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ENERGY

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Proceedings of the ERDA Contractors' Review Meeting on Chemical Energy Storage & Hydrogen Energy Systems

Airlie House
Airlie, Virginia

November 8 & 9, 1976

ENERGY RESEARCH &
DEVELOPMENT ADMINISTRATION

OFFICE OF THE ASSISTANT ADMINISTRATOR
FOR CONSERVATION

Division of Energy Storage Systems

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Prepared By
BROOKHAVEN NATIONAL LABORATORY

FOREWORD

This Meeting was called by Dr. James H. Swisher, Chief of the Chemical and Thermal Energy Branch, Division of Energy Storage Systems at ERDA Headquarters, for the purpose of informing Contractor personnel of the background, goals and status of the work on hydrogen technology being sponsored by the Division of Energy Storage Systems. The various program presentations made by twenty-nine of the seventy-one participants also provided an insight to the problems which presently limit applications. And, importantly, there was ample opportunity for participants to discuss directly their special program interests with others.

In addition to the twenty-nine manuscripts contained in this Proceedings, there is a collection of Contractor Fact Sheets in the Appendix. The Fact Sheet for each Contractor provides pertinent information on the program including its goals and status.

The Meeting was planned by personnel of Brookhaven National Laboratory as part of its management role, delegated by ERDA, for a major portion of the Chemical Energy Storage Program. As Coordinator for this Meeting, I especially thank all persons who made presentations and thereby contributed to the success of the Meeting. To Dr. Swisher, and to Frank J. Salzano of Brookhaven, I express my appreciation for their guidance in assisting with plans for the Meeting. For their valuable assistance in handling the many details associated with the Meeting, I thank Diane Capuano and Mary-Faith Healey. Lastly, I am grateful to Mary-Faith Healey for her detailed efforts on the Proceedings.

Plans for publication of the Proceedings were made in advance so that the information would be available to the public shortly after the Meeting.

Gerald Strickland,
Meeting Coordinator
Brookhaven National
Laboratory
Upton, New York 11973
December 30, 1976

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THE CHEMICAL ENERGY STORAGE PROGRAM IN PERSPECTIVE

James H. Swisher
Division of Energy Storage Systems
Energy Research and Development Administration
Washington, D.C. 20545

Energy storage is a key element in energy systems for which either the supply or the demand for energy is intermittent. It is particularly important in the use of solar energy, but utility, transportation, and other applications sectors can also use energy more efficiently through effective use of storage technology.

ERDA's Energy Storage Program, first as a part of the Division of Applied Technology in the AEC, and then as a part of the Division of Conservation Research and Technology in ERDA, grew over a period of just a few years to a division-size effort. In June, 1976, the Division of Energy Storage Systems was formed with a budget for Fiscal Year 1976 of $19M, including the transition quarter. If the ERDA Authorization bill for FY 1977 is passed without change, the budget will be $31M. The corresponding budgets for Chemical Storage are $3.2M in FY 1976 and $4.6M in FY 1977. The other subprograms in the Division are Battery, Electrochemical, Thermal, Advanced Physical Methods and Applications Analysis.

An effort is now being made by ERDA to make more effective use of laboratories in the field by the delegation of project management responsibilities. Headquarters personnel will set the policy, decide program priorities, formulate budget submissions, allocate available funds, and interface with the staff of OMB and Congress. Although manpower growth in the Division of Energy Storage Systems has not kept pace with program growth, every effort will be made to maintain close communication with program participants so that our decisions are not made in isolation. We will utilize the technical and managerial capabilities of the national laboratories and other laboratories in the field for program planning, technical monitoring and related project management functions within ERDA guidelines.

The projects in Chemical Energy Storage, most of which are tied to Hydrogen Energy Systems, are subdivided into two large groups, plus a small number of special projects. The project elements in the two groups are listed in Table 1. For "Electrolysis-Based Hydrogen Systems", the lead organization is Brookhaven National Laboratory, and for "Thermochemical-Based Hydrogen Systems", the National Aeronautics and Space Administration, with the involvement of the Jet Propulsion Laboratory, is the lead organization.

TABLE 1

PROJECT MANAGEMENT RESPONSIBILITIES AND PROGRAM ELEMENTS FOR HYDROGEN ENERGY SYSTEMS

A. ELECTROLYSIS-BASED HYDROGEN SYSTEMS

- Natural Gas Supplementation
- Electrical Utility Load Levelling
- Production via Electrolysis
- Storage Systems
- Hydrogen Occluder Materials
- Systems Studies

B. THERMOCHEMICAL-BASED HYDROGEN SYSTEMS

- Production via Thermochemical Cycles
- Production via Advanced Concepts
- Transmission and Distribution Systems
- Containment Materials
- Systems Studies

In Brookhaven's area of responsibility, the engineering subsystems under development have potential for industrial implementation in the near to intermediate time frame. They also will provide the technology base in hydrogen occluder materials and storage components for hydrogen energy systems regardless of time frame for implementation.

In NASA's area of responsibility, the components and processes under development are generally applicable to the intermediate and long-term energy program. Technology base responsibilities are mainly in containment materials for hydrogen. In both project management areas, systems studies will be included.

In the overall program plan, implementation of hydrogen energy systems is considered to follow a stepwise scenario with the following applications as the main thrusts:

- Natural gas supplementation.
- Storage of hydrogen for utilities load levelling.
- Industrial market for hydrogen both as a chemical and as a fuel.
- Vehicular applications.
- Direct substitution for natural gas in all sectors where natural gas is used today.

For near-term projects, most of the effort is directed toward the design, construction, and evaluation of engineering prototypes. In the longer term projects, the emphasis is on identifying the pacing problems and working toward their solutions. All applications depend very heavily on improved hydrogen production processes. Approximately half of the FY 1977 budget will be allocated for hydrogen production projects.

There are a number of accomplishments in the Hydrogen Program during the past year that should be highlighted.

- The Ad Hoc Committee for Hydrogen Supplementation of Natural Gas was formed to judge the technical and economic feasibility of adding approximately 10% hydrogen to our natural gas pipeline system. Full implementation could result in a 5% reduction in oil imports by 1985. A report summarizing the Committee's recommendations is now being prepared.

- Work was initiated on a hydrogen-halide electric energy storage system for load levelling. A reversible electrolytic cell, with hydrochloric acid as the electrolyte, combines the functions of the water electrolysis component and the fuel cell component in systems considered previously. This system modification is expected to reduce capital costs considerably.

- Some promising cycles for the thermochemical production of hydrogen from water have been identified. There is sufficient thermodynamic and kinetic data now available to justify starting engineering development on a small scale.

- The feasibility of using two hydride storage beds in a closed loop process for building heating and cooling applications has been demonstrated.

- A prototype hydrogen pipeline has been constructed to evaluate structural steels and fabrication techniques already studied in the laboratory. The beneficial effects of coatings, liners, and gaseous inhibitors in minimizing hydrogen damage to the steels are under investigation.

During the coming year, tentative plans have been made to start new projects on underground storage of hydrogen and on photochemical hydrogen production. An expanded effort is planned on light weight hydrides and other hydrogen occluders for use in motor vehicles. Presently our only sponsored project in this area is on the development of magnesium alloy hydrides. Some consideration may also be given to light weight hydride container materials for transportation applications.

Thus far, no mention was made of activities in the special projects category. One project on the storage of solar energy in organic materials continues to show promise. A reversible chemical change in the material is the storage mechanism. Another special project is a systems study of the feasibility of producing ammonia and fertilizer from hydrogen produced by electrolysis. This project was transferred from NSF to ERDA a few months ago.

During the past year, two projects were transferred from the Chemical to the Thermal Storage Program. Both were in the area of heat storage and transmission in chemical heat pipes.

This summary of ERDA's progress in Chemical Energy Storage last year and plans for the coming year should set the stage for the remainder of this report in which virtually all projects in the Chemical Storage Program are described.

HYDROGEN TECHNOLOGY DEVELOPMENT PROGRAM AT THE BROOKHAVEN NATIONAL LABORATORY

Frank J. Salzano
Brookhaven National Laboratory
Upton, New York 11973

The Brookhaven National Laboratory has major project management responsibility for that segment of the chemical sub-program, in ERDA's Division of Energy Storage Systems, designated "Electrolysis-Based Hydrogen Storage Systems." I will explain that program, the general scope of the overall effort, how the program is organized at BNL, as well as how we will interact with industry, other research institutions, and universities interested in participating in this program through BNL.

The ERDA Program Manager in this area is Dr. James H. Swisher, Chief of the Chemical Storage Branch at ERDA. The BNL Program encompasses the electrolytic production of hydrogen from all energy sources, storage of hydrogen, delivery and utilization. This effort is comprised of supporting work on research and development, as well as related systems analysis. The management responsibility includes the establishment of projected goals and objectives in relation to ERDA's overall program goals. BNL is responsible for the administrative and control functions necessary to implement projects, as well as for carrying out the liaison activities needed to encourage and stimulate the cooperative efforts of private industry and universities.

Brookhaven has a background in hydrogen technology development which goes back at least ten years, and we will continue to maintain a strong and relevant in-house program in this area. As of last year, an increasing fraction of the total BNL effort is being subcontracted. During FY 1976, one third of the total funding available to BNL was subcontracted to industry and universities. The percentage of the subcontract effort will approximately double in FY 1977, and a further increase is expected in subsequent years. The chart shown in Figure 1 lists the range of activities in progress or to be completed in FY 1976.

Production

- Industrial development of advanced electrolysis processes, e.g., alkaline and solid polymer systems, involvement with IEA cooperative R&D program.

Storage

- Commercialization of metal hydride (MH_x) H_2 storage.
- Identify conversion applications for MH_x, e.g., waste heat utilization, heat pumps, etc.

Applications

- H_2 for natural gas supplementation or industrial applications.
- Energy exchange between gas-electric systems.
- Electric-to-electric storage, e.g., H_2 - O_2 and HCl electrolysis.

Utilization

- Fuel cell research and development, e.g., high-temperature solid oxides, catalysts for low-temperature aqueous systems.

Test and Demonstration

- HYTACTS (Hydrogen Technology Advanced Components Test Systems).

Systems Studies

- Role of H_2 in the U. S. energy system.
- Cost goals for energy-storage devices and impacts.
- Role and cost goals for fuel cells.

Figure 1. Hydrogen Technology Program.

A key objective of the program is the industrial development of advanced electrolytic-hydrogen-production processes with the prime focus on solid-polymer and alkaline electrolyte systems. At the present time there is no large-scale electrolytic equipment supplier in the U. S.; and it is our objective to stimulate the establishment of this technology within U. S. industry. Beyond national interests, an effort is presently underway to initiate international cooperative R&D programs in association with the International Energy Agency. Most of you who work in this technical area know about the efforts underway; I will be happy to make information available to any interested party not familiar with the work in progress.

In the area of hydrogen storage, BNL has emphasized work on the metal-hydride storage of hydrogen. Work on hydrogen storage will be expanded into the area of underground storage of hydrogen. Although BNL has capability in the area of liquid-hydrogen production and storage, it is our view that this storage method is too costly and too energy-intensive for most applications, excluding the use in air transport systems, which is outside the scope of BNL responsibility. In connection with metal hydride (MH_x) storage, it is our goal to develop and establish the base for commercialization of this technology in the very-near term. Commercialization of MH_x for transportation applications is already in progress, and most of you are familiar with the product line turned out by Billings Energy Research Corporation.

Metal-hydride systems using hydrogen as the working fluid in a closed system have a number of other prospective applications, among them being thermal storage, heat pumps and electric conversion; we are looking into the prospects for end-use applications along these lines.

In the area of applications the BNL effort is concerned with relatively near term needs. A study is in progress considering the production of hydrogen by electric utilities from spinning reserve, or off-peak power, for injection into existing natural gas lines as supplemental fuel. This effort is linked with the concept of energy exchange between gas and electric systems, as discussed by

Jack Casazza et al. of Public Service Electric and Gas of New Jersey, Roosevelt Fernandes of Niagra Mohawk Power Company, and personnel at BNL.

One of the primary goals of the BNL program is to study the feasibility of electric-energy storage via the use of hydrogen-oxygen systems. The concept has been studied in detail by BNL, with support from industry. Our conclusion is that in the form considered, even anticipating advanced-electrolysis and fuel-cell-technology development, this concept is not expected to be an economically viable alternative in the near term, based on current cost projections relative to the required cost goals. However, electric to electric storage is still a major goal of the Division of Energy Storage Systems. Hydrogen systems in several different forms have potential viability and flexibility for use as long-term electric storage cycles, i.e., weekly cycles. In an effort to overcome the short-comings of the hydrogen-oxygen system, BNL, in collaboration with industry, has begun to examine the H_2-Cl_2 system because of its electrochemical reversibility and potential for H_2O electrolysis. Dr. Srinivasan will describe the system in detail.

BNL has a related but small program on fuel-cell development supported by ERDA's Division of Conservation Research and Technology. Another major focus of BNL's in-house program is on our Hydrogen Technology Advanced Components Test Systems (HYTACTS) Program. This facility will test hydrogen technology hardware supplied by industrial partners involved in cooperative efforts. The emphasis this year is on engineering design and testing of metal-hydride hydrogen-storage vessels. This HYTACTS facility will also be used to test electrolysis equipment, and eventually storage and conversion hardware related to advanced systems such as the HCl electrolysis concept.

Last, but not least, I would like to mention work in the area of systems studies which are being conducted to define the role of electrolysis-based hydrogen systems. This work includes system definition, cost goals, economic and environmental impacts, as well as synergistic effects in common with other aspects of the U. S. energy system.

During the past fiscal year the study has concentrated on near-term industrial applications of hydrogen. A recent study by Exxon Research and Engineering Company, prepared under subcontract to BNL, will be presented at this meeting.

In addition to the personnel involved in the current BNL technical program, a project management team has been assembled to direct these specific efforts.

In summary, it is of value to point out the names of key individuals who are working in the management and technical support of the program; their names are shown on the chart in Figure 2. You should note that it is the lead technical people, and their supporting personnel carrying out the in-house technical program, who will be involved in the technical monitoring of the BNL subcontract efforts.

Project Management

G. Strickland - In-House Projects and Technical Monitors

M. Bonner - Contracts Management and Coordination

Technical Projects

S. Srinivasan - Electrochemistry

J. Reilly - Metal Hydride Materials

A. Beaufrere -- Engineering Design and Coordination A/E's

C. Braun - Systems Studies

C. Waide - Automotive Storage

Figure 2. Project Responsibilities for the Hydrogen Program.

This work was carried out under the auspices of the United States Energy Research and Development Administration.

WORK OF THE AD HOC COMMITTEE EVALUATING THE USE OF HYDROGEN AS A SUPPLEMENT TO NATURAL GAS

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The Ad Hoc Committee was established at the invitation of ERDA to study the feasibility of producing hydrogen to supplement natural gas supplies. Membership was solicited from a broad base of utilities, agencies, and government to assure expertise and a balanced input to the project. Although sponsored by ERDA, the study is intended to reflect industry appraisal. Activity began with an organizational meeting on April 21, 1976.

By June 3, the Committee had defined its charge and was arranged into five Task Groups. In essence, the Committee was to advise whether or not hydrogen supplementation is a viable goal for commercialization within the mid-term, that is, 1985-2000. If affirmative, a program for demonstrating the technical ability to accomplish this goal was to be formulated. Work was oriented to problem definition and appraisal of magnitude, the supply-demand relationship, economic evaluation and planning. Problem solutions in depth were not considered other than a review of state-of-the-art and pending developments. A target date of January, 1977 was set for completion of the study.

The following listing of the Task Group scopes will give an idea of the comprehensive approach to this study.

Motivation

To place into perspective the factors relating to the natural gas and electric power supply-demand situations which make hydrogen supplementation appear to be a viable concept for the conservation of energy and natural resources.

Supply

To evaluate the problems associated with hydrogen production. This consideration to include all techniques stemming from the use of various energy sources. Commercial hydrogen production by any means also to be reviewed.

Interface - Supply to Transmission and Distribution

To evaluate the problems associated with the handling of hydrogen from the outlet of its source to injection into a natural gas pipeline. This consideration to include the injection system and controls which extend to monitoring of the blend downstream of the injection point.

Transmission and Distribution

To evaluate the problems associated with the handling of natural gas supplemented with various percentages of hydrogen. This consideration extends from the receipt of the blended mixture to its delivery on the outlet side of the meter at the consumer's premises.

Utilization

To evaluate the problems associated with the end use of hydrogen as a supplement to natural gas. This consideration extends from the outlet of the meter at the consumer's premises through the house line and final consumption. All types of appliance usage, i.e., domestic, commercial and industrial are included.

All of these Task Groups were asked to develop the technical considerations involved with their charge. They were also to assess the impact of vital non-technical considerations, such as, Safety, Environmental, Legal, Costs, Codes and Regulatory. The assessment was to proceed through five Exercises namely:

I - Present State of the Art
II - Realistic Immediate Goals and Recommendations
III - Real World Physical Applications
IV - Alternative Operating Arrangements
V - Long Range Possibilities

During the course of work, a sixth Task Group was established to provide guidelines for costing methods. These guidelines would be applied uniformly in developing the economic analysis of the hydrogen supplementation concept.

The people carrying out this study do represent a wide cross-section of industry and government. Participating organizations are listed below:

Industry

Baltimore Gas & Electric Co.
Columbia Gas System Service Corp.
Commonwealth Edison Co.
Consolidated Edison of New York
Consumer's Gas of Toronto
Elizabethtown Gas Co.
Exxon Co.
Niagara Mohawk Power Corp.
Pacific Gas and Electric Co.
Public Service Electric & Gas Co.
Southern California Gas Co.
Texas Gas Transmission Co.

Agencies

American Gas Association
Electric Power Research Inst.
Institute of Gas Technology
Gas Appliance Manufacturers Ass.

Government

Energy Research and Development Adm.
Brookhaven National Lab.
Jet Propulsion Lab.
Lewis Research Center
Sandia Lab.

Committee members have wrestled with this question and themselves since June. Coordinating this activity with many diverse, busy and geographically separated people has proved to be a stimulating experience. Despite the vicissitudes of vacations, meeting conflicts, communication breakdowns and a tight schedule, a remarkable amount of work has been done. We are now at the crucial stage of the investigation - putting together the outputs from the various Task Groups and focusing the activity to get a clear picture. It is fair to say that any statement as to the final recommendations are speculative at this time. Certain aspects of the study, however, are in perspective. These are given below:

1. There is a very high degree of confidence in the ability of gas burning equipment to utilize up to 10% of hydrogen by volume in a mixture with historic natural gas without readjustment. The latter is taken as 1030 BTU, 0.58 specific gravity gas generally distributed at this time. Work is presently being funded by ERDA to get a better handle on the upper limits. A field demonstration involving domestic appliances of various ages, types and applications "in-situ" would be valuable in confirming the interchangeability criteria now in use. Industrial equipment is in the same category except for some applications

where input rate, flame pattern and combustion atmosphere are critical. Most industrial equipment is monitored and adjusted under present conditions so this would not be an overriding consideration.

2. Distribution systems in the past have utilized manufactured gases containing hydrogen in the order of 30% and more. In fact some operate today with significant percentages of hydrogen without difficulty. Also there are straight hydrogen pipelines which have operated successfully for a number of years. However, no pipelines have operated with this particular blend of natural gas and hydrogen. Since there is still concern about adverse effects, particularly at higher pressures, such as encountered with transmission lines, a field demonstration involving such facilities would be of value.

3. The handling of pure hydrogen at an interface facility and blending controlled percentages into a flowing natural gas stream is clearly within present technology. Storage other than in "buffer" quantities is not included in this consideration. Compression, if needed from near atmospheric levels, would impose severe equipment and cost penalties. A field demonstration would be of value particularly with respect to resolving the environmental, code and regulatory questions.

4. For mid-term commercialization, the use of advanced electrolyzers operating on "spinning reserve" and "off peak" electric generation appears to be the only meaningful concept. The physical feasibility, that is, matching of availability versus demand and the economics are under intensive scrutiny at this time.

This latter consideration is where the critical judgement must be made. The Ad Hoc Committee will do its utmost to present the case for hydrogen supplementation in a fair and balanced manner. As is often said - there is nothing quite so irresistible as an idea whose time has come. Many of us believe that hydrogen will have its time. The question is when.

BLENDING OF HYDROGEN IN NATURAL GAS DISTRIBUTION SYSTEMS

C. R. Guerra, J. E. Griffith, K. Kelton and D. Nielsen
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80 Park Place
Newark, NJ 07101

The objective of this study is to experimentally evaluate the concept of supplementation of natural gas with hydrogen to extend the amount of pipeline quality gas which can be delivered by utility systems.

Background

Gas, at present, is a major primary source of energy, accounting for approximately 1/3 the total energy used in the U.S. The current U.S. gas supply picture is dominated by the production and expected reserves of gas fields in the producing states.

The available information suggests that most utilities in the U.S. can expect shortages in gas deliveries to continue. Pipeline curtailments to PSE&G averaged 30% during the winter of 1975 and curtailments by pipelines to the Northeast are expected to range up to 40% during 1985-1995. To offset these curtailments, utilities are involved in a range of projects to develop additional sources of pipeline quality gas.

In the near term (1985), additional gas supplies are expected to result from the importation of liquified natural gas (LNG), Alaskan gas, Canadian gas, offshore gas, gas from advanced fracturing, and substitute natural gas (SNG) from coal, petroleum and wastes. By most accounts all new gas will be expensive.

Hydrogen is attractive as a supplement to natural gas because it is suited to existing gas distribution/utilization systems and can be derived from various primary energy sources. It can be instrumental in the smooth transition in gas delivery operations from a fossil to a nonfossil economy. The current systems for distribution of essentially pure methane may be adapted to the distribution of blends containing methane and hydrogen in the near term and eventually pure hydrogen in the long term. The large investments in gas T&D pipeline networks and customer utilization equipment could thus be most economically used.

Project Description

This investigation consists of two tasks. Task I aims to evaluate the maximum levels of hydrogen that can be blended with natural gas and require minimal or no adjustment or conversion of typical utilization devices operating from the utility network. Task II aims to determine flow patterns from hydrogen blending points in a utility distribution system and the effectiveness in hydrogen containment by typical pipeline materials and components. Concurrent with these tasks certain nontechnical aspects related to safety and regulatory requirements are being examined.

The work in interchangeability indices and combustion tests is being carried out at PSE&G's Gas Utilization Laboratory. The work in hydrogen blending and containment, which requires larger gas volumes, is being set up at PSE&G's Harrison Gas Production Plant. This site has accessibility to gas of various compositions (SNG, refinery gas, oil gas) which need to be considered for multicomponent gas blends. The network analysis will be carried out using a Univac 1106 employed for system flow studies.

Status

This report summarizes the first 5 months of the project essentially covering most of the proposed combustion studies.

The following gas interchangeability indices (Weaver) were calculated to determine the suitability of gas mixtures of interest in meeting desirable combustion criteria.

1. Little change in heat input (J_H)
2. No lifting of flames (J_A)
3. No flashback of flames (J_F)
4. No excessive yellow tipping (J_Y)
5. No incomplete combustion (J_I)
6. Primary air requirements (J_A)

The combustion test included the following equipment:

1. Tests with hydrogen blends of eleven pilot burners including aerated, monaerated and target designs.

2. Tests with hydrogen blends of thirteen main burners including the following designs: drilled port, slotted port, single port, ribbon, target and luminous flame.
3. Tests with hydrogen blends of seven appliances including range, water heater, clothes dryer, furnace, and boiler, some with electric ignition.

The variety of utilization equipment tested is thought to be representative of what is supplied by a utility network. Burner performance was determined with natural gas and six test mixtures (6, 10, 14, 20, 25 and 30% hydrogen) at a line pressure of 5 inches water gauge.

Results

The burner tests demonstrated satisfactory interchangeability with natural gas (NG) of the following blends:

- 10% H_2 + 85% NG - the limiting concentration using target pilots at a line pressure of 5" water gauge. No modifications required.

- 15% H_2 + 85% NG - the limiting concentration using target pilots at a line pressure of 7" water gauge. Same concentration can be used by changing orifice of target pilot if line pressure is kept at 5" water.

- 20% H_2 + 80% NG - the limiting concentration determined by the main burner of appliance and can be achieved by changing target pilots and a line pressure of 7" water gauge.

A review of the experience by PSE&G in the commercial distribution of hydrogen containing refinery gas (RG) in blends with natural gas indicates the following:

- The heavier hydrocarbons in refinery gas tend to balance the combustion changes brought about by hydrogen added to natural gas. Thus 3-12% H_2 in the blends (RG + NG) have been found satisfactory.

- The experience since 1971 (30 x 10^6 SCF/D refinery gas with 12 to 32% H_2 from Exxon's Bayway Refinery blended with natural gas by PSE&G at Linden, NJ) has shown no significant problems in the transmission (15 miles) and distribution (10 miles) of the blends in a utility network or in customer acceptance.

Plans

The work will continue as planned with some updating as suggested by the experience with multicomponent gas blends.

SOLID POLYMER ELECTROLYTE WATER ELECTROLYSIS DEVELOPMENT STATUS FOR BULK HYDROGEN GENERATION

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Direct Energy Conversion Programs
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Because of the high cost of electrolytic hydrogen, it has been used primarily for specialized applications in food processing and semi-conductor manufacture which require high purity gas. Virtually all other requirements for hydrogen in this country have been supplied by reforming of natural gas. Projections of demand for hydrogen show it continually increasing between now and the end of the century while prospects for natural gas feedstock to the hydrogen industry indicates probable reductions in availability and significant increases in prices. Therefore, it would seem to be appropriate to reexamine the prospects for improving the cost and efficiency of electrolyzer technology so that it not only might be able to pick up some of the future shortfall in meeting the chemical/industrial demand for hydrogen feedstock but also become a candidate for energy storage systems to help meet peak load demands in electric utility networks, as well as for bulk hydrogen generation to supplement natural gas over a wider spectrum of energy applications.

With present funding support from ERDA and some electric utilities supplementing that of General Electric, we are extending the development of the solid polymer electrolyte (SPE) water electrolysis technology, originally developed for aerospace applications, to try to meet performance and economic goals which could make electrolytic hydrogen a viable alternative for such applications.

As the name implies, the SPE electrolysis cell which was developed by General Electric, uses a solid sheet of perfluorinated polymer plastic as the sole electrolyte. The electrodes consist only of thin films of catalyst pressed onto the surface of the electrolyte sheet.

In the cells designed for aerospace applications, multilayer expanded metal screens form the anode and cathode chambers and serve as current collectors as well as for electrolyte support. A solid metal separator is then used between the anode chamber of one cell and the cathode chamber of the adjacent cell to complete a bi-polar configuration.

There is no liquid electrolyte, and plain water is the only liquid in the cell. Water is circulated through the anode chamber at a sufficiently high rate to remove the waste heat as well as provide for the electrolysis reaction, so no separate cooling fluid is needed, making a very simple and compact cell design.

This technology was originally developed for space fuel cell applications and was first used in the Gemini spacecraft in the 1960's. However, its unique features also make it ideally suited to a wide range of other electrochemical applications including water electrolysis and oxygen or hydrogen concentration. A prototype oxygen concentrator was delivered earlier this year to the Navy for aircraft applications, and some of the present water electrolysis applications include oxygen generation for space station and submarine life support systems and a small commercial hydrogen generator for gas chromatographs and other laboratory uses.

The SPE cells are also applicable for electrolysis of HCl, NaCl and Na_2SO_4 for production of chlorine, hydrogen and caustic and offers similar advantages over current equipment used in these applications as it does in the field of water electrolysis.

The most significant feature of the SPE cell for water electrolysis is the very high efficiency as compared with conventional electrolyzers, as shown in Figure 1, and the capability for operating at high current densities (1000 - 2000 amps/ft^2). The high efficiency will result in savings in electrical power, or operating costs and the high current density will provide lower capital costs, the combination possibly resulting in the means for making electrolytic hydrogen competitive for many chemical/

industrial applications and perhaps, depending on the power source, even to be considered as a supplement to natural gas as a clean energy source.

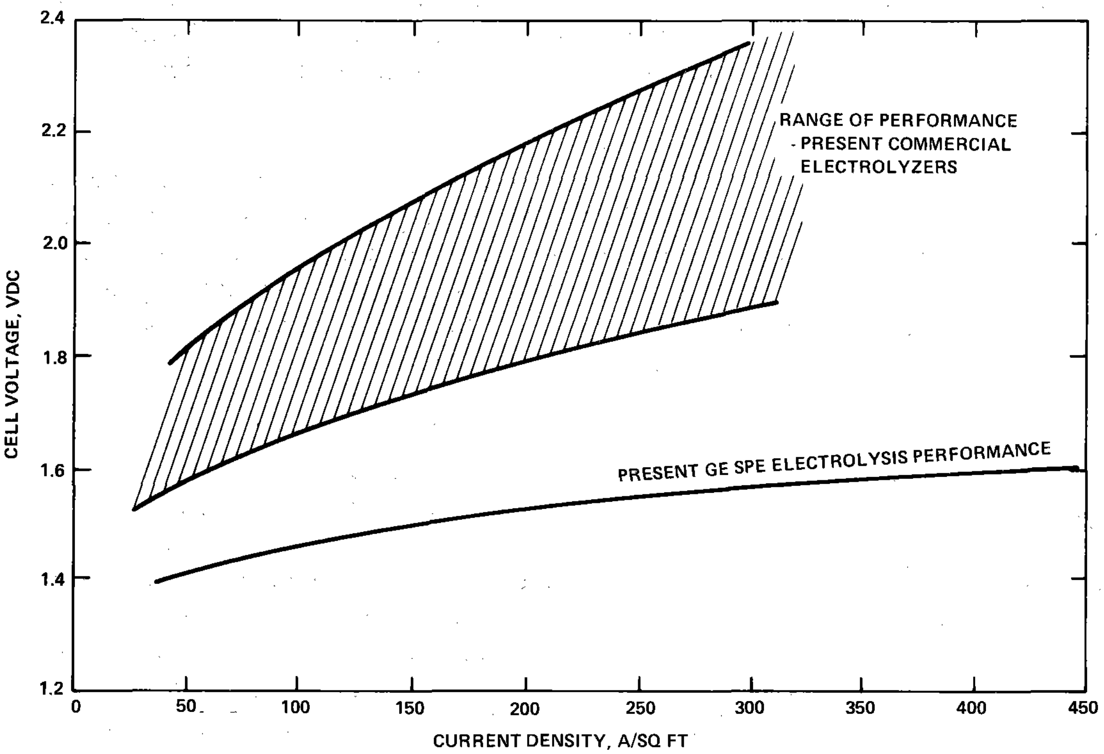

Figure 1. Electrolysis Cell Operating Performance Comparison.

The goals for the development program are to achieve an overall electrolysis system efficiency of 85 to 90% and a capital cost (in production) of less than $100/KW. If the program proceeds as planned, this capability is to be demonstrated in a 500 KW prototype system in 1980 and in a 5 MW system in 1981.

At the outset of the program, a preliminary system study was conducted to get a rough assessment of the possible economics of a large size SPE electrolysis plant. The system requirements assumed for the study were as follows:

Hydrogen Generation Rate	3250 lb/hr (58 MW out)
Pressure	40 atm
Temperature	100°F
Dew Point	-70°F
Capacity Variation	0 - 100% of rated
Duty Cycle	40%
Cost of Electricity	10 mil/KWH
Capital Cost Write-Off	17%/Yr

A schematic flow diagram for this system is shown in Figure 2 and an artist's conception of such an installation is shown in Figure 3. The floor space required for this system is approximately 40' x 90', excluding the transformer/rectifiers and switch gear. These require an additional 20' x 40', but can be installed outdoors and do not need building space.

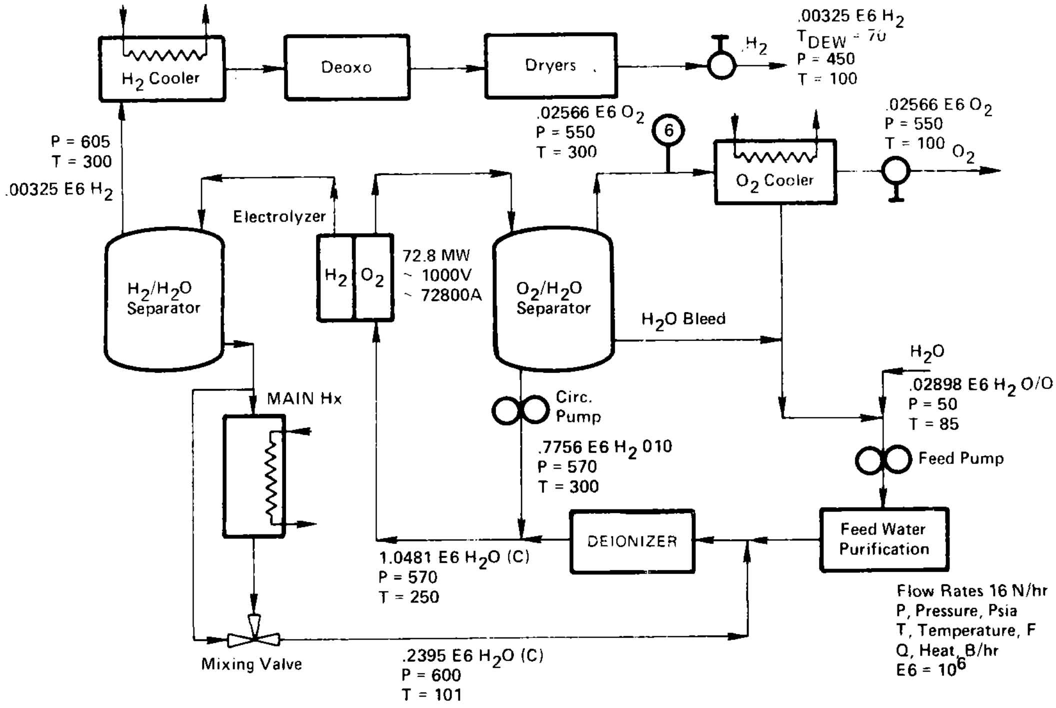

Figure 2. System Fluid Schematic.

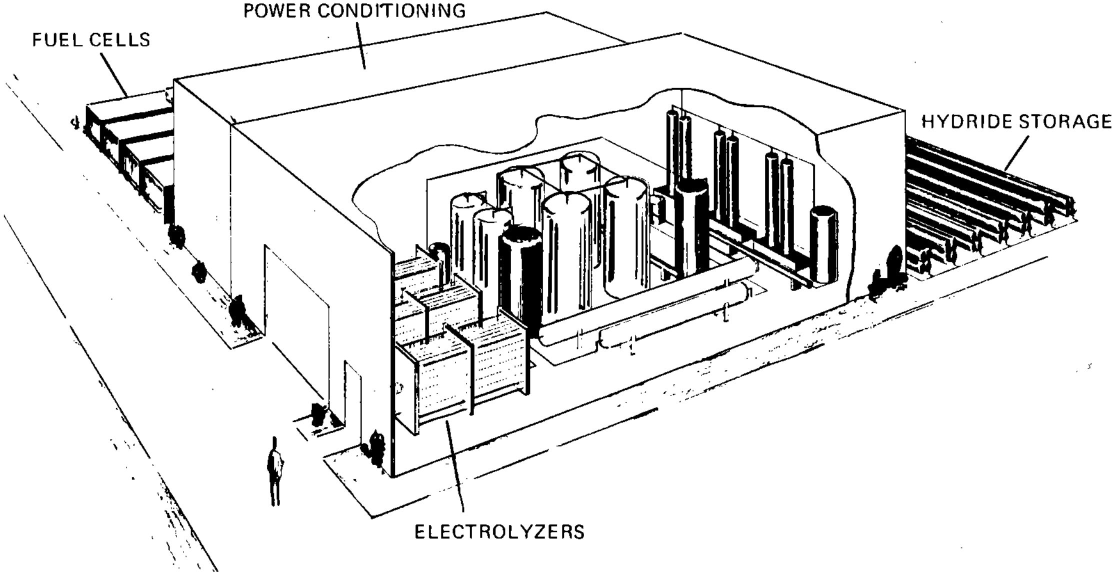

Figure 3. 58 MW SPE Electrolysis System for Energy Storage Substation.

The study did not factor in any future improvements in performance due to improved catalyst and SPE development. However, it did consider the development of the lower cost cell design and materials which we expect to realize as a result of the current development effort. The resulting calculation of system costs, using actual vendor quotations for most of the ancillary components, is shown in Table I, indicating a potential capital cost, excluding land and buildings, of less than \$80/KW. The total cost for the hydrogen, then, would be as shown in Figure 4 as a function of the electrical power cost. At 10 mil/KWH the cost of hydrogen would be between \$4 and \$5/10^6 BTU.

As an alternative to the use of off-peak power, the Institute of Gas Technology earlier this year reported on a study considering the use of a dedicated nuclear plant for production of electrolytic hydrogen, the results of which are shown in Table II. This also indicates that electrolytic hydrogen can be produced at a cost in the order of magnitude of \$5/10^6 BTU.

Table I. System Cost Breakdown.

	Cost* ($1000's)	Specific Cost $/KW**
Electrolysis Module	473	8.15
Power Conversion and Switch Gear	2484	42.76
Ancillary Equipment	1050	18.08
Installation***	480	8.26
Total	4487	77.25

* 1975 dollars

** Equivalent KW output based on HH V of hydrogen

*** Does not include land or buildings

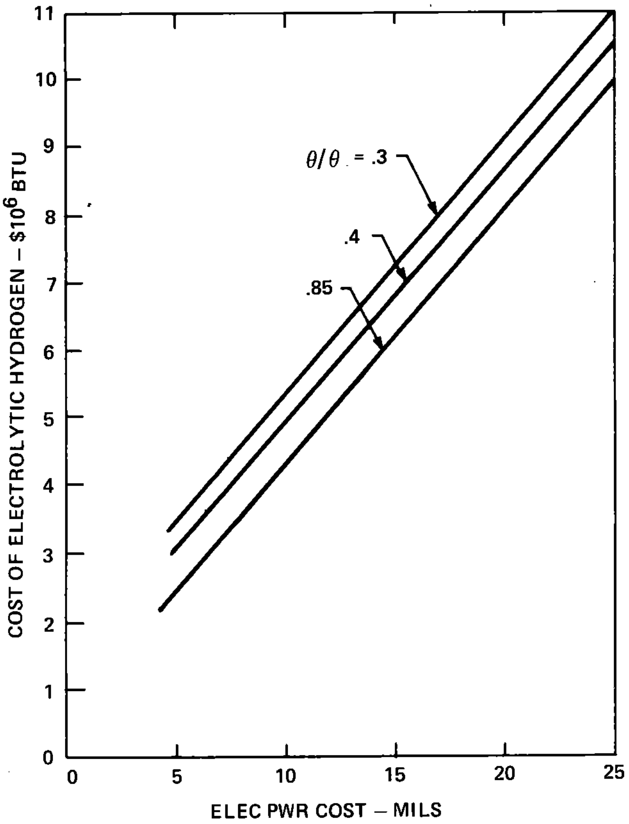

Figure 4. Gas Cost as Function of Off Peak Electric Power Cost.

