

IEA Agreement on the Production and Utilization of Hydrogen

Annual Report 1998

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Overview: International Energy Agency Hydrogen Implementing Agreement

The International Energy Agency

The International Energy Agency (IEA) was established in 1974, following the first oil crisis and is managed within the framework of the Organization for Economic Cooperation and Development (OECD). The mission of the IEA is to facilitate collaborations for the economic development, energy security, environmental protection and well-being of its members and of the world as a whole. The IEA is currently comprised of twenty-four member countries, eleven of which are participants in the program focused on the Utilization and Production of Hydrogen.

The Hydrogen Program, or Implementing Agreement, has been in existence for twenty years. Its mission is to advance hydrogen technologies and accelerate hydrogen's acceptance and widespread utilization. Past collaborations have been in the areas of Thermochemical Production, High Temperature Reactors, Electrolysis, Storage, Safety, and Markets.

The following countries/organizations participate in the Hydrogen Implementing Agreement: Canada, European Commission, Germany, Italy, Japan, The Netherlands, Norway, Spain, Sweden, Switzerland, United States.

Hydrogen

Today, hydrogen is primarily used as a chemical feedstock in the petrochemical, food, electronics, and metallurgical processing industries, but is rapidly emerging as a major component of clean sustainable energy systems. It is relevant to all of the energy sectors - transportation, buildings, utilities, and industry. Hydrogen can provide storage options for intermittent renewable technologies such as solar and wind, and, when combined with emerging decarbonization technologies, can reduce the climate impacts of continued fossil fuel utilization. Hydrogen is truly the flexible energy carrier for our sustainable energy future.

As we enter the new millennium, concerns about global climate change and energy security create the forum for mainstream market penetration of hydrogen. Ultimately, hydrogen and electricity, our two major energy carriers, will come from sustainable energy sources, although, fossil fuel will likely remain a significant and transitional resource for many decades. Our vision for a hydrogen future is one of clean sustainable energy supply of global proportions that plays a key role in all sectors of the economy. We will implement our vision with advanced technologies including direct solar production systems and low-temperature metal hydrides and room- temperature carbon nanostructures for storage.

Production

Hydrogen can be produced directly from sunlight and water by biological organisms and using semiconductor-based systems similar to photovoltaics (PV). Hydrogen can also be produced indirectly via thermal processing of biomass or fossil fuels. Global environmental concerns are leading to the development of advanced processes to integrate sequestration with known reforming, gasification, and partial oxidation technologies for carbonaceous fuels. These production technologies have the potential to produce essentially unlimited quantities of hydrogen in a sustainable manner.

Storage

Storage of hydrogen is an important area for cooperative research and development, particularly when considering transportation as a major user and the need for efficient energy storage for intermittent renewable power systems. Although compressed gas and liquid hydrogen storage systems have been used in vehicle demonstrations worldwide, the issues of safety, capacity, and energy consumption have resulted in a broadening of the storage possibilities to include metal hydrides and carbon nano-structures. Stationary storage systems that are high efficiency with quick response times will be important for incorporating large amounts of intermittent PV and wind into the grid as base load power.

Integration

Achieving the vast potential benefits of a hydrogen system requires careful integration of production, storage and end-use components with minimized cost and maximized efficiency, and a strong understanding of environmental impacts and opportunities. System models combined with detailed life cycle assessments provide the platform for standardized comparisons of energy systems for specific applications. Individual component models form the framework by which these system designs can be formulated and evaluated.

Current and Completed Annexes of the IEA Hydrogen Implementing Agreement

Annex 1	Thermochemical Production	1977-1988
Annex 2	High Temperature Reactors	1977-1979
Annex 3	Assessment of Potential Future Markets	1977-1980
Annex 4	Electrolytic Production	1979-1988
Annex 5	Solid Oxide Water Electrolysis	1979-1983
Annex 6	Photocatalytic Water Electrolysis	1979-1988
Annex 7	Storage, Conversion and Safety	1983-1992
Annex 8	Technical and Economic Assessment of Hydrogen	1986-1990
Annex 9	Hydrogen Production	1988-1993
Annex 10	Photoproduction of Hydrogen	1995-1998
Annex 11	Integrated Systems	1995-1998
Annex 12	Metal Hydrides for Hydrogen Storage	1995-2000
Annex 13	Design and Optimization of Integrated Systems	1999-2001

REPORT OF THE CHAIRMAN

Mr. Neil P. Rossmeissl
U.S. Department of Energy

INTRODUCTION

It was a very busy and productive year for the IEA Hydrogen Agreement and for hydrogen technologies, in general. The world has seen some significant advances in the hydrogen arena, including the continuing successes of the fuel cell bus and car programs throughout Europe, Japan and North American; General Electric's plans to produce residential fuel cell systems utilizing technology from Plug Power; Daimler-Benz and Ballard's collaboration with the Icelandic Government to establish a hydrogen economy in Iceland; and Norsk Hydro's activities to generate power using "clean" hydrogen from natural gas by sequestering the carbon dioxide in North Sea oil fields; just to name a few. The sodium aluminum hydride and carbon materials continue to show promise for meeting hydrogen storage targets for vehicle applications. Overall, hydrogen demonstration projects are expanding the international knowledge base on safety, feasibility, design, and performance parameters, paving the way for commercial applications of renewable hydrogen energy systems.

STATUS OF TASKS

Both Tasks 10 and 11 completed their activities during 1998 and are now preparing their final reports. Both collaborative activities resulted in significant advancements in hydrogen technologies. I would like to highlight just a few of the major accomplishments for each task:

Task 10 - Photoproduction of Hydrogen

- ! A solar-to-hydrogen efficiency of 12.4% was achieved using a tandem photoelectrochemical cell. Efficiencies of this level had not been previously reported. The materials used in this cell are still too costly for this to be an economically competitive technology in the near term. However, lower cost materials have shown similar promise. The results of this work were published in the prestigious journal *Science*.
- ! A process development scale photo-bioreactor was designed, built and tested at the University of Hawaii. The advantage of this reactor is its lower capital and operating costs than other designs.
- ! Two informative technical reports were published: *Solar Photoproduction of Hydrogen* by James R. Bolton, which provides standards for measuring photo efficiencies, reviews the state of the art, and assesses a number of photoproduction technologies; and *Process Analysis and Economics of Biophotolysis of Water* by John R. Benemann, which reviews the systems analysis and process economics of bioreactors for hydrogen production.
- ! The Task provided sponsorship for the BioHydrogen '97 meeting in Waikoloa, Hawaii, USA. This meeting brought together academic, industrial and governmental scientists from more than ten countries to share recent technological advances in the area of biological hydrogen production. Presentation areas included the fundamentals of biological processes, photosynthetic bacteria, cyanobacteria, green algae, fermentations and mixed-hybrid systems and photobioreactors. The Hydrogen Agreement provided support for the publication of the proceedings from the conference (published this past year).

Task 11 - Integrated Systems

- ! Twenty-seven component models were developed to model hydrogen production, storage, distribution and utilization. Guidelines were developed to assist in the design and optimization of integrated hydrogen energy systems. Standards were employed in the development of the component models to ensure that the component models could be linked to simulate fully integrated systems.
- ! Using the component models developed under the task, several integrated systems were evaluated. Intermittent renewable resources were assessed for grid-independent remote village applications: PV-electrolysis-metal hydride-PEM fuel cell system and wind-electrolysis-compressed gas- internal combustion engine generator set. Biomass systems were also evaluated for the production of hydrogen for vehicle refueling applications.
- ! Fourteen international hydrogen demonstration projects were critically evaluated and compared, with system performance measurement as the central focus. Safety and regulatory issues were also considered. Representatives of these demonstration projects provided technical data and participated in the review workshops. Additionally, the Annex participants were able to visit a number of the demonstration sites to see the facilities and meet with the project engineers.

I would like to personally thank Mr. Bjørn Gaudernack and Mrs. Catherine Gregoire Padró, Operating Agents for Tasks 10 and 11, respectively, for their outstanding leadership of these two Tasks and all of the task participants for their hard work and technical expertise.

NEW INITIATIVES

This year saw the development of proposals for five new tasks to both continue the activities and accomplishments of Tasks 10 and 11 and to address other research needs identified by the Executive Committee members:

- ! Many advances were made in the longer-term photoproduction area. This includes identification of the semi-conductor-based hydrogen production system capable of 12.4% solar efficiencies and the construction of the process development scale bioreactor. However, this work is still at the early development stage. A variety of materials and organisms remain under investigation. System design still requires a great deal of effort, as well. For this reason, task development phases were initiated to continue the work of Annex 10. A decision was made to split the photoproduction activities into two separate tasks, Annex 14, Photoelectrolytic Production of Hydrogen, and Annex 15, Photobiological Hydrogen Production, to better facilitate collaborations with other IEA Agreements, such as SolarPACES and Greenhouse Gases.
- ! Optimizing hydrogen energy systems requires careful integration of production, storage and end-use components. Minimized cost and maximized efficiency, as well as a strong understanding of environmental impacts and opportunities, are all key considerations when selecting and integrating system components. The models previously developed under Task 11 focused mainly on the efficiency aspects of system design. In Annex 13, Design and Optimization of Integrated Systems, these models will now be refined to incorporate cost measurements and detailed life cycle assessments to provide a platform for standardized comparisons of energy systems for specific applications.

- ! Hydrogen use in non-energy processes, such as the chemical, metallurgical, and ceramics industries was identified as an area where a concentrated research effort could facilitate the increased utilization of hydrogen. Annually, these industries account for nearly 50 percent of the world's 500 billion Nm³ hydrogen consumption. Process improvements and novel synthesis approaches could lead to overall efficiency improvements and reduced environmental impacts. Likewise, increased market share for hydrogen in these arenas should lead to expedited infrastructure development, a necessity for facilitating the advancement of the energy-related and renewable-based applications. Two workshops were held with industry representatives to identify research needs. A large scope of activities was identified. A questionnaire will be prepared and distributed to a variety of industries world-wide to better refine research activities and to evaluate industrial interest for task participation.
- ! Approximately 95% of the hydrogen produced today comes from carbon containing raw material, primarily fossil in origin. Most of the conventional processes convert the carbon to carbon dioxide, which is discharged to the atmosphere. The growing awareness of the impact of greenhouse gas emissions on global climate change has necessitated a reassessment of the conventional approach. Integrating carbon dioxide sequestration with conventional steam reforming will go a long way towards achieving "clean" hydrogen production from fossil fuels. Likewise, improving the robustness of pyrolytic cracking technologies for the conversion of hydrocarbons to hydrogen and solid carbon should not only improve the process economics, but also its applicability to a variety of feeds. Finally, the thermal processing of biomass can yield an economic and carbon-neutral source of hydrogen. We will work with industry and the related Implementing Agreements to better define where we might have the greatest impact in this important field.

