds of the resource base in the Northeast falls into the "small existing dams" category, as compared to one-fifth for the United States as a whole. It appears that the Northeast region is likely to be the most fruitful one to exploit.

The Economics

One of the most important considerations in determining the feasibility of falling-water hydrogen facilities is the cost of the hydrogen. The cost to the prospective hydrogen consumer will be largely dependent upon production, storage, and delivery costs.

It is very difficult to quantify storage and delivery costs until a specific market or demand is identified in detail. Delivery costs are directly dependent upon both the quantity of hydrogen and the distance delivered. Storage costs are a function of the amount and mode of storage, which depend on how closely demand profiles match supply profiles. Hydrogen production costs are more easily quantified, given some design specifications or restrictions.

Hydrogen production costs from small capacity falling-water facilities within the range of 250 to 5000 kWe capacity and 10 to 150 ft head have been estimated. Both design capacity and design head were found to have a significant effect on annual hydrogen production cost which is a function of the total capital investment, yearly operating expenditures, an assumed financing structure, and annual energy production. (The single largest investment is capital equipment.) All three main components (turbine, generator, electrolyzer) are technologically well developed. The concept of using hydroelectric power to produce hydrogen is not new. Several large-scale facilities exist throughout the world which produce hydrogen for ammonia synthesis used in fertilizer production.

A key piece of equipment that will greatly determine the economic feasibility of the falling-water hydrogen concept is the electrolyzer. Current electrolyzers, especially small capacity units, are costly and are limited to an energy efficiency of about 0.60 (based on the high heating value of hydrogen). Two types of advanced industrial electrolyzers are currently under development in the United States and are projected to be available in the near term (around 1980). An advanced bipolar alkaline electrolyte unit (Teledyne Energy Systems) and a solid polymer electrolyte (SPE) unit (General Electric Company) both promise efficiencies up to 0.85 at substantially less cost than current units.

In an analysis employing a constant head of 85 feet (26 meters), a utilization factor of 0.65, and different types and combinations of equipment, hydrogen costs varied from \$14-\$30/million Btu (at 250 kWe) to \$5-\$9/million Btu (at 5000 kWe). A separate analysis (based on General Electric's SPE electrolyzer costs) of hydrogen costs, as a function of capacity and head, is summarized in Figure 5.2. This analysis is based on several inputs, including a previous study^{4*}