Table II. Nuclear - Electrolytic Hydrogen Production Facility.

ESTIMATED ANNUAL COSTS*

Item	Annual Cost, $\$10^6$	$\$ / 10^6$ Btu of H_2 Produced
Nuclear-to-Electricity Subsystem		
Fuel	27.5	0.79
Operating and Maintenance	6.1	0.17
Fixed Capital Charges ($\$ 737 \times 10^6$ at 17.6%)	129.7	3.72
Subtotal	163.3	4.68
Electricity-to-Hydrogen Subsystem		
Production Materials	0.2	0.01
Water	0.8	0.02
Direct Labor	1.3	0.04
Maintenance Labor	1.4	0.04
Maintenance Supplies	1.4	0.04
Supervision	0.4	0.01
Administration and Overhead	5.8	0.17
Fixed Capital Charges ($\$ 69 \times 10^6$ at 17.6%)	12.1	0.35
Subtotal	23.4	0.68
Total Cost	186.7	5.36
Possible Oxygen By-Product Credit ($10/short ton)		.64
Net Cost		4.72

*from "Efficiency and Cost Advantages of an Advanced Technology Nuclear – Electrolytic Hydrogen – Energy Production Facility" – T.D. Donakowski & W.J.D. Escher. ACS Centennial Meeting, Apr 4-9, 1976.

The development program to date has concentrated on the technology areas required to achieve further improved performance and reduced cost. Figure 5 shows a comparison of of the past, current and projected performance curves. The goal for this program is to achieve the 1980 level shown on this figure and the development efforts to achieve it are directed toward higher temperature operation (up to 300°F), improved anode catalysts and reduced electrolyte resistance.

To date, cells have been operated at 300°F for more than 3000 hours without any serious problems, with a demonstrated performance improvement of around 150 MV at

1000 ASF. Life testing is continuing. In addition, a 50 to 100 MV improvement from newer catalyst materials and 50 to 75 MV from a possible new electrolyte material have been demonstrated in short term testing. Additional development and life tests are also continuing in these areas.

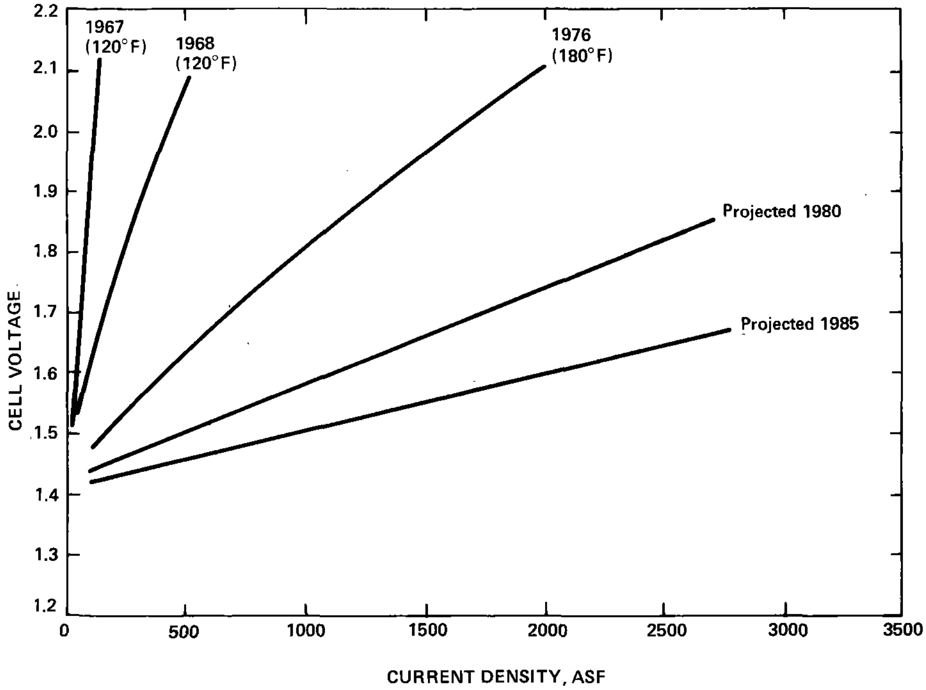

Figure 5. Historical and Projected Comparison of Performance Curves.

Thus it still appears that the performance goal for the 1980 period is realistic.

The major element of cost in the SPE cells as now designed for the aerospace applications is the expanded metal screen packages and gaskets used to form the fluid cavities and serve as current collectors. We now have on test a molded carbon current collector similar to those used in other electrochemical cells which represents an order of magnitude reduction in cost. Reduced noble metal catalyst loadings on the cathode have been demonstrated which would correspond to an additional \$30/ft and the new SPE material samples which are on test may represent an additional $10/ft^2 saving. Therefore, based on results which have been demonstrated to date, it is estimated that the production cost for the electrolyzer would be in the order of $80/ft^2 of active area as compared with $260/ft^2 for the original configuration. Continuing development during the course of this program is expected to further reduce these costs to approach the goal of $20/ft^2 by 1980.

The effect of the electrolyzer cost, in $/ft^2, on the cost of the resulting hydrogen produced is shown in Figure 6.

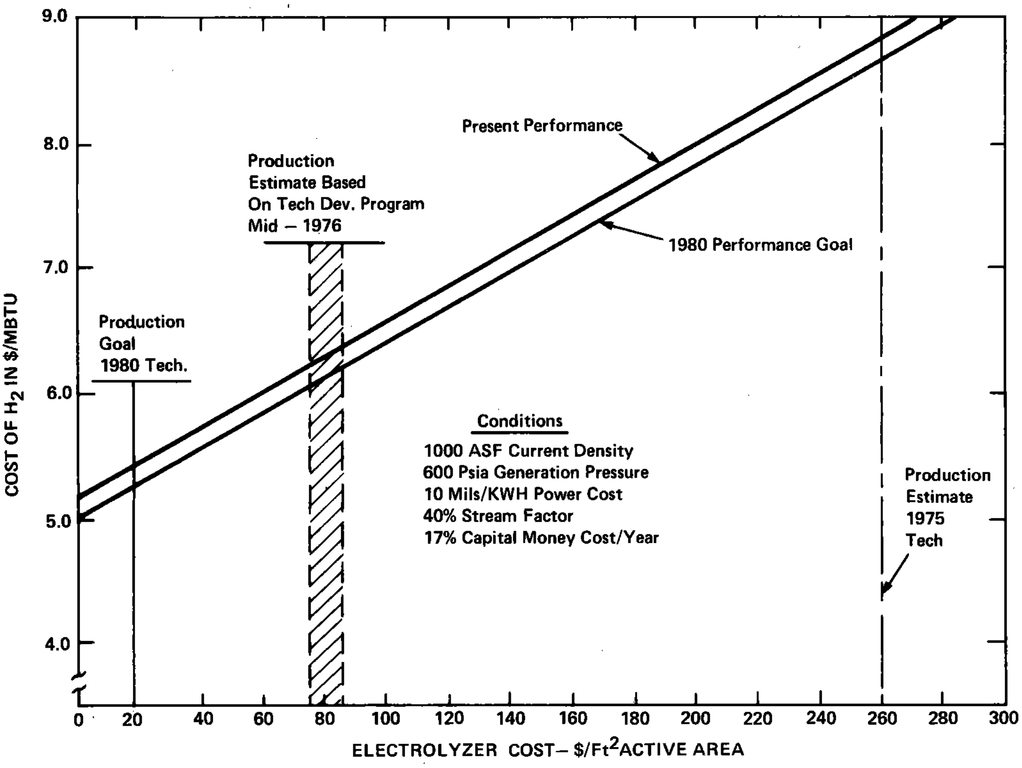

Figure 6. Cost of Hydrogen - SPE Water Electrolysis.

Thus the progress to date, essentially one year into the development program, has been most encouraging and has confirmed the feasibility of meeting the performance and economic goals and objectives. As mentioned previously, it is planned to demonstrate this capability in large scale systems in the 1980 - 1981 time period which we expect will establish electrolytic hydrogen as an economic alternative for energy storage and other energy related applications - including the possible use as a supplement to natural gas where availability of low cost electrical power exists or can be developed.

ADVANCED ALKALINE ELECTROLYSIS CELL MATRIX DEVELOPMENT

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Hydrogen plays a meaningful role in today's economy as an active chemical commodity. However, hydrogen prepared by electrolysis of water occupies only a small fraction of the market in that production costs are excessive compared to purchasing hydrogen from natural gas or hydrocarbon conversion plants. Although the electrolytic H_2 market segment is at present small, the primary attractiveness is that (a) quite high purity gas can be produced at negligible extra cost and at a price quite competitive with other supplies of high purity H_2, and (b) once the psychological barrier to user/H_2 producer is crossed, on-site generation of H_2 has much to offer with respect to production control, availability, and maintenance of purity.

To meet the existing specialty H_2 gas market needs, Teledyne Energy Systems is currently manufacturing two models of commercial alkaline electrolysis systems. The smaller HG series generators produce from one-quarter to one standard liter of H_2 per minute. These units are designed for laboratory use, to supply fuel for gas analysis instrumentation. The HS series produces from 20 to 200 standard liters of H_2 per minute and is used in industrial applications where high purity reducing atmospheres are necessary. From a module/cell performance viewpoint, these commercial models are not very efficient when compared to some of the high performance systems currently being built for military programs. By the same token, the commercial systems are relatively inexpensive in terms of dollars per square foot of cell area.

The role of H_2 in the future energy schemes, the needs for H_2 within tomorrow's technology, these areas have been discussed at length by many authors from many distinct viewpoints. The usefulness of electrolytic H_2 most analysts agree is tied to high production efficiencies, i.e., low cell voltages. Most analysis efforts have shown that the existing approaches to the commercial cell designs result in low capital costs. The major objective of this (or any) program is to lower the electrolytic cell operating voltage with no or quite low increases in the capital cost.

Two possible approaches to affect this significant improvement are (a) the use of alternative electrocatalysts, or (b) the increase in operating temperature from the present, historically established value.

At present, the large scale commercial electrolyzers employ nickel in a variety of shapes as the essential electrocatalysts are available and new catalyst systems are under study at several facilities, these advanced electrodes will cause an increased cell/module capital cost to be realized. The overall effect on cost of H_2 will be complicated by the cost of electricity, the cost of money, a subject previously discussed (1) and (2), and beyond this abstract.

Temperature increases are the more logical and immediate approach for improved H_2 production energetics. Several previous studies have shown the voltage efficiency improves linearly with increasing temperature. This general effect is observed with a variety of electrocatalysts as one would expect from both thermodynamic and electrokinetic considerations. Most of the existing cell materials are satisfactory with respect to performance and life characteristics at moderate and intermediate temperatures. The present commercial inter-electrode separator (or cell matrix) does have a life limiting temperature of approximately 82°C (180°F). The current work sponsored by ERDA/BNL is concerned with establishing an acceptable substitute for this asbestos cell matrix, capable of withstanding higher temperatures and thus improving overall cell efficiencies.

From previous work with structural polymers (3), two materials were selected for the initial evaluation. Polysulfone, supplied by Union Carbide, and polyarylsulfone, purchased from Carborundum Plastics, are processed from solution into thin fiber form by FRL (Fiber Research Laboratories). This 13 μm (0.51 mil) thread/yard is subsequently cut and processed into a matt or porous matrix 0.076 cm (0.03 in.) thick for evaluation of pore structure, compressive stress-strain and electrochemical characteristics. Additionally, lengths of the parent yarn are being subjected to aging studies with the KOH/H_2, KOH/O_2 environments. Chemical changes as well as mechanical characteristics changes are being measured to evaluate the material effectiveness.

This is the essence of the Task One effort. The Task Two effort will continue the evaluation of two additional polymers, Polyphenylenesulfide (RYTON) produced by Phillips Petroleum and Polyethersulfone (PES) produced by ICI America. The RYTON polymer requires melt spinning technology and it is anticipated the PES fiber would be prepared via melt technology as reference.

With an advanced high temperature matrix established, the second phase of the program, the construction and life testing of large area, high temperature, high efficiency electrolysis cells would be conducted. Satisfactory performance for 4000 hours (minimum) would allow sufficient basis for pilot plant demonstration when warranted.

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SELECTION AND EVALUATION OF CELL MATERIALS FOR ADVANCED WATER ELECTROLYZERS*

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1. Introduction

For hydrogen production by water electrolysis to be competitive with conventional methods, it is necessary to reduce capital costs of plants and approach 100% energy efficiencies. The main factors which limit the current densities in water electrolysis cells and reduce the energy efficiencies are the slowness of the hydrogen and oxygen evolution reactions at the electrodes and the ohmic losses in the electrolyte. Studies of hydrogen and oxygen overpotential at nickel electrodes, from potassium hydroxide, as a function of temperature in the range from 80 to 265°C shows that by simply raising the operating temperature from 80°C, which is commonly used in commercial water electrolyzers, to about 150°C, it should be possible to lower the cell potential for water electrolysis from about 2 volts (energy efficiency about 75%) to about 1.6 volts ($E > 90\%$). By increasing the operating temperature, one also lowers the ohmic losses in the cell. Teledyne Energy Systems is following this approach in the development of advanced alkaline water electrolyzers. A novel but even more promising route to developing low cost, high efficiency electrolyzers is being followed by the General Electric Company. By impregnating high surface area catalyst particles on a thin layer of a highly acidic solid polymer electrolyte, activation and ohmic overpotential losses are minimized

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* This work was done under the auspices of the United States Energy Research and Development Administration

even at extremely high current densities (>1 amp cm^{-2}). The central problem in the development of efficient advanced alkaline or acid water electrolysis cell operating at temperatures over 100°C is in finding suitable cell materials (e.g. electrocatalysts, separator materials, current collectors, cell frames, gaskets, seals, etc.). The present paper summarizes some aspects of these efforts being made at Brookhaven National Laboratory. (1-3)

2. Research and Development of Advanced Alkaline Water Electrolysis Cells Operating at Temperatures 120 and 150°C.

One of the most serious problems in raising the operating temperature from 80°C to over 100°C is in finding a substitute for asbestos as the separator material. Over 35 organic and inorganic materials have been tested in KOH as the electrolyte. Potassium titanate and Nafion are the most promising. With Nafion as the separator material, ohmic losses are less with NaOH than with KOH as the electrolyte for the same ionic concentration in both cases. A potential candidate for cell construction materials is polysulfone for cells operating at temperatures of 120-150°C. The main problem encountered to date in the construction of small test cells is in finding a gasket material, stable in the strong alkaline environment. Viton gaskets are unstable, while ethylene-propylene gaskets are resistant to chemicals and heat but are poor sealants. By measurements of half-cell potentials as a function of time, it was shown that the cathode performance is affected to a considerably greater extent than that of the anode by electrolyte contamination. The potential-current density relations for water electrolysis, in cells designed and fabricated at BNL with potassium titanate as a separator, as a function of temperature are shown in Figure 1. From the point of view of finding suitable cell construction materials at a reasonably improved cell performance over that at 80°C, an operating temperature of 120°C is recommended.

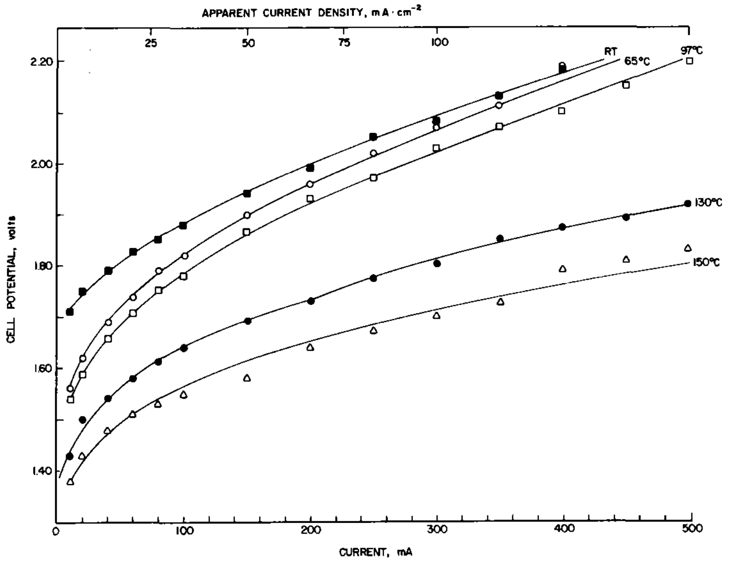

Fig. 1 CELL POTENTIAL-CURRENT DENSITY RELATIONS FOR WATER ELECTROLYSIS FROM 35% KOH WITH NICKEL ELECTRODES AND POTASSIUM TITANATE SEPARATOR

3. Electrocatalysis of the Oxygen Evolution Reaction

Activation overpotential for the oxygen evolution reaction is one of the main reasons for efficiency losses in water electrolysis cells. It is more significant in acid than in alkaline electrolytes. The choice of electrocatalysts in the acid environment is restricted to the noble metals or their alloys. In acid electrolytes, the exchange current density for oxygen evolution on Ir is about 1000 times higher than that on Pt. It is probable that the metal like conductivity of the IrO_2 film, which is probably formed on Ir in the potential region for oxygen evolution, contributes to its catalytic activity. Nickel is the best known electrocatalyst for the oxygen evolution reaction from alkaline solution. Recently, a number of alloys of Ni with Ir, Ru, W, Ti, Cu, Ag and Fe were evaluated as oxygen electrodes. Slight improvements in electrocatalytic activities were observed with the Ni-Ir and Ni-Ru alloys and with the intermetallic compound Ni_3Ti.

4. Mixed Oxides as Oxygen Electrodes

The oxygen electrode reactions are of special importance in water electrolysis, fuel cells and some secondary battery systems such as zinc-air, and iron-air. The only hope for developing reversible oxygen is by using oxides. Oxides with a spinel or perovskite structure are attractive because of their reasonably high electronic conductivity and stability in electrolyte environments. Three types of oxides, NiOx, $NiCo_2O_4$ (with spinel structure) and RuO_2/TiO_2 (with rutile structures) were investigated as anodes for oxygen evolution from KOH solution. The transfer coefficients for O_2 evolution on these materials is about twice that on nickel. The electrodes were prepared by the thermal decomposition or the freeze drying method. Teflon bonded electrodes of the latter type with $NiCo_2O_4$ showed considerable promise.

5. Optical and Electrochemical Properties of Films Formed on Metals in the Oxygen Evolution Region

The oxide layer, formed on an electrode surface during the anodic polarization, can be of the major sources of efficiency losses in water electrolyzers. The properties of this layer, such as electronic conductivity and thickness, may determine the kinetics of the oxygen evolution reaction which always takes place on oxide covered films. For this reaction on a mechanically polished Pt in IN H_2SO_4, ellipsometric studies were carried out in situ to characterize the anodized oxide films. After polarization at 2.2 volts versus the reversible hydrogen electrode, two types of oxide films, designed as α and β, were found to be present on the electrode surface. Film β, which was found to grow on film α, was found to be a poor electronic conductor and porous. However, this film was found to catalyze the oxygen evolution reaction. Its appearance causes a decrease of the observed Tafel slope from 115 to 80 mV.

Prior to the oxygen evolution reaction, the anodic oxide layer formed on Ni electrode in IN KOH was investigated using ellipsometry. The plots of changes of ellipsometric parameters vs. the electrode potential are shown in Figure 2. The initial formation of $Ni(OH)_2$ layer

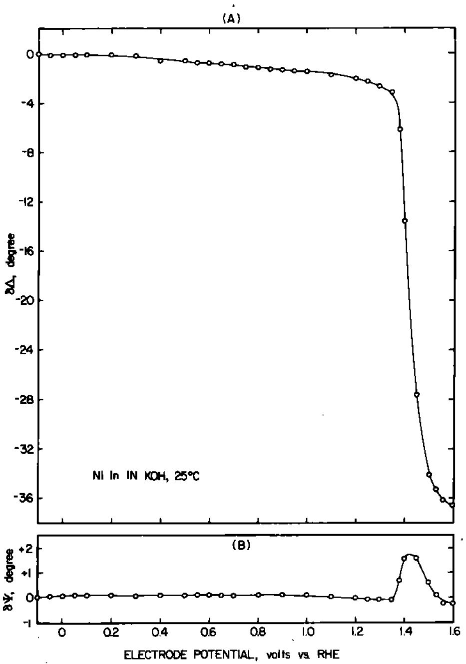

Fig. 2 VARIATION OF THE ELLIPSOMETRIC PARAMETERS WITH THE POTENTIAL OF MECHANICALLY POLISHED NI ELECTRODE ($\phi = 65^{\circ}$ and $\lambda = 5461$ Å)

(starting at ~ 0.2V) and the further oxidation of $Ni(OH)_2$ to β-NiOOH in the potential range of 0.8 ~ 1.3V results in steady and slight decrease in Δ, but no significant change in ψ. However, at the potentials higher than 1.38V, the measured Δ and ψ undergo remarkable changes arising from the formation of β-NiOOH on the Ni substrate. These observations indicate that the $Ni(OH)_2$ layer formed at lower potentials is thin (a few Å) and non-absorbing film, while the β-NiOOH film on which the oxygen evolution reaction takes place is light absorbing and thus a good electronic conductor. On anodization of Ni-electrode at 1.50V for 20 hrs, a layer of β-NiOOH of ~ 250A in thickness was found exhibiting the optical constants as follows: n = ~ 1.41 and K = 0.14 ± 0.02. The Tafel plot for O_2 evolution on this oxide layer was determined using the steady state potentiostatic method. Compared with Pt electrode on which poorly conducting films are observed (for the film β, K = 0.00 ~ 0.01), the measured exchange current density for O_2 evolution reaction on Ni electrode are higher than that for this reaction on Pt electrode by an order of $10^3 \sim 10^4$. These results show that the electronic conductivity of oxide films plays a significant role in the determination of electrocatalytic activities of electrode materials for O_2 evolution.

6. Proposed Studies for FY 1977

The three major tasks in FY 1977 will include research and development of (i) solid polymer electrolyte electrolysis cells; (ii) advanced alkaline electrolysis cells; and (iii) mixed oxides as oxygen electrodes. In the first, the subtasks will deal with the GE cell, i.e., determination of efficiencies for hydrogen production, electrocatalysis, and evaluation of anode current collector materials. Studies will also be extended on the correlations between optical properties of films formed on Pt, Ir and Ru, and their electrocatalytic activity in trifluoro methane sulfonic acid. In the second task, emphasis will be on the design and fabrication of single cells for operation at about 120°C for the long-term study of separator and construction materials. Electrocatalysis and ellipsometric studies will also be included. The third task is of vital importance to water electrolyzers, fuel cells, and secondary metal-air batteries. Transition metal and rare earth oxides will be studied, including life tests on $NiCo_2O_4$, and correlations between electrocatalytic activity and magnetic properties will be investigated.

Acknowledgements

The authors wish to thank Drs. S. Gottesfeld, M. H. Miles, and A. C. C. Tseung for their contributions to this work. The work on mixed oxides was initiated in our Laboratory by Dr. G. Singh (deceased). Discussions and helpful suggestions made by Mr. F. J. Salzano are acknowledged.

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A PROPOSED FAILURE MECHANISM OF ASBESTOS SEPARATOR MATERIAL

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The failure of asbestos separator material at elevated temperatures (>105°C) has generally been attributed to an increase in the dissolution rate of asbestos in the potassium hydroxide electrolyte. A recent paper presented at the First World Hydrogen Energy Conference (1) suggested that the potassium hydroxide electrolyte could be saturated by dissolving potassium silicates and effectively reduce the dissolution rate. Various opinions exist on this phenomenon.

Failure occurs when holes develop in the separator that allow the passage of electrolysis product gasses from one side of the cell to the other. The mechanisms by which the holes develop are not rigorously understood. Initial investigations in our project indicated two important factors on which the scope of the project was based. First, observation by scanning electron microscopy at 200X and 2000X showed no physical difference in fibers of an unexposed separator and those of a totally decomposed separator. This apparent similarity in fiber morphology indicated no severe chemical attack. Secondly, the presence of nucleated gas pockets within the asbestos diaphragm was observed. Research efforts were then undertaken to investigate the effect of these gas pockets on separator instability.

The number and size of nucleated gas pockets within the diaphragm increased with temperature as predicted by nucleation and growth theory. The nucleated gasses are believed to be gasses dissolved in the electrolyte and/or water vapor particularly when the electrolyte approaches its boiling temperature. The increase in nucleated gas pockets with temperature was investigated by estimating the percentage of surface area containing bubble pockets of a thin diaphragm. An inverse correlation was found for the approximate percentage of surface area affected and the wet tensile strength of the asbestos separator as a function of temperature. The correlation is illustrated in Figure 1.

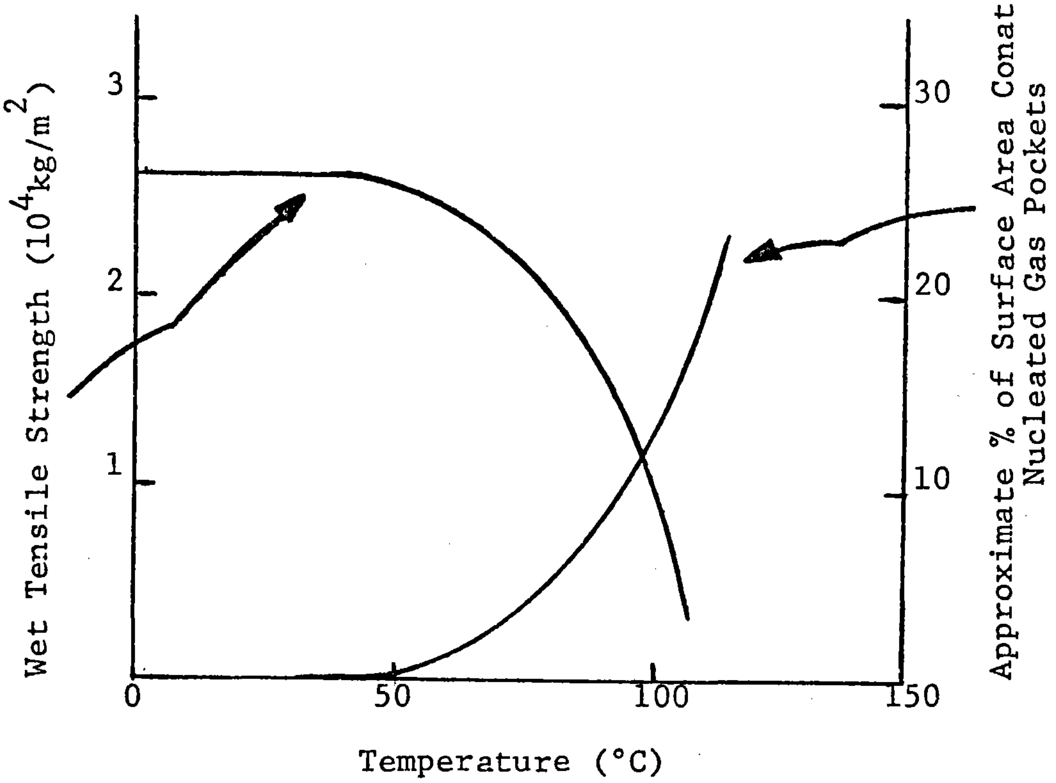


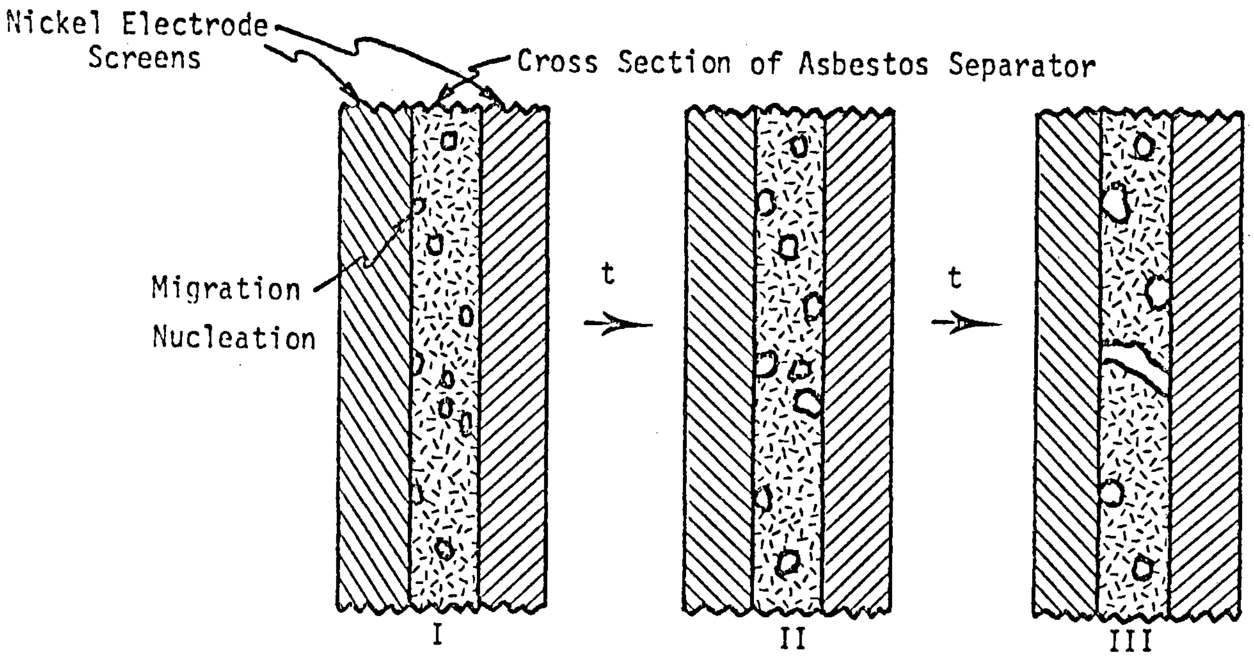
Figure 1. Correlation of the wet tensile strength of asbestos separator material and the amount of nucleated gas pockets present in the separator as a function of temperature.

A second effect was noticed in a separator which had been subjected to electrolysis. Small gas pockets were observed on the surface of the matrix. These gas pockets are formed by the migration of electrolysis product gasses into the separator. This effect was observed in a laboratory cell where the electrode screens pressed lightly against the separator and the separator had a maximum pore size of approximately 10μ. The effect was also observed for asbestos diaphragm with a maximum pore size of approximately 5μ. The effects of temperature and electrolysis time on the wet tensile strength of the asbestos diaphragm were studied and related to the number of gas pockets present from internal nucleation and product gas migration. The internal nucleation was found to be primarily temperature dependent. The migration effect increased with temperature, electrolysis time and current density.

As adjacent gas pockets increase in size they tend to accumulate. By the accumulation of migration and nucleation pockets a hole develops through the separator as illustrated in Figure 2. It has not been determined if the mechanisms of gas pocket formation and accumulation are responsible for hole formation in commercial asbestos diaphragms. However, to whatever extent they do occur they will contribute to the failure of the diaphragm. Furthermore, both of the gas pocket mechanisms are accelerated at higher temperatures.

A second phase of the research attempted to modify the asbestos separator such that the nucleation and migration mechanisms would be discouraged. The application of a suitable wetting agent would reduce nucleation sites and increase the diaphragm's hydrophillicity. This would decrease the likelihood of bubbles clinging to the separator and thus reduce the migration effect. An accelerated test was designed to evaluate the ability of various wetting agents to discourage nucleation of gasses within the separator. Asbestos was supported in plexiglass "picture frame" brackets, submerged in 30 wt. % KOH and subjected to increasing temperature. Nucleation was first noticeable in an untreated asbestos diaphragm around 3/4 of the boiling temperature (approximately 80^{o}C for 30 wt. % KOH at atmospheric pressure) and increased rapidly from that point. Rupture occurred near the boiling temperature in less than 10 minutes for untreated asbestos. Treatment with non-volatile surfactants such as quaternary ammonia salts and other organic wetting agents did not prolong the failure to any great extent.

Physical Failure Mechanism in Electrolysis Cell



I - Migration begins adjacent to the electrodes
II - With time the migration proceeds, nucleation and migration pockets begin to accumalate
III - With time failure occurs, complete hole through separator

Figure 2. Hole formation by gas pocket accumulation

A fairly new and uncommon inorganic wetting agent, tin hydrosol, was also used as a treatment and the results were encouraging. The separators treated with the tin hydrosol lasted much longer than those asbestos diaphragms receiving other treatment and in most cases survived the accelerated test without asbestos separator failure. No evidence of nucleated gasses was observed within the tin hydrosol treated diaphragms. At this point an investigation to determine if the tin hydrosol treatment had strengthened the asbestos separator material began. This was accomplished by measuring the wet tensile strength of treated and untreated asbestos. An increase in wet tensile strength was observed and was found to increase with tin hydrosol concentration to a maximum at around 10% concentration. The degree of polymerization (D.P.) of the polymeric tin hydrosol was another variable investigated for its effect on the wet tensile strength (T.S.) of asbestos. It was found that a higher D.P. resulted in a higher wet T.S.

At this point, a process was developed to effectively and readily treat asbestos diaphragms with tin hydrosol for commercial evaluation. Some degree of difficulty was experienced at first in treating the larger and heavier commercial diaphragms, but a successful process was developed. To treat the separators, tin hydrosol was aspirated through them and then they were rinsed in the same manner. Polymerization of the tin hydrosol and drying of the diaphragm was accomplished by forced hot air. The process allowed treatment of the commercial diaphragms without damaging or distorting them as previously employed treatment methods did. A commercial evaluation was then done. These tests indicated that the tin hydrosol had increased the diaphragm resistance by about 5%. However, the diaphragms sent for commercial evaluation were treated with a high concentration of tin hydrosol (about 10%) and had a high D.P. Further tests were conducted at U. Va. to determine if a lighter treatment would be effective. The successful prevention of failure in the accelerated test occurred for concentrations of tin hydrosol above approximately 3% and for all but the very small D.P.'s.

At this point, an investigation began to determine an optimum concentration and D.P. of tin hydrosol such that the diaphragm resistance could be minimized. It is expected that the % increase in diaphragm resistance can be reduced by treatment with a lower concentration and/or lower D.P. of tin hydrosol. Upon successful optimization and evaluation at U. Va. more diaphragms will be obtained, treated, and resubmitted for commercial evaluation. Following successful evaluation, life tests will be conducted in order to investigate the treatment's effectiveness in preventing the physical mechanisms from causing failure.

During the next phase of our research we plan to carry out the following:

1. Optimization of tin hydrosol treatment for lowest possible increase in separator contribution to cell resistance.

2. Commercial evaluation of improved treatment

3. Begin life tests.

4. High temperature evaluation of effectiveness of tin hydrosol treatment.

5. Investigation of the individual electrode overpotentials as affected by the presence of various concentrations and D.P.'s of tin hydrosol.

6. Scanning electron microscopic study of the effect of the tin hydrosol treatment on the porosity of asbestos diaphragms.

7. Investigation of the effectiveness of other available hydrosol wetting agents as treatments for asbestos separator material.

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SEASONAL ENERGY STORAGE REQUIREMENTS

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The objective of this project is the assessment of seasonal energy storage requirements, and therefore the conclusions drawn from its development have a much broader relevance than to just chemical energy storage. None of the tasks are directly related to an assessment of any particular storage system; instead an attempt has been made to provide parameters for the realistic evaluation of storage options. Quantification of the residential heating and cooling markets, including their seasonal variations, shows how much storage is actually required and when. In addition, a survey of oil and gas storage economics provides a much needed guideline as to the level that storage costs must attain to be economically feasible. Finally, a survey of slow-withdrawal electrical-energy storage systems and their applicability to seasonal variations in demand is made to answer the questions that are logically generated from an analysis of the demand and storage-economic sections of the report.

Variations in Energy Demand for Residential Space-Heating and Cooling

Time and economic limitations precluded any attempt to derive functional relationships for residential space-heating and cooling demands. Therefore, a methodology relying on published data to ascertain residential energy sales was developed. Although it is important to be able to present energy sales data and storage requirements on a national basis, quantification of the data in a national overview would only mask the disparities in regional seasonal variations. Therefore, the data were developed from a regional perspective and then combined to form the national overview.

An analysis of the data used in the study shows that more than 95% of residential heating demand is satisfied by four fuels: natural gas, fuel oil, liquefied petroleum gas (LPG), and electricity. Natural gas is by far the largest source of residential heating energy, accounting for more than 60% of the total sales for space-heating of the four major fuels. Fuel oil is second largest with 29% of demand, and the remainder is supplied by LPG (7%) and electricity (3%). However, recent trends indicate that electricity is assuming an increasingly larger sector of the new home market; more new homes were built in 1974 to heat with electricity (49%) than with any other fuel.

These additions to the rolls of electric heating are not causing any increase in electricity prices because they are increasing the load factor for generating capacity built to serve peak cooling needs. However, a changeover to electricity as the primary residential heating fuel would cause a shift in peak demand from summer to winter. Because of the huge disparity between the heating and cooling loads, this changeover would face major obstacles, such as a lack of storage capability, low-load factor, and inefficient conversion of primary fuels, which would result in prohibitively high prices.

For example, the highest regional peak and annual heating sales occurred in the East North Central region where energy sales in the peak month reached over 333 trillion Btu and annual energy sales for heating were estimated at almost 1735 trillion Btu. In that same region, peak monthly cooling demand was just over 8 trillion Btu while total annual cooling sales were only 19 trillion Btu. If all residential heating were done by electrical resistance heaters, almost 107,000 megawatts of generating capacity operating at a 75% capacity factor would be required, or almost 25 times the amount necessary to provide for the peak summer cooling month.

The highest regional peak cooling sales occurred in the West South Central region where the monthly peak was over 18 trillion Btu and annual sales of energy for cooling were 74 trillion Btu. Heating sales for the peak month in the same region were over 90 trillion Btu while annual heating energy sales were only 355 trillion Btu. This region is more adaptable to an "all-electric" changeover but would still require 3 times as much generating capacity to service a winter peak relative to a summer peak.