MEMBERSHIP

There were ten active members of the Hydrogen Agreement during 1998: Canada, the European Commission, Germany, Japan, the Netherlands, Norway, Spain, Sweden, Switzerland, and the United States. Italy remains an official member, but has been inactive for some time. The United Kingdom's withdrawal from the Agreement became official this year.

The Executive Committee regrets to announce that Germany will terminate their participation in the Hydrogen Agreement upon completion of the current five year term (June 1999). Germany's participation will be greatly missed. Both the Hydrogen Agreement and the hydrogen community at large have benefitted greatly from the significant research and development efforts undertaken by Germany. I would personally like to thank Germany and their Executive Committee members Dr. Norbert Stump and Dr. Piotr Malinowski for their many contributions over the years, particularly their task leadership and the perspective they brought to the Executive Committee meetings. The Hydrogen Agreement will maintain an open invitation to Germany to renew their participation should their interest return to supporting international collaborations in the hydrogen area.

SAFETY

Safety continues to be a focus for the Agreement. Dr. Addison Bain, hired as a consultant, completed his initial work for the Executive Committee. Dr. Bain canvassed the U.S. industry, trade and technical associations, academia, insurance companies, fire departments, and government agencies to obtain opinions, recommendations, interest and willingness to share data and support an international safety-related activity. He made a number of

recommendations to the Executive Committee, primarily to assess and support the ongoing International Organization for Standardization (ISO) activities and to use the joint Canadian/United States Sourcebook for Hydrogen Applications project as a foundation for some type of international activity to compile codes and standards related to hydrogen applications. Both Japan and the European Commission are expected to undertake activities similar to the Sourcebook. The Hydrogen Agreement will look for opportunities to provide input to the various efforts and to prepare a summary of the North American, Japanese and European activities.

EUROPEAN HYDROGEN ASSOCIATION

Progress has been made on the formation of a European Hydrogen Association. Planning meetings were held during 1998 and the drafting of statutes has begun. It is expected that this Association will link together the individual country organizations already in existence throughout Europe, as well as represent the remainder of the European Union members who do not currently have hydrogen associations in place. The framework for the Association should be complete during 1999.

INTERNATIONAL GAS UNION

The International Gas Union, an industry group of gas producers, established a Study Group to investigate the role of the industry in hydrogen energy technologies. Mrs. Catherine Grégoire Padró was chosen to serve as the U.S. representative to the group. Her role as Operating Agent for our Integrated Systems tasks also brings the IEA perspective into the Study Group activities.

When the International Gas Union was first established in 1913, the gas industry of all member countries was based primarily on the production of town gas from coal. In the 1950s and 60s, natural gas began to replace town gas in many parts of the world, due largely to its widespread availability and superior properties over town gas from coal.

In the 1990s, the industry experienced significant growth when the global economic expansion demanded not only low cost energy, but also reliable and clean energy for fueling economic growth around the world. The gas industry in some parts of the world is experiencing deregulation and market competition, not only from other gas companies but also from other energy industries. It is recognized that a well-informed gas industry will be in a position to play a major role in the future of the energy industry worldwide.

In parallel with the steady increase in world energy consumption, global environmental problems have become a major concern for energy policy planners. Population increases and aspirations for higher living standards worldwide will exacerbate the problem and drastic energy policy changes must take place to ensure the survivability of the planet. The 21st century will require a judicious mix of energy sources to provide a transition from unsustainable fossil fuels to sustainable energy sources that will solve both local and global environmental problems. Although all fossil fuels produce anthropogenic carbon dioxide and are available in finite amounts, natural gas is considered to be the least environmentally damaging fossil fuel. In addition, its resource base might be secure for the long term by the enormous amount of natural gas estimated available in gas hydrates (methane trapped in cage-like structures existing in enormous volumes in the arctic and deep oceans). With the increase in demand for

clean fuels and the possibility of very large increases in resource volume, it is clear that the natural gas era is just beginning. In light of the study of the Intergovernmental Panel on Climate Change (IPCC, a United Nations Organization) on the effects of carbon emissions, natural gas is also the logical transition fuel to low-carbon-content fuels, given its high hydrogen-to-carbon ratio. It is the natural transition fuel to hydrogen energy systems.

The IGU asked the Study Group to answer several questions, in order to survey the thoughts and intentions of the gas industry regarding hydrogen. The results of the investigations will be presented at the World Gas Conference in Nice, France in June 2000. The questions of interest to the IGU are:

- What specific role can hydrogen assume in meeting global energy demand?
- What will be the most likely captive markets (regional, niche or others)?
- After markets have been identified, which [primary energy source and] production processes appear to be the most promising (solar, hydro, nuclear, biomass, wastes)?
- What role should IGU take or play?

INTERNATIONAL MEETINGS

International Symposium on Metal-Hydrogen Systems:

This year, the Hydrogen Agreement helped sponsor the *International Symposium on Metal-Hydrogen Systems* in Zhejiang, China. This meeting brought together numerous international experts on metal hydride materials and their applicability to hydrogen storage and was attended by several of our Task Participants. Our own Task 12 Operating Agent, Dr. Gary Sandrock, is a founding member of this informative series of international symposia.

World Hydrogen Energy Conference:

The 12th World Hydrogen Energy Conference took place this past year in Buenos Aires, Argentina. Many of our task experts gave presentation on their IEA-related activities, including overviews of Tasks 10 and 11. All of the presentations were well received and generated interest that we expect to lead to increased participation in our Agreement in the coming years.

An important activity held in conjunction with this meeting was the brainstorming session organized by Shell International to generate ideas for Shell's move into hydrogen energy. Executives from Shell International met with about a dozen recognized international hydrogen experts. This move towards hydrogen energy follows closely with Shell's establishment of the Shell International Renewables Division last year. This is an excellent example of a large international oil company taking an active role in seeking out energy opportunities with favorable environmental benefits.

Electrical Energy Storage Applications and Technologies:

The Electrical Energy Storage Applications and Technologies (EESAT) Conference was held in Chester, United Kingdom in June 1998. Over 130 people attended the meeting, representing government, academia, and industry from Europe, North America, and Asia. The conference was held as part of the IEA Implementing Agreement on Energy Conservation through Energy

Storage Annex IX - Electrical Energy Storage Technologies for Utility Network Optimization.

In the Fuel Cell/Electrolyser Systems Session, chaired by Mrs. Catherine Grégoire Padró, three papers were presented on hydrogen energy systems, two of which were authored by Annex XI experts. Dr. Thomas Schucan (PSI, Switzerland) proposed a system for long-term energy storage using chemical carriers for seasonal renewables (such as hydro). Ms. Victoria Putsche (NREL, USA) presented a comparative study of three hydrogen storage technologies for a renewable energy system using photovoltaics and electrolysis for hydrogen generation.

Although the papers were well-received and the discussion period was lively, the primary focus of the conference, and the Storage Annex, was power conditioning. In general, the audience was concerned with, at most, 2-4 hours of storage. No emphasis was placed on grid-independent systems, or on storage needs when intermittent renewables reach >20% penetration (the point at which most experts think grid instabilities will occur). Contacts will be maintained with this IEA activity, although there seem to be few opportunities for close interactions at this time.

IMPLEMENTING AGREEMENT REVIEW

All active Implementing Agreements are reviewed by the IEA every four years. During 1998, the Renewable Energy Working Party (REWP) undertook the review of eight of the Agreements over which it has oversight. These included the Hydrogen, Bioenergy, Geothermal, Hydropower, Photovoltaic Power Systems, Solar Heating and Cooling, Solar Power and Chemical Energy Systems (SolarPACES), and Wind Turbine Systems Agreements.

This review was very timely for the Hydrogen Agreement as we are nearing the end of the current extension and preparing for the next five years. Some of the general comments directed towards all of the Agreements included the lack of industry participation, especially on the Executive Committees. The Hydrogen Agreement is, in fact, one of the few that actually has industry representation on its Executive Committee. Attracting more non-IEA Member Countries to the Agreements was indicated as an overall desire. Energy storage was cited as a key cross-cutting issue requiring further investigation. This is an area where we feel hydrogen could play a key role. Specific to the Hydrogen Agreement, the REWP recommended better collaboration with the Photovoltaic and Bioenergy Agreements, particularly related to our work in the photoproduction area. These are all areas on which we will focus attention during 1999.

HIGHLIGHTS FOR THE 1998 EXECUTIVE COMMITTEE MEETINGS

39th Meeting in Montreux, Switzerland, 2-5 June 1998.

! Dr. Edward Scerri of the Institute for Energy Technology at the University of Malta participated in the meeting as an observer. Although, to date, there has not been much effort on hydrogen production, storage and utilization in Malta, they have done a great deal of work in photovoltaics and wind research and have recently launched an effort in the photoelectrochemical hydrogen production field. Dr. Scerri will remain in contact with the Executive Committee and will look for collaborative opportunities between Malta and the Hydrogen Agreement.

- ! Proposals were presented for five new tasks: Photobiological Production of Hydrogen, Photoelectrolytic Production of Hydrogen, Design and Optimization of Integrated Systems, Hydrogen Use in Process, and Hydrogen from Carbon Containing Materials. All five proposals were given approval for task development.
- ! A recruiting drive was launched to try and solicit new membership for the Implementing Agreement. Each Executive Committee Member was assigned a number of countries for which they would identify research interests and governmental points of contact. It was agreed that a new brochure would be prepared to send to the contacts, highlighting the new activities under development.
- ! The Executive Committee welcomed Dr. Giampiero Tartaglia as the alternate for the European Commission. Dr. Tartaglia will replace Dr. Abraham Bahbout as Executive Committee Member for the European Commission upon Dr. Bahbout's retirement following the October 1998 Executive Committee meeting in Ispra, Italy.

40th Meeting in Ispra, Italy (sponsored by the European Commission), 27-30 October 1998.