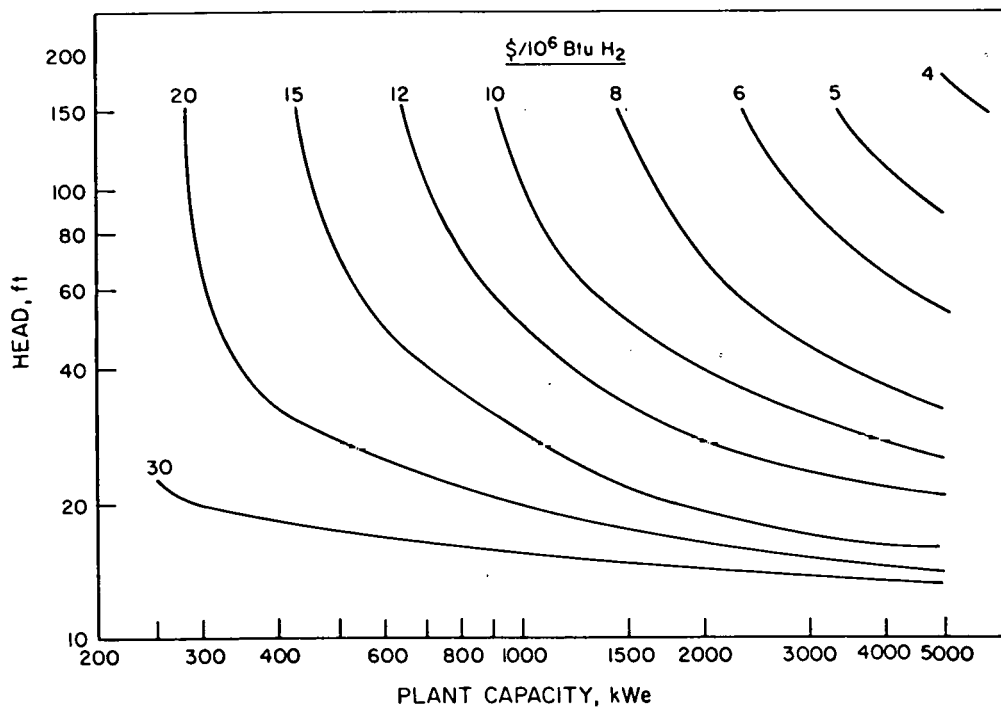


Figure 5.2. Hydrogen production cost estimates

*A 1978 update of the referenced study reports significantly lower electrical energy costs (especially in the lower head and capacity range). This, of course, would result in lower hydrogen costs.

that parametrically analyzed electrical energy costs from small capacity hydroelectric facilities.

It should be noted that the cost analyses conducted were not based on a thoroughly optimized design. Even when using conventional equipment, it was observed that there was ample opportunity for significant system improvements.

Falling-Water Hydrogen For Regional Use

In the near term, falling-water hydrogen has the potential to compete with industrial commodity (merchant) hydrogen production. The small-scale user (less than about 80,000 SCF/month) currently pays well over \$10/1000 SCF (\$30/million Btu)⁵ for commodity hydrogen. The price to the small-scale user is high, due to high storage (usually cylinder storage) and delivery costs from central producer plants. Since most of the falling-water resource is in the Northeast, where there is a large industrial population, the resource may be closer to the market than the merchant hydrogen industry's production facilities in the West and South. In an ideal situation, if a user facility is very close to an appropriate falling-water site, a short pipeline could be constructed to provide low delivery costs and lead to greatly reduced storage costs at the same time. One factor that must be taken into account is the inherent characteristic of seasonal and yearly fluctuations in deliverable hydrogen. Because the variable hydrogen supply rate may not be compatible with some industrial needs, an economic trade-off must be made between such aspects as implementation of on-site storage and purchase of supplemental merchant hydrogen during low production periods.

An added incentive to the commodity use of falling-water hydrogen is that most of the industrial hydrogen used in the United States is produced from central plant steam-reformed natural gas. The falling-water hydrogen would displace this feedstock use of natural gas and thus indirectly supplement our natural gas supply.

In the mid-term period ahead there is a strong indication that some of the larger capacity higher head sites could produce hydrogen that could be economic as an energy from in addition to its commodity potential. Hydrogen can easily be assimilated into the energy grid, as a supplement to natural gas, through direct mixing. There is evidence⁶ that conventional natural-gas combustors can be fueled with a natural gas-hydrogen mixture with up to 10% (by volume) hydrogen without using device modifications. The hydrogen could conceivably be tapped into a nearby existing gas distribution line to service a limited area.

As a supplement, this hydrogen should only be compared on an economic basis with other supplemental or alternative fuels or less accessible sources of natural gas (e.g., SNG, LNG, Arctic pipeline gas). The most favorable hydrogen costs (about \$5/million Btu) are comparable with those that gas utilities occasionally pay for natural-gas supplements when demand exceeds conventional supplies. Another valid comparison is with "new natural gas." For instance, the cost of Arctic gas (via the proposed new pipeline) at the Canadian/U.S. border is projected to be \$3.65-\$5.65/million Btu⁷.

5.2 Natural Gas Supplementation with Hydrogen

Under contract with the U.S. DOE and with funding support from Public Service Electric and Gas Company (PSE&G), various aspects concerning the delivery of blends of hydrogen with natural gas, via existing utility systems, have been studied. The study focused on the following: (1) the limitations which the use of hydrogen blends bring about in customer appliances and equipment, (2) the operation of a utility grid distributing hydrogen blends, (3) the selection of suitable points for injecting hydrogen into the distribution systems, (4) the effectiveness in hydrogen containment by typical components of a utility grid and (5) certain nontechnical aspects related to safety and regulatory requirements.