The residential energy consumption data generated in the study shows that in 1975 winter peak heating demand was 12 times greater than summer peak cooling demand. (See Figure 1.) Annual energy sales for heating in 1975 were 19 times as large as air-conditioning energy sales for the same year. These data represent actual sales to residential customers and do not reflect the efficiencies at which these fuels were consumed. For purposes of illustrating the effect of a changeover to electricity as the primary residential heating fuel, we considered two electrification scenarios: all-electric resistance heating and all-electric heat pump. The all-electric resistance heating and air-conditioning option resulted in reduced consumption of secondary energy in the residential sector by almost 40%, but this scenario still required an unacceptable increase in necessary electric generating capacity. The other scenario assumed all heating was done with electric heat pumps having an average performance coefficient of 2.0; this would have reduced 1975 secondary energy sales for heating to less than 2000 trillion Btu. This is less than one-third of the actual combined primary and secondary energy sales for residential space-heating in 1975. The extent of the reduction in seasonal variation in monthly energy demand resulting from each of these scenarios is graphically displayed in Figure 2.

Three scenarios for future growth in residential energy demand for space-heating and cooling were considered. For the sake of brevity, only the high- and low-demand scenarios will be presented here.

The low-demand scenario assumes that the average growth in heating and cooling demand experienced from 1970 to 1975 will continue through 1980. Thereafter,

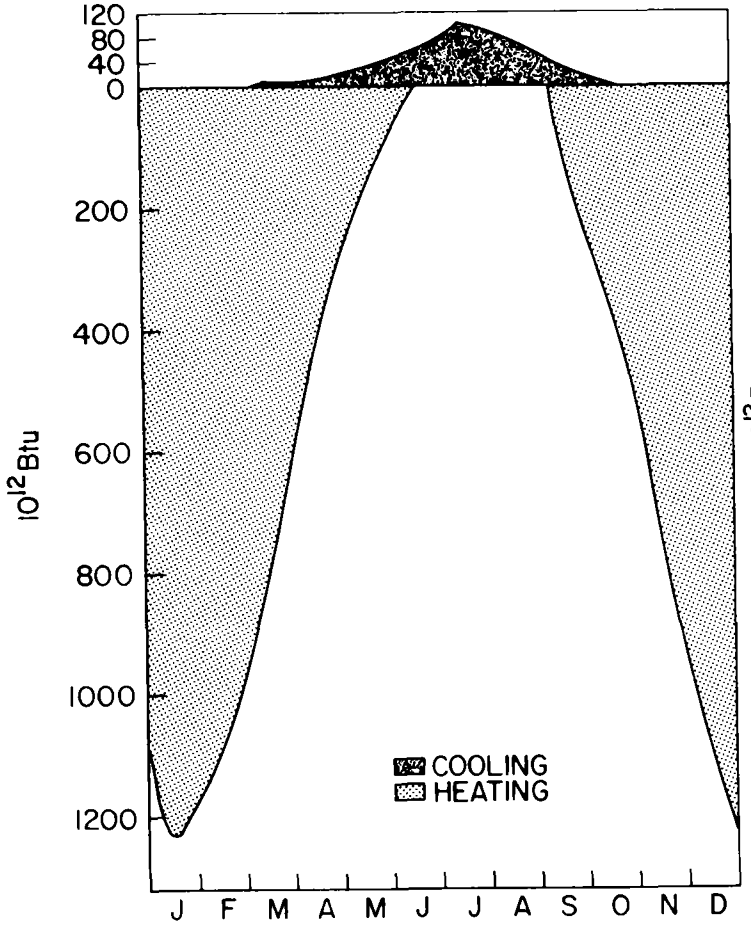

FIGURE 1

SEASONAL ENERGY SALES FOR
RESIDENTIAL HEATING AND
COOLING, 1975

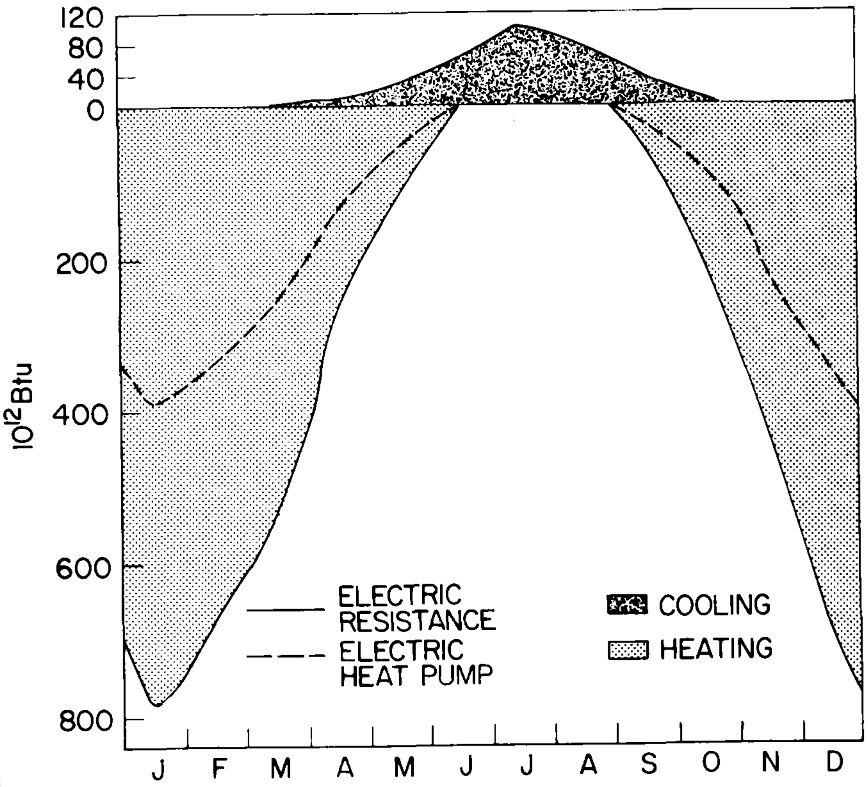

FIGURE 2

SEASONAL ENERGY SALES FOR
RESIDENTIAL HEATING AND
COOLING, 1975 (Under an
Electrification Scenario)

reduced growth rates are estimated through 1990 because of an expected reduction in the rate of construction of new housing, impending saturation of the cooling market, changes in new construction, and retrofitting insulation in existing dwellings. Air-conditioning energy sales would still increase at a faster rate than space-heating energy sales, reducing the disparity between them from 19:1 in 1975 to 10:1 in 1990. A further reduction in that ratio to approximately 6.5:1 would occur if electrical resistance became the sole source of residential space-heating energy.

The high space-heating demand scenario forecasts an increase in space-heating growth of over 50% between 1975 and 1990. It used the natural gas consumption forecasts prepared by the Gas Requirements Committee and published by the University of Denver Research Institute. Forecasts for growth in residential space-heating consumption of other fuels were adopted from the Federal Energy Administration's "best guess" or "$13 reference case," as presented in their 1976 National Energy Outlook released earlier this year. The effect of the growth in consumption of these fuels on seasonal monthly demand disparity would also reduce the ratio of space-heating energy sales to cooling-energy sales from the 1975 level of 19:1 to a 1990 level of 14:1. If all residential space heating were done by electrical resistance heating, the disparity would be reduced to a ratio of about 8:1.

Summarizing the conclusions of this analysis, seasonal monthly demand disparities are likely to be reduced under any reasonable space-heating growth scenario. This will make an electrification scenario more reasonable, but apparently still impractical without the widespread adoption of electric heat pumps and the ability to store at least a third of the energy required for winter space-heating.

Natural Gas and Oil Storage

The maximum capacity of natural gas reservoirs in the contiguous United States was over 6600 trillion Btu at the end of 1975. This capacity is well in excess of annual residential consumption, but is only about 40% of gas utility industry sales. However, it is in excess of variable sales levels related to weather, which are about 4000 trillion Btu. Still, all of the reservoir capacity is not available to meet demand. A portion of the total injected gas is required to maintain pressure levels and is termed "cushion gas." This portion amounted to approximately 2300 trillion Btu in 1975, but the real drawable reservoir capacity still exceeded total seasonal energy heating sales by a small margin.

The costs for underground storage, however, are not insignificant. A typical pipeline operation of great magnitude was recently estimated to contain imbedded historical capital investment in storage facilities of $1.75 to $1.80 per 1000 CF of gas withdrawn annually, or about $0.88 per 1000 CF of gas injected and withdrawn on a total basis. Operating and maintenance expenses for the storage operations (excluding depreciation, return, income taxes, etc.) amounted to approximately $0.09 per combined 1000 CF of gas withdrawn from storage use. Depreciation, including amortization of the approximately 60% of total reservoir gas that was utilized as cushion gas, would amount to about $0.07 per 1000 CF withdrawn, and the return and income taxes portion of the cost of service are each between $0.205 and $0.210/1000 CF. The total cost of service for underground storage services, not including the cost of gas that was already purchased by the customer separately, is between $0.65 and $0.70/1000 CF for large-scale operation of an existing, relatively mature, and hence low-cost, installation. Recently reported was an expansion of storage facilities requiring an investment of approximately $1.78 for each 1000 CF of added storage capability when growing from 123 billion CF to 134 billion CF (1000 CF $\approx$ 1 million Btu).

Distillate fuel oil is the second most popular energy form in the residential heating market. Because it is used for little else in the residential sector, peak residential seasonal demand is even more pronounced than for natural gas. The National Petroleum Council (NPC) estimates that minimum operating inventory levels for distillate fuel oil are 100 million bbl, with an additional 120 million bbl (primarily east of the Rockies) being required to build essential inventories by the beginning of the peak season (November).

Distillate fuel oil inventories and storage capacity are surveyed by the NPC on a periodic basis; the latest reports, released in 1974, showed the following: Distillate fuel oil inventories reported to the NPC as of September 30, 1973, as compared to those reported as of September 30, 1969, increased to 187.1 million bbl from 185.4 million bbl -- an increase of only 1.7 million bbl. For the same period, the increase in unavailable stocks (those not available for consumption, but needed to insure continuity of operation) was 1.1 million bbl. Seasonal variations for distillate fuel oil from March 31, 1973 to September 30, 1973, showed an increase of 76.8 million bbl, from 110.3 million bbl to 187.1 million bbl. According to the NPC, an additional 45 to 50 million bbl of distillates were added by November 1, 1973. Therefore, seasonal buildup was more than half completed by September 30. Storage capacity assigned to distillates in March of 1973 was 284.7 million bbl; by September it had increased to 302.1 million bbl.

Refinery and terminal storage capacity serves the dual purpose of enabling the oil refining industry to meet summer peak gasoline demand and winter peak heating demand. After depleting gasoline inventory during the summer peak demand period, available storage is loaded with fuel oil in anticipation of winter peak heating demand. A typical storage installation, including pumps and loading facilities, costs approximately $4.75/bbl to install. This figure can increase to as much as $15/bbl, given the diseconomies of scale. If the storage facilities are fully utilized (fully loaded to meet peak summer gasoline demand and peak winter fuel oil demand), the cost of operating the storage facility, exclusive of investment in inventory, will add 1.5¢ to 2¢/gal to the cost of fuel oil stored at the installation. Similarly, storage at smaller installations can add as much as 4.5¢

to 5¢ for every gallon. As a rule of thumb, the cost per gallon multiplied by a factor of 7.2 yields the cost per million Btu.

Fuel oil storage at the refinery does not describe the total fuel oil storage operation, as refinery inventories are transferred to terminal inventories and from there to oil storage tanks in the residential consumer's home. If we assume the average residential storage capacity to be 500 gallons, and to require two fills to meet seasonal heating requirements (140 million Btu), the homeowner pays more than a penny per gallon to amortize the installation cost of storage over a 20-year life. Depending on the size of the storage facilities throughout the transfer of fuel oil from the refinery to the homeowner, storage can add between 5¢ and 10¢ to the cost of each gallon of fuel oil consumed by residential customers.

Electrical Energy Storage Options

The last portion of the study briefly describes electrical energy storage systems and their applicability to seasonal storage. While none except pumped-hydro are in commercial operation, only hydrogen and the operation of batteries are currently advanced enough to meet electrical energy storage requirements. Pumped-hydro is already economical but is limited in site availability. Batteries large enough to meet seasonal load variations require prohibitively high initial capital investment. The primary shortcoming of hydrogen is low overall efficiency. None of the technically feasible storage alternatives presents a clear-cut economic advantage at this point, precluding a judgement as to the most advantageous storage system.

PRODUCTION ECONOMICS FOR HYDROGEN, AMMONIA, AND METHANOL DURING THE 1980-2000 PERIOD

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The objectives of this study are:

(1) to predict quantities of hydrogen needed in the U.S. during the 1980-2000 period for refinery hydrogen, ammonia, methanol, the manufacture of other chemicals, and for uses requiring ultrahigh purity hydrogen that are usually provided by electrolytic hydrogen;

(2) to compare hydrogen, ammonia, and methanol manufacturing economics during this period for natural gas reforming, resid partial oxidation, coal gasification, and electrolysis;

(3) to predict quantities of industrial hydrogen that are likely to be produced by each process during this period assuming manufacturing economics will control the choice of processes;

(4) to identify technology developments that are likely to have an impact during this period in reducing the consumption of natural gas and petroleum in the manufacture of hydrogen; and

(5) to suggest how ERDA resources could be used to develop technology that would reduce the consumption of natural gas and petroleum for hydrogen manufacture.

The process economics data used in this study were published as multi-client studies by Chem Systems, Inc. in November, 1974 and December, 1975. Our study was recently completed and a draft report was sent to Brookhaven for review. A few days later we were informed by Chem Systems that their process economics data had been revised to reflect the unprecedented capital cost escalations that will occur in the 1975-80 period. These revisions resulted in increasing the investments in hydrogen manufacturing plants by 57% for natural gas reforming; by 51% for resid partial oxidation; by 40% for K-T coal gasification; by 44% for improved (new) coal gasification; and 12% for SPE type electrolysis. In view of these substantial investment changes our study is being revised.

Table 1 shows the U.S. industrial hydrogen requirements for the 1980-2000 period. These hydrogen requirements for ammonia and methanol are the stoichiometric quantity of hydrogen contained in these products. The natural gas feed required to manufacture these quantities of hydrogen and hydrogen containing products are also shown. Assuming all industrial hydrogen (except electrolytic hydrogen) is made by reforming, the natural gas requirements will increase from 0.70 MB/D (crude oil equivalent) in 1980 to 1.60 MB/D in the year 2000, a growth rate of 4.2%/year. In the year 2000, this natural gas requirement will correspond to 18% of the projected U.S. natural gas consumption, or 7% of the U.S. crude oil consumption, or 15% of the U.S. crude oil imports. In that year the requirements for electrolytic hydrogen will be 256 MSCF/D; this will require 1341 mw of electricity.

In this study the escalation of coal and electricity prices and construction costs are projected to be 5%/year during the 1980-2000 period. Escalation rates for natural gas and oil prices are forecast to be 6.5%/year due to combined effects of increasing demand and decreasing reserves, and also because the price for imported crude oil is expected to follow world inflation rates rather than those for the U.S. Production costs for the 1980-2000 period are calculated in this study in constant 1980 dollars. Due to the increase in natural gas and oil prices during the period, with constant prices for coal and electricity (in 1980 $), natural gas reforming and resid partial oxidation will become less favorable compared to coal gasification and electrolysis.

Table 2 shows the feed stock prices assumed in this study. The prices of natural gas (or alternative light hydrocarbon liquids), high sulfur resid, electricity and construction costs are assumed to be equivalent in all geographical areas. However, coal mining costs and coal transportation costs vary from one area to another thereby resulting in different prices for coal delivered to plant sites on the East Coast, Midcontinent, Gulf Coast, and West Coast.

The Koppers Totzek process is now used at 15 ammonia plants located outside the U.S. Although this process is not attractive for industrial hydrogen production in the U.S., an improved K-T process is being developed that should make hydrogen manufacture by coal gasification more attractive. In this improved process (called new coal gasification) the gasification is conducted at 450 psig rather than atmospheric pressure now used. This will reduce plant investment by about 20%.

Although the new coal process will improve coal gasification economics, and the price of light hydrocarbon feed stocks will increase relative to coal, natural gas reforming will continue to be more attractive than coal gasification for refinery hydrogen production throughout the 1980-2000 period. These data are shown in Table 3 wherein the advantage of methane reforming over new coal gasification is shown for the East Coast, the location most favorable for coal gasification, and the Gulf Coast, the least favorable location. These advantages are shown for the most likely, the high, and the low feed stock prices and sensitivities of investment cost and the escalation of construction prices and coal prices. At the East Coast location reforming has a cost advantage in 1980 relative to new coal gasification of about $2.00/MBtu or 25%. This advantage decreases to $0.52/MBtu or 7% by the year 2000. Advantages for natural gas reforming are substantially greater for the Gulf Coast location.

Hydrogen manufacture by resid partial oxidation will be somewhat more expensive during the 1980-2000 period than by natural gas reforming. Resid partial oxidation will probably not be used to any significant extent during this period.

Electrolytic hydrogen costs are substantially higher than those for natural gas reforming. The market for electrolytic hydrogen will be limited to essentially those uses that now require ultra-high purity.

As this report goes to press, data using the revised investments are being developed for ammonia and methanol manufacture.

It appears that additional process improvements are needed to provide attractive economics for the use of coal as a source of industrial hydrogen. ERDA should continue to identify promising processes for coal gasification for hydrogen manufacture and assist in their development. It is also appropriate for ERDA to assist in the development of improved electrolysis processes.

TABLE 1

U.S. INDUSTRIAL HYDROGEN REQUIREMENTS, 1980-2000

Year	1980	1990	2000
Hydrogen Requirements, 1015 Btu/yr, for			
Petroleum refining	0.21	0.38	0.56
Ammonia	0.46	0.66	0.90
Methanol	0.08	0.14	0.23
Other chemicals	0.14	0.23	0.37
Ultra-high purity (electrolysis)	0.01	0.02	0.03
Total	0.90	1.43	2.09
Natural Gas Feed Stock Required to Manufacture Hydrogen*, MB/D Crude Equivalent			
Petroleum refinery hydrogen	0.15	0.27	0.39
Ammonia	0.36	0.51	0.70
Methanol	0.09	0.16	0.25
Hydrogen for other chemicals	0.10	0.16	0.26
Total	0.70	1.10	1.60
Electricity Required for Electrolysis, mw	350	660	1300

*Assuming natural gas reforming is used to manufacture all industrial hydrogen except for electrolytic hydrogen.

TABLE 2

U.S. ENERGY PRICES IN THE 1980-2000 PERIOD
($/MBtu, 1980$)

Prices		Minimum	Most Likely	Maximum
Natural gas	1980	2.50	3.15	3.40
	2000	3.37	4.24	4.58
High sulfur resid	1980	1.57	2.35	2.75
	2000	2.11	3.17	3.70
High Sulfur Coal, 1980-2000				
East Coast		0.73	1.04	1.31
Midcontinent		0.65	0.96	1.35
Gulf Coast		1.24	1.54	1.66
West Coast		0.95	1.25	1.37
Electricity, ¢/kwhr, 1980-2000				
Continuous		2.0	2.7	3.0
Off-peak		0.5	1.0	1.5

TABLE 3

ADVANTAGES FOR NATURAL GAS REFORMING OVER NEW COAL GASIFICATION FOR REFINERY HYDROGEN PRODUCTION, 1980-2000

(100 MSCF/D Plants, 1980 $)

	Advantage of Natural Gas Reforming Over New Coal Gasification, $/MBtu	
	1980	2000
East Coast Location		
Most likely feed prices	1.86	0.44
High feed prices	2.03	0.49
Low feed prices	2.13	1.00
10% additional investment	2.17	0.75
Construction costs escalate +1%/yr.	--	1.31
" " " -1%/yr.	--	-0.78
Coal prices escalate +1%/yr.	--	0.86
" " " -1%/yr.	--	0.10
Gulf Coast Location		
Most likely feed prices	3.73	2.31
High feed prices	3.82	2.28
Low feed prices	4.22	3.09
10% additional investment	4.14	2.54
Construction costs escalate +1%/yr.	--	3.44
" " " -1%/yr.	--	1.39
Coal prices escalate +1%/yr.	--	2.89
" " " -1%/yr.	--	1.84

DEVELOPMENT OF A PRACTICAL PHOTOCHEMICAL ENERGY STORAGE SYSTEM

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Introduction

The concept of a fuel source based on photochemical reactions which generate products of high energy content (which can in turn be reconverted at will to the original material) is exceedingly attractive in that a virtually inexhaustible source of energy (sunlight) is converted into a usable form with no net consuption of resources. The photosensitized conversion of norbornadiene to quadricyclene (Figure 1) is a promising method for storing energy from sunlight. A device based on this reaction requires two steps: (1) Energy storage through the sensitized photolysis of norbornadiene to quadricyclene in an endothermic reaction; (2) Energy release through the catalyzed reconversion of quadricyclene to norbornadiene in an exothermic reactions. Sensitizers for the first step must absorb strongly in the region of available solar energy be thermally and photochemically stable and, of course, efficiently effect the desired sensitization. Ideal catalysts for the reverse reaction must also meet stringent criteria including long term stability along with the obvious requirement of effecting rapid and clean conversions. Many of the best available candidates are prohibitively rare and expensive. Introduction of the sensitizer and catalyst onto separate polymeric supports facilitates the construction of an actual device by keeping the sensitizer and catalyst separate from each other. An energy storage device based on these principles could result in the practical use of solar energy for heating buildings and related applications.

The Solar Energy Storage Program at the University of Georgia is directed towards the development of this promising system. The efforts of the research group can be classified into four categories:

1. Sensitizer Development
2. Catalyst Development
3. Polymeric Anchoring of Sensitizer and Catalyst
4. Prototype and Test Systems

Each of these phases will be discussed with respect to results attained to date and future plans.

Sensitizer Development

The fact that the absorption spectrum of norbornadiene does not overlap at all with the solar radiance spectrum precludes the direct conversion of norbornadiene to quadricyclene. This apparent obstacle is easily circumvented by use of a photosensitizer. The sensitizer should ideally absorb a large fraction of available solar energy and at the same time efficiently effect the desired transformation. Our efforts have concentrated on (1) surveying a wide variety of potential candidates and (2) studying the mechanism of sensitization in order to intelligently design new candidates offering improved characteristics. The best available candidate is 4-(N,N-dimethylamino)-benzophenone which sensitizes with 100% quantum efficiency and absorbs out to 435 nm (capturing 10.2% of available solar energy).

We have also considered transition metal compounds as sensitizers for the desired energy storage step, since (1) they can strongly absorb light in the near ultraviolet-visible wavelength region, (2) they possess binding sites which may promote new, low energy pathways, and (3) they are known to undergo a variety of thermal reactions which can lead to useful catalytic schemes. Results to date indicate that complexation of norbornadiene to a metal provides a potentially useful route to sensitization. Thus several copper (I) compounds have been found to sensitize the conversion of norbornadiene to quadricyclene with high quantum efficiency. Work in progress is aimed at (i) increasing the stability of the metal toward destructive side reactions, and (ii) binding a strongly absorbing chromophore to the metal so as to increase absorption in the wavelength region of available solar energy.

Catalyst Development

An important aspect of this project is the development of catalysts of high activity, high specificity, and low cost for the conversion of quadricyclene to norbornadiene. We have therefore been searching for new structures with the desired catalytic acitivity.

At the start of this project the two known most active types of catalysts were certain rhodium (I) complexes and cobalt (II) porphyrins. In order to gain a more detailed insight into the structure-activity relationships for the rhodium (I) catalyzed conversion of quadricyclene to norbornadiene, numerous rhodium (I) complexes were screened for catalytic activity. In general, the introduction of tertiary phosphine or cyclopentadienyl ligands was found to decrease markedly or even destroy the catalytic activity of the rhodium (I) complexes apparently by blocking coordination positions needed for the catalytic action.

A drawback of rhodium complexes as catalysts in a practical solar energy storage system is the high cost of the metal. We are searching for similar complexes of less expensive metals with the desired catalytic activity. A promising lead is our observation of the high catalytic activity of the triphenylcyclopropenylnickel complexes $[(C_6H_5)_3C_3Ni(CO)X]_2$ (X=Cl and Br) as well as their products with alkylmagnesium halides in tetrahydrofuran which might be the alkyls $(C_6H_5)_3C_3Ni(OC_4H_8)_2R$ ($R=CH_3, C_2H_5$, $(CH_3)_2CH$, $(CH_3)_3C$, and C_6H_5). Further work is in progress in connection with the characterization of these catalytically active triphenylcyclopropenylnickel complexes as well as the preparation of additional triphenylcyclopropenylnickel derivatives for evaluation of their catalytic activities.

Polymeric Anchoring of Sensitizer and Catalyst

Implementation of the norbornadiene-quadricyclene interconversion as a practical device requires a number of considerations. The need to physically constrain the catalyst for the heat-releasing reaction to the "catalytic chamber" is obvious. Similar confinement of the photosensitizer to the "irradiation chamber" is desirable for a number of simple reasons. The absolute quantity of sensitizer needed can thus be reduced by several orders of magnitude. Periodic replacement of the photochemical fluid would not necessitate replacement of the sensitizer and vice versa. Undesirable interactions with the catalyst (in the catalytic chamber) would also be avoided. We have begun investigations concerning achieving the desired immobilization by covalent attachment of the catalyst and sensitizer to insoluble polymeric matrices.

At the outset of our studies little was known about the feasibility of efficient polymeric catalysis and photosensitization. We have successfully achieved the synthesis of a polymeric catalyst and several polymeric sensitizers, and each has been shown to perform satisfactorily. However, studies concerning optimization of the large number of parameters involved are in their infancy. The best available candidates are shown in Figure 2.

Prototype and Test Systems

The requirement that a practical solar energy storage system based on the norbornadiene-quadricyclene interconversion can be repeatedly cycled without degradation of the key components (sensitizer, catalyst, storage medium) is quite stringent. If one percent of norbornadiene (or quadricyclene) is lost per cycle via conversion to side products, only 37 percent of the original C_7 hydrocarbons will remain after 100 cycles. Sensitizer and catalyst candidates which appear to function cleanly on the basis of initial screening experiments may therefore prove to be unsatisfactory upon several repetitions of the energy storage-energy release steps. For this reason it is of key importance to test the ability of system to be cycled numerous times without significant losses of any of the components.

Such testing will be undertaken utilizing a small scale laboratory model now under construction. The design of the model (Figure 3) allows considerable breadth as to the types of experimental information which can be obtained. For example, losses of norbornadiene or quadricyclene via undesired side reactions can be monitored during repeated cycling of the system. In addition, sampling valves located before and after the photochemical and reversion chambers allow the conversion efficiency of a single energy release step to be determined. A decreasing efficiency would be indicative of a loss of activity of the sensitizer or catalyst. The use of a variable speed pump also allows the conversion efficiency to be monitored as a function of the flow rate in the system.

Information obtained from the laboratory model will be useful in suggesting improvements in the overall functioning of the system. Ultimately, these improvements can be incorporated in the design of a commercial energy storage prototype.

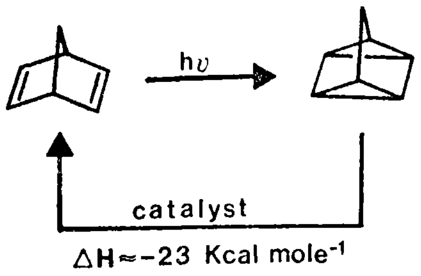
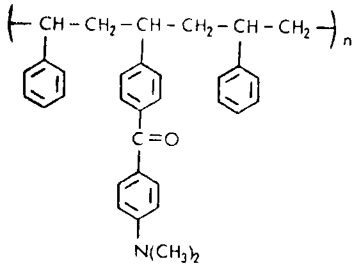


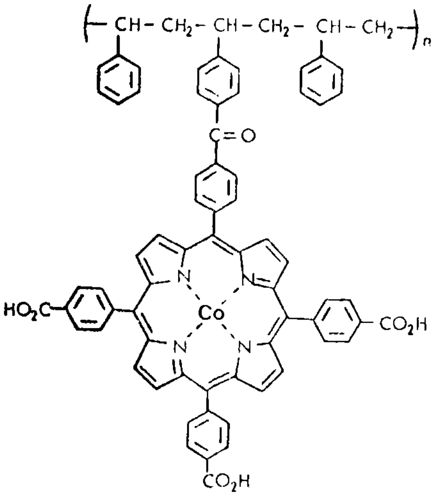
Figure 1

Figure 2

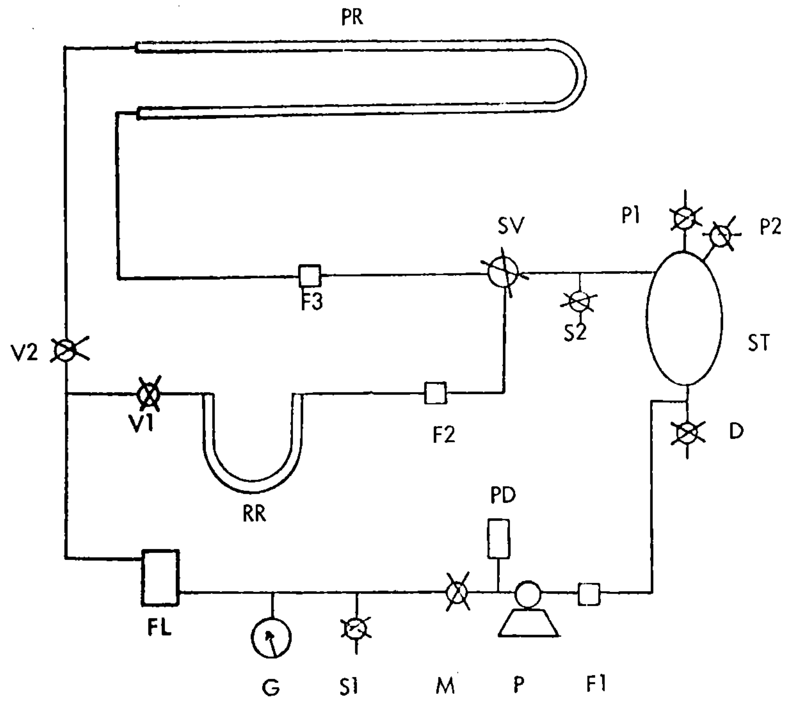
Polymeric Sensitizer



Polymeric Catalyst



Prototype Test System - Schematic



LEGEND

PR - Photochemical Reactor
RR - Reversion Reactor
ST - Storage Tank
F1, F2, F3 - 140 micron filters
S1, S2 - Sampling Valves
P - Variable Stroke Pump
M - Metering Valve

G - 0-100 psi pressure guage
FL - Flow Meter
V1 and V2 - Shut-off Valves
SV - Switching Valves
P1 and P2 - Gas Purge Valves
D - Drain Valve
PD - Pulse Damper

Figure 3

THE METAL HYDRIDE HYCSOS SYSTEM FOR SOLAR HEATING, COOLING AND ENERGY CONVERSION.(≠)

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I. Introduction

Thermal energy storage in the low temperature region (< 150°C) is a fertile area for advances over existing technologies, particularly in the hitherto virtually neglected field of chemical bond energy storage. For this purpose, the metal hydrides represent a class of potentially interesting materials. Their use in an integrated system for thermal storage, space conditioning and refrigeration as well as for power production is described in this paper. The initial description of the overall concept has been given.(1) A thermodynamic analysis of the efficiency of the energy conversion cycle has also appeared.(2) A recent paper discussed in detail the various functions of the total system with the help of heat transfer fluid and hydrogen gas flow diagrams.(3) An analysis of certain special features associated with the use of alloy hydrides which make them virtually unique for solar energy applications was also given.

II. Special Features of the HYCSOS System for Solar Energy Utilization

Two aspects of solar energy, its diffuse and intermittent nature, dictate optimization in all of the systems employed in the utilization of this renewable resource. Although solar energy is usually considered to be ideally matched to the task of direct space heating, collector temperatures, particularly in the case of high performance collectors for space cooling purposes, exceed the requirements for optimum second law efficiencies. A system operating on the heat pump principle could make optimum use of higher collection temperatures to store thermal energy, for space conditioning and for reasonably efficient conversion of heat into work. The two metal hydride or HYCSOS concept is such a system and offers the possibility of reducing the required solar collector area by 40% compared to thermal storage systems not utilizing the heat pump principle. Because of the three possible modes of operation, HYCSOS can make flexible use of the widely varying supply of solar energy. Furthermore, the use of heat transfer fluids allows ready substitution of electric power for solar energy and efficient use of both energy sources for heating or cooling purposes because of heat pump operation. A hybrid system for space heating and cooling involving the use of solar as well as electrical energy has often been considered and appears to be very attractive for use with the HYCSOS concept. A hybrid system has the desirable feature of reducing the troublesome problems associated with long term or seasonal thermal energy storage.

Some of the special features associated with the HYCSOS system for solar energy applications are listed below.

1) High second law efficiencies by heat pump action in both thermal storage and cooling modes.

2) The consequence of heat pump action in the thermal storage mode is that collector temperatures (≈ 140°C) can be used to decompose the high temperature hydride while at the same time using the heat of formation of the low temperature hydride at ≈ 50°C for space heating. The full heat of formation of the high temperature hydride is recovered by heat pump action in the absence of insolation. If the solar collector is to provide one Btu for space heating during the day while at the same time placing one Btu into thermal storage, the theoretical reduction factor in solar collector area is $1 - \Delta H_{low}/\Delta 2H_{high}$. Since the heats of formation of $MnNi_5$ and $LaNi_5$ are in the ratio 5.6/7.2, the solar collector area could be reduced 40% with this particular hydride combination compared to equivalent collector operation with non heat pump storage materials.

3) In the cooling mode, direct conversion of thermal energy into cooling power by heat pump action can be achieved, thus circumventing for example primary conversion of solar thermal energy to work in a Rankine cycle for subsequent operation of the compressor of a conventional air conditioner.

4) The application of materials engineering to alloy hydride systems so as to "tailor" them for optimum performance over preselected temperature limits. Calculations on the $LnNi_5$ - $LaNi_5$ pair show that operation

between ∿ 100°C and -20°C is possible offering the opportunity for space conditioning and refrigeration applications at modest collector temperatures.

5) Straightforward substitution of electric for solar energy to operate the system, thus offering integration into an electric utility network.

6) Hybrid operation using both solar and electrical energy with high second law efficiencies provides the opportunity for minimizing long term thermal storage capacity while maximizing energy utilization in a flexible manner.

7) Operation in the energy conversion mode, if competitive with photovoltaic or other solar energy conversion schemes, could help to meet residential electrical energy needs. Much development work needs to be done in this applications area. The possibility of HYCSOS operation in heating, cooling and conversion modes in a single system provides an incentive to develop hydride technology for use in this flexible manner.

8) Since metal hydrides decompose over a range of temperatures, thermal storage is not critically dependent on collection temperature. These materials offer thermal storage capabilities achieved only in so-called "cascade" collection systems which employ more conventional thermal energy storage materials.

9) In common with other chemical bond storage materials, metal hydride storage materials require no insulation and provide indefinite storage of thermal energy.

10) The metal hydrides possess quite high volumetric thermal energy storage capacities and compare favorably with the best phase change media so far available.

11) The incorporation of heating, ccoling and power conversion functions into a single system based on metal hydride technology may offer economic advantages over separate systems each designed to perform only one of these three functions.

III. Conceptual Operation of a Hydride Conversion and Storage System (HYCSOS)

Because of their desirable properties, binary metal as well as alloy hydrides have been proposed as media for the storage of thermal energy (1-4) as well as for thermal energy conversion cycles. (1-3, 5-8)

Metal hydrides were proposed and are being tested (9, 10) as off-peak energy storage systems. In this application, the large volumetric storage capacity of some metal hydrides for hydrogen is combined with the high free energy of formation of water from hydrogen and oxygen to furnish electrical power through a fuel-cell-electrolysis cycle. The application of metal hydrides for storage of thermal energy imposes different constraints on the hydride system chosen, requiring an optimization of thermal energy stored at temperatures and pressures compatible with solar energy collection.

Schematic diagrams of the two metal hydride concept for solar energy applications were shown and described in earlier papers. (1-3) Thermal energy from a solar collector is used to decompose a hydride (M_1H) such as $LaNi_5H_6$, which becomes the primary solar energy unit. The released hydrogen is stored as a hydride (M_2H) such as $LnNi_5H_6$, where Ln stands for another lanthanide metal.

The use of a system of reversible metal hydrides offers a variety of possibilities for solar energy use and conservation. With three units in tandem, solar energy can converted directly to electricity. Operation in a reversed "heat pump" mode allows the system to be used in space conditioning and in refrigeration applications. Each of these functions will be discussed in turn in the following sections.

A. Thermal Energy Storage Mode

For solar energy storage and recovery heat transfer fluid coming from the solar collector is pumped through the heat exchangers of two storage units filled with M_1H ($LaNi_5H_6$). Heat is absorbed from the fluid by M_1H which thermally decomposes to give $M_1 + H_2$. The H_2 is allowed to flow into two storage units filled with M_2($LnNi_5$) where it reacts to form M2H ($LnNi_5H_6$). The heat of reaction is removed by fluid coming from a second heat transfer loop. The M_2 storage units are maintained at 50°C so that the heat of the reaction $2M_1 + H_2 = 2M_1H$ is available at that temperature for space heating. Thermal decomposition of M_2H can occur at temperatures of 0°C and below by heat absorption from the ambient environment.

B. Space Conditioning and Refrigeration Mode

The ability of metal hydride systems, and in particular the $LaNi_5$-$LnNi_5$ pair, to function in space conditioning and refrigeration applications has also been discussed. (2,3) In operation heat transfer fluid from the solar collector at temperatures of 105°C or higher is circulated through $LaNi_5H_6$ decomposing it and storing the hydrogen in $LnNi_5$ while rejecting the heat of recombination to outdoor ambient at 35°C. At the same time, $LnNi_5H_6$ in another container releases hydrogen by absorption of heat from indoor ambient at temperatures down to -24°C. This hydrogen is stored in $LaNi_5$ in a fourth container while rejecting the heat of recombination to outdoor ambient at 35°C. A continuous flow of hydrogen can be maintained and therefore continuous cooling power can be provided by switching the flows of heat transfer fluid as well as the hydrogen gas flows. (3)

To estimate the cooling power obtainable with the $LaNi_5$- $LnNi_5$ demonstration system, one needs to know the heat of dissociation of $LnNi_5H_6$, and the number of moles of hydrogen dissociating per unit time. Taking the heat of dissociation to be 5.6 Kcal, the quantity of hydrogen to be 33 moles and a cycle time of 4 minutes gives a cooling power (down to -24°C) of $\sim$ 3200 W. The minimum heat input at the minimum collector temperature of 105°C is 4142 W. However, a small loss ($\sim$ 15%) of cooling power arises from the necessity to cool the container with $LnNi_5$ from 35°C to the lowest temperature in the cooling cycle.