- ! The Executive Committee unanimously agreed to request that the Governing Board approve a five year extension of the Agreement on the Production and Utilisation of Hydrogen. This extension would take the Agreement through June 2004.
- ! Annex 13, Design and Optimization of Integrated Systems, was unanimously approved by the Executive Committee, with the United States, represented by Mrs. Catherine Gregoire Padró, as Operating Agent.
- ! Task Development continued on the other four proposed Tasks: Photo-biological Hydrogen Production, Photoelectrolytic Hydrogen Production, Industrial Uses of Hydrogen (formerly known as Hydrogen Use in Process), and Hydrogen from Carbon Containing Materials.
- ! After the Task 12 Operating Agent, Dr. Gary Sandrock, reported that the task target of 5 weight percent hydrogen storage at 1 atm and 150°C had essentially been met, a new target of the same storage capacity and pressure at 100°C was set. [The material that met the earlier target was a reversible sodium aluminum hydride material developed at the University of Hawaii, following the Bogdanovic' approach. (See the Annex 12 section of this report.)]
- ! This marked the final meeting for Dr. Abraham Bahbout. The Executive Committee expressed its sincere gratitude to Dr. Bahbout for his many contributions and insights and wished him the best of luck with his retirement.**

ELECTIONS

Our meeting in Montreux, Switzerland, marked the completion of my first three-year term in office as Chairman of the Executive Committee. I was very pleased by my election to a second term and would like to take this opportunity to thank my fellow Executive Committee members for their continued support and faith in my leadership. Once again, our Executive Committee elected two Vice-Chairs, Dr. Giampiero Tartaglia, from the European Commission and Mr. Hurami Arai, from Japan. [Mr. Arai has since been replaced on the Executive Committee and as Vice-Chair by Mr. Yoshitaka Tokushita.]

SUMMARY

I am very enthusiastic about the current state of our Implementing Agreement activities. The unanimous agreement to request a five year extension and the preparation of proposals for five new tasks clearly demonstrates the commitment of our member countries to pursue collaborative research projects and to advance hydrogen technologies at the international level. We have lost two members whose contribution we greatly valued, but we are confident that the new tasks, enthusiasm and international recognition of hydrogen as an energy carrier for the future will draw new members to the Agreement.

We will spend the coming year preparing for our new five-year term. We will revisit our strategic plan and set some firm objectives for the coming year. Task development will continue on our new initiatives. Task 12 will continue developing these new sodium aluminum hydride formulations and carbon materials that are showing so much promise for hydrogen storage. The next phase of integrated system modeling will begin with the start of Task 13 in January 1999. Finally, we hope our membership drive and new tasks will attract new participants in our Agreement's activities and help us to increase the impact of the advances resulting from our various efforts.

As we enter the new millennium, the growing concerns about the impact of greenhouse gases on global climate change have turned world attention to the environmental benefits of hydrogen. Our opportunities have never been better for increasing awareness of available hydrogen technologies and gaining support for hydrogen penetration within the mainstream energy market. Combined with emerging decarbonization and sequestration technologies, hydrogen can play a key role in minimizing the environmental impact of continued fossil fuel utilization and, at the same time, facilitate the transition to a renewable-based energy supply.

***** In May 1999, prior to publication of this report, the Executive Committee learned of the passing of Dr. Abraham Bahbout. Dr. Bahbout was a man of great vision and insight whose leadership lead to significant contributions to the international technical community in several fields, including the advancement of hydrogen technologies. Dr. Bahbout brought a unique perspective to our Executive Committee, challenging all of us to see outside of our respective program objectives to hydrogen's potential in the international arena. We are all better leaders, and individuals, for having the benefit Dr. Bahbout's intelligence, perspective, guidance and companionship. He will be sorely missed by all of us. Our deepest regrets to his family, friends and colleagues.***

TASK 10 – PHOTOPRODUCTION OF HYDROGEN

Bjørn Gaudernack

Institute for Energy Technology

Operating Agent for the Research Council of Norway

Task Description

The objective of this Task is to investigate and develop processes and equipment for the production of hydrogen by direct conversion of solar energy. Such processes have the potential to be efficient, economically competitive and environmentally benign, and may provide the basis for hydrogen as an energy carrier in future, sustainable energy systems. Both photo-electrochemical and photobiological processes are studied in this Task, comprising the following Subtasks:

Subtask A: Photoelectrochemical Hydrogen Production

This includes two main activities:

- Development of innovative concepts for water splitting (involving evolution of hydrogen and oxygen).
- Evaluation of non oxygen-evolving systems, emphasizing the potential of combining hydrogen production with waste degradation.

Subtask B: Photobiological Hydrogen Production

This involves the metabolic production of hydrogen by micro-organisms (algae or bacteria) using light as an energy source. The Subtask includes the following activities:

- Screening and characterization of hydrogen-producing micro-organisms;
- Establishing an Internet data bank based on information from literature and available culture collections;
- Genetic studies of such micro-organisms aimed at increasing their hydrogen production capacities;
- Development of photobioreactors; and
- Feasibility studies and cost estimates of photobiological hydrogen production.

Subtask C: Standardization of Methods for Measurement, Calculation and Reporting of Efficiencies.

This Subtask was finished and reported during 1996. (J. R. Bolton: "Solar Photoproduction of Hydrogen", IEA/H2/TR-96.)

Duration

Task 10 started on 1 March 1995 and was terminated by 1 October 1998.

Participation

Participants in Task 10 have been: Japan, Norway, Sweden, Switzerland, the United Kingdom and the United States.

Activities and Progress During 1998

Two regular Experts Meetings were held:

- The Spring Experts Meeting was held in Oslo, Norway, on 4-6 March. The first day focused on Subtask B, the last day on Subtask A, with common discussions and a technical tour arranged on the day in between. The tour included visits to the Institute for Energy Technology, the Norwegian Water Research Institute (research on photobiological hydrogen production), and the Norwegian Research Council. The meeting was attended by ten Task 10 Participants and two observers.
- The Fall Experts Meeting was held at NREL in Golden, Colorado, on 7-9 October. This was the last Experts Meeting of Task 10 and was mainly used for the summing up of results, decisions on final reports, and planning for future collaborations. The Experts recommended to continue Task 10 activities in two new, separate Tasks under the Hydrogen Agreement: Task 14 on Photoelectrolytic Production of Hydrogen, and Task 15 on Photobiological Production of Hydrogen. Dr. Andreas Luzzi (a Swiss citizen engaged at the University of Australia) was proposed as Operating Agent for Task 14; Dr. Yasuo Asada of NIBH, Japan, was proposed as OA for Task 15. (Dr. Asada has since changed employment and has been replaced as task organizer by Dr. Peter Lindblad of Uppsala University, Sweden.) The meeting was attended by seven Task 10 participants and two observers, and included a very interesting tour of some of the NREL laboratories

Other relevant "Hydrogen Events" in 1998:

- 12th WHEC (World Hydrogen Energy Conference) took place in Buenos Aires on 21-25 June. This conference was attended by the Operating Agent and two of the experts of Task 10, all of whom gave presentations (see list of publications). The presentations were well attended. There were several other interesting papers on the photoproduction of hydrogen, and a number of presentations by Task 11 experts.
- IPS-12, Berlin 9-14 August was attended by some of the Task 10 experts. This conference focused on two main areas: TiO_2 and related materials for photodegradation of organic pollutants and dye-sensitized PV cells. Both of these areas are quite relevant to the present and future photoproduction work.

Subtask A: Photoelectrochemical Hydrogen Production

The following institutions participated in Subtask A: National Renewable Energy Laboratory (NREL), Hawaii Natural Energy Institute (HNEI), Florida Solar Energy Center (FSEC) - all in the USA; Geneva University, Bern University, Federal Polytechnic School of Lausanne - all in Switzerland; National Institute of Materials and Chemistry Research (NIMC), Japan; and Uppsala University, Sweden.

Different approaches to photoelectrochemical hydrogen production have been pursued:

- Water splitting in particulate photo-catalyst systems;
- Photoelectrolysis of water with multijunction semiconductor devices; and

- Water splitting and combined hydrogen production/waste degradation in a combined PEC/PV device.

Particulate photocatalyst systems: At NIMC in Tsukuba, Japan, water splitting by photocatalysts enhanced by sodium carbonate addition was studied. Using UV light, water splitting has been demonstrated with more than twenty different photocatalysts. A mechanism for the enhancement obtained by the carbonate has been proposed. Water splitting by sunlight was also demonstrated. The best results were obtained with 3wt% NiO/TiO₂ and 2.2M Na₂CO₃. The quantum efficiency was only 1.7%, but, with a pond of 100m x 100m area, 4200 L of hydrogen would be produced on a sunny day. The concept is regarded as interesting due to the low cost of the materials involved. Another novel, two-step water splitting system, involving oxide semiconductors and redox pairs such as Fe²⁺/Fe³⁺, was also studied at NIMC.

At FSEC in Florida, a dual bed water splitting system, based on particulate photo-catalysts, is under development. TiO₂ has been used in the oxygen-evolving bed, but has limited efficiency due to its large bandgap. As a part of the Task 10 collaboration, tests have been made with WO₃, produced by a method developed at the University of Geneva. The hope was that replacing TiO₂ with WO₃ would improve the efficiency, since WO₃ has a somewhat smaller bandgap. However, no improvement was obtained. Part of the explanation may be that WO₃ requires an acid environment, which may have been detrimental to the redox mediator employed. Alternative mediators and photo-catalysts are being investigated. This work will continue under the new Task 14.

At Uppsala University, studies of light-induced oxygen evolution on nanostructured hematite electrodes have been initiated.

Photoelectrolysis of water with multijunction devices: Two types of semiconductor devices were studied. One is based on highly efficient III-V semiconductors, specifically GaAs/GaInP₂, developed by Dr. John Turner's group at NREL. With a double junction PV/PEC device based on these materials, a water splitting efficiency of 12.4% was obtained, as reported in the 1997 Annual Report. These results were published in *Science* in April 1998, a publication that has raised a great deal of interest. Even higher efficiencies are predicted with this type of photoelectrolyser, which is very promising. The major drawback of this system is the high cost of the materials.

Multijunction α -Si material, commercially available for use in PV systems, has been adapted for the photoelectrolysis of water. Using this lower cost device, HNEI has demonstrated 7.5% water splitting efficiencies. Development of similar devices is also taking place at NREL. The collaboration in Task 10 has been focused on the development of catalytic and protective layers on the surfaces in contact with the electrolyte.

A feasibility study on the photoelectrolysis of water, conducted at NREL, indicated that at 14% efficiency, considered to be obtainable, the production cost will be 3 USD/kg hydrogen.