Combustion Tests of Blends in Burners and Appliances

The objective of this investigation was to determine the maximum amount of hydrogen that could be blended in natural gas, maintaining the reliability and efficiency of typical utilization devices with minimal or no adjustment or conversion.

Although interchangeability criteria, which may be calculated from the gas analysis, are available, these methods are not mutually consistent and were developed over 20 years ago. Since that time, new varieties of burners have been developed, and others have been modified, and burners which were critical are no longer used. In addition, use of these criteria to predict ignition or extinction noise; flashback on rapid turn-down or short-cycling; faulty ignition performance, with either thermal elements or flash tubes; and unfamiliar gas odors have not been successful. The preferred method of assessing interchangeability, is to (1) determine the possible interchangeable mixtures using established criteria, (2) set up in a laboratory selected burners/appliances representative of the most critical types served and (3) operate the proposed mixtures on the critical burners/appliances.

A preliminary study, using Weaver Indexes of Interchangeability, indicated that mixtures containing up to approximately 20% hydrogen should be interchangeable with natural gas. Of the five conditions which must be met for satisfactory interchangeability, [(1) little change in burner input, (2) no lifting of flames, (3) no flashback of flames, (4) no excessive yellow tipping of flames, (5) no incomplete combustion] it appeared that these mixtures would be critical with respect to flashback. Laboratory tests were undertaken to substantiate the preliminary finding.

Determination of Gas Distribution System Flows

This study examined the ability of a typical utility distribution system to deliver hydrogen while conforming to the pressure limitations of a system designed for natural gas. Natural gas is distributed in the U.S. today by means of a well integrated network of transmission lines operated by pipeline companies and by the distribution systems of hundreds of utilities which carry the gas to the ultimate user. The moving force which causes the gas to flow from wellhead to customer is the difference in the pressure of the gas from one point in the system to another. Different gases, since they have different characteristics such as heating value and specific gravity, require different pressure differentials for the delivery of an equivalent amount of energy.

Table 5.1 lists the principal elements of the natural gas T&D system from the wellhead to the customer's appliance. In the network studies, two subsystems of primary concern with regard to the flow of gas blends were examined in detail:

- (1) A distribution pressure subsystem involving a large PSE&G feeder main network;
- (2) a utilization pressure subsystem involving a medium sized PSE&G grid.

Network analyses were carried out for 100% natural gas at peak load conditions and for blends containing 10% and 20% hydrogen at peak load conditions. Comparisons of the results were made to determine the system modifications needed to carry the different gas blends. The service pressure subsystem was only briefly examined because it is expected that excess capacity is available to accommodate the flow of gas blends.

Table 5.1
PRINCIPAL ELEMENTS OF THE NATURAL GAS T&D NETWORK

Gas Well
Pumping Station
Underground Storage
Transmission Line
Metering Station
High or Medium Pressure Feeder Main
Distribution Regulator
Utilization Pressure Main
Service Main
Service Regulator
Customer Meter
Customer Line
Customer Appliance or Equipment

Points of Potential Hydrogen Admission

The selection of the points at which hydrogen should be admitted to a distribution system to supplement natural gas is closely related to the requirements of the State Utility Commission. Aside from safety considerations, the utility commission's chief concern will most likely be that customers receiving

the lower heating value blend are billed accordingly. To this end, the commission will probably require that the limits of the area receiving the blend are clearly defined so that these customers can be easily identified. From the utility's standpoint, the simplest way to define these limits would be to supply the blend to an entire distribution system, or if this cannot be done, at least to some easily defined subsection of the distribution system. This can be done most easily if the utility blends hydrogen with natural gas at the meter stations supplying a particular distribution system.

Leakage Performance of Gas Distribution Equipment

Gas leakage through pipeline joints raises concern when considering the distribution of hydrogen blended with natural gas which is primarily methane. Certain differences in gas characteristics are expected to affect joint leakage and associated hazards. Hydrogen is much lighter than methane, having a specific gravity of 0.0695 compared to methane's 0.555. This characteristic would make hydrogen rise, or travel, much faster than methane. Hydrogen, having a diffusion coefficient of 0.63 CM²/sec. compared to methane's 0.2 CM²/sec., would also escape more readily than methane through a crack, micropores or pervious material, all other conditions being equal. The range of flammability for hydrogen (4.1%-74% in air) is much broader than that for methane (5.3%-15% in air) and thus a hydrogen leak could be more easily ignited than a methane leak. Further hydrogen needs only about 1/15 the amount of energy required to ignite methane (20 J vs. 300 J). Because of these differences, it was thought important to determine if leakage from joints used in natural gas distribution systems would increase with hydrogen blends.