C. Energy Conversion Mode

The HYCSOS system also lends itself to conversion of thermal energy into useful work as electricity. The mechanical work could be used to drive the compressor of a conventional air conditioning system. Alternatively, electrical energy for home use could be generated. In the energy conversion cycle, high pressure H_2 at $\sim$ 50 atm generated by passing hot fluid coming from the solar collector through the first of three M_1H storage units, is allowed to do work in an expansion engine. The cooler, lower pressure H_2 exiting from the expansion engine is fed into a second storage unit containing M_1 where it reacts to form M_1H. (For maximum Carnot efficiency, the temperature of the reacting unit should be kept as low as possible. However, in practice it may be desirable to generate electricity and to provide space heating at the same time. In the event, the reacting unit could be kept at 50°C at a sacrifice of some conversion efficiency). After the reaction $2M_1 + H_2 = 2M_1H$ is complete in the second unit, the hot fluid flow is directed through the heat exchanger in this unit. The high pressure H_2 produced by thermal decomposition is now fed into the third storage unit containing M_1. While the hydriding reacting is occurring in unit three, the first storage unit is cooled to reaction temperature. By using three storage units which are alternately desorbing hydrogen at a lower temperature and lower pressure, a practically constant flow of hydrogen should be maintained through the expansion engine and therefore a steady power generation should be achieved. The cycle time is determined primarily by the time needed for absorption which in turn is strongly dependent on the heat transfer from the cooling fluid to the absorbing metal powder. In cyclical fashion, one unit is always desorbing, one is absorbing, and one is in the process of heating up or cooling down. (11-13) By expansion of the high pressure hydrogen through a suitable expansion engine, a certain amount of work is produced. For a top temperature of 140°C and absorption at ambient temperature, 298.2 K, the maximum efficiency is

$$\varepsilon = \frac{413.2-298.2}{413.2} = 0.28,$$

i.e., 28% of the heat absorbed by the hydrogen during dissociation can in principle be converted to electricity.

It is of interest to estimate the performance of a small scale system based on ∿ 30 lbs. of $LaNi_5$ involving a total of 33 moles of hydrogen. The dissociation pressure is given by the equation

$$\log_{10} P_{atm} = -\frac{1587}{T} + 5.60,$$

resulting in an equilibrium dissociation pressure of 57.2 atm at 140°C, and of 1.9 atm at 25°C. In practice, the equilibrium pressure calculated using the above equation is an upper value. During desorption at 140°C the H_2 pressures are strongly composition dependent and absorption at ambient temperature will require a pressure head. It will be assumed here that hydrogen at 50 atm is available for operation of the expansion engine. The low-pressure at which absorption takes place is assumed to be 3 atm.

The heat of dissociation is 30.3 kJ/mol of hydrogen. During decomposition of 33 moles of hydrogen, therefore, 1000 kilojoules of heat have to be supplied. Assuming the expansion engine to be 90% efficient means that 33 moles of hydrogen yield 197.3 kilojoules of electricity, i.e., 19.7% of the heat supplied during desorption was converted into work.

Under actual conditions losses will be incurred during the warming and cooling of the hydride containers. Part of the heat that has to be removed from the hot container during cooling could be recovered and used to raise the temperature of the unit to be heated next. For this purpose a buffer volume of heat exchange fluid is needed. The temperature of the buffer fluid can be cycled in a range intermediate between 25°C and 140°C, e.g., between 70 and 90°C. To cool a unit from 140°C the 70° warm fluid can be circulated until a temperature near 90°C is reached. To cool the unit further, coolant can be used without heat recovery. Similarly, if a unit is to be heated subsequently, the buffer fluid at 90°C can be used to reach a temperature near 70°C. In this fashion at least part of the internal energy of the hydride containers can be cycled between the three units in a regenerative way.

The burden of unavoidable heat losses for the complete cycle is estimated to be 15% of the heat required for the dissociation of the hydride.

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THERMO-CHEMICAL ENERGY CONVERSION AND STORAGE

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The overall objectives of the program are to design, construct, and operate a pilot scale version of a processing scheme by which thermal energy may be absorbed, stored, and retrieved on demand. The thermal energy will be stored in high energy Chemical Bonds. Energy retrieval and absorption stages will be accomplished through the cleavage and formation of chemical bonds that take place during a reversible chemical reaction. After reviewing a number of candidate reactions, the reaction which appeared most promising to us is the vapor phase hydrogenation of benzene to cyclohexane

$$C_6H_6 + 3H_2 \rightleftarrows C_6H_{12} \quad (-\Delta H_R) = 49.25 \text{ Kcal/g -mole}$$

The choice was based on the following considerations.

a. The reaction is catalytic and both the forward and reverse reactions represent existing commercial technology. Catalysts are readily obtainable and data on the kinetics of the forward reaction exists in the literature.

b. Both benzene and cyclohexane are liquids at ambient temperature and pressure so that separation of the hydrogen from the mixture will be straightforward and relatively inexpensive. Hydrogen will be stored as a compressed gas or in hydride form.

c. The reaction proceeds at $400\text{-}600^{\circ}F$ at 1 atm, which is within the temperature range capabilities of existing solar concentrator designs and waste heat streams from existing nuclear reactors.

d. The dehydrogenation step is endothermic and will be used as the energy absorption step while the hydrogenation step is exothermic and will be used as the energy recovery step.

e. The energy recovery step can take place in a pressurized boiler of conventional design (boiler-reactor).

The result will be a programmed flow of saturated steam which can be used for electrical power generation by conventional means.

Before an adequate pilot plant design can be formulated, however, several questions must be answered. The most important of these for design purposes concern the intrinsic kinetics of the dehydrogenation (endothermic) reaction. Although kinetic data are available in the literature for the catalytic hydrogenation of benzene (exothermic) which can be used for design, very little useful design data exists for the catalytic dehydrogenation reaction and must be developed. Other areas for investigation concern catalyst deactivation, catalyst attrition during cycling and side reactions. Although there is no evidence of side reactions occurring in this system, there may be some cracking of the cyclohexane and benzene rings if the reaction is run at high enough temperature. Next the whole question of control of such a process must be investigated. Even during periods of regular operation, a solar driven thermal energy storage-recovery system would be operated cyclicly. The control algorithms which would take the process from the storage to the recovery mode or vice-versa must be developed since these involve the non-steady state operation of catalytic reactors. Moreover, if the system is to respond to demand or supply (cloud cover) changes, these must be incorporated into a rational control scheme. Finally, since hydrogen is one of the products (reactants) in the process, a hydrogen storage facility must be designed. The question then arises as to how is the best way to store hydrogen. Should we design a conventional compressed gas storage facility? Should hydrogen perhaps best be stored as a liquid? What about hydride storage and recovery? Each of these storage modes have assets and limitations and involve different energy and economic contributions to the overall process design.

The objectives of the initial phase of the study are twofold.

a. To experimentally obtain the apparent kinetics of cyclohexane to benezene and hydrogen. Apparent kinetics in lieu of intrinsic kinetics, which are partially available in the literature, are most appropriate for the design of full-scale reactors.

The data will be taken at atmospheric pressure in the temperature range of 400-600°F over a commercially available naphtha reforming catalyst. The effect of a nitrogen diluent, which may be used for flushing during shutdown of a commercial unit, will be investigated. Catalyst deactivation and attrition during cycling will be investigated in the proposed reaction environment.

The experimental apparatus is a fully instrumented internal recirculation (gradientless) reactor connected to a gas chromatograph. The catalyst testing facility is also planned for later use in obtaining or verifying available benzene hydrogenation kinetics (exothermic step) and for the evaluation of other chemical systems that appear to be appropriate for the collection and storage of thermal energy.

b. A model that will realistically describe the transient behavior of a gas phase catalytic reactor dedicated to the collection of thermal energy will be formulated and computerized. The model will have the capability of accepting measured transient data of solar isolation and ambient temperatures as well as parameters which describe the collection system. The collection system is envisioned in this study as being a solar collection device whose performance has already been characterized. The model will be applied to the cyclohexane dehydrogenation system for the purposes of evaluating startup, shutdown, and control algorithms.

The model will be used in the later stages of the development program for pilot plant design and control. It can also be utilized for the evaluation of other chemical systems and for the application of the converter to other thermal energy sources, such as waste heat from a nuclear reactor installation.

STATUS OF PROGRAM

Experimental: The internally recirculated (gradientless) reactor has been set up and instrumented for temperature, pressure and flow control. A gas chromatograph with a programmable automatic sampling valve has been attached to the reactor and a chromatographic separation column has been calibrated for the system benzene-cyclohexane. A calibration curve has been prepared relating % area under each curve to % cyclohexane in the sample over the range of data expected.

One run has been made at 600°F and 1 atm over the naphtha reforming catalyst and gave an equilibrium conversion of 98%(based on cyclohexane).

Theoretical: A model has been formulated which describes the transient behavior of a gas phase catalytic reactor dedicated to the collection of thermal energy.

Most heat exchangers including solar collectors, involve the passage of thermal energy through the wall of a circular pipe into a heat transfer fluid which flows through the pipe. Differences lie primarily in things external to the pipe.

The approach that has been taken is to develop the analysis for the circular pipe and a reactive working fluid while the external geometry is reflected in appropriate model parameters. In this way, the model is not unnecessarily burdened with a particular energy source configuration and has the flexibility of evaluating different alternatives. However, since the primary thrust of the overall effort is directed toward solar applications, the external configuration is assumed to be a solar collector. Minor modifications will be required for other applications such as waste heat-collection from nuclear reactors.

The model consists of the following dynamic equations for a single reversible catalytic reaction of arbitrary stoichiometry and number of components in which the activity of the catalyst is constant. The continuity equations (mass balances) are given by:

$$\frac{\partial C_i}{\partial t} \quad \frac{\partial (qC_i)}{\partial V_R} = \nu_i r \qquad i = 1,2,\ldots, n-1 \qquad (1)$$

In general, only n-1 equations are required since an overall mass balance then yields the nth component.

where $\Sigma \nu_i A_i = 0$ *

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* $\nu_i = 0$ for inert components (e.g., N_2) so that all species are included in this formulation.

q - volumetric flowrate based on the total reactor volume and may vary with position and time

n - number of components plus number of inerts

C_i - molar concentration of species i

r - overall rate of reaction (moles/sec/ft^3)

V_R - total reactor volume

The reaction kinetics are assumed to be "apparent kinetics" so that internal diffusional and heat transfer restrictions are automatically included. However, external heat and mass transfer effects are excluded and will have to be evaluated at a later stage. The reactions rate r is, in general, a nonlinear function of the concentrations of the n species and temperature.

One now needs an independent equation for the flowrate, q. While any valid equation of state can be used; for simplicity and as a reasonable approximation an ideal equation of state is assumed. A further reasonable assumption is that the pressure is constant with distance (the pressure drop in the tube is small), but may vary with time since the feed flowrate will be used as a control variable to compensate for variations in solar energy and ambient temperatures. This yields a differential equation for q as follows:

$$\sum_{k=1}^{n-1} (M_k - M_n) \frac{\partial C_k}{\partial t} - \left(\frac{M_n P(t)}{RT^2}\right) \frac{\partial T}{\partial t} + \sum_{k=1}^{n-1} q(t)\,(M_k - M_n) \frac{\partial C_k}{\partial V_R} - \left(\frac{M_n P(t)}{RT^2}\, q(t)\right) \frac{\partial T}{\partial V_R} + \hat{\rho}(t) \frac{\partial q}{\partial V_R} = - \frac{M_n}{RT} \frac{\partial P(t)}{\partial t} \tag{2}$$

$$\hat{\rho}(t) = \sum_{i=1}^{n} M_i C_i = \sum_{i=1}^{n-1} (M_i - M_n)\, C_i + \frac{M_n P(t)}{RT} \tag{3}$$

M_k - molecular weight of species k

M_n - molecular weight of species n

$P(t)$ - total pressure in reactor - considered constant with distance

T - absolute temperature

R - gas law constant

The pressure derivative in eq'n. (2) will be imposed on the system and will be directly related to the inlet flowrate.

An energy balance over the reactor ignoring viscous dissipation and axial conduction yields

$$\frac{\partial T}{\partial t} + \frac{\partial T}{\partial V_R} = \frac{(-\Delta H_R)}{C\ C_p^*}\, r + \frac{q_v}{C\ C_p^*} \qquad (4)$$

$(-\Delta H_R)$ - heat of reaction

C_p^* - molar heat capacity of the mixture (assuming ideal mixture)

C - molar density of mixture - $\Sigma\ C_i$

q_v - energy input rate per unit volume of the tube

An energy balance on the tube wall yields

$$q_v = \frac{4\ h_i/D_i}{h_o + D_i h_i/D_o} \{ \varepsilon\ q_s(t) - h_o\ (T - T_s)\} \qquad (5)$$

ε - efficiency factor which is a function of collector design. This represents the "effective area" of the collector per unit area of outside tube surface.

q_s - solar flux, which will be a function of time

h_o - outside film heat transfer coefficient

T_s - temperature of surroundings

h_i - inside film heat transfer coefficient

D_i, D_o - inside and outside diameters of pipe

Here a pseudo-steady state assumption for the wall temperature was made and radient energy loss was neglected.

Equations (1), (2), (4) and (5) may be written in compact notation as:

$$\{ A \} \frac{\partial \vec{x}}{\partial t} + \{ B \} \frac{\partial \vec{x}}{\partial V_R} = \{ \vec{d} \} \qquad (6)$$

where the dimension of the system is n + 1 and

$$x_i = \begin{cases} C_i, & i = 1,2,\ldots, n-1 \\ T & i = n \\ q & i = n + 1 \end{cases} \qquad (7)$$

$$a_{ij} = \left\{ \begin{array}{ll} \left.\begin{array}{ll} \delta_{ij} & i = 1,2,\ldots, n-1; \forall j \\ M_j - M_n & i = n; j=1,2,\ldots, n-1 \end{array}\right\} & \text{Lower} \\ -M_n P/RT^2 & i=n; j=n+1 \\ 0 & i=n; j=n+1 \\ \delta_{nj} & i=n+1; \forall j \end{array} \right] \begin{array}{l} \text{Triangular} \\ \text{Matrix} \end{array} \qquad (8)$$

$$
b_{ij} = \begin{cases} \delta_{ij}\, q + \delta_{j,n+1}\, C_i & i=1,2,\ldots,\ n-1;\ \forall_j \\ q\,(M_j - M_n) & i=n;\ j=1,2,\ldots,\ n-1 \\ -M_n Pq/RT^2 & i=n;\ j=n \\ \rho & i=n;\ j=n+1 \\ q\ \delta_{nj} & i=n+1;\ \forall_j \end{cases} \qquad (9)
$$

$$
d_i = \begin{cases} \nu_i\, r & i=1,2,\ldots,\ n-1 \\ -(M_n/RT)\,\dfrac{\partial P}{\partial t} & i=n \\ \left(\dfrac{-\Delta H}{C\, C_p^*}\right) r + \left(\dfrac{1}{C\, C_p^*}\right)\left(\dfrac{4h_i/D_i}{h_o + D_i h_i/D_o}\right)\{\varepsilon q_s - h_o(T-T_s)\} & 1=n+1 \end{cases} \qquad (10)
$$

Eq'ns. 6,8,9 and 10 then constitute a model for the gas phase catalytic reactor which will accept experimental kinetic data and allow us to simulate the effects of such variables as collector design (ε), solar flux variation (q_s), pressure changes, reactor diameter (D_i), heat transfer effect (h_i, h_o) and ambient temperature variation (T_s) on the startup, shutdown and performance of the thermal converter.

Equations (6) may be normalized by dividing both sides by $\{B\}^{-1}\ x_{n+1}$ to give a set of coupled quasilinear hyperbolic equations. These, along with the appropriate boundary and initial conditions, may be solved using either a standard finite difference technique (2) or by the method of characteristics (3). The latter approach involves transforming the independent variables so that the partial differential equations become ordinary differential equations along the characteristic curves. This will yield a faster, more accurate numerical integration algorithm and will be the technique we will follow.

Presently the equations are being programmed for solution on the Stevens PDP-10 digital computer.

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CONVERSION AND STORAGE OF WIND ENERGY AS NITRATE FERTILIZER

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Estimates of present fuel resources and forecasts of future energy consumption forebode a growing inability for the nation to cope with the demand in coming decades. In the search for alternate energy sources, wind is an attractive candidate, but its energy must be captured and stored in sufficient quantities during windy days to provide for the demand during quiescent times. The National Science Foundation has awarded Lockheed-California Company a contract to study a unique method for storing wind energy, one which converts it to a useful energy product, nitrate fertilizer. This compound can be manufactured, stored and distributed at a cost competitive with similar compounds currently made from fossil fuels. In Lockheed's concept, the wind energy is captured by a wind turbine, combined with water and air, converted to anhydrous ammonia, and then to ammonium nitrate solution. These high energy fertilizer compounds are, in a sense, the final storage medium for the wind energy.

The research study is investigating technical and economic feasibility for the concept, identifying the technical obstacles requiring solution, and defining a program for demonstration.

Depletion of fossil fuels is having tremendous impacts on other parts of the nation's economy and life style. In particular, nitrogen fertilizer manufacture is a high energy user, but more important, it uses natural gas as the primary source of hydrogen for ammonia and nitrate. The cost of nitrogen fertilizers has tripled in the last three years, primarily because of the natural gas shortage and rising cost. Since nitrogen compounds constitute 60% of all agricultural fertilizer(Ref. 1) and fertilizer can in many instances more than double the average crop yield, the beneficial impact of fossil fuel conservation and development of alternate energy sources is easily understood.

The proposed program is a unique combination of state-of-the-art technologies that makes optimum use of each technology through the synergism of the combination.

Wind energy conversion systems achieve their maximum potential when energy storage is provided to smooth the variability of wind power availability. Storing wind energy in the form of hydrogen obtained through electrolysis of water is a proven concept and state-of-the-art (Ref. 2). The chemical processes for creating ammonia and nitrates from hydrogen and nitrogen have been used for many years (Ref. 3). Large centralized processing plants have evolved to achieve production economy, but these require additional energy to solidify the ammonium nitrate from its water solution state and to transport the product over very long distances.

In Lockheed's concept, wind energy is captured by a wind turbine and converted to electricity. The electricity generates hydrogen and oxygen by water electrolysis. These products are stored in sufficient quantities to serve as a constant source of chemical ingredients and energy to manufacture ammonia and ammonium nitrate. The process is illustrated in the flow diagram in Figure 1. A major feature of the process is provision for purging vented effluents to eliminate environmental pollution.

The system advantages are obvious:

- Wind energy can be converted directly to a useful product.
- It can be stored and used on a demand basis.
- Raw materials are abundant and essentially free.
- Process sites are numerous and wide spread.
- Products can be manufactured in local proximity to agricultural areas, independent of fuel supplies. The energy required for distribution can be conserved.
- The small initial investment enables agricultural organizations to acquire their own fertilizer plants and benefit from self sufficiency.

Other advantages are:

- Assistance in solving a critical agricultural problem, the shortages and rising costs of nitrogen fertilizers.
- Improved safety through use of an aqueous solution of ammonium nitrate rather than the unstable dry chemical.
- A self help product would become available from the United States for the emerging nations of the world. These countries need an indigenous fertilizer source before anything else to reduce their dependency on imported fertilizer or on fossil fuel with which to make fertilizer.

Although each element of the proposed fertilizer system is based on proven concepts and is within the state of the art, questions remain concerning the efficiency of small fertilizer plants and their economic viability. Lockheed has teamed with Jacobs Engineering Company of Pasadena, California, and other reputable consultants to analyze these problems. Lockheed is responsible for wind energy conversion, costing, economic analysis, hardware development and systems management. Jacobs Engineering Company is contributing with design and analyses of the ammonia, nitric acid, and ammonium nitrate processing equipment. Expertise in high pressure electrolysis systems is being provided by Jack Allison from Oklahoma State University.

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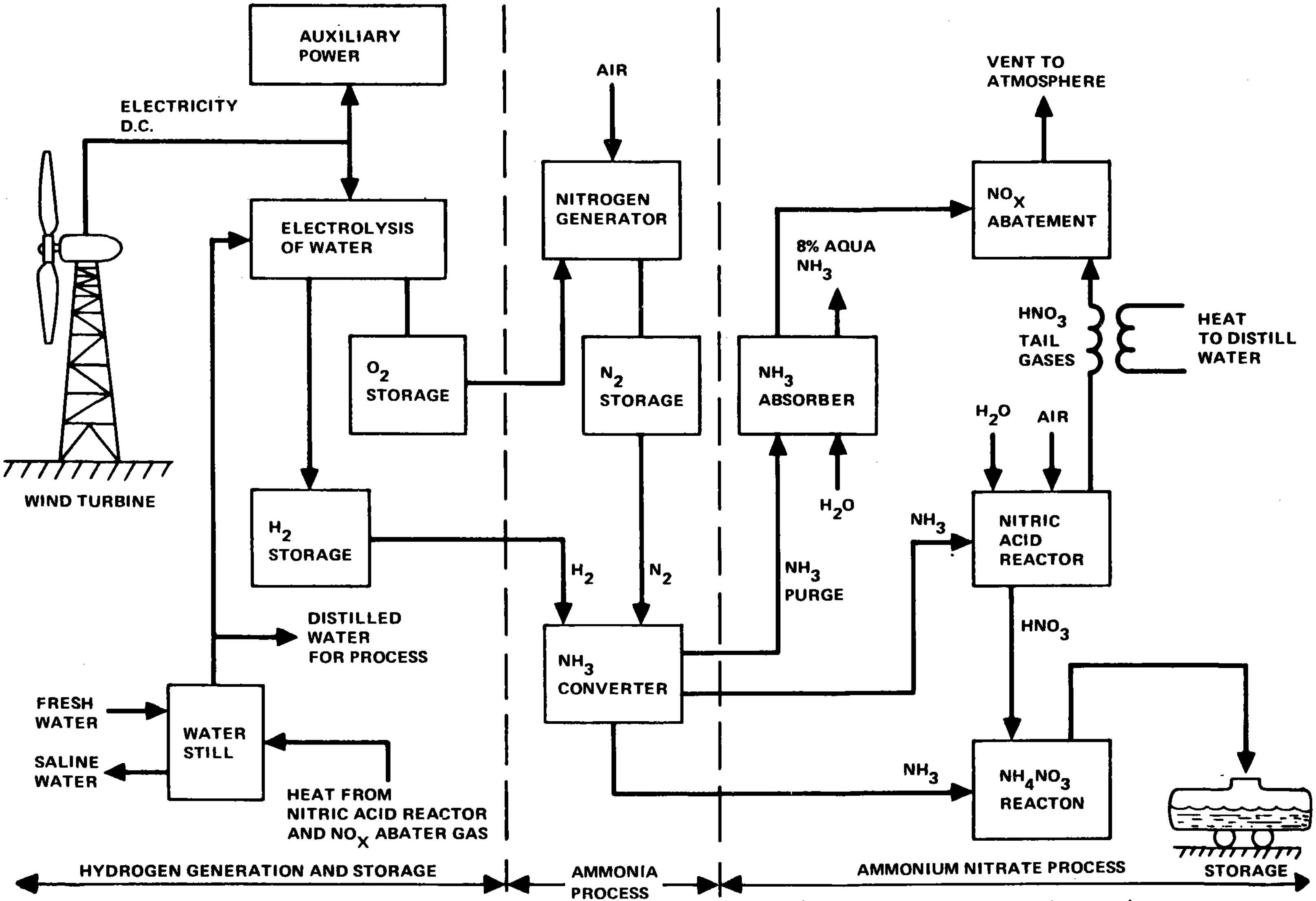

Figure 1. Conversion of Wind Energy, Air and Water to Ammonium Nitrate.

ENGINEERING STUDIES WITH METAL-HYDRIDE TEST BEDS*

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INTRODUCTION

Metal hydrides have proven to be an efficient and convenient way of storing hydrogen without the disadvantages of low temperature or high pressure. The best candidate for wide-scale use today is iron titanium hydride ($FeTiH_x$) because the reaction kinetics are adequate at readily available temperatures, and there is an ample supply of raw materials and some hope that their cost can be appreciably reduced.

Recent studies at BNL have concentrated on determining the long-term and dynamic behavior of $FeTiH_x$ for a time cycle related to energy storage for an electric-utility application (10-hour charge or discharge). The work has consisted of experiments with individual test beds, or heat-transfer cells, a group of which comprises a hydride reservoir. Most of the work has been done with units in which the heat-transport fluid (water) is on the outer boundary of a cylindrical cell rather than on the inner boundary or longitudinal axis. In the long-term tests the service life and the effect of attrition were of primary interest. The rate information obtained in the dynamic tests is equivalent to determination of the power rating of the device.

Another important factor in design of a commercial hydride reservoir is the cost of the container material. Tests are under way to determine if a low-cost steel can be used to replace stainless steel or aluminum as the material of construction for an $FeTiH_x$ reservoir. The selected material must resist hydrogen embrittlement which results in loss of ductility and crack growth.

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* This work was carried out under the auspices of the United States Energy Research and Development Administration.

LONG-TERM STUDIES AND PHYSICAL BEHAVIOR

The first series of tests conducted on $FeTiH_x$ consisted of determining the extent of attrition and the change in storage capacity during accelerated hydride-dehydride cycling. Early in this work capacity losses were experienced; small leaks and a cylinder of impure hydrogen were the causes. Since conversion to welded and O-ring-seal joints, as well as the use of high-purity hydrogen ($\geq$99.999%), no loss of storage capacity has been discernible after 3500 cycles, using fresh hydrogen for each hydriding. Tests made by Reilly (1) in determining the effect of oxygen added to hydrogen have shown that there is still a significant capacity loss at levels as low as 10 ppm oxygen. Thus hydrogen to be stored as $FeTiH_x$ has to be very highly purified.

The main result of extended cycling is extensive attrition and a large increase in pressure drop. Attrition occurs because the FeTi alloy is embrittled by hydrogen and expands about 15%. There is more rapid break-up in deep beds (depth = several bed diameters) because the particles tend to interlock and cannot readily expand to the free surface of the bed during hydriding. Thus they are crunched against each other and break up where embrittlement has occurred.

A related problem in deep beds is that the volumetric expansion is accommodated by some decrease in the void space, some vertical expansion toward the free surface, and more detrimentally, some lateral expansion which can result in vessel bulging. Comparison tests with deep vertical beds have shown that both moderately- and loose-packed beds can cause vessel bulging, with the rate being appreciably greater in the more dense bed. This behavior poses a problem for large-scale beds because it can limit the container arrangement and bed depth. Ways of safely accommodating this volumetric expansion, without greatly increasing the cost, need to be found.

Pressure-drop measurements taken at various times during the accelerated-cycle tests with $FeTiH_x$ have shown an increase from a fraction of an inch of water/in. of bed height (length) to several psi/in. An equation was developed for calculating the differential pressure vs. particle diameter at various hydrogen flow rates (2). The agreement between the calculated values and those measured in a small test unit was within 6% over the range examined. From particle-size measurements made on $FeTiH_x$ at various stages of attrition, it was estimated that after 4000 cycles (design life of 15 years) the average particle diameter would be 10 μm (microns). Using the correlation developed, the differential pressure in the bed would be 2 psi/in. for the design flow rate, 2.49 SCFM/ft^2. Data for other conditions are shown in Fig. 1. It is evident that the differential pressure increases very rapidly for average particle sizes $\leq$ 10 μm. Additional filter area will have to be provided where the differential pressure is considered excessive.

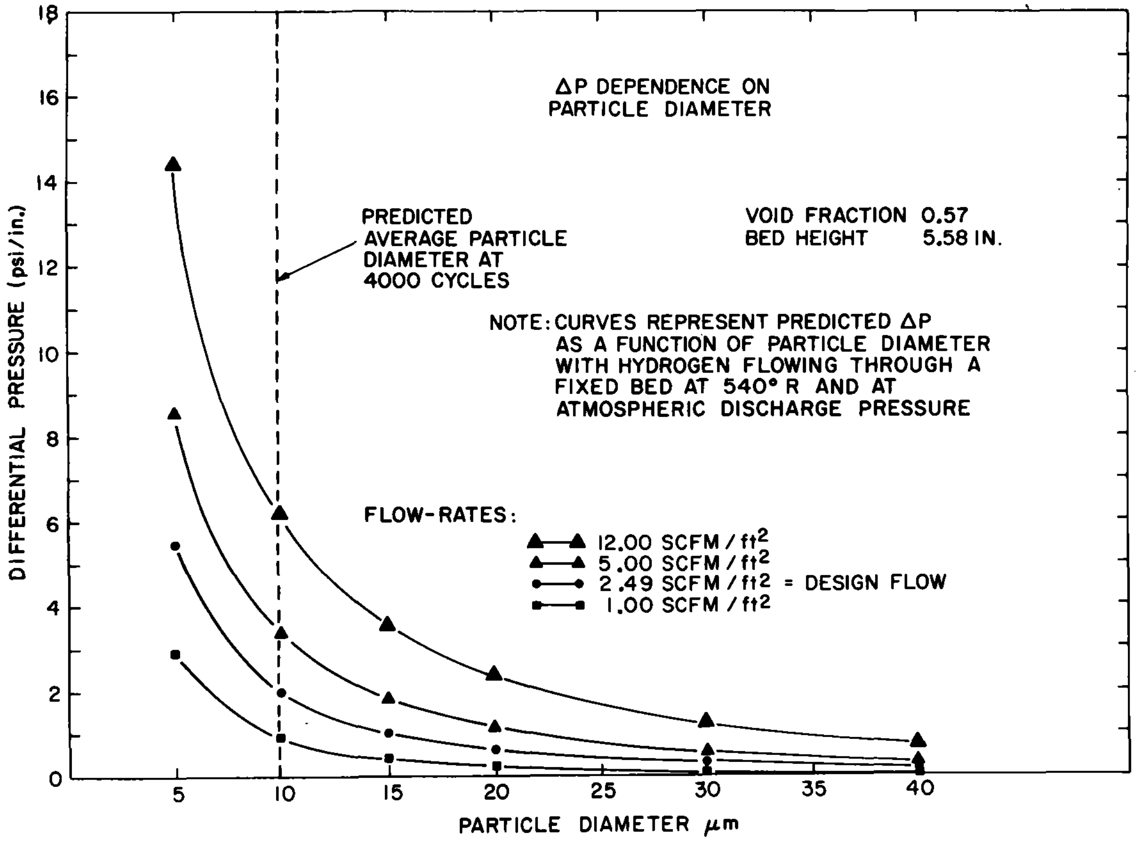

FIG. 1 Pressure Drop vs. Particle Size for Hydrogen Flow through a Fixed Bed.

FIGURE 1.

Pressure Drop vs. Particle size for
Hydrogen Flow through a Fixed Bed.

RATE STUDIES

The most extensive rate studies were made with a 6-in. diameter test bed* which is about 30 in. tall (3). It consists of a cylindrical vessel having an axial porous-metal tube and a water jacket. The main advantage of this design is that the water is adjacent to the major area of the bed; whereas in the usual water-tube design the water is adjacent to the minor area of the bed. This test bed contains 84 lbs. of FeTi alloy and has a working capacity of 1 lb. of hydrogen. Tests have shown that its 10-hour rating (constant flow rate) is 9 standard liters per minute (SLPM) for hydriding or dehydriding, using water at 30° and 50°C, respectively. By using hotter water during the dehydriding part of the cycle, a higher discharge rate can be sustained for a shorter period, or a higher terminal discharge pressure can be attained. At the highest flow rate tested, 40 SLPM, steady flow was maintained for 72 minutes during charging and 79 minutes during discharging. Tests were also made at intermediate flow rates, and another interesting test was made for comparison with the performance of a battery at the half-discharged condition. When the reservoir was half discharged at its 10-hour design rating of 9 SLPM, using water at 80°C 176°F), the flow rate was suddenly increased to 45 SLPM (limit of meter was 50 SLPM); the rate was sustained for 31 minutes and the terminal pressure was 43 psia. This 31-minute performance (at 100% efficiency) is equivalent to that of the best lead-acid battery in the standard 15-second discharge test (130 W/kg). Thus an $FeTiH_x$ reservoir can release much more power upon sudden demand than can the lead-acid battery under the test conditions specified; or it can sustain the equivalent power for a longer time.

Modeling studies of the ESEERCO Test Bed utilizing experimental values of pressure and a measured, but fixed, value of thermal conductivity have shown that good agreement can be attained between the analytical and experimental values for both the hydrogen discharge rate and the amount of hydrogen discharged. The agreement on temperature profiles was generally fair to good.

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* It is known as the ESEERCO Test Bed because the Empire State Electric Energy Research Corporation contributed substantially to its construction and operation.

CONTAINER MATERIAL TESTING

Five container materials are being exposed to an $FeTiH_x$ environment as part of a cooperative test program with Sandia Laboratories (SL) (4). The self-loaded tensile specimens were supplied by SL, and the candidate materials are those which had passed screening tests in hydrogen at SL. The materials being exposed are: carbon steels A106B (pipe material) and A516 Grade 70 (plate material), low-alloy steel 2¼% - ½% Mo, aluminum alloy 6061-T6, and stainless steel type 304. The latter two are being used for reference because their behavior in hydrogen is known in detail. Smooth and notched specimens, in plain and welded form, are included in the test matrix along with welded specimens having a solder (Sn-Pb) coating. The stress levels used were the ASME Code stress and a level 50% greater. Accelerated-cycle (hydriding-dehydriding) operation equivalent to about three years of exposure will be performed before the 80 specimens are sent to SL for examination and tensile testing.

HYDROGEN TECHNOLOGY ADVANCED COMPONENT TEST SYSTEMS (HYTACTS) PROGRAM

The objective of this program is to design, construct, test and evaluate advanced components of hydrogen-energy storage systems for the purpose of obtaining process, heat transfer and mechanical data which will assist industry in designing cost-effective components. Initially the work will center on metal-hydride energy storage devices for automotive and electric-utility applications. The first storage device designed for this program is known as the Variable-Parameter Test Unit. It is a hydride storage vessel which can be provided with various internal heat-exchanger configurations, and for added versatility it has a water jacket. The first configuration will probably have a group of U-tubes connected to inlet and outlet headers, each of which is connected to a nozzle on one head. The shell is 2 feet in diameter and will be 3-5 diameters long. Axial porous-metal tubing is used as the gas distributor and particle barrier (filter). Other configurations designed to enhance heat transfer will be tested and evaluated. Different configurations will be designed for the automotive application. The behavior of hydrides and system components will be examined, and performance studies will be made under a variety of operating conditions for several heat-exchanger configurations.

Subsequently preprototype electrochemical devices for generating and utilizing hydrogen will be added to the system to determine their performance and to investigate interface problems in the energy storage system. All of the major components will be fabricated commercially and incorporated in the test system at BNL.

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THE HYDROGEN-HALOGEN ENERGY STORAGE SYSTEM: PRELIMINARY FEASIBILITY AND ECONOMIC ASSESSMENT*

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1. Introduction

In 1964, Bianchi had suggested(1) that the hydrogen-chlorine (H_2-Cl_2) cell can be utilized as an electric energy storage battery. Recently, this system was proposed(2) for energy storage applications in electric utilities with the following advantages over the batteries and the hydrogen-oxygen (H_2-O_2) system which are being considered for the same purpose: (i) since the electrode reactions of H_2 and Cl_2 are quite reversible, one can expect an overall efficiency (electric → electric) of over 75%; (ii) the same electrodes can be used as electrocatalysts in both modes (chemical and electricity generation). Therefore, the same electrochemical cell can be used for both functions, which reduces the capital costs; (iii) the reactants for chemical and electricity generation are stored outside the cell which appears beneficial for a weekly cycle. A preliminary technical and economic feasibility assessment of the hydrogen-halogen battery as an electric energy storage system was undertaken, in our Laboratory, with support from the General Electric Company (GE), Energy Development Associates (EDA), Gould, Inc., and Bechtel Corp.

2. Conceptual Design of Energy Storage System

The conceptual design of a 20MW electric storage system, evolved for this study, is based on data furnished by the subcontractors; namely, Cl_2 cell characteristics and cost data by GE; Cl_2 storage and system characteristics by EDA; bromine (Br_2) system characteristics by Gould, Inc.; and system engineering analysis by the Bechtel Corp. This design appears satisfactory for a preliminary assessment. Because the Cl_2 and Br_2 systems are quite similar and Cl_2 technology is well developed, the H_2-Cl_2 system was used for the reference design. The process flow schematic for this reference design is shown in Figure 1.