Water splitting and waste degradation in PEC + PV device: The Swiss group collaborating in Task 10, including scientists from the Universities of Geneva, Bern and Lausanne, have developed and studied a device comprising a photoelectrochemical cell (PEC) connected in series with a special type of PV cell, a so-called Grätzel cell (a dye sensitized liquid junction photovoltaic cell). The PEC consists of a WO₃ photoanode for oxygen evolution and a Pt counterelectrode for hydrogen evolution. The Grätzel cell is incorporated to provide the necessary voltage bias for water splitting. The two cells are superimposed, taking advantage of

their complementary light absorption in the visible range. The thin film nanocrystalline WO_3 absorbs the blue part of the solar spectrum, and the dye-sensitized TiO_2 electrode absorbs the green and red parts of the spectrum. The latter is placed directly behind the WO_3 film, capturing the light transmitted through the WO_3 electrode.

This device has been applied to pure water splitting, giving efficiencies of about 4%. However, efficiencies as high as 9% have been obtained when operating the device in a 0.01M solution of methanol. In this case the anode reaction is an oxidation of methanol to CO_2 instead of the oxidation of water to O_2 . This indicates a useful capability for depollution of organic pollutants, particularly in dilute solutions that are otherwise difficult to decontaminate. Degradation of other organic pollutants, such as formic acid, formaldehyde and EDTA, was also demonstrated. The advantages of this procedure over conventional electrolytic degradation are that much (an order of magnitude) less energy is required and that sunlight can be utilized directly. In the case of photoproduction of hydrogen, feeding the anodic compartment of the PEC with a solution of an organic pollutant instead of the usual supporting electrolyte, will bring about a substantial increase of the photocurrent at a given illumination. In other words, the replacement of the photo-oxidation of water by the photodegradation of organic waste will be accompanied by a gain in solar-to-chemical conversion efficiency and hence a decrease in the cost of the photoproduced hydrogen. Taking into account the benefits and possible revenues obtainable by the waste degradation, this would seem to be a promising approach to the photoproduction of hydrogen.

Subtask B: Photobiological Hydrogen Production

The following institutions participated in Subtask B: National Institute of Bioscience and Human-Technology (NIBH), Japan; Hawaii Natural Energy Institute (HNEI), USA; Oak Ridge National Laboratory (ORNL), USA; Norwegian Institute for Water Research (NIVA), Norway; Uppsala University, Sweden.

The collaborative research in Subtask B was organized into three main areas: Screening and surveying of potential hydrogen producing micro-organisms, including establishment of a data bank on relevant strains (B1); genetic and enzymologic studies aimed at genetic engineering to improve hydrogen production capabilities (B2); and development of photobioreactors, process analyses and economic estimates (B3).

Data bank of H_2 -producing micro-organisms: The data bank was established on the Internet in 1997, as reported in the Annual Report for that year. This was done under the supervision of Dr. Asada at NIBH, which is also the location of the data bank.

This catalogue of data for hydrogen-producing strains available in culture collections (e.g. those at HNEI in Hawaii and at NIVA in Norway) was expanded and upgraded during 1998. It lists strains available to the Task 10 participants with basic information about these strains, including their origin, maintenance protocol, taxonomy, and the experimental results currently available. The catalogue also contains information in a standardized format about important literature references on biohydrogen. Addresses and access to other culture collections are provided.

The data bank will allow input of information by users, and limit the access to certain types of information to the participating organizations. The bank was originally restricted to data on cyanobacteria, but will be expanded to include relevant green algae and photosynthetic bacteria. Maintenance and upgrading of the data bank will continue as an activity under the new Annex on Photobiological Production of Hydrogen.

Genetic and enzymologic studies: Certain enzymes, such as nitrogenase and reversible/bidirectional hydrogenases, are essential to the hydrogen production by micro-organisms. With sufficient knowledge of the genetic coding of these enzymes, genetic manipulation of specific strains to improve their hydrogen production capability may become possible. One useful modification would be to increase the oxygen tolerance of these enzymes, since their sensitivity to oxygen is a limitation to the hydrogen-production efficiency. Recent results indicate that this is possible by genetic manipulation. Another objective is to reduce the light-harvesting or "antenna" pigments of the organisms, in order to allow for higher light saturation and, thereby, increased photosynthetic efficiencies - implying also higher hydrogen production efficiencies.

Collaboration in this area in Subtask B proceeded under the direction of Dr. Peter Lindblad, Uppsala University and involved scientists at HNEI, Hawaii and NIVA, Norway. The cooperation has involved exchange of genetic sequence information, probes, samples, and organizing joint training in methods useful for the development of molecular genetic techniques relevant for strengthening photobiological hydrogen production.

Photobioreactor development and process analysis: The development of efficient and inexpensive photobioreactors is another crucial element in the pursuit of commercial photobiological hydrogen production. As an activity under Subtask B, a U.S. Department of Energy-funded project at the University of Hawaii (HNEI) has comprised the design, installation and initial testing of a pilot stage photobioreactor. This was done in close cooperation with Prof. Mario Tredici at the University of Florence, Italy, who conceived the original design. This is a so-called NHTR (near-horizontal tubular reactor) design with internal gas exchange and water spray cooling. The reactor installed in Hawaii consists of 8 parallel plastic tubes, 20 m long and with a slope of about 10%. The fundamental advantages of this photobioreactor design are not increased productivities, but lower capital and operating costs than other designs.

The approach followed at HNEI is to use a single organism (a cyanobacteria called *Spirulina* or *Arthrospira*) for the production of hydrogen by biophotolysis of water. Key stages are the growth of the biomass, the dark induction of the hydrogenase system, and the subsequent generation of the hydrogen in light. So far only the first stage, i.e. the biomass growth, has been tested in the pilot photobioreactor. A final report on this work was submitted by project leader Dr. Oscar Zaborsky in October. It was concluded that sustainable hyperintensive cultivation of *Arthrospira* sp. is possible in outdoor tubular photobioreactors of this type, under Hawaiian conditions of climate and insolation. Also, hydrogen production under laboratory conditions (dark, anaerobic) was demonstrated using *Arthrospira* isolated from a commercial culture.

The system is also amenable to a single-stage, indirect process whereby hydrogen can be produced in the same bioreactor configuration. A detailed analysis and cost estimate of such a process was performed, assuming a high insolation location (21 MJ/m²/day of solar energy) and a 10% solar conversion efficiency. This analysis projects biohydrogen costs of some 15 USD/GJ, exclusive of any gas purification, handling or storage costs. A study of a two-stage process, using open ponds for the biomass growth stage, was conducted by Dr. John Benemann and published as an IEA Technical Report (see list of publications). In this study, also based on very favourable assumptions, the cost estimates indicated a production cost of about 10 USD/GJ for the biohydrogen.

Future Activities

Since Task 10 was officially terminated by 1 October 1998, no further activities (except the finalising and publishing of the final reports) are planned under this Annex. Although valuable results have been obtained and some conclusions have been drawn, the fundamental and long-term nature of the research performed implies that it should be continued. Much effort has been spent in establishing collaboration projects and world-wide research networks that should be maintained. All parties involved have expressed interest in this. As mentioned, two new Tasks have been proposed for the Photoelectrolytic and Photobiological production of hydrogen. These proposals are being finalized, including the drafting of Programmes of Work and confirmation of participation. It is expected that both tasks will be approved and will start work before the end of 1999.

Publications

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TASK 11 - INTEGRATED SYSTEMS

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Introduction

Task 11 was completed this year, successfully developing over two dozen component models; evaluating the technical aspects of a number of integrated systems; analyzing, in detail, ten hydrogen demonstration projects throughout the world; and developing a systematic design procedure for evaluating and comparing hydrogen energy systems. This report describes the activities undertaken in this effort, and the implications for hydrogen energy systems. Follow-on work is also discussed.

Task Description

The objective of this effort was to develop a tool to assist in the design and evaluation of potential hydrogen demonstration projects and in the optimization of existing hydrogen demonstration projects. Emphasis was placed on integrated systems covering all components, from input energy to end use. The activities were focused on near- and middle-term applications, with consideration of the transition to sustainable hydrogen energy systems.

Systems considered included stand-alone and grid-connected hydrogen production and hydrogenation systems; hydrogen and oxygen transport and storage systems; conversion devices including fuel cells, turbines, combustors, and hydrogenation units; electric load leveling systems; and general characteristics of mobile applications.

The task participants undertook research within the framework of three highly coordinated subtasks. This work was carried out in cooperation with other IEA Implementing Agreements, where appropriate.

Subtask A: Case Studies

Hydrogen energy systems were critically evaluated and compared, with system performance measurement as the central focus. Safety and regulatory issues were considered where appropriate.

The data base of demonstration projects was updated and extended to include new projects and additional data according to requirements of Subtasks B and C. A case study report will be produced, with detailed reports on the hydrogen demonstrations given below:

Project
Solar hydrogen demonstration at Neunburg vorm Wald
Markus Friedl solar hydrogen plant on residential house
Photovoltaic hydrogen production - Alexander T. Stuart renewable energy test site
Phoebus Jülich demonstration plant
Schatz solar hydrogen plant
INTA solar hydrogen plant
Clean Air Now: solar hydrogen fueled trucks
SAPHYS: stand-alone small size PV hydrogen energy system
Hydrogen generation from stand- alone wind-powered electrolysis systems
Palm Desert renewable hydrogen transportation project

Additionally, short reports will be made of several other hydrogen demonstration projects.

Subtask B: Analysis Tools

Subtask B focused on simulation activities, building on existing modeling efforts. Using data collected in Subtask A, component models were developed and validated.

The component models were then adapted into the integrating platform, and parametric studies were conducted to identify promising strategies for improving the performance of selected components. A report describing the models will be produced and the component models will be organized into a library that will be made available to the participating countries. The component models are given below:

Technology	Team Lead
Production	
PV-Electrolysis	Spain
Wind-Electrolysis	USA
Grid-Electrolysis	USA
Steam Methane Reforming	USA
Biomass Gasification	USA
Biomass Pyrolysis	USA
Coal Gasification	Netherlands
Storage	
Pressurized Gas	Canada
Metal Hydrides	USA

Technology	Team Lead
Liquefaction	Japan
Chemical Storage	Netherlands
Chemical Hydrides	Switzerland
Distribution	
Transport Tanker	Japan
Pipeline (trunk and distribution)	USA
Tank Truck	Japan
Methanol Transport	Netherlands
Utilization	
PEM Fuel Cell	Canada
Phosphoric Acid Fuel Cell	Spain
Solid Oxide Fuel Cell	USA
Molten Carbonate Fuel Cell	USA
Gas Turbine	USA
Internal Combustion Engine	USA
Refueling Station	USA

Subtask C: Design Guidelines

Guidelines were developed to assist in the design of future demonstration plants to meet operating and user requirements, and to facilitate the systematic integration of hydrogen into the energy system.