Summary of Results and Conclusions

The results show that main burners can burn blends with up to 20-25% hydrogen in natural gas, but target pilots limit the hydrogen concentration to 6-11%. After modification of pilot orifice or increase in gas supply pressure, blends with up to 20% hydrogen were found satisfactory for use in most burners and appliances. The flow studies indicate that natural gas with up to 20% hydrogen could be readily adapted to utility operations at the gas pressure and flows used in the distribution, utilization and service subsystems of the grid. The metering station appears to be the most suitable site for introducing hydrogen

into the distribution system. Blends of natural gas with up to 40% hydrogen by volume do not result in increased rates of gas leakage through pipeline joints when compared with leakage rates for straight natural gas.

Impact of Regulatory Standards

An analysis of the Regulatory Commission rules in one state (New Jersey) reveals few problems with regard to distributing hydrogen blends, but certain topics need further study.

1. Possible conflicts with a variety of existing codes, including piping and plumbing codes, welding codes, electrical codes, and compressor station codes.
2. Gas detector calibration could be difficult when the percentage of hydrogen in the blend is constantly varying.
3. Odorizing hydrogen-natural gas blends could present problems.
4. Purging mains for hydrogen-natural gas blends may need development of special procedures.
5. Heating value calculations for billing purposes will be more complicated.

Regulatory standards regarding gas distribution and hydrogen handling may vary significantly among states and localities and further studies should be made in this regard.

REFERENCES
5.0 SYSTEMS STUDIES AND END-USE APPLICATIONS

1. Johnson, D.G., and Escher, W.J.D. Hydrogen From Small Existing Falling-Water Sites: An Initial Feasibility Assessment, Final Report prepared for the U.S. Department of Energy, (Brookhaven National Laboratory, Contract No. BNL42332-S), Institute of Gas Technology, Chicago, Illinois, April 1978.
2. Tippetts, Abbett, McCarthy and Stratton, New York Polytechnic Survey of Hydropower in Nine Northeastern States, April 30, 1977.
3. McDonald, R.J. Estimate of National Hydroelectric Power Potential at Existing Dams, U.S. Army Corps of Engineers, Institute for Water Resources, July 20, 1977.
4. O'Brien, E. Small hydroplants for the northeast. Electrical World, 61-62, August 15, 1977.
5. Biederman, N.P., et al. Utilization of Off-Peak Power to Produce Industrial Hydrogen, Final Report prepared for the Electric Power Research Institute under Project No. EPRI-320-1. Institute of Gas Technology, Chicago, Illinois, August 1975.
6. An Evaluation of the Use of Hydrogen as a Supplement to Natural Gas, prepared by the Ad Hoc Committee, ERDA Report No. TID-27747, June 1977.
7. Koran, N. \$5.65/MCF? Rolled in pricing may become vital to Alaskan gas future. Oil Daily, January 13, 1978.

6.0 PROJECT MANAGEMENT

6.1 Project Planning and Liaison with Industry

The bulk of the activities described in this report were implemented in accordance with the FY 1978 Hydrogen Program Operating Plan prepared in late 1977 by BNL for the DOE Division of Energy Storage Systems. Two planning documents were prepared this year for DOE approval. These are a Summary Plan submitted in September 1978, which provides the program rationale and funding requirements, and an Annual Operating Plan, which provides details on the individual contracts and projects. These plans, which serve as working documents for the program, are subject to periodic revision and, therefore, are not published formally. Figure 6.1, which was abstracted from these documents, gives an overview of the program by funding and technical area.