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*This work was done under the auspices of the United States Energy Research and Development Administration

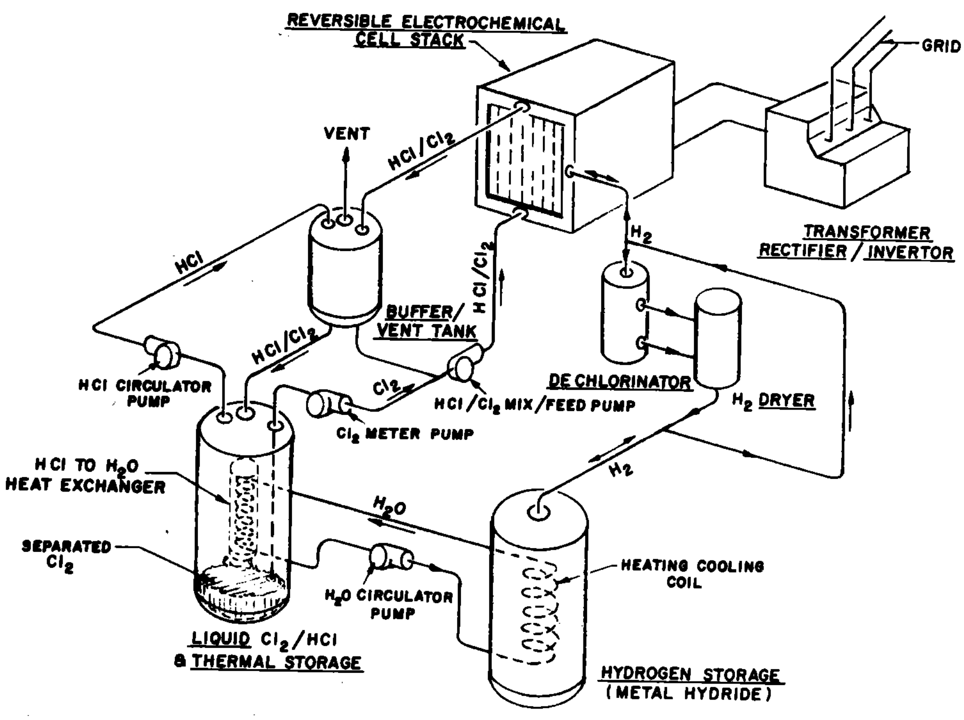

FIGURE I. H_2- Cl_2 ELECTROCHEMICAL ENERGY STORAGE POWER PLANT SCHEMATIC

The major components assumed for this system are: (i) a solid polymer electrolyte (SPE) electrochemical cell stack operating at pressures up to 600 psi and temperatures up to 200°F; (ii) a combination AC-DC convertor/DC-AC inverter with power control; (iii) an iron titanium (FeTi) metal hydride hydrogen storage subsystem; (iv) a combined liquid Cl_2 hydrochloric acid (HCl) storage subsystem; and (v) heat transfer and fluid transfer equipment. The high pressure capability of the GE SPE cell allows cost effective storage of the H_2 without the complication of mechanical compressors and the storage of Cl_2 as a liquid without the use of high pressure pumps. The HCl/Cl_2 storage also acts as a thermal storage system that not only can serve to store heat generated in the fuel cell mode for maintaining the proper temperature of the electrochemical subsystem, particularly in the electrolysis mode, but also can be used to desorb the H_2 from the metal hydride. Thus, no external heat is added to the system and a high overall system efficiency can be attained (>70%). Furthermore, this system seems to meet most of the important requirements of an electric-load-leveling-energy-storage system, i.e., high reliability and safety, long life, low maintenance, low cost, and the capability of operating on a daily and weekly storage cycle at a typical substation site. The latter requires high power and storage densities. This, together with the demand for near absolute safety, leads to the vertical storage tank installation with the heavier Cl_2 being stored underground so as to avoid dispersion of accidental Cl_2 leaks. The Cl_2 storage is well separated from the H_2 storage subsystem, as an additional safety measure.

3. Electrochemical Studies

In the H_2 and Cl_2 half cell studies, it was found, as expected, that the ionization reactions are highly diffusion controlled, whereas this is not the case with the gas evolution reactions. Platinum is a better electrocatalyst than graphite for both electrode reactions. However, RuO_2/TiO_2 is superior to Pt for the Cl_2 electrode reaction. In the cell provided by GE, for evaluation, it was found that the activation overpotential loss is quite small and one can expect high overall electric-to-electric efficiency while operating as an electrochemically regenerative system. The limiting current density in the discharge mode was found to be strongly dependent on the mass transfer of dissolved chlorine to the electrode and, thus, by the electrode configuration. Cell potential-current density relations in the GE SPE cell, during the charging and discharging modes, are shown in Figure 2.

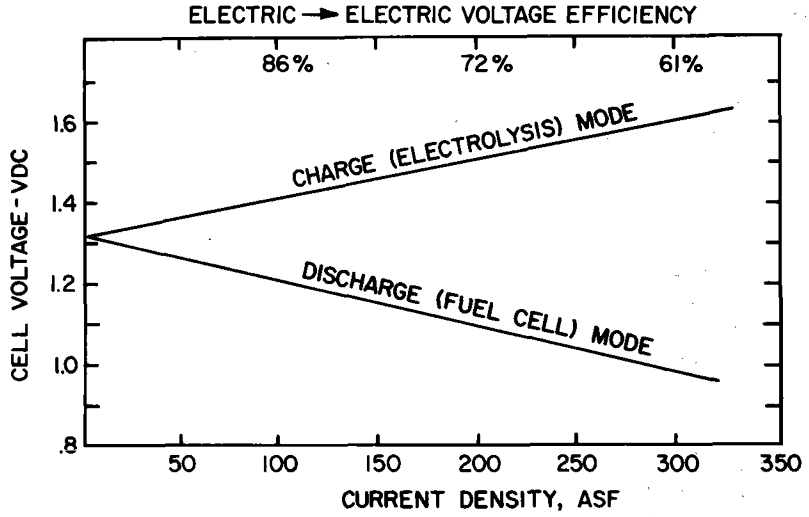

FIGURE 2. G.E. HYDROGEN CHLORINE BATTERY PERFORMANCE (OCT. 1976)

4. Hydrogen Storage Subsystem

The FeTi metal hydride storage system was selected for the following reasons: (i) near absolute safety from explosion (tests prove it will not explode even under gun fire); (ii) high storage density per unit volume; (iii) use of basically low-cost plentiful materials such as found in ilmenite ore; and (iv) the critical hydrogen desorption temperature and absorption pressure are compatible with the SPE electrochemical subsystem. The design chosen for this study was similar to the one developed at BNL as part of the BNL/ERDA Hydrogen Technology Program. Several salient details of the design worth noting are: all carbon steel construction for low cost; all welded x-rayable construction; no large mechanical seals; few prefabricated modules requiring only standard proven manufacturing and process techniques, except for a low-cost processing method which must be developed to refine the FeTi ore (ilmenite).

5. Halogen (Chlorine) Storage System

Similarly for the Cl_2 storage subsystem, as for the H_2 subsystem, the high pressure capability of the GE SPE cell leads to a reliable pressurized liquid storage subsystem without the use of high pressure mechanical pumps. The adaptation of a high pressure system also leads to a cost effective combination thermal and HCl/Cl_2 storage. Even though Cl_2 and HCl are stored in the same plastic-lined-steel tank, proper monitoring and feed of the Cl_2 to the electrochemical cells is easily accomplished because the heavier Cl_2 separates to the bottom of the storage tank. Based on these principles, the Gordon Hart (EDA) concept, involving steel storage vessel with a water-jacketed plastic liner/bladder, was evolved. The water in the jacket not only serves to control the heat generation by the electrochemical system, but also to concurrently transfer heat to the hydrogen storage system. This plastic-type liner also serves as a cost effective control of the system expansion and, in turn, the pressurization of the entire HCl/Cl_2 storage system. A similar storage system for storing the H_2-Br_2 can be evolved based on the above. Although it is a liquid at much lower pressures, its storage volume will be significantly larger.

6. Economic Assessment

Energy storage systems for electric-load-leveling applications are highly capital intensive and heavily dependent on the utilization time. In light of this, a simple cost figure of merit, dollars per kilowatt hour ($/KWh), was used in this first economic assessment (Table 1). The base assumptions were that a near-term development (early 1980's) would yield a system capable of >5000 hr design life, an overall efficiency of >70%, near absolute safety and reliability, high power (>250 amp/ft^2) and storage (>40KWh/ft^3) density.

Table I

20 MWe HYDROGEN-HALOGEN ENERGY STORAGE PLANT
FOR INSTALLATION AT EXISTING SUBSTATIONS (1/2 ACRE)

UNINSTALLED COSTS IN 1976 $/KWh

	H_2/Cl_2		Cost ($/KWh)	H_2/Br_2	
	10hrs*	5hrs*		10hrs	5hrs
1. Electrochemical Subsystem @ $80-100/KW	8	16		9.5	19
2. Power Conditioning Control @ $80/KW	8	16		8.5	17
3. Hydrogen Storage Subsystem (Based on Metal Hydride at $1/lb)	12	12		14	14
4. HCl/Cl_2 Storage Subsystem (Based on Liquid Chlorine at 450 PSI)	13	13		10	10
Total Capital Cost	41	57		42	60

According to Table I, it appears that there is little cost difference between the H_2/Cl_2 and H_2/Br_2 systems. Secondly, the cost is a stronger function of the utilization or discharge time for daily cycles (5 hrs discharge or less) where the major costs are in the power-related equipment. For the 10 hr discharge or weekly cycle, the storage and power-related costs are about equal. The latter results suggest that a 10 hr discharge time is near the optimum condition for this system.

7. Future Plans

(i) Electrochemical Studies

One of the important problems to be studied is the corrosion of the cell components, particularly the electrode materials. Also to be investigated is the effect of the Cl_2 partial pressure on the limiting current density, and on the off-setting effect of increased diffusion losses. The effect of temperature on cell performance is fairly well known, i.e., the higher the temperature, the lower the ohmic overpotential and the higher the diffusion losses. Also the higher the temperature the lower the solubility of Cl_2 in HCl which, in turn, decreases the limiting current density. It has been found that the concentration of HCl around 18-25% will minimize the overpotential, but an optimal concentration range should be determined for a cell employing the SPE technology.

Certain corrosion resistant metals, such as Ta and Nb (especially with addition of trace amounts of Fe), and alloys seem promising but are expensive. The application of certain polymer coatings for reducing corrosion rate will be investigated. Parasitic losses due to shunt currents, etc., on overall efficiency at different electrolyte conditions will also be determined.

(ii) Engineering Studies

Optimum system conditions will be established based on further experimental investigation of the electrochemical cell. The system conditions will also be established from a cost effective design analysis of the Cl_2 storage system and its interfacing problems, particularly those involving heat transfer and the H_2 storage subsystem. Based on these optimum system conditions, preliminary engineering designs of the major components, interconnecting piping, controls, and auxiliaries will be determined and the overall system costed. In this study (to be made in conjunction with the subcontractors and an Architect/Engineers Firm), particular attention will be given to obtaining an inherently safe and low-cost installation for electric load levelling at a typical substation. The corrosion resistance and creep properties of various plastics, such as the fluorocarbon polymers, will be investigated as to their suitability for liners of pipes and the HCl/Cl_2 storage tanks. A cost effective manufacturing method for low-cost production of these liners, for large tanks, will also be investigated. It is also important to assess the prospects of producing

FeTi directly from ilmenite ore.

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Acknowledgements

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THE LASL THERMOCHEMICAL HYDROGEN PROGRAM:
STATUS ON OCT. 31, 1976

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Introduction

The overall thermochemical hydrogen program at LASL may be described as two complementary programs. The first is a program of research in thermochemistry designed to provide the data base for the conception or identification, theoretical evaluation and preliminary development of thermochemical cycles for hydrogen production. The general procedures include theoretical, thermodynamic analyses of reaction types and specific reaction cycles that are potentially useful and a vigorous experimental program to evaluate and test specific chemical reactions; to determine reaction rates and reaction yields; to develop catalysts for specific reactions; and to determine experimentally, thermochemical data required for thermodynamic analyses. The second program is an application of results from the research program in the engineering of practical, efficient and economically sound processes that are optimized for each potential heat source.

Many of the cycles conceived and tested in the LASL program have been described by members of the hydrogen group in publications and in presentations at national and international scientific meetings (1-10). The program was also summarized, and some of the engineering problems identified, at the First Hydrogen Information Meeting for ERDA Contractors at BNL in April (11).

This paper will be limited to a brief summary of activities in the applied program since the first meeting. Most of the effort has been directed toward engineering design and analysis of two different systems of thermochemical cycles and to experimental studies in direct support of the engineering program.

Sulfuric Acid-Sulfur-Sulfide Systems:

The General Atomic Company (under contract to ERDA) has performed a preliminary engineering design and analysis of the LASL Baseline Cycle utilizing data and conditions from the LASL experimental program (12). The Baseline

Cycle may be described by the following reactions.

1. $1.5SO_2 + H_2O \longrightarrow H_2SO_4 + 0.5S$
2. $H_2SO_4 \longrightarrow H_2O + SO_2 + 0.5O_2$
3. $1.5S + H_2O \longrightarrow H_2S + 0.5SO_2$
4. $H_2S \longrightarrow H_2 + S$

In our experimental program, we had observed the following:

1. Through the use of iodine as a homogeneous catalyst, sulfuric acid had been produced in reaction 1 to a concentration near 12 moles. The reaction time was considered too slow for a practical cycle. However, it seemed probable that the rate of reaction 1 could be increased by higher temperatures and higher SO_2 pressures. Accordingly, 70% sulfuric acid from reaction 1 was specified for the General Atomic study.

2. Near equilibrium decomposition of sulfuric acid (using catalyst) had been demonstrated at LASL and also more extensively at GA and at Westinghouse.

3. The reaction between sulfur and water vapor had been demonstrated with good yield at 550-600°C. Methods for separating the SO_2 and H_2S products had not been demonstrated. Nevertheless, it was agreed that reaction 2 would be assumed to occur as written for the GA study and LASL continued laboratory work to develop separation methods.

4. Reaction 4 had been demonstrated at LASL. The reaction rate was found to be rapid and initial results suggested somewhat better yield than predicted by literature data. Literature data were used for the GA study.

The GA study indicated a heat efficiency of 27% for hydrogen production from a 3000 $MW_{(t)}$ nuclear plant. Actually, this is a reasonably encouraging number for a preliminary, nonoptimized design. However, the study also indicated a thermochemical plant cost of about three times the cost of the reactor. Most of this cost is attributed to the heat exchangers required for the cyclic decomposition of H_2S in reaction 4 above and, to a lesser extent, equipment required for drying H_2SO_4 produced in reaction 1.

It is probable that some improvement can be made in each of these conceptual systems. However, the realities of experimental study have indicated that the assumptions for reaction 3 were too optimistic. The only method we have demonstrated experimentally for completing reaction 3 involve the following reactions.

5. $CaCO_3 + 1.5S = CaS + 0.5SO_2 + CO_2$

6. $CaS + H_2O + CO_2 = CaCO_3 + H_2S$

Reaction 5 can be conducted at $\sim 600^\circ C$ in the presence of water vapor. Reaction 6 is a low temperature reaction.

Design studies have continued to determine possible improvements in the system for drying sulfuric acid and to assess the costs resulting from substituting reactions 4 and 5 for reaction 3. These results are not yet available. Nevertheless, it seems reasonably clear that the baseline cycle is unlikely to offer advantages over other known cycles (including the GA prime cycle) until improved reactions can be substituted for reactions 4, 5 and 6 and, (probably) iodine can be eliminated from the cycle and a different homogeneous catalyst used in reaction 1. Therefore, the baseline cycle has been returned to the experimental research portion of the LASL program.

Cerium Chloride Systems

A thermochemical cycle based on the Reverse Deacon Reaction and the hydrolysis of cerous chloride was identified in our experimental research program. The cycle may be described by the following reactions:

7. $Cl_2 + H_2O \longrightarrow 2HCl + 1/2\ O_2$ (high temp.)

8. $2CeO_2 + 8HCl \longrightarrow 2CeCl_3 + 4H_2O + Cl_2$ ($\sim 200^\circ C$)

9. $2CeCl_3 + 2H_2O = 2CeOCl + 4HCl$ ($\sim 600^\circ C$)

10. $2CeOCl + 2H_2O = 2CeO_2 + 2HCl + H_2$ (high temp)

The cycle has been demonstrated experimentally except for the possibility that CeO_2 from reaction 10 will not be sufficiently reactive in reaction 8. Up to the present, CeO_2 used in reaction 8 has been prepared by decomposing $Ce_2(CO_3)_3$. Good yields can be achieved for all of the reactions except reaction 10. This reaction exhibits a positive ΔG^0 even at 1200 K and the gases evolved from the reaction contain 10-12 molecules of H_2O per molecule of H_2. The hydrolysis step (reaction 10) in the cerium chloride cycle is quite similar to the hydrolysis step in some iron chloride cycles. Since the remainder of the cerium chloride cycle seems simpler than iron-chloride cycles, it is believed that the cerium chloride cycle may offer advantages.

During this past summer at LASL, Professor D. L. Ulrichson of Iowa State University prepared different flow sheets and made preliminary design evaluations of the cerium chloride cycle. The completed report is not yet available, but the following interesting features are clearly apparent:

> It is rather expensive in terms of equipment and process heat to process large volumes of $HCl-H_2O$ mixtures where concentration and/or condensation steps are required. In particular, it is difficult to remove H_2 from the H_2O-HCl mixture evolved in reaction 10 in an efficient and economical way.

In view of the apparent disadvantages of the cerium chloride cycle as written above, the following variation has developed from continued laboratory experimentation.

11. $Cl_2 + H_2O = 2HCl + 1/2\ O_2$

12. $2CeO_2 + 8HCl = 2CeCl_3 + 4H_2O + Cl_2$

13. $3CeCl_3 + 3H_2O = 3CeOCl + 6HCl$

14. $3CeOCl + 3CO_2 \longrightarrow Ce_2(CO_3)_{3\,(ppt)} + CeCl_3(\text{solution})$

15. $Ce_2(CO_3)_3 + H_2O \longrightarrow 2CeO_2 + 3CO_2 + H_2$

The apparent disadvantage of this variation is the necessity for drying the $CeCl_3$ solution from reaction 14. The apparent advantages derive from:

1. The fact that all reactions can be conducted under conditions where ΔG^0 is negative.

2. The fact that the H_2 separation is from H_2O-CO_2 mixtures rather than $HCl-H_2O$ mixtures.

3. The fact that very high HCl/H_2O ratios are produced in reactions 11 and 13 and concentration steps do not appear to be necessary.

It is interesting to note that the decomposition of moist (or hydrated) $Ce_2(CO_3)_3$ from reaction 14, decomposes on heating via the following reactions:

16. $Ce_2(CO_3)_3 + H_2O = 2Ce(OH)CO_3 + CO_2$

17. $2Ce(OH)CO_3 = Ce_2O_2CO_3 + H_2O + CO_2$

18. $Ce_2O_2CO_3 = 2CeO_2 + CO$

The reactions occur successively at different temperatures and (therefore) accept heat over a range of temperatures. Reaction 18 can be conducted as written. In this case the reactions constitute a cycle for splitting carbon dioxide. Alternatively, water vapor can be added during reaction 18 and hydrogen (with some CO and some CH_4) is evolved.

The preparation of flow sheets, together with engineering design activities, are continuing for the cerium chloride cycle and the different versions of the cerium-chloride-carbonate cycle.

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THE THERMOCHEMICAL WATER-SPLITTING PROGRAM AT GENERAL ATOMIC

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General Atomic (GA) is developing a promising thermochemical water-splitting cycle for hydrogen production. This cycle, which is based on a main reaction involving iodine and sulfur, can be conducted as an all liquid and gas process, and has heat requirements that are compatible with the high-temperature gas-cooled reactor (HTGR).

In addition to developing its own cycle, GA has been supporting the Los Alamos Scientific Laboratory (LASL) by performing engineering on selected LASL cycles. Both the engineering support provided LASL and the GA program will be described in this abstract.

LASL CYCLES

Work for LASL was first initiated under ERDA funding in CY 1975. The goal of that work was to do a preliminary engineering design and cost estimate for the LASL baseline sulfuric acid-sulfur-oxide-sulfide cycle. This four-step cycle is represented by the following set of equations.

$$H_2S \rightarrow H_2 + S \qquad (1)$$

$$\frac{3}{2} S + H_2O \rightarrow H_2S + \frac{1}{2} SO_2 \qquad (2)$$

$$\frac{3}{2} SO_2 + H_2O \rightarrow H_2SO_4 + \frac{1}{2} S \qquad (3)$$

$$H_2SO_4 \rightarrow H_2O + SO_2 + \frac{1}{2} O_2 \qquad (4)$$

Assuming the HTGR as a heat source, a complete flow sheet was prepared for the cycle, along with heat and mass balance.

Major equipment items were sized from the flow sheet and used as the basis for a first-order cost estimate.

The nonoptimized thermal efficiency was 27%. For the flow sheet as developed, the chemical plant costs were heat-exchange dominated and of the order of 3.5 times the cost of the nuclear heat source. Details are provided in the final report. (1)

In July, 1976, GA began work under a LASL subcontract to do engineering on a modification to the LASL baseline cycle, preliminary engineering on an additional LASL cycle, and investigate vapor-liquid equilibria and metallurgy for sulfuric acid. This contract is scheduled for completion November 15, 1976. The sulfuric acid work was also a part of the GA cycle development program.

The modified LASL baseline cycle is represented by the following set of equations.

$$H_2S \rightarrow H_2 + S \qquad (5)$$

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (6)$$

$$CaO + \frac{3}{2} S \rightarrow CaS + \frac{1}{2} SO_2 \qquad (7)$$

$$CaS + H_2O + CO_2 \rightarrow CaCO_3 + H_2S \qquad (8)$$

$$\frac{3}{2} SO_2 + H_2O \rightarrow H_2SO_4 + \frac{1}{2} S \qquad (9)$$

$$H_2SO_4 \rightarrow H_2O + SO_2 + \frac{1}{2} O_2 \qquad (10)$$

where Eqs. 6, 7, and 8 have replaced Eq. 2 of the baseline cycle. This modification is under consideration by LASL because of difficulty in separating the products of Eq. 2.

The additional LASL cycle investigated by GA is also a six-step cycle, and is represented by the following set of equations.

$$\frac{3}{2} SO_2 + H_2O \rightarrow H_2SO_4 + \frac{1}{2} S \qquad (11)$$

$$H_2SO_4 \rightarrow H_2O + SO_2 + \frac{1}{2} O_2 \qquad (12)$$

$$\frac{1}{2} S + Cu_2O \rightarrow 2\ Cu + \frac{1}{2} SO_2 \qquad (13)$$

$$2\ Cu + 2\ HBr \rightarrow 2\ CuBr + H_2 \qquad (14)$$

$$2\ CuBr + MgO \rightarrow MgBr_2 + Cu_2O \qquad (15)$$

$$MgBr_2 + H_2O \rightarrow MgO + 2HBr \qquad (16)$$

This has been designated the copper-copper bromide-oxide sulfide, magnesium bromide-oxide, sulfuric acid-sulfur oxides-sulfur cycle. A reason for doing preliminary engineering on this cycle was to assess the impact of an extensive solids handling requirement.

Although a complete flow sheet section meshing and heat balance was not prepared for the modified baseline cycle, the thermal efficiency is estimated to be around 20%. For the additional cycle, a non-optimized flow sheet was prepared, and the preliminary heat balance yields an efficiency of 9.6%. If extensive heat recuperation is implemented, the efficiency could rise to around 15%. With other projected improvements the efficiency might rise to around 20%. The following other conclusions have been drawn from these engineering efforts: 1) Due to irreversibilities, the more steps a cycle has the more difficult it is to make it efficient; 2) If a cycle has too few steps then there is trouble in matching it to the heat source; 3) The amount of solvent or inert gas recycle must be kept to a minimum because it reduces efficiency and/or increases capital cost; 4) In order to confidently design solids handling steps it is necessary to have a large mass of empirical data on solids and particulates properties.

GA CYCLE

General Atomic first became interested in thermochemical water-splitting because it characteristically requires high temperature heat input, and represents a possible application for the HTGR. It also now appears that GA's fixed mirror solar concentrator (FMSC) and Doublet fusion reactor concept could also be applied to water splitting.

In October, 1972, GA began the development of a computer code that could search thermodynamic and thermochemical data for combinations of chemical reactions that could form closed hydrogen-producing cycles (2). This search, supplemented by manual evaluations and feasibility demonstrations in the laboratory, resulted in the selection of the three-step cycle represented by the following set of equations.

$$2\ H_2O + SO_2 + xI_2 \rightarrow H_2SO_4 + 2\ HI_x \quad \text{Aqueous} \qquad (17)$$

$$H_2SO_4 \rightarrow H_2O + SO_2 + \frac{1}{2}\ O_2\ (1089\ K) \qquad (18)$$

$$2\ HI_x \rightarrow xI_2 + H_2 \qquad (572K) \qquad (19)$$

The HI_x in Eq. 17 represents the average of several HI_n compounds formed in the reaction. The HI is a good solvent for iodine, and the resulting HI_x solution is not miscible in H_2SO_4. As the reaction proceeds, H_2SO_4 rains upward, leaving behind a lower component rich in HI_x. The acids can be readily separated and thermally decomposed to obtain the hydrogen and oxygen products and the iodine and SO_2 for recycle.

The first public disclosure of this cycle was in March, 1976 (3). General Atomic is cooperating with the American Gas Association and Northeast Utilities Service Company, and hopes to cooperate with ERDA, to develop around this cycle a thermochemical water-splitting process that can be demonstrated to be a commercially feasible source of hydrogen. Progress of the development program through September, 1976 was described at a recent technical conference (4). This development program currently includes work in chemistry, chemical engineering, and materials of construction corrosion.

The conditions to maximize the yield of the H_2O-SO_2-I_2 reaction have been determined. By conducting the reaction at around 368 K with the solution saturated in iodine a sulfuric acid concentration of around 48 wt % is produced. It also reduces tramp H_2SO_4 in the HI_x phase to around 0.03 wt %, and the HI_x can be vacuum degassed of dissolved SO_2.

High pressure distillation and extractive distillation are two methods that are being investigated for recovering HI from HI_x. HI cannot be efficiently distilled out of the HI_x at atmospheric pressure because of the formation of an azeotrope. The high pressure work has consisted of capillary distillations, and the equipment has been built for conducting single-plate distillations. Extractive distillation studies have been employing phosphoric acid as the dehydration agent.

Experimental studies of catalytic cracking of HI have demonstrated a particular catalyst to be functional at temperatures where I_2 could be produced as a liquid. This catalyst is very effective and does not appear to be easily poisoned.

Studies of H_2SO_4 catalytic decomposition with platinum have demonstrated that decomposition is very dependent on a catalyst, and that once the gases are disentrained from the catalyst, cooldown can be accomplished without substantial back reaction of SO_2. Hardware is under construction to investigate in greater detail the catalytic decomposition of H_2SO_4.

Studies of H_2O-H_2SO_4 vapor-liquid equilibria at elevated pressure were undertaken with LASL funding to find out whether there is an appreciable shift of azeotropic concentrations and to define conditions around the azeotrope for column design purposes. The shift has been found to be from 98.5 wt % at atmospheric down to 97.3 wt % at 23 atm. The vapor-liquid equilibria exhibit a considerable spread between liquid and vapor curves indicating that separation of H_2O and H_2SO_4 will be relatively easy.

In the next year, with ERDA funding, it is intended to begin bench-scale tests of key steps in the cycle. Two engineering flow sheets have been prepared; the first, completed late in 1974, and based on optimistic chemical data estimates, resulted in an estimated thermal efficiency of 52%. Another flow sheet was completed in April, 1976, and incorporated some of the laboratory-derived data. The estimated thermal efficiency for this flow sheet was 41%. In the next year, with ERDA funding, it is intended to revise the flow sheet, incorporating new chemical data and improving the heat utilization between various portions of the process. It is anticipated that the thermal efficiency will eventually rise to between 45 and 50%.

A test program is in progress to evaluate the corrosion performance of possible construction materials in the process fluid environments. Some industrial experience has been found on the successful containment of SO_2 and SO_3 gaseous environments at elevated temperature. No industrial experience has been found for a HI + I environment at elevated temperature.

A pyrex and quartz materials test rig was constructed to subject material samples to the high temperature decomposition products of sulfuric acid. With private and LASL funding, a thousand hour test of several materials was conducted, including bare samples, and samples with three types of aluminized coating. In addition to weight change data taken during the course of the test, metallography was performed and revealed Incoloy 800 with an aluminized coating to be the most promising candidate. It developed an outer oxide with very little internal oxidation, had no sulfur within the coating, and a diffusion zone between the coating and base metal that showed only a small widening with time. No cracks were observed in the coatings.

A test apparatus has been constructed for evaluating the corrosion behavior of materials at the liquid-vapor interface of a boiling HI_x solution. Although this apparatus has not been used, preliminary tests of several hundred hours duration in a room temperature solution, and other exposure tests of about 5-hr. duration and within a temperature range of 572 to 772 K, and pressures of 136 to 204 atm have shown the metals titanium, molybdenum, tantalum, and Inconel 600 to exhibit moderate to rapid corrosion in the liquid phase. Thus, the HI_x environment may just be the most demanding of all the process environments from a corrosion viewpoint.

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ANALYSIS AND EVALUATION OF THERMOCHEMICAL HYDROGEN PRODUCING PROCESSES

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As outlined in Figure 1, this paper presents a summary of the history and present state of the Hydrogen Energy Programs at the University of Kentucky. A brief statement of the work being planned for the future is also included.

The earliest work on the thermochemical production of hydrogen from water at the University of Kentucky was done in 1964-65 under contract to General Motors as a part of the Energy Depot project. This work dealt with thermodynamic aspects of the problems and techniques for preliminary process evaluation. The work is reported in references 1 and 2.

From 1968-71 a program dealing with fluid mechanics in water electrolyzers was sponsored by the National Science Foundation. Experimental data were obtained describing the void fraction, slip ratio and current density distribution. This kind of information will be important in the design and/or analysis of high performance water electrolyzers and is reported in references 3, 4, and 5.

In early 1973 NASA-Lewis contracted with the University of Kentucky for a program dealing with the development and evaluation of thermochemical processes. The process evaluation technique resulting from this activity is embodied in the HYDRGN computer program which operates with a thermodynamic data bank and two NASA programs which handle thermodynamic properties and determine equilibrium composition. The HYDRGN evaluation procedure requires as input the chemical reactions comprising the process and the operating temperature and pressure for each. The output includes:

1. Changes in enthalpy, entropy, and Gibbs function for each step--including heating and cooling--of the process.

THE THERMOCHEMICAL HYDROGEN PROGRAM AT THE UNIVERSITY OF KENTUCKY

1964-65	ENERGY DEPOT PROJECT (General Motors) - Thermodynamics of Hydrogen Production from Water Using Thermochemical Cycles
1968-71	FLUID MECHANICS IN WATER ELECTROLYZERS (National Science Foundation) - Void Fraction, Slip Ratio, Current Density
1973	HYDRGN COMPUTER PROGRAM (NASA-Lewis) - A Computerized Technique for the Analysis of Thermochemical Water-Splitting Cycles
1974	PARAMETRIC STUDY OF THE WESTINGHOUSE SULFUR CYCLE - (Westinghouse)
	DEVELOPMENT OF CYCLES BASED ON SULFUR CHEMISTRY - (NASA)
1975	A TECHNOECONOMIC ANALYSIS OF LARGE SCALE THERMOCHEMICAL PRODUCTION OF HYDROGEN (Electric Power Research Institute)
	LABORATORY WORK ON CHEMICAL REACTIONS OF A Fe/Ba/S CYCLE - (University of Kentucky/NASA)
1976	DEVELOPMENT OF A "HEAT PENALTY" ANALYSIS OF THERMOCHEMICAL WATER-SPLITTING CYCLES - (Univeristy of Kentucky/Electric Power Research Institute)
	REVISION OF HYDRGN COMPUTER PROGRAM (ERDA) - 1) Allow for the Use of Elevated Pressures 2) Allow for a "Topping Cycle" to Produce Useful Work 3) Calculate Loss Coefficients and Individual Stage Efficiencies
FUTURE WORK	CONTINUOUS EVALUATION OF PROMISING THERMOCHEMICAL CYCLES 1) State of Experimental Work on Chemical Reactions (reaction conditions, side reactions, kinetics) 2) Flowsheet Development 3) Heat Penalty and Efficiency 4) Economics

FIGURE 1

2. Magnitude of the recycle streams and an estimate of the work of separation as a function of approach to equilibrium and inlet ratio of the reactants.

3. A scheme for internal process heat recovery which matches heat requirement and availability in the various streams.

4. Two estimates of the process thermal efficiency employing different assumptions concerning efficiency of separation.

The HYDRGN program has been favorably received and is being used at IGT and the University of New Mexico as well as by other organizations. It provides a starting point for more detailed studies. It was modified to perform parametric studies on the hybrid sulfuric acid process for Westinghouse (6) and was used in a technoeconomic study being performed for the Electric Power Research Institute (7). Results from the HYDRGN procedure were used in the preparation of an appendix for the Jet Propulsion Laboratory study reported under the title "Hydrogen Tomorrow" (8).

The results of University of Kentucky efforts to devise a number of efficient sulfur cycles have been published (9) and experimental work has been conducted on the hydrogen producing step of one of these cycles (10).

A new "Heat Penalty" analysis of thermochemical cycles has been formulated by Professor K. F. Knoche of the Technical University at Aachen, West Germany during his work at the University of Kentucky from March to September of 1976 (11 - 14). An example of the application of this technique to the Westinghouse Sulfur Cycle is shown in Figure 2.

Part of the present work being conducted consists of improvements to the HYDRGN computer program. This work which is being sponsored by ERDA consists of modifying the program to allow for the following:

1. Use of Elevated Pressures

2. Use of a "Topping Cycle" to Produce Useful Work

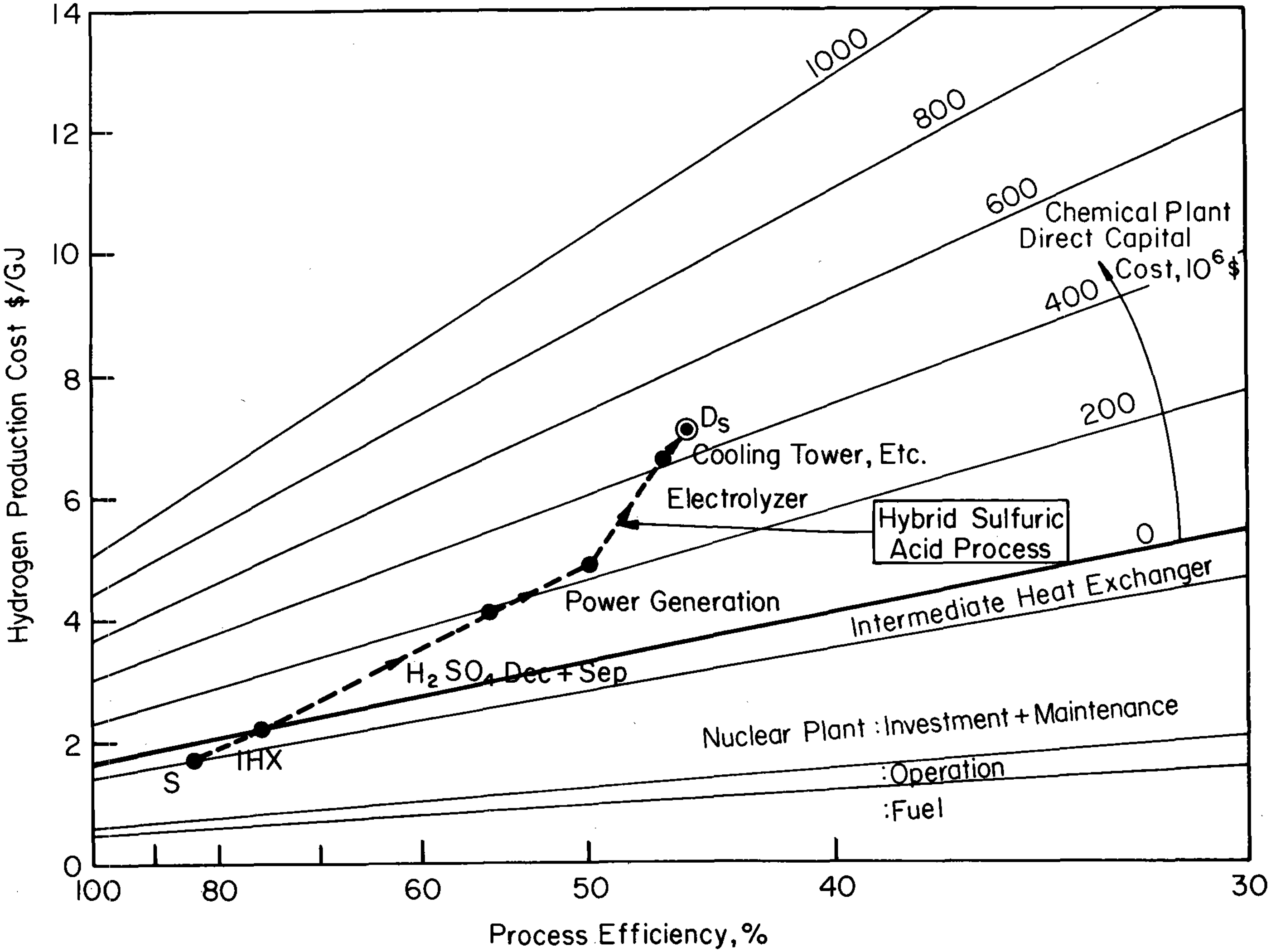

FIGURE 2. PRODUCTION COST VERSUS PROCESS EFFICIENCY FOR THE HYBRID SULFURIC ACID PROCESS

3. Calculation of Loss Coefficients and Individual Stage Efficiencies

In the future, the University of Kentucky plans to be part of a group which will evaluate and review the current state of development of various processes and make independent preliminary estimates of process efficiency and economics. In particular, this group would provide evaluations in the areas of:

1. Chemistry

2. Flowsheet Development

3. Heat Penalty and Efficiency

4. Economics

The permanent members of the University of Kentucky hydrogen group include J. E. Funk, W. L. Conger, and R. H. Carty. Others who have worked in the program include: J. F. Thorpe, now at the University of Cincinnati; R. Barker, now at Oak Ridge National Laboratory; Kenneth E. Cox, now at the University of New Mexico; F. Nakano, now at the Osaka Gas Company; and M. Soliman, now at the University of Riyadh, Saudi Arabia. Professor K. F. Knoche of the Technical University at Aachen, West Germany, has worked with the University of Kentucky group for seven months (March-September) during 1976 and Dr. K. Ota of the University of Tokyo has joined the program on a post-doctoral appointment. The group has participated in the formation of the International Journal for Hydrogen Energy and is represented on the editorial board.

In addition to the references cited, sixteen other publications have resulted from the Hydrogen Program at the University of Kentucky.

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THE ZNSE THERMOCHEMICAL CYCLE

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Abstract

Scientific feasibility of the ZnSe thermochemical cycle was clearly established through laboratory experimentation 2 years ago. Since that time we have continued experimentation that has lead to refinement and improvement of the cycle. Recently, through a joint effort with United Engineers and Constructors, we conducted a preliminary process definition and economic analysis of the cycle. The study allowed us to better define problem areas and set directions for future development. Thus, critical problem areas are: 1. optimization of cycle efficiency and economics, 2. process design development for main chemical reactors in the cycle, and 3. evaluation of selenium resources. Further, the study indicated that an area of major improvement exists in this cycle if we can reduce the number of moles of $ZnSO_4$ from 2 to 1 for each mole of H_2 produced. This would substantially reduce the high grade energy required for the cycle, and increase ideal cycle efficiency from 49 to ~70%. We are in the process of exploring this approach, and have two potential methods that show promise.