System models were built in the integrating platform, based on individual component models developed in Subtask B. Base case validation and optimization runs were conducted and the results compared to data collected in Subtask A.

A report will be prepared that includes recommendations for the optimization of existing hydrogen systems and design guidelines for new, promising, and desirable hydrogen systems.

Duration

The Task was formally begun on 1 August 1995 and ended on 15 November 1998. This represents an extension of 3.5 months from the original schedule, and was authorized by the Executive Committee on 12 November 1997.

Results

The collaborative efforts of Task 11 will result in the following outputs:

- C Case study report to document hydrogen energy system demonstrations;
- C Report describing the component models, including the required inputs and the expected outputs, and limitations and capabilities of the models, with a library of component models for use in the common integrating platform; and
- C Report of recommendations for optimizing existing hydrogen energy systems and the set of design guidelines for planning future integrated hydrogen energy systems.

These reports will be published as IEA reports in 1999.

Participation

Seven countries participated in Task 11: Canada (Subtasks A and B); Italy (Subtasks A and C); Japan (Subtasks A, B, and C); the Netherlands (Subtasks B and C); Spain (Subtasks A and C); Switzerland (Subtasks A and B); and the USA (Subtasks A, B, and C).

The Lead Countries for Subtasks A, B, and C are Switzerland, the USA, and the Netherlands, respectively.

Activities and Progress during 1998

Activities during 1998 were focused on completion of data collection, model development and validation, system integration, and increasing technology transfer and dissemination activities.

The Spring Experts Meeting was held in Italy on March 25-26, 1998. The meeting was conducted at ENEA (Italian National Agency for New Technology, Energy and the Environment) in Casaccia, Italy.

Continuing the highly successful seminars on hydrogen demonstrations, four hydrogen demonstration projects were presented: Stefano Galli (ENEA) presented the SAPHYS Project; Geoff Dutton (Rutherford Appleton Laboratory, UK) and M. Falchetta (ENEA) presented the Wind-powered Electrolysis System; Felipe Rosa (INTA, Spain) presented the PV-Hydrogen System; and Dieter Meissner (KFA, Germany) present the PHOEBUS Jülich project:

Stefano Galli of ENEA presented the results of the **SAPHYS** project, a joint project of ENEA (Italy), IFE and ABB Energi (Norway), and KFA (Germany) supported by the European Commission within the framework of the Non-Nuclear Energy Programme Joule-II. Started in 1994, the project consists of a photovoltaic array that supplies energy to a variable simulated load, battery storage for short-term energy variations, water electrolysis for production of hydrogen when the batteries are charged and the PV array produces excess energy, and a PEM fuel cell for production of electricity when the solar input is not sufficient and the batteries are nearly completely discharged. The system was designed to operate in a stand-alone (fully automated) mode, with appropriate computer controls and data acquisition. The project lasted 36 months (7/94 - 6/97).

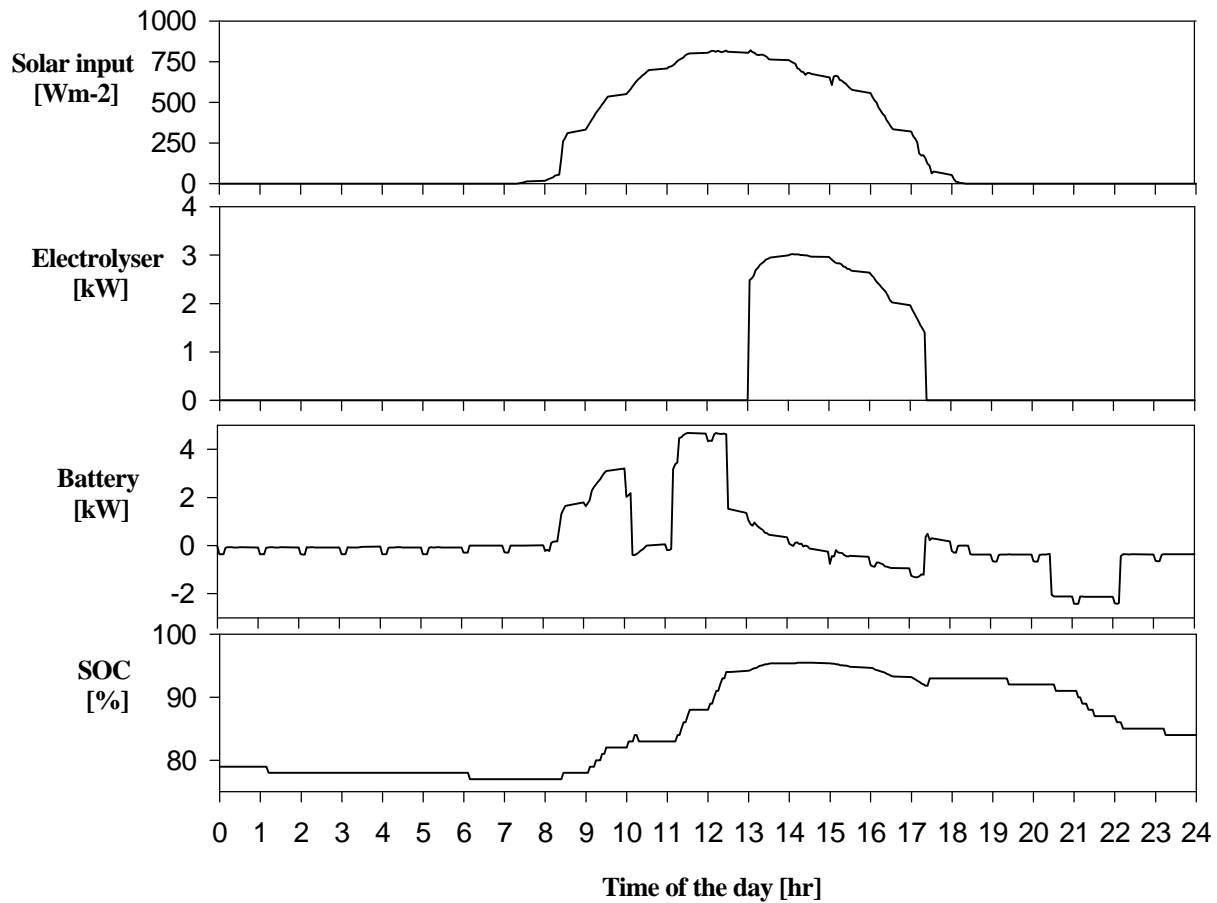


Figure 1 - SAPHYS data for sunny day

The PV array is rated at 5.6 kW, and the 5 kW (peak) electrolyzer operates at 20 bar pressure and 80°C. Up to 300 Nm³ of hydrogen at 20 bar are stored for use in the 3 kW Ballard fuel cell. The hydrogen/air fuel cell operates at 30 psi and 75°C. Experimental data for a typical sunny are shown in Figure 1.

Geoff Dutton of Rutherford Appleton Laboratory (RAL) and Massimo Falchetta (ENEA) presented the results of a project to generate hydrogen from a **stand-alone wind-powered electrolysis** system. Funded in part by the European Commission within the framework of the Non-Nuclear Energy Programme Joule-II, with partners RAL (UK), ENEA, DLR (Germany), and the University of Leicester (UK), this project was operated from 4/94 - 12/96.

The system consisted of a 5.2 kW single blade, variable speed wind turbine, 300 Amp-hours (36 kWh) of lead-acid batteries, and a 2.25 kW electrolyzer operating at 20 bar, along with appropriate data acquisition and controls. The produced hydrogen was not stored in this project, but was vented through a 5 meter pipe. At low current and after some hours of standby operation, the electrolyzer produced hydrogen with high levels of oxygen, and oxygen with significant hydrogen contamination. The basic scheme for the project is shown in Figure 2.

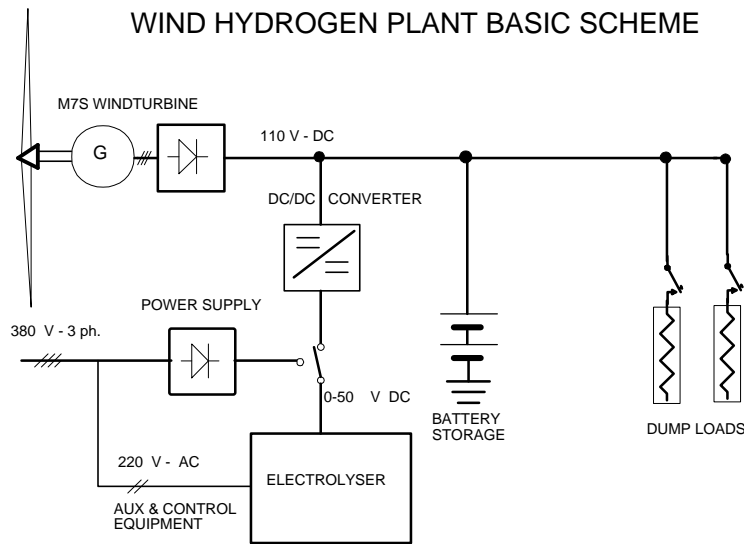


Figure 2 - Layout of stand-alone wind-powered hydrogen demonstration.

Cell redesign resulted in improved hydrogen purity, even at low current. Operational experience resulted in a minimum permanent current of 20-25 amps, which was half of the nominal value, to keep the hydrogen contamination of the oxygen stream below 3%.

Several conclusions drawn from the project are: computer modeling of the system was useful in developing control strategies for intermittent systems; further development is required to implement a truly autonomous system; electrolyzer operation is impacted by intermittent energy sources, although not a short time scale (fluctuation on the order of several minutes, not several seconds). This project site was also visited during the technical tour.

Felipé Rosa (INTA) presented the **Solar Hydrogen** Project located in Huelva, Spain. The motivation for the development of the stand alone project was for electricity production and storage for a space station concept. Components include a PV array (Figure 4), an electrolyzer operating at 6 bar, various types of hydrogen storage, and a phosphoric acid fuel cell. Both the PV and the fuel cell would be connected to the grid, with the water produced in the fuel cell recycled to the electrolyzer.

In order to operate at the maximum power point (MPP) of the PV array, the electrolyzer was operated with a variable number of cells. This same effect can be obtained by using DC/DC converters to match the MPP. The overall efficiency of the system during a one-year operating period was 6.7% (photons to hydrogen).

A new project, called the Hispania Project, is under development. This 3-year, \$4 million project involves the use of renewable hydrogen (PV-electrolysis) in a modified 4-wheel-drive vehicle. A 20 kW PEM fuel cell fueled by compressed hydrogen (at 200 bar) will be installed in a hybrid battery configuration.