The major liaison activity during the period was the conduct of the Annual Contractors' Review Meeting, held in November 1978 in the Washington, D.C. area (Dulles Marriott Hotel). Over 40 contractors and Principal Investigators presented papers, which are available as published proceedings through either BNL or DOE/STOR.

One major procurement activity was undertaken with the issue of a Request for Proposal (RFP) for work in "Hydrogen Production from Small Hydropower Sites." Proposals were received and evaluated by BNL supported by reviewers from outside organizations and the solicitation resulted in two potential contractors, New York State ERDA and Air Products, with contract awards scheduled for first quarter 1979.

A workshop was planned and coordinated by BNL on the subject of "Metal Hydride Hydrogen Storage Vessel Design." Approximately 40 representatives of Government, National Laboratories, and industry participated in the two-day session to discuss current problems, design approaches and operating experience for various applications. A summary of the discussions and responses to prepared questions is available in the form of BNL internal reports. A total of 10 unsolicited proposals/preproposals were evaluated by the BNL staff and selected reviewers from outside organizations. Of these proposals, five were rejected for either technical or programmatic reasons and the decision on the remaining five is pending with two tentatively accepted for funding support when it becomes available.

6.2 Contract Management and Technical Monitoring

BNL managed and provided technical monitoring for a total of 18 contracts amounting to a funding level of about \$3.2 million. The largest of these contracts was with General Electric (~\$1 million) for work in large-scale water electrolysis technology development. The technical monitoring consisted of evaluating the contractor's progress, conducting contract reviews, visits and inspection of development facilities and approval of final reports. A listing of the contract actions in 1978 is provided in Figure 6.2.

FY 78		FY 79 (for planning only)	
Budget \$3,200K	\$K	Budget \$3,800K	\$K
H ₂ Production 1,400	GE--1,055 Teledyne--125 Univ. of Va.--20 BNL--200	H ₂ Production 1,800	GE--1,500 Teledyne--100 Univ. of Va.--20 BNL--180
H ₂ Storage Systems 600	Foster-Wheeler--70 BNL--365 Teledyne Motors--15 ORNL--10 IGT--140	H ₂ Storage Systems 370	Foster-Wheeler--20 BNL--170 Teitel--100 ORNL--10 IGT--70
H ₂ Storage Materials 480	DRI--120 INCO--35 Air Products--92 BNL--150	H ₂ Storage Materials 430	DRI--100 INCO--75 Air Products--120 BNL--140
End Use/Applications 330	PSE&G--70 GE--45 BNL--60 Billings--125 IGT--30	End Use/Applications 835	Low Head Hydro--TBD* Fork Lift--100 BNL(FRG)--60 TBD*
Systems Studies 200	PSE&G--20 Systems Science/ Chem Systems--30 Teitel--60 BNL--85	Systems Studies 90	Remote Hydro--60 OTEC/WECS--TBD* TBD*
Project Management 200	BNL--200	Project Management 300	BNL--300

*To Be Determined

Figure 6.1. Hydrogen project budgetary breakdown

<u>Contractor</u>	<u>Work Area</u>	<u>Approx. \$ Value</u>
Systems, Science, Software	Underground Storage (Consultation Support)	30K
Air Products (Cont. from RFP award)	Hydride Storage (Automotive Applications)	92K
Clarkson College	Storage (Hydrogen-Halogen)	24K
Foster-Wheeler	Storage	60K
Teledyne Energy Systems	Alkaline Electrolysis	60K
R. J. Teitel	Storage (Microspheres)	65K
General Electric	SPE Water Electrolysis	1.5M
International Nickel Co.	Hydride Metallurgy	90K
Institute of Gas Technology	Underground Hydrogen Storage	144K
Oak Ridge National Laboratory	Heat/Mass Transfer Hydride Beds	15K
Oronzio De Nora	Hydrogen-Halogen	60K
Denver Research Institute (SRSA)	Hydrides Research	100K
Chem Systems	RFP Evaluation Support	10K
<u>Unsolicited Proposals</u> (Contract Renewals not included)		
10 received		
5 rejected		
5 pending (2 accepted pending availability of funds)		

Figure 6.2. Contract activities for calendar year 1978