Background

Thermochemical cycles for production of hydrogen have been under study at the Lawrence Livermore Laboratory for the past five years. Studies have been concentrated on selenium based cycles because of the favorable thermodynamic criteria for these cycles. For the past 2-1/2 years, under funding provided by ERDA's Division of Physical Research, we have carried out laboratory experimentation on a cycle based on ZnSe. Scientific feasibility of the ZnSe cycle was established 2 years ago through small batch type laboratory experiments, and refinement of the cycle chemistry is currently underway. Under the sponsorship of Division of Energy Storage Systems, we have recently conducted a process definition and economic analysis of the cycle.

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The ZnSe cycle was selected for development at LLL because of its favorable chemistry and thermodynamics, and because of its prospects for high thermal efficiency (>40%), minimal separative work, and reasonable materials requirements. Work in the laboratory has shown that the cycle clearly works. Free energy changes are negative for all of the reactions, and reaction rates are fast (about 5 to 15 minutes). Conversions are high and free of undesirable by-products, separative work is low, and materials problems are minimal.

Goals

We plan to conduct selected engineering development studies on the ZnSe thermochemical cycle with the objective of evaluating its suitability for 1. bench scale closed cycle demonstration, and 2. economic viability of a commercial plant. More specifically, we plan to conduct studies in the following areas:

- Optimization of the cycle for efficiency and economics
- Process design/development for the main chemical reactors in the cycle ($ZnSO_4$ decomposer, ZnO-Se-SO_2 reactor, and ZnSe hydrolyser).
- Evaluation of solar concentrators as an alternate heat source for the cycle.
- Evaluation of selenium resources.

Cycle Chemistry

The ZnSe cycle is described by the following major reaction steps:

	$\Delta H^\circ 298$ (kj/mol)
(1) $2ZnO + Se(\ell) + SO_2(g) \xrightarrow{800K} ZnSe + ZnSO_4$	-159
(2) $ZnSe + 2HCl(g) \xrightarrow{350K} ZnCl_2(aq) + H_2Se(g)$	-69
(3) $ZnCl_2(aq) + SO_3(g) + H_2O(\ell) \xrightarrow{400K} ZnSO_4 + 2HCl(g)$	-39
(4) $2ZnSO_4 \xrightarrow{1200K} 2\ ZnO + SO_2(g) + SO_3(g) + 1/2O_2(g)$	576
(5) $H_2Se(g) \xrightarrow{750K} Se(\ell) + H_2(g)$	-23

We have experimentally studied the chemistry in some detail for reactions (1) and (2), and results have been submitted for publication (1). Detailed data have also been obtained recently on reactions (3) and (5), but have not yet been published. A substantial literature exists on reaction (4).

Reaction (1) proceeds in ~15 min. at 800K and is free of side reactions. Degree of completion of the reaction depends primarily on intimacy of mixing of ZnO/Se and ranges from 60% for poorly mixed material to better than 95% for well mixed material. Reaction rate is also accelerated by increased SO_2 pressure. Reactions (2) and (3) both occur in less than 5 min. at greater than 95% yield. Reaction (4) is calculated from literature data (2) to be 30% complete in 1.3 min. and 98% complete in 16 min. at 1200K. The reaction proceeds in two stages. In the first stage $ZnSO_4$ is decomposed to an oxysulfate ($ZnO \cdot 2\ ZnSO_4$), which then in the second stage goes to ZnO. For reaction (5), we find that H_2Se is 60% decomposed in 5 min. at 750K.

Although additional chemistry refinement and better definition of reaction mechanisms and kinetics are needed on all of these reactions, the more critical need from a mission-oriented standpoint is to evaluate the reactions in continuous mode operations. This type of operational data is essential for process design, and for providing a more realistic input for cost analyses. Data is especially required for reaction (4), which is the primary heat consuming step in the cycle, but is also vitally important for reactions (1) and (2) because they will require novel process designs.

Engineering Development

Engineering development on this cycle is at an early stage: 1. preliminary process definition and economic analyses have been carried out in a joint in-house and contractual effort with United Engineers and Constructors, and 2. planning and experimentation are just beginning on continuous process operations.

The economic analysis was carried out on a limited time and funding basis, and within these constraints it was only possible to carry out the study on a once-through basis. A number of details could not be adequately completed, let alone exploration of alternate design approaches and process optimization. Cycle efficiency, after correcting for unused high temperature process and isentropic heats in the analysis, is about 32%. An ultra-conservative estimate of the hydrogen production cost is $\$28/10^6$ BTU. Not much significance can be attached to the absolute values of cycle efficiency or hydrogen costs, particularly hydrogen costs, at this stage of analysis. More realistically, for an optimized cycle we would expect cycle efficiency to be ~40% and hydrogen production costs ~\$9/10^6 BTU.

Although not quantitative, the results of the analysis have been very useful in indicating areas of the cycle that are readily achievable, and in identifying other areas where substantial improvements can be made. For the process as it stands, the major cost items are: 1. the $ZnSO_4$ decomposer, 2. the $ZnSe/ZnSO_4$ separator, and 3. the $ZnCl_2$ to $ZnSO_4$ convertor. Availability of selenium in large quantities is also a problem, and we need to better evaluate selenium resources. Finally, a major improvement in cycle efficiency can be achieved if $ZnCl_2$ can be converted directly to ZnO without going through a $ZnSO_4$ step. This would reduce the moles of $ZnSO_4$ in the cycle from 2 to 1 for each mole of hydrogen produced, and increase the ideal thermal efficiency from 49 to ~70%. It would further reduce costs on two major equipment items. More detailed comments are given next on the $ZnSO_4$ decomposer design, and on methods for conversion of $ZnCl_2$ to ZnO.

The $ZnSO_4$ decomposer design for purposes of the economic analysis was assumed to be an isothermal fluidized bed operated at 1200K in a reaction vessel containing a bundle of heat exchanger tubes heated by circulating He. Decomposition product gases were partially recirculated to fluidize the bed. Significant design improvements can be achieved here by decomposing the $ZnSO_4$ over a larger ΔT in order to couple better with the heat source, and going to a moving bed type of process to lower gas circulation costs and move the $ZnSO_4$ through faster.

In order to develop an optimum design for the $ZnSO_4$ decomposer, we need to determine the kinetics of $ZnSO_4$ decomposition under conditions simulating a moving bed design. The current literature is inadequate in that it deals with the case of $ZnSO_4$ powder contained in a boat in a tube furnace with a slowly flowing gas stream passing over it. An insulating oxide layer develops on the surface of the powder and both heat and mass transport become seriously limited as decomposition proceeds. We anticipate that decomposition rates will be markedly accelerated in a moving bed system, and are planning experiments to investigate this. We calculate that radiant heat transport for 100 μm particles should be sufficiently rapid to heat up and decompose the particles in less than 1 sec. if kinetics permits.

Two possible approaches for conversion of $ZnCl_2$ to ZnO are presently under study. The first involves the following reactions:

(6) $ZnCl_2(\ell) + 2\ HBO_2(\ell) \xrightarrow{650K} ZnO \cdot B_2O_3(s) + 2\ HCl(g)$

(7) $ZnO \cdot B_2O_3(s) + H_2O(\ell) + CO_2(g) \xrightarrow{300K} ZnCO_3(s) + 2\ HBO_2(aq)$

(8) $ZnCO_3(s) \xrightarrow{700K} ZnO(s) + CO_2(g)$

We have made preliminary measurements of reaction (6) in the laboratory and have detected HCl given off, but quantitative studies have not been made. All of the reactions can be predicted to proceed from thermodynamics.

In the second approach, we are considering conversion of $ZnCl_2$ to ZnO by a process described in the literature (3) in which concentrated aqueous solutions of $ZnCl_2$ are evaporated to produce HCl(g) and a series of hydroxychlorides. A number of these hydroxychlorides have been characterized by X-ray, e.g., Zn(OH)Cl, $Zn_5(OH)_8Cl_2$, and $Zn_5(OH)_{8.75}Cl_{1.25}$ (4). We need to quantitatively explore these reactions in the laboratory, as well as methods for separation of ZnO from the hydroxychloride.

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SULFUR CYCLE WATER DECOMPOSITION SYSTEM

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The objective of this program is to assess the technical and economic feasibility of a hydrogen generation process based upon the electrolysis of sulfurous acid. To do this, a multi-task program is being carried out to experimentally determine the operating characteristics of key process steps in the hydrogen generating cycle and to perform engineering and economic analyses to evaluate the system.

The process being evaluated called the Sulfur Cycle Water Decomposition System, is a two-step hybrid electrochemical/thermochemical cycle. The process, in its most general form, consists of two chemical reactions - one for producing oxygen and the other for producing hydrogen. The production of oxygen occurs via the thermal reduction of sulfur trioxide obtained from sulfuric acid.

$$H_2SO_4 \longrightarrow H_2O + 1/2\ O_2 + SO_2 \qquad (1)$$

The equilibrium for Reaction 1 lies to the right at temperatures above 1000K. Catalysts are available for accelerating the rate of sulfur trioxide reduction to sulfur dioxide and oxygen. The process is completed by using the sulfur dioxide from the thermal reduction step to depolarize the anode of a water electrolyzer. The overall reaction occurring electrochemically is

$$2H_2O + SO_2 \longrightarrow H_2 + H_2SO_4 \qquad (2)$$

This is comprised of the individual reactions:

		E^o
Cathode:	$2H^+ + 2e^- \longrightarrow H_2$	0.00 Volts
Anode:	$H_2SO_3 + H_2O \longrightarrow 2H^+ + H_2SO_4 + 2e^-$	-0.17 Volts

The net result of Reactions 1 and 2 is the decomposition of water into hydrogen and oxygen. Sulfur oxides are involved as recycling intermediates. Although electrical power is required in the electrolyzer, much smaller quantities than those necessary in conventional electrolysis are needed.

The process is shown schematically in Figure 1. Hydrogen is generated electrolytically in an electrolysis cell which anodically oxidizes sulfurous acid to sulfuric acid while simultaneously generating hydrogen at the cathode. Sulfuric acid formed in the electrolyzer is sent to a surge tank from where it is fed to two vaporizers in series. The first of these is a recuperative heat exchanger heated by the effluent from the high temperature sulfur trioxide reduction reactor. The second is heated by a high temperature heat source. The sulfur trioxide-steam mixture from the second vaporizer flows to an indirectly heated reduction reactor where sulfur dioxide and oxygen are formed. These gases are subsequently cooled against the incoming acid and unreacted sulfur trioxide is recovered as sulfuric acid in a knock-out system. Wet sulfur dioxide and oxygen flow to the separation system. Steam is first condensed and recycled, following which the SO_2/O_2 mixture is compressed and subsequently separated. A conceptual design and cost estimate for a large hydrogen production facility using this process (NASA-CR-134976, April 1976) has shown that hydrogen could be produced at overall thermal efficiencies in excess of 45 percent.

The experimental studies being conducted under this contract {E(49-18)-2262} are concentrated in those areas important to the success of the process. These studies are concerned with the sulfur acid electrolyzer (membrane analysis, anode development, and cell demonstration), acid concentration (alternate concentration systems and materials for the sulfuric acid vaporizer), and sulfur trioxide reduction (catalyst evaluation). In addition, engineering trade-off studies are being performed.

Considerable progress was made in each of the major program areas since the inception of this contract in May, 1976. These results are summarized in the paragraphs below.

ELECTROLYSIS

Membrane Evaluation Program

In order to prevent the migration of sulfurous acid from the cell anolyte to the cathode, with the subsequent deposition of sulfur, a membrane is used to separate these two cell compartments. A slight overpressure of sulfur-dioxide free catholyte permeates the membrane and excludes sulfurous acid penetration. In addition to being chemically and mechanically stable in concentrated sulfuric acid, an ideal membrane will possess both low permeability less than .01 cc liquid/cm^2 surface-min and ohmic losses of less than 100 mV at 200 mA/cm^2. These two goals are contrary to one another and trade-offs are required. The thicker the membrane, the less permeation. Work conducted on asbestos membranes indicated that ohmic losses in the order of 80-100 mV are achievable with, however, permeation rates in the order of .04 to .05 cc liquid/cm^2-min. The present work conducted shows that microporous rubber membranes are capable of reducing permeation below .01 cc/cm^2-min. Cell ohmic losses, however, of 200-300 mV are incurred. Further membrane evaluation will consider materials such as ion exchange membranes and ceramics.

Anode Development Program

In the electrochemical step of the Sulfur Cycle, sulfur dioxide and water are reacted to produce hydrogen and sulfuric acid. The primary contribution to voltage inefficiency within the electrolyzer occurs at the cell anode where sulfurous acid is oxidized to sulfur acid. Contributions to overall cell voltage from cathode overvoltage and cell ohmic losses are within acceptable bounds. The present work has emphasized the evaluation of platinum as an anode electrocatalyst employing both flooded and flow-through electrodes.

At the start of the program, anode overvoltages (measured relative to a Hg/Hg$_2$ SO$_4$ reference) were between +100 mV to +300 mV for flooded platinized carbon electrodes and between 0 to +150 mV for flooded platinized platinum electrodes. As the program progressed, initial polarizations for each flooded electrode were comparable, ranging between -100 mV to +100 mV. Aging characteristics, however, were dramatically different. The platinized platinum electrodes were highly irreproducible, with polarizations of subsequent days between 100 to 500 mV above the initial values. The platinized carbon electrodes, in contrast, were extremely reproducible with polarizations changing by less than 5 mV over a two week period.

More recently, initial polarizations obtained using flow-through electrodes constructed with platinized carbon

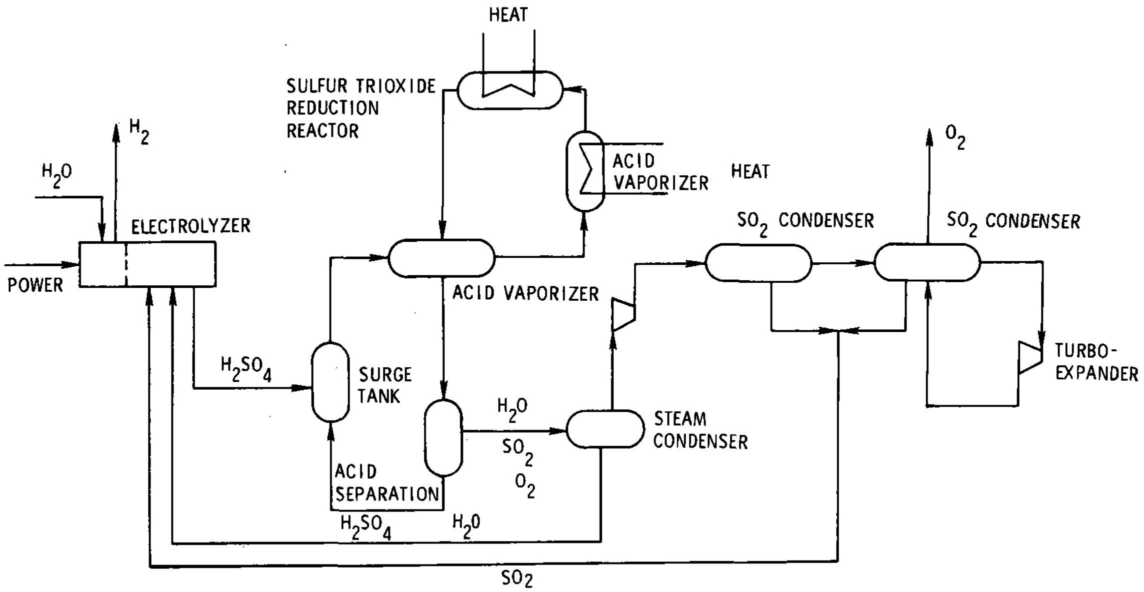

Figure 1. Hydrogen Generation Schematic Diagram.

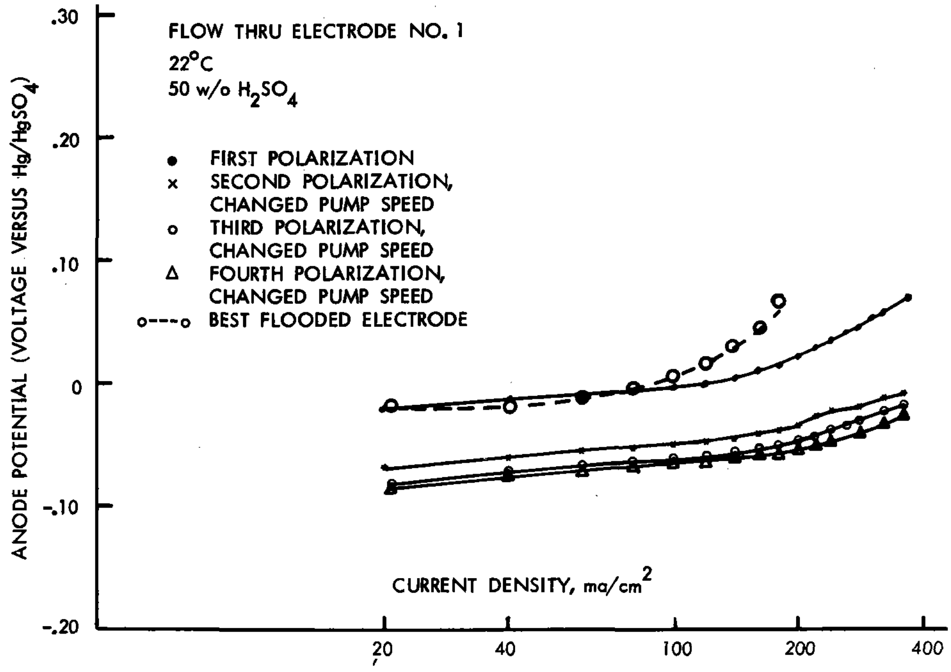

Figure 2. Potential of Anode as Function of Current Density and Anolyte Flow.

bettered the best flooded electrode results to date. This is shown in Figure 2. As before, no aging or deterioration of anode performance was observed over a two week period.

Summary of Electrolysis Program

Total electrolyzer performance can exceed the targets established at the beginning of the program. At that time, the goal was to demonstrate cell voltages below 900 mV at current densities of 200 mA/cm^2. Using the best of the presently tested electrodes and membranes, at 200 mA/cm^2 in 50 w/o sulfuric acid at 25°C, cell voltages (excluding ohmic losses) of 700 to 800 mV appear attainable. Allowing another 100 mV for ohmic losses (albeit with membranes currently exhibiting greater than desired permeabilities) leads to total cell voltages in the range 800 to 900 mV. Effort in the future will be directed towards reducing these voltages even further.

ACID CONCENTRATION

Membrane and/or Resin Concentration

Mechanical methods, as well as the chemical and thermal methods, are being investigated as potential means of concentrating sulfur acid solutions. Electrodialysis has emerged as a potentially attractive process. Provisions are now being made to undertake a limited test program to assess the characteristics of the process.

Thermal Concentration

The practicality of a thermal concentration system depends upon the identification of suitable structural and heat transfer materials to withstand the extremely corrosive environment of high pressure boiling sulfuric acid. An initial effort is being undertaken to screen candidate materials for suitability for this application. A test capsule configuration has been designed, materials ordered, and initial tests are now underway.

SULFUR TRIOXIDE REDUCTION

The evaluation of platinum as a catalyst for the thermal reduction of sulfur trioxide into sulfur dioxide and oxygen is proceeding. Tests at space velocities of 1000, 5000, 10,000, and 30,000 hr^{-1} indicate that platinum does not possess as high an initial activity as does the vanadium pentoxide catalyst tested earlier. This, in addition to its greater cost per catalyst volume, places platinum at a disadvantage to vanadium pentoxide with respect to process first costs. These include the cost of initial catalyst fill as well as the incremental capital costs associated with a proportionately larger thermal reduction reactor. In spite of this, platinum may still be the preferred thermal reduction catalyst. Should life testing, now underway, indicate a much lower deactivation with time than that observed with vanadium pentoxide, the longer time between catalyst refills may offset the higher initial costs.

ENGINEERING AND ECONOMIC STUDIES

Work on a revised process flowsheet is in progress. Three major departures from the flowsheet provided in the NASA conceptual design are anticipated. The first concerns the sulfur dioxide-oxygen separation system where scrubbing rather than condensation will be used for sulfur dioxide removal. The second modification will be in the high temperature thermal reduction reactor. Rather than a single large indirectly heated reactor, two smaller reactors will be employed. The first will be indirectly heated by the process heat source and the second will be recuperatively heated with the high temperature effluent. The third process modification will be in the acid vaporizers which will be cascaded to provide better heat economy.

METAL HYDRIDE MATERIALS PROGRAM
AT BNL -
CURRENT STATUS AND FUTURE PLANS*

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Over the past year, our materials development program has been focused on a number of areas. These include the effect of a third alloying metal on the properties of iron titanium hydride, the effect of alloy microstructure on hydride properties, the change in activity of pertinent alloys towards hydrogen as a function of the number of hydriding-dehydriding cycles, the poisoning effect of O_2 in the hydrogen gas and the outgassing temperature required to activate virgin materials. Several of these areas have been covered in detail recently and will not be referred to here (1), (2). Our attention at this meeting will center on unreported data involving both ferrotitanium and other alloys and a discussion of our future plan of work.

High Cycle Testing: In addition to pressure-temperature-composition relationships there exist many other system properties which are important with respect to the performance of a practical hydrogen storage reservoir. Perhaps the most important of these are:

(1) the change of activity of the alloy toward hydrogen as a function of the number of such cycles,

(2) the physical attrition of the alloys as a function of the number of hydriding-dehydriding cycles, and

(3) the poisoning effect of impurities such as O_2, N_2, CO, etc., in the hydrogen gas.

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*This work was carried out under the auspices of the United States Energy Research and Development Administration.

In order to investigate these variables a laboratory high cycle test apparatus was built. This system was capable of subjecting simultaneously three alloy samples to five complete hydriding-dehydriding cycles per hour with a composition swing per cycle of 1 H/Ti unit. Our initial objective was to determine whether there is any inherent deterioration of FeTi or similar materials as a function of hydriding-dehydriding cycles when pure hydrogen is used. The data shown in Table 1 establish that no such deterioration occurs.

Table 1.

High Cycle Test

Material	Complete Cycles	Temperature Change/Cycle ^{o}C, Avg.	Pressure Change/Cycle Psia, Avg.	Composition Change/Cycle $\Delta H/Ti$, Avg.
FeTi	19568	-1 to +100	428-459	1.11
$TiFe_{.79}Mn_{.15}$ (INCO #2)	28411	-1 to +100	179-211	1.08
$TiFe_{.76}Mn_{.14}$	26319	-1 to +100	87-114	0.96

The high cycle apparatus was also used to measure the effect of O_2 in the hydrogen gas phase on the reactivity of FeTi towards hydrogen. The results of these experiments are summarized in Table 2.

Table 2.

Poisoning Effect O_2 in H_2

Initial O_2 Conc. in H_2	% Reduction in Composition Change ($\Delta H/Ti$) Cycle	
Mol %	After 5 Cycles	After 40 Cycles
1.10	90	90
0.10	40	80
0.01	6	20
0.001	2	9

As expected these data indicate that FeTi is very sensitive to the presence of oxygen (which may be converted to H_2O) in the gas phase. However, in all cases it was possible to restore the alloy to its original activity by subjecting it to the usual activation procedure.

With respect to the rate of physical attrition (Table 3), the highest rate occurs in the first few cycles after which it slows considerably. It is also apparent that pure FeTi is much more resistant to physical attrition than any of the ternary manganese alloys tested. In this connection, it should be noted that the FeTi sample was finally removed after 19,568 cycles. Qualitative examinations indicated that while a substantial decrease in particle size occurred, it was not of a magnitude which would constitute a serious engineering problem. This sample is now undergoing extensive physical and chemical characterization.

Table 3.

Particle Size Distribution
$TiFe_{0.7}Mn_{0.18}$ (INCO #1) and FeTi (NL-2)
As a Function of Hydriding-Dehydriding Cycles

Screen Classification, Mesh	Weight Percent		
	$TiFe_{0.7}Mn_{0.18}$*		FeTi*
	5 Cycles	1115 Cycles	5478 Cycles
+ 16			11.4
+ 20			2.9
+ 30			2.1
+ 40			4.3
+ 60	5.3	6.4	14.7
+ 80	2.0	0.6	16.4
+100	1.5	2.1	11.0
+140	10.1	12.4	
+200	32.2	25.5	23.0
+275	19.3	21.5	4.2
+325	17.1	11.8	2.3
-325	14.1	19.7	7.7

* Initial particle size range -10 +16 (U.S. Standard Sieve).

Activation

The usual procedure for activating FeTi specifies high temperature outgassing (300°C). Such a requirement can impose difficult problems in large hydride reservoirs where activation in situ is desirable. Thus a series of experiments were carried out with manganese containing ferrotitanium alloys to determine minimum activation temperatures. This alloy type was chosen because it is of interest for our particular purpose (stationary storage) and also because it was apparent from our previous work that such alloys could be readily activated. The results of this work are shown in Table 4.

Table 4.

Low Temperature Activation Experiments

Sample	Maximum Temperature (°C)	Elapsed Time at 500 psi(hr)	Final H/M
$TiFe_{0.7}Mn_{0.2}$	50	3.5	0.94
$TiFe_{0.9}Mn_{0.1}$	25	27.5	0.98
$TiFe_{0.85}Mn_{0.15}$	25	19.0	0.98
$TiFe_{.70}Mn_{.18}$ (INCO #1)	25	25	0.91

Current and Future Work

The primary goal of the Brookhaven Metal Hydride Development Program has been revised. Simply stated it is to discover and develop new metal hydride compounds having thermodynamic properties similar to that of iron titanium hydride, but with significantly greater hydrogen fuel storage capacities and which would be attractive for automotive applications.

Our investigation will be concerned primarily, but not exclusively, with two separate alloy systems, i.e., those of magnesium and titanium. Currently, three Mg alloys are of interest as lightweight hydrogen storage media; i.e., Mg_2Ni, Mg_2Cu and magnesium itself, catalyzed with a small amount of Ni or Cu. Unfortunately, all of these hydrides require relatively high decomposition temperatures, the most favorable case being the Mg_2Cu-H system which has a dissociation temperature (the temperature at which equilibrium dissociation pressure is 1 atm) of 239°C. All of these systems were defined several years ago (3). Since that time, a large number of lightweight alloys have been examined, but none were found to be more attractive for automotive storage (4). Nevertheless, a re-examination of certain low melting alloys, of the type MgM_x may be profitable. Such alloys were originally investigated using accepted alloy activation techniques, i.e., outgassing and contacting the sample with H_2 at temperatures which were high relative to the melting point of the alloy. Under such conditions the metal atoms have appreciable mobility and if a hydride phase forms, it is likely to be the phase which is most thermodynamically favored; i.e., MgH_2 rather than a less stable ternary hydride system. A known example of such disproportion is as follows:

$$2Mg_2Cu + 3H_2 \rightleftarrows 3MgH_2 + MgCu_2$$

Thus, we will re-examine such alloys using a new approach, i.e., a low temperature activation technique. Such a procedure, if successful, could result in the syntheses of several ternary alloy hydrides having properties substantially more attractive for our purpose than any currently available.

In the case of titanium alloys, the same considerations hold, particularly for those that are titanium rich (e.g., Ti_2M type). We have also recently noted (5) the existence of a novel hydride having a composition corresponding to $TiCr_2H_{3.7}$. This material, originally discovered as part of our fundamental research program,* is interesting in several respects; it contains 2.4 wt % H, the presence of Cr enhances the hydrogen sorption capacity and it is extremely unstable as shown by the thermodynamic data listed in Table 5. In fact, it is probably too unstable for automotive purposes, but it may represent a new class of hydrides, the properties of which can be modified

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*Supported by the Division of Physical Research, U.S. Energy Research and Development Administration by the addition or substitution of a third metal component. Indeed, we have preliminary data (Fig. 1) supporting this contention in which Mn is substituted for Cr to give an alloy composition corresponding to TiCrMn.

Table 5.

Relative Partial Molal Quantities Per Gram-Atom of Hydrogen (298°K) for the Formation of $TiCr_2H$ from $TiCr_2$

Comp.	$(\overline{H}_H - \frac{1}{2}H_{H_2}^o)$	$(\overline{S}_H - \frac{1}{2}S_{H_2}^o)$	$(\overline{F}_H - \frac{1}{2}F_{H_2}^o)$	A[a]	B[a]
$TiCr_2H_{0.90}$	-1.81	- 9.1	+0.91	-1824	+ 9.1927
$TiCr_2H_{1.50}$	-2.49	-13.2	+1.45	-2502	+13.3014
$TiCr_2H_{2.10}$	-2.55	-13.8	+1.56	-2562	+13.8620
$TiCr_2H_{3.30}$	-2.21	-15.0	+2.25	-2224	+15.0794

[a] Constants in the equation $\ln P_{atm} = (A/T) + B$.

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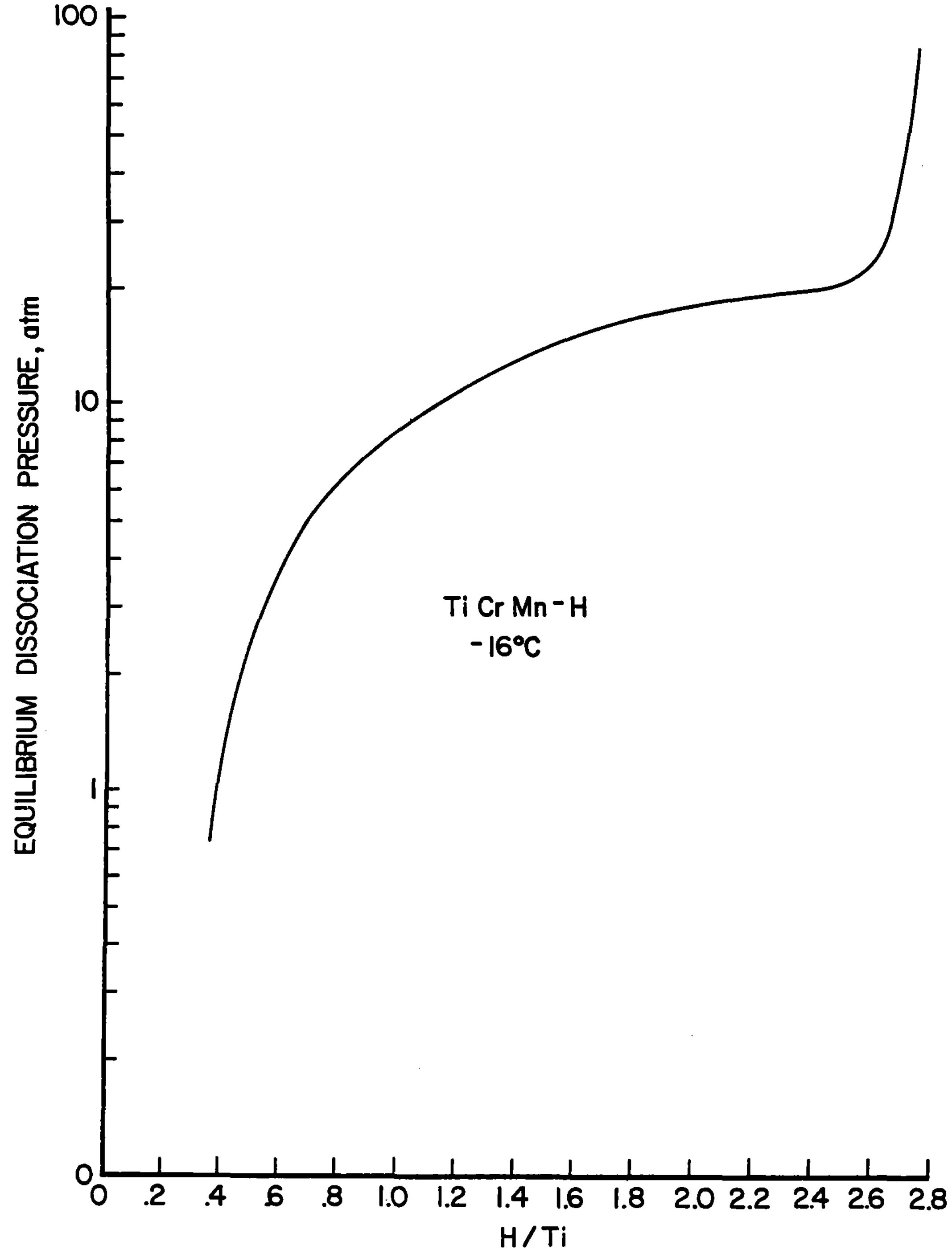

H Concentration in Alloy

Figure 1. Pressure-Composition Isotherm for the TiCrMn-H System.

THE ENGEL-BREWER CORRELATION APPLIED TO THE FORMATION OF METAL HYDRIDES

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Our current program is based on the idea that the characteristics of a particular metal hydride are controlled by the specific electron distributions within the parent alloy. These distributions are deduced from a logical interpretation of what happens as the electron structure of a free atom changes to accommodate the lattice geometry and are deduced with the idea that they occur from linear combinations of the hybridized atomic orbitals. The idea is based strongly on the type of approach used by Professor Neils Engel and Professor Leo Brewer, which I want to discuss briefly, and leads to the strong implication that the reacting species in hydrogenation is the metal phase, and that the hydride characteristics are not necessarily predictable from the characteristics of the constituents taken alone.

A plausible basis for the Engel-Brewer argument comes from the interpretation of the results of the quantum mechanics as is presented by Pauling. He says that the fundamental principle governing the "natural" states of matter is that the total energy of the system must be minimized. He demonstrates, as an explanation of the covalent bond type, that where equivalent states are available the total energy may be minimized by considering the linear combination of available states. He concludes with the starting point of the E-B correlation with the development that in general, each additional electron pair formed within a molecule tends to stabilize the molecule further. The most stable state of a molecule is then that state wherein all of the stable orbitals are used in either bond formation, or for the formation of internal pairs.

Engel and Brewer basically start at this point. From their observation on ^{11}Na, ^{12}Mg, ^{13}Al, ^{14}Si they have proposed that 1, 2, 3, and 4 outer electrons correspond to the bcc, hcp, fcc and diamond structures respectively. You will notice that the ground states generally involve paired 3s electrons which are promoted so that the maximum utilization of the valence group is realized.

Ground State Electron Configurations

^{11}Na	$1s^2;\ 2s^2,\ 2p^6;\ 3s^1$
^{12}Mg	$1s^2;\ 2s^2,\ 2p^6;\ 3s^2$
^{13}Al	$1s^2;\ 2s^2,\ 2p^6;\ 3s^2,\ 3p^1$
^{14}Si	$1s^2;\ 2s^2,\ 2p^6;\ 3s^2,\ 3p^2$

Promoted Electron Configurations Proposed by
Engel and Brewer

Element	Configuration	No. of Bonding Electrons	Structure
^{11}Na	$1s^2;\ 2s^2,\ 2p^6;\ 3s^1$	1	bcc
^{12}Mg	$1s^2;\ 2s^2,\ 2p^6;\ 3s^1,\ 3p^1$	2	hcp
^{13}Al	$1s^2;\ 2s^2,\ 2p^6;\ 3s^1,\ 3p^2$	3	fcc
^{14}Si	$1s^2;\ 2s^2,\ 2p^6;\ 3s^1,\ 3p^3$	4	diamond

In his observation on the structures of the elements, Brewer observes that, in general, where the ls orbital is clearly singly occupied the bcc structure is the only structure observed. For the case of the transition metals he regards the d band as a flexible sink to allow the ns^2 pair to dissociate such that the promotion from $(n-1)d^{(m-2)};\ ns^2$ to $(n-1)d^{(m-1)};\ ns^1$ and hence to $(n-1)d^{(m-2)};\ ns^1,\ np^1$...etc. occurs in order that maximum utilization of the outer electrons occurs with minimum expense of energy. (n=principle quantum number of outermost shell, m=number of s+p+d "valence" electrons). The most stable state is apparently predicted, where the greatest difference occurs between the promotional energy expended to excite the atoms to the higher levels and the bond energy gained by utilization of the promoted electrons. From correlations based on extrapolation of the binary phase diagrams which are known, Brewer has suggested that the various structures occur over a range of outer (s+p) electron concentrations.

i.e.	$m < 1.5$	bbc
	$1.7 < m < 2.12$	hcp
	$2.5 < m < 3$	fcc

Although the observations are not based as yet on strong first principle postulates, the fact that they do work strongly contributes to their credibility. In our own work, they have been used to form alloy hydrides close to the $FeTi_2H_4$ composition. The Engel-Brewer correlation works best in the metals of the first and second transition series where there is little doubt about the nature of the promoted electron distributions. To illustrate our approach, I would like to discuss its application to the formation of $FeTiH_2$.

Engel-Brewer Approach to FeTi

The application of the Engel-Brewer correlation to the FeTi alloy is most convincing of its application to the study of metal alloy hydrides. The method considered the electron distribution in the ground state of the free atom, promotes the electrons to near energy configurations, and balances the expended promotional energy per mole of atoms against the energy gain from the additional bonds that may be formed.

Iron, in the ground state, has a nonbonding $3d^6$; $4s^2$ outer electron configuration when it exists as a free atom. It has available a $3d^7$; $4s^1$ and a $3d^6$; $4s^1$, $4p^1$ configuration with the expense of 20-23 and 55-70 Kcal/mole promotional energy. The number of bonding electrons go from

0 in the $3d^6$; $4s^2$ to 4 in the $3d^7$; $4s^1$ to 6 in the $3d^6$; $4s^1$, $4p^1$ configurations.

Titanium, in the ground state, has a nonbonding $3d^2$; $4s^2$ configuration with a promoted state of $3d^3$; $4s^1$. Note that regardless of the promotional energy expense beyond this state, no more than four bonding electrons become available. There will be four electrons available for bonding in each of iron and titanium with each in its lowest bonding state. In each case, the bond set consists of three d electrons and one s electron, forming sd^3 hybrid bond sets. This bond type has four equivalent orbitals projecting into space with exact tetrahedral symmetry about the atom, i.e., four bonds are formed each 109° 28' from the others, projecting to the corners of a regular tetrahedron with the atom at its center, and this coincides exactly with the FeTi lattice structure.

FeTi is an ordered cubic alloy with an occupied body center. The two equivalent sites in the lattice are at the cube corners, and at the cube center. The resonance bonding which occurs between the two sets of equivalent bond groups further stabilizes the structure with the result that substantial lattice contraction of about 12% results compared to the normal atomic volumes occupied by iron and titanium alone.

If one considers the localized bond configurations of iron and titanium in light of the available promoted configurations, the localized configurations for the elements can be developed more completely.