Dieter Meissner (KFA) presented the results of the **PHOEBUS** Jülich Project, which supplies grid-independent solar-generated electrical energy to the Central Library of Research Center Jülich throughout the year. Hydrogen and oxygen are produced and stored in the summer by electrolysis of water, using excess PV power. Electrical energy is produced by a hydrogen/oxygen fuel cell in the winter to compensate for the power deficit from the PV system in this low-solar-insolation period.

The PV system consists of 312 m² in four fields, separately managed, for a total rated capacity of 43 kW (peak). A Siemens alkaline fuel cell was used, but has been replaced by two PEM fuel cells. The electrolyzer was developed by KFA in a earlier program. A thorough safety report was completed by KFA's nuclear safety experts. The system is not isolated in special enclosures or buildings.

The hydrogen compressors proved problematic, as did the inverters/converters. Because of the very small gas volumes and the inefficiency of small compressors, the compression energy requirements were 80% of the energy contained in the hydrogen; 40% of the losses were due to the inverters/converters.

An extension of the PHOEBUS plant to a hybrid operation using photovoltaics and wind for combined heat and power generation takes advantage of the complementary aspects of these intermittent renewable resources (often the wind blows more in the evening and nighttime than in the daytime). PHOEBUS 2 will be placed in the Visitors Center of a former military facility. The system will be simplified: inverters/converters will be replaced by high-speed switches from Siemens; and the compressor will be eliminated in favor of a high-pressure electrolyzer. Since batteries make up the majority of the storage system, the overall efficiency (electricity to electricity) is 65%. [Note: this overall efficiency is significantly higher than that of a system where all the renewable electricity is used to make hydrogen, with the hydrogen used in a fuel cell to generate electricity when needed. The roundtrip efficiency (electricity to electricity) on such a system is on the order of 30-35%.] PHOEBUS 3 will be a home cogeneration system, using PV-wind hybrid systems, with heat pumps.

With the modeling work nearly complete in all areas, we increased our technology transfer efforts through presentations and publications at international conferences. A paper was presented at the National Hydrogen Association's Annual Hydrogen Meeting (March 1998) on the selection of system components for grid-independent renewable power systems. The results of a comparison of three storage subsystems for a grid-independent renewable hydrogen system in a remote Central American village was presented at the EESAT conference in the United Kingdom (June 1998). Four papers were prepared for oral presentation or poster presentation at the World Hydrogen Energy Conference in Buenos Aires (June 1998). In addition, a poster was developed for use at the Village Power 98 conference, held at World Bank headquarters in Washington, DC. Finally, a paper was presented at the Colorado Renewable Energy Conference.

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Future Plans

Comparison of different system configurations for a particular application requires a set of criteria on which the comparison can be made. This can include efficiency, environmental impacts, economic impact, capital and operating costs, and other measures of importance to the analyst. In all cases, these parameters can be reduced to a comparison of costs, given that appropriate value can be assigned to the individual criteria. It is important to develop consistent cost models for the various hydrogen components so that fair assessments can be made of alternative designs. This is particularly important when comparing dissimilar systems at very different levels of development and commercialization.

A Programme of Work was developed for the continuation and expansion of this effort. Approved for commencement on 1 January 1999, Task 13 will address the design and optimization of integrated hydrogen systems. The work will be carried out in two highly integrated subtasks.

Subtask A will include improvement to existing component models, development of additional component models, and the development of cost models for each component model. The basis for the development of consistent cost models will be established, including the appropriate size ranges, scaling factors, installation factors, operating and maintenance costs, etc. This basis will be used throughout this activity to insure consistency and fairness. Cost models based on existing non-proprietary data and standard engineering procedures will be developed for each component. This activity will include development of ASPEN-based cost

models, spreadsheet models, and/or graphical representations. A range of sizes will be identified for the components, so that the cost models will be applicable for a range of integrated system sizes. These models will include non-proprietary projections for future costs based on cost-reduction parameters (such as mass production, market size, and technological advances) that will be defined as part of this activity (based on literature values to the largest extent possible). In addition to developing traditional engineering cost models, this activity will also address the issue of externality costs. Specifically, a set of cost parameters will be developed for important greenhouse gas emissions, so that the benefits of renewable hydrogen production systems can be compared to fossil-based production systems. Some effort will also be directed to assigning value to other intangible benefits such as job creation, energy independence, etc.

Subtask B activities involve the identification of candidate configurations (in cooperation with Subtask A), design of the system using the design guidelines developed in Task 11, modeling of the integrated systems using the tools developed in Task 11, and evaluation of the performance, costs, and environmental benefits of hydrogen energy systems.

The value of hydrogen energy systems is often linked to environmental improvements (greenhouse gas reductions, and CO, NO_x, and SO_x reductions, etc.) or other intangible benefits (job creation, energy independence, etc). Quantification of some of these benefits can be made using life cycle assessment (LCA) comparisons. LCA is a systematic analytical method to identify, evaluate, and help minimize the environmental impacts of a specific process or competing processes. Material and energy balances are used to quantify the emissions, resource depletion, and energy consumption of all processes between transformation of raw materials into useful products and the final disposal of all products and by-products. The results are then used to evaluate the environmental impacts of the process so that efforts can be focused on mitigating possible effects. In this activity, the scope of an LCA for hydrogen systems will be defined, based on established (published) LCA methodologies. The measures to be considered include comparison of CO₂ and other gaseous emissions, and determination of net energy ratio (amount of energy produced per unit of fossil fuel input). Case studies will be identified and LCA performed to enable comparison of different hydrogen technologies. These results will also be compared to existing (published) LCA studies for other non-hydrogen-based technologies (i.e., biomass power plants and coal-fired power plants). In addition to comparative analysis of process efficiencies, cost and emissions analysis will be performed using the models developed in Subtask A.

TASK 12 - METAL HYDRIDES AND CARBON FOR HYDROGEN STORAGE

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Task Description

The use of hydrogen as a vehicle fuel requires a storage means that has inherent safety and both volumetric and gravimetric efficiency. Metal hydrides and carbon offer alternatives to the storage of hydrogen in gaseous and liquid form. They store hydrogen in an essentially solid form and offer the potential for volume efficiency, high safety, low pressure containment and ambient temperature operation.

Unfortunately, all known hydrides are either heavy in comparison to the hydrogen they carry or require high temperature for hydrogen release. One purpose of this Task is to develop hydrides for on-board storage that have a combination of improved gravimetric capacity and lower temperature release of hydrogen. In addition, the option of reversible electrochemical hydrogen storage is included, although that was the minority component of the Task 12 activity in 1998.

Recent advances have been reported for the use of various forms of carbon as hydrogen storage media. Whereas carbon was once considered only as a cryoadsorbent for hydrogen, there is growing belief it can be used at ambient temperature. In response to this belief, carbon was added to Task 12 late in 1997 and two projects in that area were started in 1998.

The specific targets of the Task are as follows:

- The identification of a formulation technique for a metal hydride or carbon material that is capable of 5 wt.% hydrogen capacity with a desorption temperature of less than 100EC. [The target temperature was reduced from the original 150EC in 1998.]
- The development of a metal hydride surface treatment such that high-efficiency, reversible electrochemical reactions can be accomplished over thousands of cycles.

The wt.% target is currently the same for metal hydrides and carbon; however, it is hoped that it can be met at room temperature with carbon.

The Task is highly experimental in nature and is centered around two general efforts: (1) the synthesis of new and different materials and (2) the characterization of those new materials relative to their ability to store hydrogen. When promising new materials are clearly identified, there will also be studies of their manufacturing technology and potential applications in areas other than vehicle storage.

Project Descriptions

There were sixteen distinct hydride projects active in 1998, fourteen on metal hydrides and two on carbon. Each project is led by one or two of the Task 12 Experts and usually involves

experimental contributions by other Experts on an international basis. Brief descriptions and national participations of the projects are as follows:

- # **Project 1: Destabilized magnesium nickel hydride** [Leader: D. Noreus (Sweden); co-participants: USA, Japan]

Mg₂NiH₄ formed above 240EC develops a microtwinned structure upon cooling, but is twin-free if formed below 240EC. The purpose of this project is to experimentally determine if the twin-free microstructure results in a destabilization effect that is manifested in decreased hydrogen desorption temperatures. This project also attempts to improve the electrochemical properties of Mg₂NiH₄.

- # **Project 2: Vapor phase synthesized Mg₂Ni** [Leader: G. Thomas (USA); co-participants: Japan, Norway, Sweden, Switzerland]

Sandia National Lab has a process to make single phase Mg₂Ni by the reaction of Ni powder with Mg vapor. This material exhibits higher hydrogen desorption kinetics and slightly higher plateau pressures. This project is concentrating on determining the structure and potential of V.P. Mg₂Ni. (*Project completed in 1998*).

- # **Project 3: Fine-structured RE(Mn,Al)₂ alloys** [Leader: L. Schlapbach (Switzerland); co-participants: Canada, Japan, Norway, Sweden, USA]

RE(Mn,Al)₂ alloys (RE=rare earth elements) offer the possibility of low-cost, high-capacity hydriding alloys. However, alloys made by conventional melting do not show distinct advantages over the prior art. This project is attempting to improve the gas and electrolytic hydriding properties by introducing fine (nanocrystalline) microstructures using unconventional techniques, particularly high-energy ball milling and rapid solidification. (*Project completed in 1998*).

- # **Project 4: Laves phase CaAl_{2-b}X_b alloys with substitutional and interstitial elements X** [Leader: I. Uehara (Japan); co-participants: Sweden, Switzerland]

The AB₂ Laves phase CaAl₂ offers the possibility of high hydrogen storage capacity with extraordinarily low materials cost, at least in principal. Unfortunately, CaAl₂ has anomalously low H-capacity. The purpose of this project is to attempt to correct this problem by the partial replacement of Al by other elements. (*Project completed in 1998*).

- # **Project 5: Preparation and characterization of titanium-aluminum alloys as potential catalysts for reversible alkali metal - aluminum hydrides** [Leader: A. Maeland (Norway); co-participants: Canada, USA]

Bogdanovic' (Germany) showed in 1996 that the normally nonreversible complex hydrides of Na and Al can be made reversible by incorporating Ti catalysts. The purpose of this project is to test the theory that it is really the in situ formation of Ti-Al compounds (e.g., Ti₃Al, TiAl, etc.) that is responsible for the catalytic activity. See also related Projects 6, 10 and 14. (*Project completed in 1998*).

- # **Project 6: Structural investigations of intermediates and end products in the synthesis of Ti-doped alkali metal - aluminum hydrides** [Leader (acting): D. Noreus (Sweden); co-participants: Japan, Norway, Sweden, USA, Germany (unofficial)]

Ti-doping renders the normally nonreversible NaAlH_4 and Na_3AlH_6 hydrides reversible. Although the kinetics are low, along with possible cyclic stability problems, Ti-catalyzed alkali metal - aluminum hydrides are close to meeting the capacity-temperature target of Task 12. This project aims at developing a clear understanding of the chemistry of the system so that reasonable judgments can be made toward the design of improved catalysts. See also related Projects 5, 10 and 14.

Project 7: Comprehensive Hydride Review and Associated IEA Databases [Leader: G. Sandrock and G. Thomas (USA), co-participants: Switzerland, Japan]

This project is aimed at cataloging past work on hydriding materials and applications in support of IEA Task 12 and its search for new and innovative hydriding materials. It is also aimed at encouraging hydride R&D throughout the world by making past results widely and easily accessible via the Internet in the form of on-line IEA databases. The databases can be reached at the Sandia National Laboratories' Hydride Information Center:

<http://hydpark.ca.sandia.gov>

Project 8: Mechanical destabilization of metal hydrides [Leader: A. Zaluska (Canada); co-participants: Sweden, Norway]

This project explores the mechanical destabilization of hydrides. Destabilization is induced by the local structural changes in the hydride (not metal) phase by mechanical treatment (ball milling) to produce strain and other defects. The stored energy may be released during heating, thus assisting hydrogen desorption. (*Project completed in 1998*).

Project 9: Ball milling under reactive atmosphere [Leader: E. Akiba (Japan); co-participant: USA]

This project explores ball milling during hydriding as a possible technique to improve the hydrogenation properties of hydrogen absorbing alloys, as well as to form novel hydrides. The initial purpose of this project is to clarify the conditions that determine the products of reactive milling of Mg_2Ni . This work differs from Project 8 in that ball milling is done while hydriding, not after. It is complimentary and represents another approach, experimentally and theoretically. (*Project completed in 1998*).

Project 10: Application of polyhydride catalysts to Sodium Aluminum hydrides [Leader: C. Jensen (USA); co-participant: Canada] (*Project completed in 1998*).

Bogdanovic' (Germany) recently demonstrated a novel family of hydrogen storage media based on the complex hydrides NaAlH_4 and Na_3AlH_6 doped with Ti catalysts. Further kinetic improvements are necessary to produce a system that is suitable for practical vehicular applications (e.g., to feed hydrogen to a fuel cell). The purpose of this project is to test whether polyhydride and other novel catalysts are effective for the hydrogenation and dehydrogenation of Na-Al. See also related Projects 5, 6 and 14. (*Project completed in 1998*).

Project 11: High pressure synthesis of new hydrogen storage materials [Leader: K. Yvon (Switzerland); contributor to Swiss effort: Russia]

For several years, the University of Geneva has concentrated on discovering new saline and complex metal hydrides. Some have hydrogen storage capacities greater than 5 wt.%, but decompose only above 300EC, while others decompose below 100EC, but are too heavy or expensive for H-storage applications. The goal of this new project is to synthesize new lightweight metal hydrides based on inexpensive 3d-elements, such as Mn and Fe, by using high-pressure techniques. The ultra-high-pressure (several kbar) facilities of Lomonosov Moscow State University (V. Verbetsky) will be used to help achieve experimental conditions hitherto unexplored.

Project 12: Ball milling effects during fluorination of the eutectic alloy Mg-Mg₂Ni [Leader: S. Suda (Japan), co-participants: Sweden, Switzerland, USA]

Kogakuin University (KU) has developed the application of fluorination (F-treatment) to enhance the surface properties of hydriding alloys. This new project combines ball milling (shown in other IEA 12 projects to increase hydriding/dehydriding kinetics and possibly pressure) with F-treatment (shown by KU to provide surface protection, increased kinetics and improved activation). The alloy chosen (Mg-23.5 wt.% Ni) for the study is a two-phase mixture of Mg and Mg₂Ni that is capable of meeting the wt.% target of Task 12.

Project 13: Ca-based ternary alloys [Leader: I. Uehara (Japan); co-participants: Sweden, Switzerland]

The objective of this new project is to search for reversible hydrides based on ternary alloys consisting of cheap and light metals, e.g., Ca, Mg, Al and transition metals. Sample materials will be prepared by sintering methods and evaluated for hydrogenation characteristics and metallurgical structures.

Project 14: Catalytically-enhanced sodium aluminum hydride [Leader: C. Jensen (USA); co-participant: G. Thomas (USA)]

This new project is an extension of Project 10, now successfully completed. It continues the work on Ti/Zr catalyzed NaAlH₄ with the following two objectives: (1) Determine the mechanism of the catalytic action and (2) Demonstrate the feasibility of a moderate scale hydrogen storage system.

Project C-1: Optimization of single-wall nanotube synthesis for H₂ storage [Leaders: M. Heben (USA) and P. Bernier (European Commission)]

Carbon has received considerable recent attention as a possible storage medium for hydrogen (physical and chemical). The purpose of this new carbon project is to optimize the production and purification techniques of single-wall nanotubes (SWNTs) for physical hydrogen storage in the vicinity of room temperature. It makes use of an alliance of new Task 12 Experts Heben (U.S. National Renewable Energy Laboratory) and Bernier (France's University of Montpellier). It will carefully survey both arc and laser ablation processes for SWNT production, as well as purification techniques.

Project C-2: Hydrogen storage in fullerene-related materials [Leaders: R. Murphy and R. Loutfy (USA)]

Although fullerenes (for example, C₆₀ and C₇₀) have the potential for high gravimetric and volumetric hydrogen storage densities, the high activation energies associated with chemical

adsorption and desorption processes pose potential difficulties in the realization of such attractive storage performance at desired conditions. Considering the Task 12 Target of 5 wt.% recoverable at 100EC, the main objective of this project will be to reduce the activation energies and associated process temperatures for reversible hydrogen storage, especially via the use of catalysts. This new carbon project makes use of an alliance of new U.S. Task 12 Experts Murphy (Oak Ridge National Laboratory) and Loutfy (MER Corporation).

Duration

Task 12 was initiated September 1995, for a duration of three years. In late 1997, the Task was extended for two years and it is now scheduled to end in September 2000.

Participation

The participants during 1998 were Canada, the European Commission, Japan, Norway, Sweden, Switzerland and the USA. Norway withdrew in late 1998. The European Commission's participation in 1998 was active, yet tentative and unofficial. Canada changed its expert at the end of the September. The official experts, past and present, are as follows:

Canada:	R. Chahine, <i>University of Quebec</i> A. Zaluska*, <i>McGill University</i>
(European Commission):	(P. Bernier, <i>University of Montpellier</i>)
Japan:	E. Akiba, <i>National Institute of Materials & Chemical Research</i> S. Suda, <i>Kogakuin University</i> I. Uehara, <i>Osaka National Research Institute</i>
Norway*:	A. Maeland*, <i>Institute for Energy Technology</i>
Sweden:	D. Noréus, <i>Stockholms University</i> (B. Bogdanovic', <i>Max-Planck-Institute für Kohlenforschung</i>)
Switzerland:	L. Schlapbach, <i>University of Fribourg</i> K. Yvon, <i>University of Geneva</i> (V. Verbetsky, <i>Moscow State University</i>)
United States:	M. Heben, <i>National Renewable Energy Laboratory</i> C. Jensen, <i>University of Hawaii</i> R. Loutfy, <i>MER Corporation</i> F. Lynch, <i>Hydrogen Components, Inc.</i> R. Murphy, <i>Oak Ridge National Laboratory</i> G. Sandrock, <i>SunaTech, Inc. (Operating Agent)</i> G. Thomas, <i>Sandia National Laboratories</i>

* indicates no longer active; () indicates unofficial

Activities and Progress During 1998

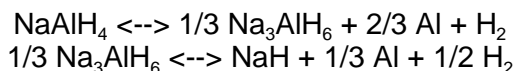
The eleven hydride projects active in 1997 were continued into 1998, with three additional hydride projects added: Projects 12 (Japan), 13 (Japan) and 14 (USA). Seven hydride

projects were completed or terminated during 1998. Two new carbon projects were started, Projects C-1 (joint USA-EC) and C-2 (USA).

Projects 1, 2, 8, 9 and 12 were conceived to try various techniques to increase the hydriding and dehydriding kinetics of Mg_2NiH_4 , and also, hopefully, decrease the temperature for desorption. All were active during at least part of the year. Various innovative techniques were used including the use of crystal structure modification (1), a vapor synthesis technique (2), mechanical milling to create nanophase structures (8,9) and surface coating (12). All of these projects were highly successful in increasing hydriding/dehydriding kinetics, but only slightly successful in decreasing thermodynamic desorption temperature. In fact, it has become reasonably clear that the Task temperature target (100EC) cannot be met by these approaches toward Mg_2NiH_4 . Therefore, projects 2, 8 and 9 were completed during 1998. Project 1 continues in a new direction, namely trying to make Mg_2NiH_4 work as a room temperature battery electrode. Project 12, which started only in 1998, continues to follow its aims to combine surface fluoride coating and mechanical milling.

Projects 3 and 4 focused on low-cost AB_2 intermetallic compounds. Interesting new fundamental information was established in the areas of crystal structure and phase relations. However, from practical points of view, it became evident that Task targets could not be achieved by these hydrides. Therefore, both projects were terminated in 1998.

In terms of the Task Target 1, the best results have been obtained with the alkali metal - aluminum complex hydrides represented by Projects 5, 6, 10, and the newly established 14. The projects are based on the two-step reversible Ti catalyzed reaction



first reported by Bogdanovic' [J. Alloys Comp., **253-254** (1997) 1]. Theoretical capacity for the above reaction is 5.5 wt.% hydrogen. Uncatalyzed alkali metal alanates are not normally very reversible, nor do they exhibit practical dehydrogenation kinetics. Bogdanovic' first showed that the addition of $Ti(OBu^n)_4$ (titanium tetra-n-butoxide), via a solution technique, resulted in significant increases in kinetics and reversibility. A dry homogenization introduction procedure for the $Ti(OBu^n)_4$ has been developed during Project 10 that gives even greater kinetics and cyclic stability than the wet Bogdanovic' technique. However, this approach is effective only for the first step of the above two-step reaction. Additional 1998 work under Project 10 identified $Zr(OPrn)_4$ (zirconium tetra-n-propoxide) to be effective for the second hydrogenation step. Thus, repeatable (10 cycles) 4.5 wt.% H-capacity and good kinetics have been achieved at less than 150EC. This was close to the original Task Target of 5 wt.% at 150EC, so the Target temperature was reduced to 100EC in late 1998. Project 10 has been completed and replaced by Project 14, which will examine catalyst mechanisms and practical hydrogen storage demonstration.