The promotional energy to the lowest excited states assumed previously correspond to 19 Kcal/mole for the d^3s configuration of Ti and 23 Kcal/mole for the d^7s configuration of Fe. This calculates to 21 Kcal/mole promotional energy needed to allow the sd^3 bond configurations which were assumed.

For titanium the bond enthalpy for an sd^3 bond is calculated allowing 53 Kcal/mole bond for the 4s electron and 30 Kcal/mole bond for each of the three 3d electrons.

The bond enthalpy for the sd^3 configuration of Ti is thus 143 Kcal/mole. For iron the bond enthalpy calculation involves on 4s and three 3d electron bonds giving 57 Kcal plus 3 x 11 Kcal for 90 Kcal/mole of iron. The calculated bond enthalpy for FeTi is then $(90 \times 143)^{0.5}$ or 113 Kcal per mole FeTi. Thus for the formation of FeTi an expense of 21 Kcal/mole is more than offset by the 113 Kcal gained from bonding and a stable structure results with an average of one/s electron per atom which Brewer predicts as bcc in accord with experimental data on the alloy.

Titanium with the sd^3 configuration is using all of its electrons in bonding. No additional bonding can occur from further promotion of the valence state and the sd^3 configuration can be considered a final approximation. For iron, however, the second promoted state would correspond to d^6sp with a promotional energy of 55-70 Kcal/mole and would provide the addition of two more electrons for bonding. These electrons probably are involved in weak next nearest neighbor bonds between the iron atoms in the lattice. Thus in the approximation one would conclude that FeTi occurs in the bcc structure with Ti in the d^3s configuration, and Fe in a minimum energy state between the d^7s and d^6sp configurations.

In the alloy, the outer electron contribution of iron and titanium are $3d^7 + 4s^1$ and $3d^3 + 4s^1$ respectively. The average electron concentration for the lattice type is $3d^5 + 4s^1$ with the d band exactly half full. For the α solid solution of hydrogen in FeTi, Brewer predicts that the electron in hydrogen will enter the lattice with about the same percentages of s and d character represented by the lattice, i.e., $d^{5/6} + s^{1/6}$. The additional electron forced into the d band reduces the number of bonding d electrons to $d^{4.17}$ and increases the s + p bonding to $s^{1.17}$. The overall bond strength is diminished and the lattice expands taking hydrogen into solution endothermally. The maximum solubility of hydrogen in the α phase should be low (in the order of $0.05 \rightarrow 0.5$ std cc/100 g). This compares with Reilly's measurements on FeTi at about room temperature of $H/m \simeq .1$ or 0.15 std cc/100 g.

The determination of the electronic states in FeTi applies directly to the prediction of its ability to form hydrides. It has been shown that Ti, in the FeTi alloy, occupies a site of tetrahedral symmetry with all electrons involved in strong nearest-neighbor bonding. Examination of the monohydride structure deduced from the diffraction work of Reilly shows that Ti remains in a site of fourfold symmetry incompatible with H-Ti bonding. Iron, on the other hand, has a predicted d^6sp configuration available with four electrons tied into nearest-neighbor bonds in the lattice and two electrons involved in weak next-nearest-neighbor bonds. These next-nearest-neighbor bonds may be broken and tied into hydrogen with hydrogen entering the octahedral sites at either the face centers or cell edges. This predication is compatible with the tetragonal distortion of the basic cell evidenced in the formation of the monohydride $FeTiH_{1.0}$. The electron configuration which has been deduced for Fe affords two electrons per Fe atom for hydrogen bonding and predicts the final stoichiometry of $TiFeH_2$, as is confirmed by the extensive efforts of Reilly who has determined that $FeTiH_2$ is the final stoichiometry of the system.

A calculation of the thermodynamic processes involved in our model give a very close approximation to the numbers published by Reilly, however, the uncertainty in some of the assumptions seriously affect the certainty with which the final result can be viewed. We must now test and refine the model so that it may be used specifically to predict the hydride formation mechanism of the proposed alloys.

NEW MELTING TECHNIQUES FOR THE PRODUCTION OF HYDRIDING GRADE FeTi

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INTRODUCTION

The BNL developed hydrogen storage alloy FeTi(1) is far more complex metallurgically than its simple formula implies. This complexity is reflected in the hydriding behavior of alloys based on FeTi. A detailed survey of the interrelations among composition, microstructure, and hydriding behavior for alloys based on the intermetallic compound FeTi was presented at the First Annual Information Meeting for ERDA Contractors in the Hydrogen Energy Program and elsewhere(2-4). Among other things, this work emphasized the role of the contaminant oxygen in producing the $Fe_7Ti_{10}O_3$ phase in the microstructure which (a) severely reduced H-storage capacity, (b) increased the rate of decrepitation (particle size breakdown), and (c) increased activation rate. Although increased activation rate was considered desirable, reduced H-capacity and increased decrepitation resulting from O-contamination were considered most undesirable for engineering applications of the alloy in hydrogen storage devices.

Thus the key to the optimum use of FeTi, and related alloys, was shown to be alloy preparation techniques that minimized final alloy O-content. Although the arc and electron beam melting techniques used today in the Ti-alloy industry are capable of producing excellent purity FeTi, lower cost, more conventional melting techniques are desirable. In this paper I report on the work under this contract which has led to two new techniques to melt high quality, hydriding grade FeTi in conventional vacuum induction and air induction furnaces: (a) the vacuum induction melting of FeTi in high purity graphite crucibles and (b) an air melting/rare earth deoxidation technique.

VACUUM INDUCTION MELTING IN GRAPHITE CRUCIBLES

Vacuum induction melting is a common and well known procedure used to produce a variety of specialty base metal alloys (e.g., high temperature Ni-base alloys). In general this procedure is not used for the melting of high-Ti alloys because of the high reactivity of Ti with common oxide crucibles such as Al_2O_3, MgO, and ZrO_2.

Using sponge Ti and electrolytic Fe as raw materials, a series of successful melts were made in graphite crucibles along the lines developed by Buehler of the Naval Ordnance Lab for the "memory alloy" NiTi(5). A priori, one would probably not expect graphite to be a useful crucible material for melting FeTi because both Fe and Ti individually have high solubilities for C in the liquid state. However, the equiatomic composition apparently has a very low solubility for C, on the order of 0.05-0.15 wt. % in the vicinity of 1425°C. High purity, high density graphite (e.g., Grade ECL) was found to give excellent results in the melting of hydriding grade FeTi as long as the melt composition was maintained in the 50-50 region. As shown in Figure 1, material so produced exhibits virtually identical hydriding properties with fairly high purity material produced by cold crucible, consumable electrode melting. Hydrogen capacities and general curve shapes are fully equivalent. In addition to FeTi, the procedure was also found to be useful in melting related alloys such as (Fe,Mn)Ti.

MELTING IN AIR INDUCTION FURNACES WITH RARE EARTH DEOXIDATION

The possibility of simple low cost melting of FeTi in conventional air induction furnaces was explored in detail. As in vacuum induction melting, crucible material was found to be important. Although a pure graphite crucible cannot be used because of its poor oxidation resistance, clay-graphite was found to be a useful substitute. Preliminary trials using crude argon blankets resulted in oxygen levels on the order of 0.3 to 0.35 wt. %, somewhat higher than our target of less than 0.1 wt. %.

Extensive work was done on melt deoxidation techniques resulting in considerable success when rare earth elements were added to molten FeTi. The relatively low cost ($3.20/lb) rare earth alloy mischmetal was found to be technically and economically superior to Ce or La. The hold time between mischmetal addition and final pour was found to be important. The best results were obtained with the 8 kg melts of this study by adding 4 wt. % mischmetal about 2 minutes before final pouring. The hydriding curve of FeTi produced by this method is fully equivalent to arc melted FeTi, as shown in Figure 2. An additional advantage of rare earth treatment is that a small amount of excess rare earth phase is present in the microstructure which greatly aids activation.

The air or argon-blanket induction melting of FeTi, followed by rare earth deoxidation respresents a simple, powerful new method of producing FeTi. We have scaled up melt size to 100 kg and see no reason why multi-ton heats cannot be made by this procedure. The procedure has also been found valid for the production of related alloys such as (Fe,Mn)Ti.

FUTURE WORK

Although this work has indicated a direction in reducing the cost of high quality, hydriding grade FeTi by allowing its production in conventional air and vacuum induction furnaces, its cost will still remain undesirably high because of the inherently high price of Ti, both primary sponge and secondary scrap. Work will continue under this contract in the directions of cost reduction. In particular efforts will be made to survey the feasibility of low cost production directly from ilmenite ($FeTiO_3$) ore, especially when combined with remelting techniques such as described in this paper.

ACKNOWLEDGEMENTS

This work was supported both by the ERDA Brookhaven National Lab (Subcontract BNL 352410S) and The International Nickel Company, Inc., on a cost-sharing basis. The work proceeded with the close cooperation and help of BNL. In particular, thanks are due J.J. Reilly (BNL Technical Monitor) and J.R. Johnson for

many helpful discussions.

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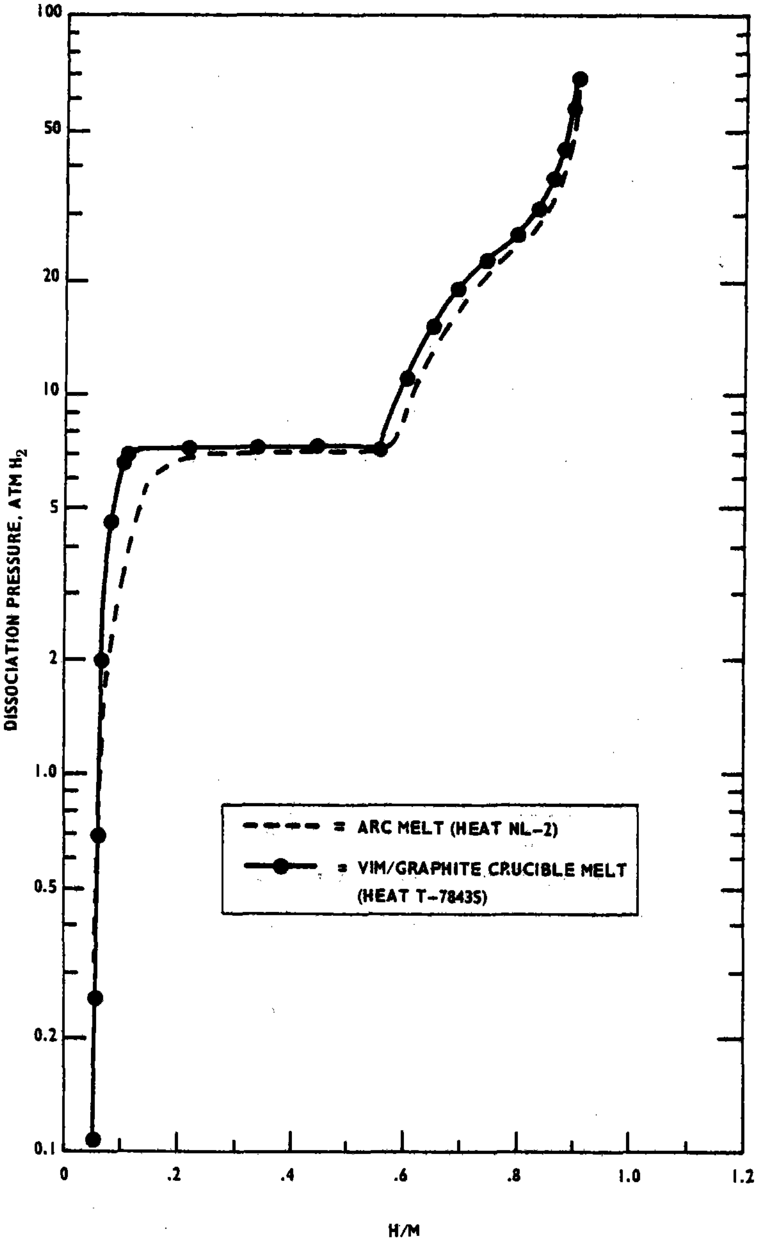

Figure 1 - Comparison of 40°C Desorption Isotherms of Vacuum Induction Melted (Graphite Crucible) FeTi and Arc Melted FeTi.

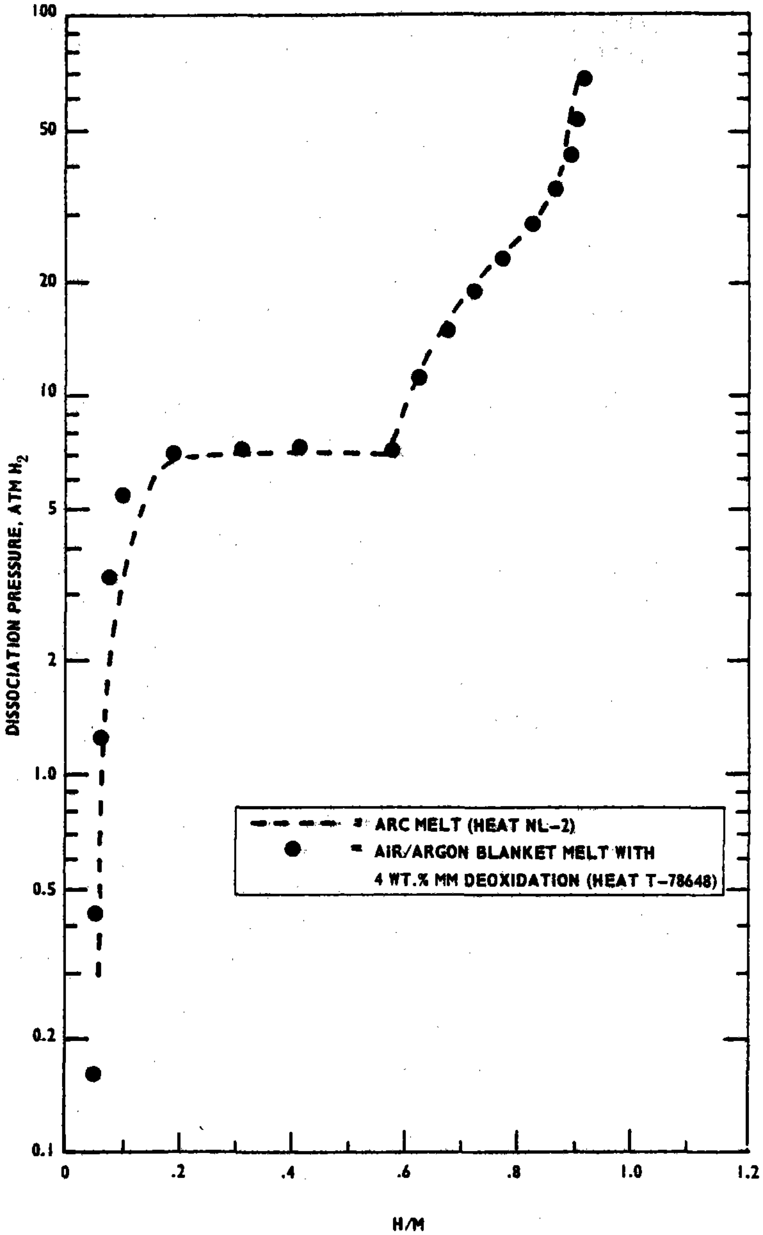

Figure 2 - Comparison of 40°C Desorption Data of Air/Argon Blanket, Mischmetal Deoxidized FeTi with Arc Melted FeTi.

HYDROGEN COMPATIBILITY OF STRUCTURAL MATERIALS FOR PRESSURE VESSELS AND PIPELINES

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The program at Sandia Laboratories is directed towards obtaining engineering data related to the use of structural steels for energy systems containing gaseous hydrogen. The work has focussed upon two applications: (1) iron-titanium hydride containment materials for the Brookhaven National Laboratories (BNL) program concerning off-peak electric energy storage, and (2) containment of hydrogen by inexpensive materials in hydrogen storage and transmission systems.

Support of the BNL program has included selection of materials for $FeTiH_x$ containment vessels. Tests performed were, tensile tests and slow crack growth tests, in both air and high pressure hydrogen, of both welded and unwelded materials. Long-term test specimens were designed, loaded and installed by Sandia in a test bed at BNL for accelerated hydride cycling. Postmortem analysis of the specimens will be performed at Sandia. A welding specification for mild steels in hydrogen service has been developed and forwarded to BNL, and modifications will be made as experience is gained.

Several efforts aimed at developing more hydrogen compatible mild steels for future energy systems have been initiated. Both alloy chemistry modification and thermomechanical treatment are being utilized. Alloy purity, alloy element distribution, inclusion character (shape and composition), microstructures, and subsequent hydrogen compatibility are the variables being explored using the matrix of materials outlined in Table 1. Initial efforts indicate that significant improvements in compatibility are possible, without sacrificing strength.

Protective coatings are often considered as a means of protecting a vulnerable structure (e.g. a weld zone) from embrittlement by hydrogen. However, the criteria which distinguish a good coating from a bad coating have not been fully identified. Further, the applicability of coatings is limited to specific structures. Other serious concerns are reliability and cost. These concerns are being addressed in this program. Protective coatings have been applied to mild steels by electroplating, plasma spraying, and pyrolysis of specific compounds such as silane gas (SiH_x), and their performance in hydrogen has been evaluated by tensile testing. Thick dense plasma sprayed aluminum coatings appear to give the best performance in tensile tests, with least preparation and cost.

An alternative approach to protection of easily hydrogen embrittled materials is to add gaseous inhibitor, which is preferentially adsorbed on the surface and allows less hydrogen to contact the material. This approach is incompatible with systems requiring high purity hydrogen, but may have applicability in less pure systems. The best inhibitor, oxygen, is usually considered unacceptable from the safety viewpoint. Other known inhibitors such as CO and SO_2 may also be unacceptable because of their toxicity. We are searching for other gaseous additives which may be more acceptable and for alloy chemistry changes which may give protection.

Welds in steels account for the most failures in hydrogen environments, since most cracks occur in the weld zone. The choice of welding parameters, filler metals, and welding processes may affect the hydrogen compatiblity of both the fusion zone and heat affected zones. Fusion zone properties vary with weld pool geometry, filler metal chemistry, number of passes and specific welding process used. The heat affected zone properties are being studied by the method of temperature profile simulation, in which the time-temperature cycles which welding imposes on the base metal are reproduced.

The primary hazard of premature failure in mild steels by hydrogen embrittlement is environmentally assisted cyclic fatigue, rather than sustained load crack growth. Significant contradictions and gaps in knowledge exist in the literature. Therefore, fatigue tests of welded and base metal mild steels are being initiated to assist predicting structural lifetimes and setting inspection criteria.

An experimental hydrogen pipeline is nearing completion. The pipeline will perform specific materials tests relating to weld quality and defect tolerance, applicability of specific joining processes and inspection requirements. Table 2 lists some of the experiments to be performed. This phase of the program addresses the use of existing natural gas lines for hydrogen transmission, and the setting of codes for future pipelines. Sandia's experience with the "real world" of nondestructive inspection will be discussed.

TABLE 1

EXPLORATORY ALLOY MATRIX

BASE METAL A516 GRADE 70

HEAT	ADDITIVES	REFERENCES	CARBON EQUIVALENT(A) (APPROXIMATE)	WORKING SCHEDULE	SULFIDE CONTROL
1	None (Melt & Cast Only)		0.38 to 0.45	Hot Worked Warm Worked	None
2	(B) (X w/o rare earth R.E.)		unchanged	"	I.S.C.
3	Sulfur level reduction		unchanged	"	Volume Red. + I.S.C.
4	0.1 w/o Ti	9-13,16,20	slight decrease	"	None
5	0.3 w/o Ti	"	0.37-0.44	"	None
6	0.3 w/o Ti, X w/o R.E.	"	(A)	Warm Worked	I.S.C.
7	0.5 w/o Si	"		Hot Worked	None
8	0.5 w/o Si + X w/o R.E.	"	(A)	Hot Worked Warm Worked	I.S.C.
9	0.5 w/o Si + lowered S level	same, particularly 20.21	(A)	"	Volume Reproduction + I.S.C
10	0.30 w/o Cu	14,15	0.39-0.46	"	
11	0.3 w/o Cu + 0.3 w/o Ni	13-15		"	None

(A) Assume base metal is 0.25 w/o C, 0.8 w/o Mn. Sulfur is not calculated, but plays a role in weldability (21). Silicon probably raises C.E. No C.E. for Ti is available. C.E. is given by reference (13).

(B) X is a parameter to be calculated from the sulfur level of the base metal, see <u>Sulfide Inclusions In Steel</u>, A.S.M. 1975 Metals Park, Ohio.

TABLE 2

MODULAR EXPERIMENTS

High stresses

Marginal Welds

Intentional flaws

Permeation

New alloy, coupling, and coating qualification

Cathodic charging effects

STUDY OF THE BEHAVIOR OF GAS DISTRIBUTION EQUIPMENT IN HYDROGEN SERVICE

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This program is part of a long-range (5-year) effort to supply needed information about hydrogen delivery in a gas-distribution system. The overall program will determine operating, safety, and materials problems associated with the use of hydrogen in conventional distribution equipment. In this program three "model" distribution systems (Residential, Commercial, and Safety Test) are being constructed with components donated or loaned by manufacturers and gas utility companies. These components will be operated under closely monitored laboratory conditions. After system assembly and leak-testing with standard procedures, the leak rates of the systems and of selected components, operating on natural gas and on hydrogen for a continuous period of about 6 months, will be compared. The model systems will be operated on hydrogen for a continuous period, after which parts of the systems will be disassembled. Chosen components will then be examined and tested to identify and document noticeable effects of hydrogen exposure.

Figure 1 presents the preliminary design of the Residential Model. As shown, the Residential Model is composed of four subloops and a bypass. The four different subloops will utilize different materials of pipeline construction: 1) steel, 2) copper, 3) plastic (high-molecular-weight, high-density polyethylene), and 4) cast iron. In operation, a single-stage compressor will feed 15 SCFM of natural gas or hydrogen to the Residential Model at a pressure between 60 and 70 psig. The compressed gases will pass through an aftercooler to reduce gas temperatures to ambient and through a surge tank to dampen pulsations. A regulator will reduce pressure to 50 to 60 psig, simulating pressures in the distribution mains and the service lines to residential consumers. In the case of cast iron construction, the pressure will be reduced further by another pressure regulator to 10 psig. At the simulated building line (i.e., the termination of the service line), the distribution pressure (50 to 60 psig and 10 psig) will be reduced further by a service regulator to 6-inches water column. The gases will then pass through a domestic gas meter, to the inlet of the compressor, and be recompressed and recycled. Flow will be controlled and proportioned through the subloops with needle valves and the bypass.

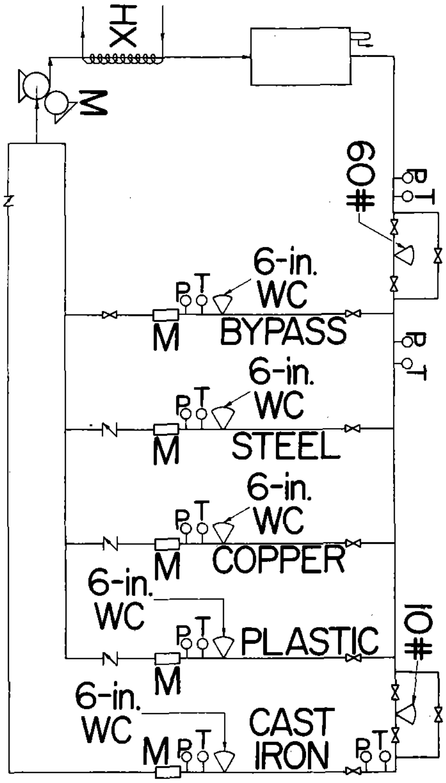

Figure 1. Residential Model.

Figure 2 presents the preliminary design of the Commercial Model. As shown, the Commercial Model consists of one loop and a bypass. The pipeline material will be steel. In operation, a two-stage compressor will feed 15 SCFM of natural gas or hydrogen to the Commercial Model at a pressure between 180 and 200 psig. The compressed gas will pass through an aftercooler to reduce gas temperatures to ambient and through a surge tank to dampen pulsations. A line regulator installation will reduce the pressure to

150 psig, simulating pressure reductions in feeder and trunk mains. Another regulator downstream, in series, will reduce the pressure further to 50 to 60 psig, simulating pressures in the distribution mains and service lines. At the simulated building line (i.e., the termination of the service line), the gas will pass through a dust filter, and the pressure will be reduced by a commercial-type service regulator to 1 psig. The gases will then pass through several commercial gas meters (e.g., diaphragm, rotary, or turbine) connected in series, to the inlet of the compressor, and be recompressed and recycled. Flow will be controlled and proportioned with needle valves and the bypass.

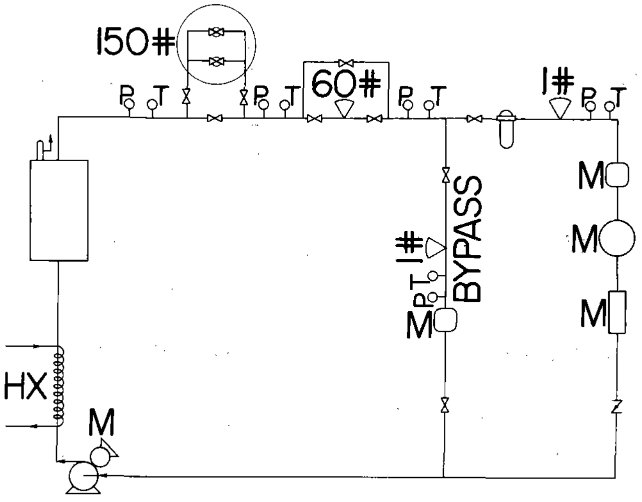

Figure 2. Commercial Model.

Figure 3 presents the preliminary design of the Safety Test Model. As Shown, this model consists of one loop with a Leak Zone and a bypass. The Leak Zone will provide a space for testing and defining problems associated with mechanical or corrosion leaks, leak clamps, ruptures, and rupture safety devices. The pipeline material will be steel, except at the Leak Zone. In operation, a single-stage compressor will feed 10 to 15 SCFM of natural gas or hydrogen to the Safety Test Model at a pressure between 60 and 70 psig. The compressed gases will pass through an aftercooler to reduce gas temperatures to ambient and through a surge tank to dampen pulsations. A regulator will reduce the pressure to 50 psig, simulating pressures in the distribution mains and service lines. The gases will then pass through the experimental setup in the Leak Zone, to the inlet of the compressor, and be recompressed and recycled. If leakage is a problem, the gas flow will terminate in the Leak Zone, and the gases will be vented to the outdoors. The Safety Test Model will be operated intermittently, whereas both the Residential and Commercial Models will be operated continuously.

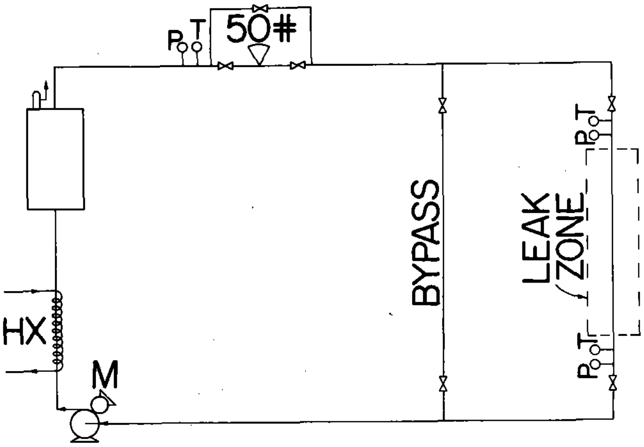

Figure 3. Safety Test Model.

Twelve manufacturing concerns and two local utilities are supplying the following items in duplicate:

- Piping (steel, copper, plastic, and cast-iron)
- Pipe couplings, fittings, transitions, and insulators
- Gas distribution valves
- Pressure regulators and reliefs
- Service connectors
- Service fittings
- Risers
- Curb/meter valves
- Filters
- Service regulators
- Meters (diaphragm, rotary, and turbine)
- Joints (welded, threaded, flanged, compression-fitting, and bell-and-spigot)

- Pipe repair clamps and sleeves
- Service rupture shutoff/safety devices
- Pressure gauges.

The three compressors were procured from the Corken Pump Co. The compressors are reciprocating piston machines with Teflon (TM) rings and Teflon (TM) dynamic seals for oil-free operation in natural gas and/or hydrogen service. They were selected over diaphragm models on the basis of costs and delivery time.

Leakage measurements on components will be accomplished by a sealed-volume technique, which consists of enclosing the component in a gas-tight constant-volume container constructed of sheet metal and/or Plexiglas (TM). The containers will be filled with an inert gas, and we will monitor the rate of rise of the hydrogen concentration. Samples will be drawn from the enclosures at varying time intervals (depending on the leakage rate) and analyzed by a mass spectrometer. Each container will be calibrated by introducing known amounts of hydrogen into the container and withdrawing samples for analysis by the mass spectrometer. The pressure and temperature of the containers will also be monitored.

Total system leakage will be determined by the pressure decay method. Pressures will be continuously monitored by strain-gauge pressure transducers in the models. Periodic calculations will be made to determine the hydrogen content of the model loops, and, when the system's hydrogen content falls below 90% of the initial charge, makeup hydrogen will be added.

Tests of leaks deliberately caused by drilling small holes, loosening fittings, and overpressurizing regulators will be conducted in the Safety Test Model devoted to these studies. Occurrence or nonoccurrence of autoignition will be noted. In some cased the leaks will be ignited, and the temperatures, apparent damage, and other visible effects to adjacent components will be noted and assessed.

After six months of operation, the model systems will be disassembled, and individual components and parts will be checked against the inventory. The parts will then be weighed, measured, and otherwise examined and compared with the unexposed duplicates to document apparent changes.

Approximately 30 to 40 selected parts and samples will be delivered to the Department of Metallurgy and Materials Engineering of the Illinois Institute of Technology (IIT) for examination and materials testing. This testing will provide a qualitative indication of mechanical and structural changes in the materials that have been exposed to hydrogen. It will lead to recommendations for further exposure and quantitative property tests in the future. The materials examination is not intended to be a study of "hydrogen embrittlement"; its purpose is merely to identify and document instances where significant changes in materials properties have occurred.

Progress Report Addendum

Twelve manufacturers and two local gas utilities were invited to participate in the program by furnishing materials and components that could be utilized in the three distribution models. All of the companies responded affirmatively; they are as follows:

- American Meter Division of Singer Company
- Republic Steel Corporation
- Rockwell International/Municipal & Utility Group
- Kerotest Manufacturing Company
- Mueller Company
- Sprague Meter Company
- Dresser Measurement Division of Dresser Industries, Inc.
- M. B. Skinner Company
- Phillips Products Company, Inc.
- Fisher Controls Company
- Dresser Manufacturing Division of Dresser Industries, Inc.
- E. I. Du Pont De Nemours and Company/Plastic Products and Resins Department

- Northern Illinois Gas
- The Peoples Gas Light & Coke Company

To date these companies have donated or loaned well over one hundred components in duplicate. The estimated value of these items is $20,000. Also, four companies are furnishing special tools and equipment and the services of trained technicians to install their gas distribution components in the models.

Twenty compressor companies were surveyed to procure laboratory type (i.e., low capacity) compressors for natural gas and hydrogen service. Five concerns furnished quotations on their units; costs ranged from $2,200 to $28,000 each and delivery was estimated to be 10 to 36 weeks. We purchased three units from the Corken Pump Company at a cost of approximately $12,300. The compressors were delivered; water and electrical power is being connected to the units.

Preliminary designs of the three distribution models were made to select components and materials from the participating companies. Three dexion-angle gratings were constructed to support the piping and components of the model distribution loops. Final assembly drawings are being prepared to layout piping and component configuration and to establish the components that are to be closely monitored.

HYDROGEN EMBRITTLEMENT -
THE EFFECT OF STRESS STATE

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The concept that "maximum triaxiality" plays a vital role in hydrogen embrittlement processes is recurrent throughout the hydrogen in metals literature. Oriani (1), for example, considers only the effect of the hydrostatic component of stress in the development of a decohesion theory for embrittlement. This theory incorporates the earlier work of Troiano (2) which suggested that hydrogen is concentrated in the regions of maximum triaxiality and that fracture process is initiated in that region. If it is assumed that the triaxiality concept means that the three principal stresses are equal, the shear stresses in the region of fracture initiation must be identically zero and dislocation motion is not feasible. Thus, the triaxiality concept excludes any role for dislocation motion in the hydrogen embrittlement process. Further, it predicts that design criteria based on uniaxial tensile loading of components exposed to hydrogen are more conservative than criteria based on either biaxial or triaxial loadings. These design predictions are in direct opposition to criteria based on a dislocation transport model for hydrogen embrittlement.

The hypothesis that dislocation motion is involved in hydrogen embrittlement processes has received increasing support in recent years (see References 3-6 for example). Shear stresses must be present if dislocation motion is to occur; thus, loadings which approach triaxiality and therefore minimize the tendency for dislocation motion should minimize the susceptibility to hydrogen embrittlement. These arguments indicate that the stress state of a particular component may play an important role in determining the susceptibility of that component to hydrogen embrittlement. However, the apparent favorability of any particular stress state depends on which embrittlement mechanism is assumed to be operative.

The most complex stress state may be reduced to a state of purely normal stresses, σ_1, σ_2, and σ_3. Furthermore it is known that the absolute maximum shear stresses are related to these normal stresses; they act on planes which bisect the principal planes and are given by

$$\tau_1 = \frac{\sigma_2-\sigma_3}{2}\ , \quad \tau_2 = \frac{\sigma_3-\sigma_1}{2}\ , \quad \tau_3 = \frac{\sigma_1-\sigma_2}{2}$$

A proper failure criteria which uses experimental data obtained from uniaxial tests to predict the failure (or yielding) of a material subjected to a triaxial stress state has been the elusive goal of researchers for many years. Defining σ_F = Stress at failure in uniaxial test, ν = Poisson's ratio, and ordering the principal stresses so that $\sigma_1 \geq \sigma_2 \geq \sigma_3$ typical failure criteria which have been used are:

A. Maximum Stress Theory. This essentially ignores all stresses except the largest one and failure is predicted when $\sigma_1 = \sigma_F$

B. Maximum Strain Theory. This theory states that failure occurs when the maximum strain is equal to the uniaxial strain at failure (note that the elastic stress-strain equations are presumed valid up to failure)
$\sigma_1 - \nu(\sigma_2+\sigma_2) = \sigma_F$

C. Maximum Shear Theory. Essentially states that the maximum shear stress alone is the controlling factor in failure, $\sigma_1-\sigma_3 = \sigma_F$

D. Strain Energy Theory. An early attempt to account for all three of the principal stresses. Assumes linear elasticity to failure

$$\sigma_1{}^2 + \sigma_2{}^2 + \sigma_3{}^2 - 2\nu(\sigma_1\sigma_2 + \sigma_2\sigma_3 + \sigma_1\sigma_3) = \sigma_F{}^2$$

E. Distortion Energy (Octahedral shear theory etc.). Considers the three values of maximum shear stress states simultaneously.

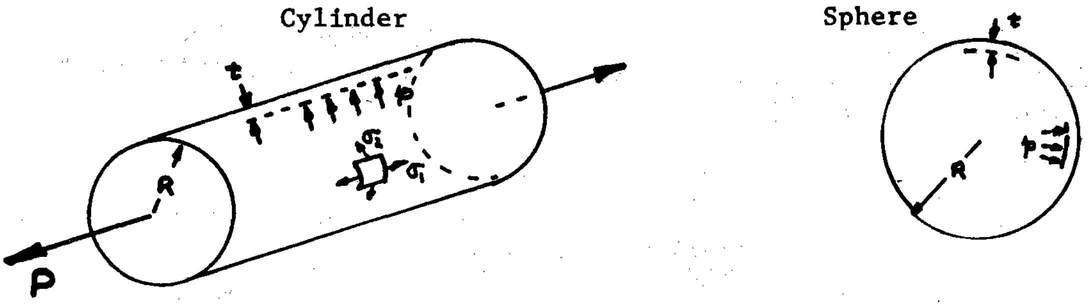
$$(\sigma_1-\sigma_2)^2 + (\sigma_1-\sigma_3)^2 + (\sigma_2-\sigma_3)^2 = 2\sigma_F{}^2$$

It is patently clear that in general the above theories will predict quite different stresses and strains for failure even in an unembrittled homogenous material. The maximum shear stress and the distortion energy theories define failure on the basis of the developed shear stresses and thus predict that failure would never occur for hydrostatic tension. Maximum stress and strain theories on the other hand relate more closely to deformation models of failure. As might be expected experience has shown that failure of ductile materials, under non hydrostatic stress states, is described by the maximum shear and distortion energy theories while failure of brittle materials is described by the maximum stress, or strain theories.

Embrittlement of materials by hydrogen or other environments further complicates the failure criteria partially because the stress state may influence whether and by how much a particular region in a load carrying member is embrittled. Furthermore, hydrogen may change the failure mode and effect deformation processes. As an illustration of the above, consider the following: Localized, high hydrogen concentrations may be developed because hydrogen diffuses to regions of maximum lattice dilatation. Such segregation is maximized by a triaxial state of stress. Failure or hydrogen embrittlement on the other hand may occur by either a brittle or ductile process. Ductile processes require dislocation motion which is minimized by the same triaxial stress state. Thus alloys, such as most austenitic steels which fail by microvoid coalesence even when severely embrittled may not show any embrittlement when the hydrogen concentrations are developed because of triaxial stress states. If, however, the localized hydrogen concentrations were developed because of dislocation motion-- which requires shear stresses--embrittlement might result because of the localized concentration. Thus, the embrittlement-failure process may be a complicated combination of stress state and hydrogen transport mechanisms.

There is experimental evidence to suggest that some materials that appear embrittled in uniaxial tension (for example A-286 stainless steel) are not as severely embrittled under the particular complex stress states such as exist in the disc rupture test (7). We are presently investigating the behavior of A-106 steel and 4340 in the presence of hydrogen in attempts to determine how the failure process depends on stress state. The information developed in this study will then be utilized to relate the actual stress state expected in service, to the particular material used and its expected propensity to hydrogen embrittlement. To demonstrate the effects of stress state, cylindrical pressurized and axially loaded test specimens will be used to study a wide range of stress states.

Consider the pressure vessels shown below where $t \ll R$



$$\sigma_1 = \frac{pR}{2t} + \frac{P}{2\pi Rt}$$

$$\sigma_2 = \frac{pR}{t}$$

$$\sigma_1 = \sigma_2 = \frac{pR}{2t}$$

Fig. 1

The resulting stresses for various loadings are given in Table I. The terms "in-plane" and "out-of-plane" have meaning due to the thinness of the material.

TABLE I

EFFECT OF LOADING ON
MAXIMUM AND SHEAR STRESSES IN TEST SAMPLES

	Max. Stress	In Plane Shear	Out of Plane Shear
Sphere	2σ	0	1σ
Cylinder $P = 0$	2σ	$\sigma/2$	1σ
Cylinder $P/2Rt\pi = \sigma$	2σ	0	1σ
Cylinder, no pressure uniaxial load	2σ	1σ	1σ

Combinations of axial loads and pressurization of the cylinder can produce (1) a uniaxial stress state,

(2) a regular cylindrical pressure vessel or pipeline, and (3) a spherical configuration. In all cases the maximum stress and the "out of plane" shear stresses would be the same.

A possible rationale for the influence of the "in plane" shear on hydrogen embrittlement susceptibility is suggested by Fig. 2.

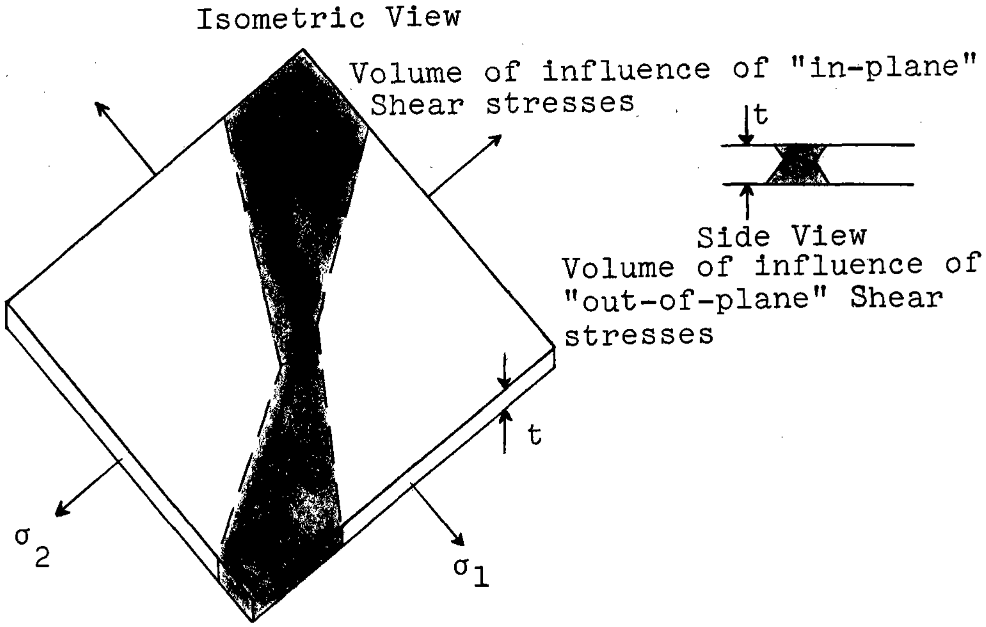


Fig. 2

Sketches indicating the relative volumes from which hydrogen could be transported by means of shear stresses.

As can be seen from Fig. 2, the volume of influence of the "in plane" as compared to the "out of plane" shear stresses is at least an order of magnitude larger, thus enabling hydrogen to be able to be drawn from a much larger reservoir and in some cases to cause embrittlement while in other cases the minimum hydrogen content necessary for embrittlement would not be achieved.

Thus,

1. If it is primarily the "in-plane" shearing forces that drive dislocations, and

2. If the dislocations indeed transport hydrogen, and
3. If the achievement of some threshold amount of hydrogen is required at some high energy site,

Then this model should, for very thin specimens, predict that in a hierarchy of severity of hydrogen embrittlement the worst case would be

1. Uniaxial tension, next would be
2. Cylindrical state and least affected would be
3. the spherical case.

There is experimental evidence which supports this hypothesis for particular materials and evidence from disc rupture tests suggests that such behavior varies from material to material.

The experimental program at Virginia Polytechnic Institute and State University is designed to address these complex stress state-embrittlement process interactions, with the ultimate goal of relating the results of our work to the development of conservative design criteria.

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AUTOMOTIVE HYDROGEN STORAGE WITH MAGNESIUM HYDRIDE

D. A. Rohy, J. F. Nachman, T. E. Duffy and A. N. Hammer
Solar Division of International Harvester
2200 Pacific Highway
San Diego, CA 92138

On-board fuel storage is a basic limitation to the use of hydrogen as an automotive fuel. Metal hydrides can store hydrogen at the same volumetric density as cryogenic methods, but generally incur serious weight penalties. Among the relatively common materials, magnesium-base alloys offer the best (lowest) weight density. The objective of this program is to develop a magnesium-base alloy to store hydrogen that meets the operating constraints of a conventional automobile with a spark ignition engine. Specific constraints include:

- Dissociation Temperature

  A maximum 200 C hydride dissociation temperature. Vehicle exhaust will be used to supply the heat of dissociation.

- Weight

  It must store 9 to 23 kg (20 to 50 pounds) of hydrogen with total weight of hydride metal plus containment tank and heat exchanger system sufficiently low to not seriously impair vehicle performance.

- Waste Heat Utilization

  The heat of dissociation and temperature pressure relationship must be in a range that allows waste heat of the engine to be utilized for hydrogen generation.

- Rate of Dissociation

  The hydride must dissociate at a rate to supply a continuous flow of hydrogen for steady state 0.62 g/sec to 1.25 g/sec (5 to 10 pph) and transient 3.15 to 6.3 g/sec (25 to 50 pph) fuel flow rates. The system must be designed to handle virtually instantaneous flow transients from idle to maximum flow.

- Cost

  The cost of the basic hydride must be compatable with automotive requirements of less than $2.20/kg ($1.00/ pound).

- Startup

  A startup system to supply hydrogen immediately from cold start must be provided.

- Storage Density

  The volume/pound of hydrogen must be sufficiently low to allow installation in a vehicle and, thus, must be close to the density of liquid hydrogen 0.07 g/cm^3 (4.4 lbs/ft^3).

There are four general methods of storing hydrogen for vehicular fuel: metal hydrides, cryogenic, compressed gas and chemical carriers. Many studies exist on these competing techniques (1). Metal hydrides can store more hydrogen per unit volume than normal high pressure or cryogenic techniques. Little energy is required to store the hydrogen in the hydride, and high stability at room temperature ensures low losses over long storage periods. Safety features of metal hydride storage are favorable. Because of its low weight and high hydrogen storage densities, modified magnesium hydride offers the greatest potential for automotive storage of hydrogen. Recent experimental and analytical work has been directed toward the optimization of this storage system.

While several hydrides have been considered for automotive use, only two, iron-titanium (FeTi) and magnesium (Mg) based alloys, can come close to satisfying the basic constraints of

- Inexpensive nonstrategic material
- Low weight density
- High hydrogen density
- Moderate dissociation temperature
- Good kinetics

The properties of these two alloys are compared in Table I.

Table I

Hydride Comparison

	FeTi	Mg Alloys
Weight for 320 km Range (lbs)	1270	420
Cost Per Vehicle ($)	1300	520
Hydrogen Capacity (%)	2	7
Dissociation Temperature (C)	0	245
Kinetics	Acceptable	Fair

Except for the high dissociation temperature and fair kinetics, the Mg alloys are better suited to a mobile system. The goal of the present program is to reduce the dissociation temperature to 200 C. To accomplish this goal we have alloyed Mg with Ni, Zn, Cu, Si, V, Ga and Ce. The effect of each addition on the dissociation temperature and kinetics has been noted.

From experimental data developed in this study, the modified Mg-Ni alloys offer the greatest potential for reaching that goal. Dissociation temperature at one atmosphere hydrogen pressures is reduced to 249 C for an alloy of Mg, Ni, Cu, V and Zn from 302 C for $Mg_{0.9}Ni_{0.1}H_x$. Nickel content has been reduced to 9.3 percent from 55 percent in Mg_2NiH_x. Another Mg alloy now under test has displayed a dissociation temperature of 233 C. Data is still being acquired on this system.

Considerable work remains before one of these alloys is found in an operation fuel storage system. This work includes a thorough study of the dehydriding kinetics and an optimization of the hydrogen capacity.

In summary, we have found metal hydrides to be viable hydrogen storage media for vehicular fuel. Among the hydrides modified magnesium alloys are the best for this application. Alloy modification studies are underway and have been successful in reducing the high dissociation temperature of these alloys. Further work on hydrogen capacity and reaction kinetics is planned.

Reference

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A PROGRAM FOR A HYDROGEN-FUELED INDUSTRIAL VEHICLE

J. T. Mehne and T. J. Pearsall
Teledyne Continental Motors
Muskegon, Michigan 49443

This paper describes a program being carried out under contract to ERDA under the Hydrogen Energy Program by Teledyne Continental Motors.

I. SCOPE

The program is structured to consist of three main phases:

A. Literature search - to compile data covering all phases of the use of hydrogen in engine-powered equipment.

B. Application selection - to select an appropriate industrial vehicle within the application field, and to determine suitable systems required to power that vehicle with hydrogen fuel.

C. Preliminary installation - to make a preliminary installation design encompassing data and systems, as defined in Phase B, within an existing industrial vehicle.

It is anticipated that this phase could lead to an actual test installation to include the latest technologies, and provide a practical near-term test bed.

II. APPLICATION FIELD

The general field of application chosen for this program is that of industrial, in-plant, internal combustion engine powered fork lift trucks.

The typical operating cycles for these vehicles encompasses a wide range of power loading and engine operating speeds, combined with a high utilization factor in terms of hours worked per day.

In addition, the in-plant fork truck is an attractive application for hydrogen fuel because of the major reduction in gaseous emissions obtainable; the established use of central fueling stations for conventional fuels; and the large amount of cast iron carried on the truck to act as a counterweight to the fork load, and which can be replaced effectively by the metal hydride storage tanks.

III. LIFE CYCLE COSTS

The costs to own, operate, and maintain a typical 4000-lb. rated fork truck with a gasoline-fueled internal combustion engine, and a battery-powered electric truck, over the life of the vehicle are as follows:

	Gasoline ICE	Battery Powered
Cost to Own, Operate and Maintain ($/Year)	$ 6117.	$ 6295.

These data are based upon gasoline at $.47 per gallon, and electricity at $.033/Kwh, and provide a base line in terms of 1976 costs upon which to compare developed costs of hydrogen-powered vehicles.

IV. KNOWN PROBLEM AREAS

The following general problem areas are known to exist, and will be considered in this program with the expectation of further defining the effect of each with respect to an industrial vehicle.

- Miscellaneous fuel leaks. Hydrogen is odorless.
- Invisible flame. Effect of ruptured hydride tanks, etc.
- Engine lubricating oil life. Hydrogenation.
- Embrittlement of critically stressed structures.
- Knock limit and back-fire prevention.
- Fuel storage, both on vehicle and at the fueling center.

In conclusion, we at Teledyne Continental Motors look forward to a continuing program of hydrogen-fueled engine research that can lead to a clear definition of the practical and economic elements that would go into the consideration of hydrogen as a long range fuel alternative.

APPENDIX

Contractor's Fact Sheets

Organization: ARGONNE NATIONAL LABORATORY

Address: 9700 South Cass Avenue
Argonne, Illinois 60439

Project Title: The Metal Hydride HYCSOS System for Solar Heating, Cooling and Energy Conversion

Principal Investigator: D. M. Gruen

Telephone No.: (312) 739-7711, Ext. 2651

Contract Officer: Paul A. Nelson, Director
Energy Storage Programs

Telephone No.: (312) 739-7711, Ext. 2577

Contract No.: ANL 189 No. 49405

Effective Date: July 1, 1975

Term of Contract: July 1975 - September 1976

Amount*: $175,000

Goal: Development, design, construction, operation and evaluation of a two metal hydride demonstration system for space heating and cooling and for the conversion of thermal to electrical energy.

Status: The two metal hydride or HYCSOS system has been designed and construction is to be completed by January 1, 1977.

Technical Monitor: P. Auh

Address: Brookhaven National Laboratory
Upton, New York 11973

Telephone No.: (516) 345-2052

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* ERDA funding in FY 1976 (including transition quarter).

Organization: BROOKHAVEN NATIONAL LABORATORY

Address: Upton, New York 11973

Project Title: Hydrogen Technology Development

Principal Investigator: Frank J. Salzano

Telephone No.: (516) 345-4458

Contract Officer: Joseph Haeg

Telephone No.: (516) 345-3151

Contract No.: Form 189 No. HC-01-07

Effective Date: Continuing

Term of Contract: One Year

Amount*: $1.45M

Other Funding: None**

Goal: To develop the technology of hydrogen production, storage and utilization systems such that it has a significant impact on the national energy system.

Status: Technology development is proceeding at a proper pace to achieve objectives defined by ERDA PAD document and by project systems analysis, economic studies and within the project budget constraints.

* ERDA Funding in FY 1976 (including transition quarter).

** Some cost sharing is being done by contractors.

Organization: BURNS AND ROE, INC.

Address: 185 Crossways Park Drive
Woodbury, New York 11797

Project Title: Conceptual Design and Cost Estimates of Metal Hydride Storage Power Plants

Principal Investigators: I. Chait and Dr. S. Fogelson

Telephone Nos.: (1) (516) 364-8800 (x357)
(2) (516) 364-8800 (x360)

Contract Officer: A. Pucillo

Telephone No.: (516) 364-8800 (x364)

Contract No.: BNL 326493-S

Effective Date: April 1, 1974

Term of Contract: To June 1977

Amount*: $44,500

Goal: To assess the technical and economic feasibility of proposed metal hydride storage power plant concepts.

Status: Two design and cost estimate studies have been completed to date. There is no work in-house at present.

Technical Monitor: A. Beaufrere

Address: Brookhaven National Laboratory
Building 120
Upton, New York 11973

Telephone No.: (516) 345-2094

* ERDA funding in FY 1976 (including transition quarter).

Organization: EXXON RESEARCH AND ENGINEERING COMPANY

Address: P. O. Box 8
Linden, New Jersey 07036

Project Title: Hydrogen Systems Study

Principal Investigator: Hampton G. Corneil

Telephone No.: (201) 474-3488

Contract Officer: E. J. Horan

Telephone No.: (201) 474-3965

Contract No.: BNL 368150-S

Effective Date: February 2, 1976

Term of Contract: To December 31, 1976

Amount*: $100,008

Goal: To conduct economic studies to predict hydrogen, ammonia, and methanol manufacturing costs by natural gas reforming, coal gasification, and electrolysis processes for the 1980 - 2000 period.

Status: Draft report has been submitted to F. J. Salzano. Data in the report will be revised to reflect recent changes in investments.

Technical Monitor: F. J. Salzano

Address: Brookhaven National Laboratory
Building 475
Upton, New York 11973

Telephone No.: (516) 345-4458

* ERDA Funding in FY 1976 (including transition quarter).

Organization: GENERAL ATOMIC COMPANY

Address: P. O. Box 81608
San Diego, California 92138

Project Title: Analysis of Thermochemical Hydrogen Processes (LASL)[1]

Principal Investigator: John L. Russell, Jr.

Telephone No.: (714) 455-2090

Contract Officer: William Kane

Telephone No.: (714) 455-2716

Contract No.: L46-48844-1

Effective Date: July 1, 1976

Term of Contract: To November 15, 1976

Amount: $81,500 (LASL)

Other Funding: ERDA(1), AGA, GA

Amounts: $50,000; $250,000(2); $150,000(2)

Goal: LASL: Perform engineering development for LASL water-splitting cycles.
GA : Develop GA water-splitting process to where it is a commercially feasible source of hydrogen.

Status: LASL: Engineering flowsheets prepared for two cycles, metallurgy and vapor-liquid equilibria investigated for H_2SO_4.
GA : Second flowsheet interation complete, still refining chemistry, conducting metallurgy testing, ready for bench tests.

Technical Monitor: M. Bowman

Address: University of California
Los Alamos Scientific Laboratory
P. O. Box 1663
Los Alamos, New Mexico 87544

Telephone No.: (505) 667-6014

(1) ERDA Funding for GA cycle development expected in FY 77.
(2) Funding in CY 1976.

Organization: GENERAL ELECTRIC COMPANY
Direct Energy Conversion Programs

Address: 50 Fordham Road
Wilmington, Massachusetts 01887

Project Title: Solid Polymer Electrolyte Water Electrolysis Technology Development for Bulk Hydrogen Generation

Principal Investigator: J. H. Russell

Telephone No.: (617) 657-4698

Contract Officer: Robert Maitner

Telephone No.: (617)657-4820

Contract No.: EY-76-C-02-2675 *000

Effective Date: June 15, 1975

Term of Contract: To October 31, 1977

Amount*: $270,000

Other Funding: Niagara Mohawk Power Corporation

Amount: $300,000

Goal: This program is initial phase toward a 5MW demonstration system with goal of 85-90% overall efficiency, < $100/KW capital cost, 40,000 hour minimum cell life.

Status: Significant progress has been made in technology development toward achieving cost and performance goals. Full scale cell design effort proposed to start during FY 1977.

Technical Monitor: S. Srinivasan

Address: Brookhaven National Laboratory
Building 815
Upton, New York 11973

Telephone No.: (516) 345-4494

* **ERDA** Funding in FY 1976 (including transition quarter).

Organization: UNIVERSITY OF GEORGIA

Address: Department of Chemistry
University of Georgia
Athens, Georgia 30602

Project Title: Development of a Practical Photochemical Energy Storage System

Principal Investigators: Richard R. Hautala and Charles Kutal

Telephone Nos.: (1) (404) 542-2626 (x 18)
(404) 542-2626 (x 75)

Contract No.: E(38-1)-893

Effective Date: June 15, 1975

Term of Contract: To June 14, 1977

Amount*: $72,198

Other Funding: NSF Amount: $50,000 (2 years)

Goal: The objective of this research program is the development of a practical solar energy storage system based upon the photosensitized valence isomerization of norbornadiene to quadricyclene. Key steps in the project include (1) the development of strongly absorbing sensitizers for the energy storage step, (2) the development of efficient catalysts for the energy release step (reconversion of quadricyclene to norbornadiene), (3) the immobilization of appropriate sensitizers and catalysts onto an insoluble polymeric support, and (4) the construction of a laboratory model which can be recycled repeatedly to test the stability of the sensitizer catalyst and storage medium. We ultimately plan to construct a prototype device for commercial development.

Status: Progress in each of the four areas described above has been achieved. Both organic and inorganic sensitizers with improved absorption characteristics have been found and several effective catalysts containing relatively

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* ERDA Funding in FY 1976 (including transition quarter).

inexpensive transition metals have been tested. Polymer immobilized sensitizers and catalysts have been prepared and shown to be effective. Current work is aimed at optimizing the performance of these heterogeneous materials. Construction of a laboratory prototype is underway, and upon its completion, recycling studies of the energy storage-energy release steps will be undertaken to test the stability of the various components in the system.

Technical Monitor: Dr. P. Russell

Address: Brookhaven National Laboratory
Building 815
Upton, New York 11973

Telephone No.: (516) 345-4518

Organization: INSTITUTE OF GAS TECHNOLOGY

Address: 3424 South State Street
Chicago, Illinois 60616

Project Title: Seasonal Energy Storage Requirements

Principal Investigators: T. M. Goff and W. C. Chambers

Telephone Nos.: (312) 567-3972 and
(312) 567-3744

Contract No.: E(11-1)-2906

Effective Date: July 1, 1976

Term of Contract: Three months.

Amount: $18,500

Goal: To quantify residential heating and cooling energy sales. Assess the cost and magnitude of natural gas and oil storage. Review electric energy storage systems amenable to seasonal application and recommend research programs for each of them.

Status: The analysis is complete and the final report is undergoing in-house draft revision.

Technical Monitor: J. Milau

Address: Brookhaven National Laboratory
Building 835
Upton, New York 11973

Telephone No.: (516) 345-3184

Organization: INSTITUTE OF GAS TECHNOLOGY

Address: IIT Center
3424 South State Street
Chicago, Illinois 60616

Project Title: Study of the Behavior of Gas Distribution Equipment in Hydrogen Service

Principal Investigators: J. B. Pangborn and W. J. Jasionowski

Telephone Nos.: (312) 567-3688 and (312) 567-3938

Contract No.: E(11-1)-2907

Effective Date: April 1, 1976

Amount*: $60,000

Goal: To identify problem areas of conventional gas distribution equipment in hydrogen service.

Status: Three model gas distribution loops were designed, collection of donated components is almost completed, and assembly of the distribution models has begun.

Technical Monitor: H. J. Saxton

Address: Division 8314
Sandia Laboratories
Livermore, California 94550

Telephone No.: (415) 455-2391

* ERDA Funding in FY 1976 (including transition quarter).

Organization: INTERNATIONAL NICKEL COMPANY, INC. (INCO)

Address: Paul D. Merica Research Laboratory (PDMRL)
Sterling Forest
Suffern, New York 10901

Project Title: The Interrelations among Composition, Microstructure, and Hydriding Behavior for Alloys Based on the Intermetallic Compound FeTi

Principal Investigator: G. D. Sandrock

Telephone No.: (914) 753-2761

Contract Officer: F. W. Schaller

Telephone No.: (914) 753-2761

Contract No.: BNL 352410-S

Effective Date: April 14, 1975

Term of Contract: To April 15, 1977

Amount*: $72,500

Other Funding: Inco Amount: $64,500

Goal:
(1) Understand the Physical Metallurgy and Melting of FeTi.
(2) Support BNL Experimental Efforts.
(3) Survey Possible Low Cost Production Techniques.

Status: Goal (1) completed and reported in final report dated June 30, 1976. Work on (2) and (3) continuing on contract extension.

Technical Monitor: J. J. Reilly

Address: Brookhaven National Laboratory
Building 815
Upton, New York 11973

Telephone No.: (516) 345-4502

* ERDA Funding in FY 1976 (including transition quarter).

Organization: UNIVERSITY OF KENTUCKY

Address: College of Engineering
Lexington, Kentucky 40506

Project Title: Evaluation of Multi-Step Thermal Processes for the Production of Hydrogen from Water

Principal Investigators: William L. Conger and
James E. Funk

Telephone Nos.: (1) (606) 258-4958
(2) (606) 257-1688 or (606) 257-2866

Contract Officer: Jack Supplee, Dale Chapman

Telephone No.: (606) 258-4666

Contract No.: F-(40-1)-5129

Effective Date: May 1, 1976

Term of Contract: To February 1977

Amount*: $25,000

Goal: The goal of this research is to develop a procedure for evaluating the thermodynamic efficiency of proposed thermochemical cycles for the production of hydrogen from water.

Status: We are in the last stage of writing the computer program HYDRGN. This program calculates a first estimate of the thermodynamic efficiency of hydrogen production cycles. Work on the final report is about to start.

* ERDA Funding in FY 1976 (including transition quarter).

Organization: UNIVERSITY OF CALIFORNIA

Address: Lawrence Livermore Laboratory
P. O. Box 808
Livermore, California 94550

Project Title: Engineering Development of the ZnSe Thermochemical Hydrogen Cycle

Principal Investigator: Oscar H. Krikorian

Telephone No.: (415) 447-1100 (x 7021)

Contract Officer: W. B. Harford

Telephone No.: (415) 447-1100 (x 7861)

Contract No.: W-7405-Eng-48

Amount*: $70,000

Other Funding: ERDA-DPR Amount: $125,000

Goal:
1. Conduct an economic analysis of the ZnSe cycle.
2. Advance the engineering development of the ZnSe cycle for a potential bench-scale demonstration.

Status: Preliminary economic analysis has been completed and engineering development studies are being initiated.

* ERDA Funding in FY 1976 (including transition quarter).

Organization: LOCKHEED-CALIFORNIA COMPANY

Address: P. O. Box 551
Burbank, California 91520

Project Title: Study of Wind Energy Conversion and Storage

Principal Investigator: Michael Dubey

Telephone No.: (213) 847-6885 or (213) 782-7209

Contract Officer: James Glenn

Telephone No.: (213) 847-3456

Contract No.: NSF-C75 22186

Effective Date: June 30, 1976

Term of Contract: To April 1976

Amount: $164,634

Goal: Investigate the technical and economic feasibility of a concept for producing hydrogen by electrolysis using wind power as the energy source, and then combining the hydrogen with air and water to manufacture ammonium nitrate fertilizer. The study will identify technical obstacles requiring solution and will define a program for a proof-of concept experiment.

Status: A baseline system is being designed as a basis for parametric performance and production cost analyses.

Organization: LOS ALAMOS SCIENTIFIC LABORATORY

Address: P. O. Box 1663
Los Alamos, NM 87545

Project Title: Thermochemical Processes for Hydrogen Production

Principal Investigators: Melvin G. Bowman and John D. Farr

Telephone Nos.: (1) (505) 667-6014
(2) (505) 667-6074

Goal: To identify and develop practical thermochemical cycles for hydrogen production.

Procedure:

I. Experimentally determine reaction yields, reaction rates and thermochemistry of individual reactions in potential cycles.

II. Prepare process flow sheets for preliminary design, cost analyses and comparative cycle evaluations.

III. Further develop and evaluate selected processes by bench-scale, closed-loop experiments to provide data for more realistic evaluation and cost analyses.

Status: Scientific feasibility has been demonstrated for several cycles by means of Step I. Three cycles are in progress through Step II in an iterative program of process definition and evaluation followed by re-design and re-evaluation. No process has been selected for Step III.

New and potentially promising cycles are in progress through Step I.

Organization: MIDDLE TENNESSEE STATE UNIVERSITY

Address: Murfreesboro, Tennessee 37132

Project Title: Hydrogen Fuel Production: Investigation of Electrocatalysts for Water Electrolysis

Principal Investigator: Melvin H. Miles

Telephone No.: (615) 898-2954 or (615) 896-4877

Contract Officer: J. Tunstill

Telephone No.: (615) 898-2940

Contract No.: BNL 347505-S

Effective Date: March 15, 1976

Term of Contract: To May 31, 1977

Amount*: $5,000

Goal: Amendment No. 3 shifts the goals to investigations of electrocatalysts for fuel cells. In particular, the oxygen reduction reaction is to be investigated on various metals, alloys, and metallic oxides in several electrolyte solutions.

Status: Anion effects on oxygen reduction have been investigated in acid and alkaline solutions. Kinetic studies of the oxygen reduction reaction on several metals in aqueous carbonate systems have been made.

Technical Monitor: F. J. Salzano

Address:
Brookhaven National Laboratory
Building 475
Upton, New York 11973

Telephone No.: (516) 345-4458

* ERDA Funding in FY 1976 (including transition quarter).

Organization: PUBLIC SERVICE ELECTRIC AND GAS COMPANY

Address: 80 Park Place
Newark, New Jersey 07101

Project Title: Blending of Hydrogen in Natural Gas Distribution Lines

Principal Investigator: Carlos R. Guerra

Telephone No.: (201) 622-7000 (x 2841)

Contract Officer: Robert Butz

Telephone No.: (201) 622-7000 (x3508)

Contract No.: E(11-1)-2925

Effective Date: June 1, 1976

Term of Contract: To August 1977

Amount*: $100,000

Other Funding: PSE&G Amount: $10,000

Goal: Determine the maximum amounts of hydrogen which can be blended with natural gas without effect on distribution system and utilization equipment.

Status: Combustion tests are near completion. Leakage, effect on materials and network analysis to be started.

Technical Monitor: C. Braun

Address: Brookhaven National Laboratory
Building 475
Upton, New York 11973

Telephone No.: (516) 345-2070

* ERDA Funding in FY 1976 (including transition quarter).

Organization: SANDIA LABORATORIES

Address: Materials Characterization Division 8314
Sandia Laboratories
Livermore, California 94550

Project Title: Hydrogen Compatibility of Structural Materials for Energy Storage and Transmission Applications

Principal Investigator: Harry J. Saxton

Telephone No.: (415) 455-2391

Effective Date: January, 1975

Amount*: $235,000

Goal: Gather hydrogen performance data for existing materials and develop new low cost materials, assembly procedures and protection schemes for hydrogen containment and transmission systems.

Status: Two low cost steels appear suitable for containment of $FeTiH_x$ reactions. Various coatings and alloy modifications are being evaluated; an experimental hydrogen pipeline facility is nearing completion.

Technical Monitor: Howard Nelson

Address: NASA - Ames Research Center
Mail Stop 240-1
Sunnyvale, California 94035

Telephone No. (415) 965-6137

* ERDA Funding in FY 1976 (including transition quarter).

Organization: INTERNATIONAL HARVESTER, SOLAR DIVISION

Address: 2200 Pacific Highway
San Diego, California 92138

Project Title: Automotive Hydrogen Storage with Magnesium Hydride

Principal Investigators: David A. Rohy and
Joseph Nachman

Telephone Nos.: (714) 238-5604 and (714) 238-6781

Contract No.: E(04-3)-1167

Effective Date: February 23, 1976

Amount*: $60,000

Goal: Develop a magnesium based alloy to store hydrogen that meets the operating constraints of a conventional automobile. Specifically the hydride must dissociate at or below 200°C.

Status: Numerous alloys have been developed and tested. The dissociation temperature has been reduced ~300°C to 232°C. Hydrogen capacity and dissoc-kinetics are being investigated now.

Technical Monitor: C. Waide

Address: Brookhaven National Laboratory
Building 120
Upton, New York 11973

Telephone No.: (516) 345-2404

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* ERDA Funding in FY 1976 (including transition quarter).

Organization: STEVENS INSTITUTE OF TECHNOLOGY

Address: Department of Chemistry and
Chemical Engineering
Hoboken, New Jersey 07030

Project Title: Solar-Chemical Energy Conversion and Storage

Principal Investigators: A. B. Ritter and G. B. Delancey

Telephone Nos.: (201) 792-2700

Contract Officer: I. R. Ehrlich, Dean of Research

Telephone No.: (201) 792-2700

Contract No.: E(11-1)-4031

Effective Date: June 1, 1976

Term of Contract: To May 31, 1977

Amount*: $31,616

Goals: a. <u>Cyclohexane Dehydrogenation Kinetics</u>

Experimentally obtain apparent kinetics of dehydrogenation of cyclohexane to benzene and hydrogen at 1 atm. and 400-600°F over industrial naphtha reforming catalyst using an internally recirculated batch reactor.

b. <u>Collector-Reactor Simulation</u>

Develop a model to realistically describe transient behavior of a gas phase catalytic reactor dedicated to the collection of thermal energy. Measured solar isolation data and parameters that describe the collection system will be inputs to the model as well as kinetic data. The model will be applied to the cyclohexane dehydrogenation system for the purposes of evaluating startup, shutdown and control algorithms as well as for the later stages of pilot plant design and possibly for evaluation of of other chemical storage systems.

A.B. Ritter, G.B. DeLancey

Status: a. gas chromatograph has been calibrated for the benzene-cyclohexane system and one run has been made over the catalyst at 600°F.

b. a transient model for the reactor has been formulated and is being programmed for computer simulation of the collector-reactor system.

Technical Monitor: Mr. Matthew J. Rosso

Address:
Brookhaven National Laboratory
Dept. of Applied Science, Bldg. 835
Upton, L.I., N.Y. 11973

Phone No. (516) 345-4506

* ERDA Funding in FY 1976 (including transition quarter).

Organization: TELEDYNE CONTINENTAL MOTORS CORPORATION

Address: 76 North Getty Street
Muskegon, Michigan 49441

Project Title: A Program for a Hydrogen Fueled Industrial Vehicle

Principal Investigators: T. Pearsall, J. Mehne and A. Karaba

Telephone No.: (616) 724-2885

Contract Officer: T. Schwallie

Contract No.: BNL 387491-S

Amount: $49,684

Goal: To define a potential near term application for hydrogen fueled engines employing metal hydride storage systems.

Technical Monitor: C. Waide

Address: Brookhaven National Laboratory
Building 120
Upton, New York 11973

Telephone No.: (516) 345-2404

Organization: TELEDYNE ENERGY SYSTEMS

Address: 110 West Timonium Road
Timonium, Maryland 21093

Project Title: Advanced Alkaline Electrolysis Cell Matrix Development

Principal Investigator: John N. Murray

Telephone No.: (301) 252-8220

Contract Officer: W. W. Wachtl

Telephone No.: (301) 252-8220

Contract No.: BNL 380750-S

Effective Date: April 22, 1976

Amount*: $41,223

Goal: Identify and test candidate alkaline electrolysis cell separator materials capable of operating at temperatures up to 350°F resulting in improved process efficiencies.

Status: Environmental testing of two candidate materials is about to begin. Conditions will include elevated temperature, caustic solutions, and exposure to both hydrogen and oxygen.

Technical Monitor: S. Srinivasan

Address: Brookhaven National Laboratory
Building 815
Upton, New York 11973

Telephone No.: (516) 345-4494

* ERDA Funding in FY 1976 (including transition quarter).

Organization: VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY

Address: Blacksburg, Virginia 24061

Project Title: The Role of Stress in Controlling Susceptibility to Hydrogen Embrittlement

Principal Investigators: M. R. Louthan, Jr. and
R. P. McNitt

Telephone Nos.: (1) (703) 951-6825
(2) (703) 951-6746

Contract No.: E-(40-1)-5255

Effective Date: September 1, 1976

Term of Contract: One Year

Amount*: $29,920

Other Funding: VPI&SU Amount: $8,950

Goal: To examine the role of stress state on the hydrogen embrittlement of two different engineering materials. Materials could be candidate materials for many applications in the hydrogen economy.

Status: Work is underway and is on schedule.

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*ERDA Funding in FY 1976 (including transition quarter).

Organization: UNIVERSITY OF VIRGINIA

Address: Department of Materials Science
Thornton Hall
Charlottesville, VA 22901

Project Title: Preparation and Characterization of New Alloy Phases for Hydrogen Storage

Principal Investigators: G. Stoner, J. Johnson, and C. Adkins

Telephone Nos.: (1) (804) 924-3462
(804) 924-3264

Contract Officer: Mr. Louis Redden

Telephone No.: (804) 924-7062

Contract No.: E-(40-1)4952

Effective Date: June 1, 1976

Term of Contract: Two years

Amount: $55,497

Goal: Development of new alloy phases for storage of hydrogen with improved H/weight and H/volume ratios.

Status: A model of the hydrogenation mechanism has been developed based on the Engel-Brewer concepts which works well applied to FeTi and will be improved with further correlations based on specific hydride characteristics of A_2B, AB, and AB_2 alloys of the first three periods of the elements.

Preparation of the phase type Ti_2Fe with hydride stochiometry Ti_2FeH_4 has been prepared and proved unstable due to dissociation of the hydride into equilibrium phases of TiH_2 and $TiFeH_2$. Stabilization of this phase type by adjustment of a d band contribution is being pursued.

Student supported by the contract has been appointed and is involved in literature study to determine most probable next structure to investigate to improve the existing model of the hydrogenation reaction.

Construction of hydrogenation hardware and alloy preparation hardware is nearing completion and will be ready to start specific investigation within the next month.

Technical Monitor: J. R. Johnson

Address: Department of Applied Science
Building 815
Brookhaven National Laboratory
Upton, New York 11973

Telephone No.: (516) 345-4502

Organization: UNIVERSITY OF VIRGINIA

Address: Department of Materials Science
Thornton Hall
Charlottesville, VA 22901

Project Title: Water Electrolysis: Studies of Separator Materials

Principal Investigator: Dr. Glenn E. Stoner

Telephone No.: (804) 924-3264

Contract Officer: Mr. Louis R. Redden

Telephone No.: (804) 924-7062

Contract No.: BNL 382793-S

Effective Date: March 1, 1976

Term of Contract: March 1, 1976 to September 30, 1976
Renewal pending

Amount: $7,000

Goal: The goal of this research is to understand the mechanisms of failure of asbestos separator material and to successfully stabilize the separator at elevated temperatures.

Status: A treatment has been developed which reduces an observed failure mechanism and optimization efforts are currently taking place. Commercial evaluation is also underway.

Technical Monitor: Dr. S. Srinivasan

Address: Department of Applied Science
Building 815
Brookhaven National Laboratory
Upton, New York 11973

Telephone No.: (516) 345-4494

Organization: WESTINGHOUSE ADVANCED ENERGY SYSTEMS DIVISION

Address: P. O. Box 10864
Pittsburgh, Pennsylvania 15236

Project Title: Sulfur Cycle Water Decomposition System

Principal Investigators: G. H. Farbman and V. Koump

Telephone Nos.: (1) (412) 892-5600 and (2) (412) 256-7636

Contract Officer: E. A. Murphy

Telephone No.: (412) 892-5600 (x 6738)

Contract No.: E(49-18)2262

Effective Date: May 17, 1976

Term of Contract: To May 1977

Amount: $384,000

Goal: The objective of this program is to assess the technical and economic feasibility of a hydrogen generation process based upon the electrolysis of sulfurous acid. To do this, a multi-task program is being carried out to experimentally determine the operating characteristics of key process steps in the hydrogen generating cycle and to perform engineering and economic analyses to evaluate the system.

Status: Electrolysis work, using an atmospheric pressure low temperature cell, has looked at both flooded and flow through electrodes and has shown substantial progress towards achievement of the 450 mV overall cell voltage selected as the target for the conceptual plant design. Catalysts for SO_2 reduction have been identified with activities that result in the reduction reactor being heat transfer limited, rather than chemical reaction rate limited. The experimental effort on material evaluation for high pressure, high temperature sulfuric acid vaporization is underway. Flow sheet optimization is now indicating overall efficiency higher than the 45.2% reported in earlier work (NASA-CR-134976).

Organization: YESHIVA UNIVERSITY

Address: Belfer Graduate School of Science
2495 Amsterdam Avenue
New York, New York 10033

Project Title: Optical Studies of Titanium Based Reversible Electrodes

Principal Investigators: Fred H. Pollak and Paul M. Raccah

Telephone Nos.: (212) 568-8400 (x 203) and
(212) 568-8400 (x 441)

Contract Officer: J. Raskin

Telephone No.: (212) 568-8400 (x 2309)

Contract No.: BNL 379095-S

Effective Date: March 1, 1976

Term of Contract: To September 30, 1976

Amount*: $8,000

Goal: Investigation of the optical properties of titanium based reversible electrodes (TiO_2, $SrTiO_3$) for a better understanding of surface interactions.

Status: Initial progress has been made in determining properties of space charge layer.

Technical Monitor: S. Srinivasan

Address: Brookhaven National Laboratory
Building 815
Upton, New York 11973

Telephone No.: (516) 345-4494

* ERDA Funding in FY 1976 (including transition quarter).

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