Other Task activities with Na- and related alanates included Projects 5 and 6. Project 5 was largely completed in 1997 and not significantly active in 1998. However, Project 6 has continued to more precisely define the reaction paths and structures associated with the two-step reaction. Bogdanovic' (especially his student A. Reiser) have unofficially participated in this effort via a Sweden-funded visit to Stockholm University.

Project 11 has continued to search for new transition metal complex hydrides by using high pressure synthesis techniques. Mg_3MnH_7 was characterized in 1998 and shown to have the first known hexahydromanganese(I) complex $[MnH_6]^{5-}$. This material contains 5.2 wt.% hydrogen and starts to decompose about 250°C. Attempts are being made to catalyze the hydriding/ dehydriding reactions. The first attempt to use $Ti(OBu^n)_4$ was not successful. Several other transition metal complex hydrides were discovered in 1998, including a new form of CuH.

Project 13 was started late in 1998 and will look at new ideas in the area of Ca-base alloys. Two new additional hydride projects (Projects 15 and 16) are planned for 1999 (see **Work Planned for 1999** below).

Two carbon projects (C-1 and C-2) were started in 1998. Project C-1 is concentrating on improved synthesis techniques for single walled carbon nanotubes and has resulted in considerable progress with both the arc and laser synthesis techniques, including chemical purification and mechanical cutting techniques. Project C-2 is focusing on catalyzed C_{60} fullerenes. Two additional carbon projects are expected in 1999.

The IEA/DOE/SNL Hydride Databases

The purpose of Project 7 is to provide a continually-updated inventory of hydride technology and other information to Task 12 experts, as well as the entire hydride R&D community, via the Internet. This will help both new and established hydride scientists and engineers to more quickly review the open literature and thus minimize duplication of effort. The information is presented in the form of specific searchable databases accessible at the URL:

<http://hydpark.ca.sandia.gov>

The data is tabulated from the open literature and presented under the auspices of the IEA with financial support from the US Department of Energy. Sandia National Laboratories supplies the Internet Server and website. Project 7 was very active during all of 1998 with the addition of new databases and updating of established ones. Following are a list of records on-line at the end of 1998, along with future plans.

Although rather thorough descriptions of the databases can be found in on-line introductory material, a brief description of each may be useful here.

Database	Records
Hydride Alloy Listings	1706
AB ₅ Intermetallic Compounds	316
AB ₂ Intermetallic Compounds	489
AB Intermetallic Compounds	147
A ₂ B Intermetallic Compounds	98
Misc. Intermetallic Compounds	279
Solid Solution Alloys	166
Mg Alloys	211
Complex Hydrides	Planned
Miscellaneous	Planned
Hydride Properties	47
References	871
M-H Organizations	22
M-H Meetings Calendar	Varies
IEA 12 Profile	Text
Hydride Applications	Planned
Hydride & Fluoride Structures	Planned

Hydride Alloy Listings - These databases are a series of comprehensive historical listings of hydriding alloys. Each is based on a metallurgical or crystallographic class of alloy and intermetallic compounds. Unlike the Hydride Properties Database (below), the Hydride Alloy Listings include only a few representative properties, mainly in the area of hydrogen-capacity and representative PCT (pressure-composition-temperatures) thermodynamic properties. Like all the other databases, it is searchable and linked to the References Database.

Hydride Properties - This database contains a limited number of alloys, at least in comparison to the Hydride Alloy Listings, but exhibits much more engineering property detail on each. The alloys represented are those that have been used for applications or have historical and special scientific interest. Properties include composition, detailed PCT, H-capacity, enthalpy and entropy of hydriding, plateau slope and hysteresis, metallurgy and synthesis, activation, kinetics, cyclic stability, morphology, gas impurity effects, commercial suppliers, known applications and selected literature citations.

References - The references used in the hydride databases are located in this separate, but linked, database. The reference database can also be used in a self-standing mode, i.e., independently of the hydride databases. It is searchable either by using the usual bibliographic fields (author, coauthor, year, journal, organization, etc.) or by key subjects.

M-H Organizations - This database consists of profiles of organizations involved in metal hydride (M-H) research, development and commercialization. The information contained in each record is exactly as prepared by the organization. Interested M-H organizations are urged to submit a profile via the on-line form for data entry.

M-H Meetings Calendar - This is a compilation of world-wide conferences and symposia in the field of metal-hydrogen systems. It includes information on the basic parameters of the meetings (date, place, organization, abstract submission, etc.), as well as Internet or other address for further information.

IEA 12 Profile - This text file covers activities in IEA Hydrogen's Task 12.

In addition to the above databases already on-line, there are more being planned. For the Hydride Alloy Listings, databases on the transition- and non-transition-metal complex hydrides are planned, as well as a miscellaneous category (amorphous, nanocrystalline, etc.). A "Hydrides Applications" database will be started in 1999. A "Hydride-Fluoride Crystal Structure" database will also be added. The latter (called HFD) will be a contribution of the private database developed at the University of Geneva [cf. Gingl et al, J. Alloys Comp., 253-254 (1997) 286] with the help of Sandia National Lab (USA) and the National Institute of Materials & Chemical Research (Japan).

The users of these databases should fully understand they represent only a door to the published literature. They are not meant to be used for the design of hydride devices. The user should carefully read the background information associated with each database and the disclaimers. The original reference sources for each datum of interest should be read before it is utilized. As always with the published literature, be wary of erroneous data.

Work Planned for 1999

Projects 1, 6, 7, 11, 12-14, C-1 and C-2 will continue in 1999. In addition, two new hydride and two new carbon projects will likely be established. Project 15 (Lynch, USA) will determine the safety related properties of the Na-Al complex hydrides and Project 16 (Akiba, Japan) will search for possible new hydrides that may be deduced from the hydride-fluoride (HFD) database. Projects C-3 (Chahine, Canada) and C-4 (Schlapbach, Switzerland) are expected to focus on various forms of carbon as possible H-storage media.

In the database area, the new complex and HFD databases will be put on-line early in 1999. The main new effort during 1999 will be the filling of a "Hydrides Applications" database that will hopefully be put on-line late in the year. Once that is established, a CD ROM version of the searchable databases will be established and made available to anyone interested in doing off-line searching.

Publications and Presentations during 1998

Code: [PU] = Publication and [PR] = Presentation

L. Schlapbach, A. Züttel, D. Chartouni, O. Kuttel, L. Diederich, O. Groning, N. Kuriyama and T. Sakai: "Hydrogen in Metals and Condensed Carbon," Spring 98 Meeting of the Materials Research Society, San Francisco, April 13-17, 1998 [PR] (Proj. 3 and C-4)

K. Gross, A. Züttel and L. Schlapbach: "Intermetallic Materials for Hydrogen Storage," Poster Paper, Spring 98 Meeting of the Materials Research Society, San Francisco, April 13-17, 1998 [PR] (Proj. 3)

S.E. Guthrie, G.J. Thomas, D. Noréus and E. Rönnebro: "Properties of Mg_2NiH_4 at 450-570K," Spring 98 Meeting of the Materials Research Society, San Francisco, April 13-17, 1998, published in Mat. Res. Soc. Symp. Proc. Vol. **513**, 1998, pp.93-98 [PR+PU] (Proj. 1)

M.J. Heben: "Hydrogen Adsorption in Carbon Nanotubes," Spring 98 Meeting of the Materials Research Society, San Francisco, April 13-17, 1998 [PR] (Proj. C-1)

- G. Thomas and S. Guthrie: "Hydrogen Storage Development," 1998 U.S. DOE Hydrogen Program Annual Review, Alexandria, VA, April 28-29, 1998, Proc., NREL/CP-570-25315, p. 419 [PR+PU] (Proj. 2)
- C. Jensen: "Hydrogen Storage via Polyhydride Complexes," Ibid., p.449 [PR+PU] (Proj. 10)
- R. Murphy, T. Wang and R. Loutfy: "Thermal Management Technology for Hydrogen Storage: The Fullerene Option," Ibid., p.459 [PR+PU] (Proj. C-2)
- M. Heben: "Carbon Nanotube Materials for Hydrogen Storage," Ibid., p.539 [PR+PU] (Proj. C-1)
- S.E. Guthrie and G.J. Thomas: "A Novel Process for Fabricating Mg₂Ni," 43rd Annual SAMPE Symposium, Society for the Advancement of Materials and Process Engineering, Anaheim, CA., May 31-June 4, 1998, published in Proceedings [PR] (Proj. 2)
- C.M. Jensen, R. Zidan, N. Mariels, A. Hee and C. Hagen: "Advanced Titanium Doping of Sodium Aluminum Hydride: Segue to Practical Hydrogen Storage Material?," Int. H. Hydrogen Energy (in press) [PU] (Proj.10)
- P. Tessier, H. Enoki, M. Bououdina and E. Akiba: "Ball-milling of Mg₂Ni under hydrogen," J. Alloy Comp., **268** (1988) 285-289 [PU] (Proj. 9)
- G. Thomas and K. Gross: "The state of R&D on metal hydrides in USA," Special Symposium, The Research Association for the Development and Application of Metal-Hydrogen Systems, Tokyo, Japan, Oct. 2, 1998 [PR] (Proj. 2)
- C. Jensen: "Na-Al based alloys as a potential hydrogen storage medium," Ibid.[PR] (Proj. 10)
- M. Heben: "Carbon materials for hydrogen storage," Ibid. [PR] (Proj. C-1)
- D. Noréus: "R&D and commercial activities of Ni-MH batteries in Europe and new Mg-based hydrogen storage alloys," Ibid.[PR] (Proj. 1)
- G. Sandrock: "A panoramic overview of hydrogen storage alloys from a gas reaction point of view," International Symposium on Metal-Hydrogen Systems, Fundamentals and Applications, Hangzhou, China, Oct. 4-9, 1998, to be published in J. Alloys Comp. [PR+PU] (Proj. 7)
- K.J. Gross, F. Fauth, D. Chartouni, A. Züttel and L. Schlapbach: "In situ neutron diffraction study of the new hydride CeMn_{1.5}Al_{0.5}D_x (0<x<4)," Ibid. [PR+PU] (Proj. 3)
- E. Akiba and P. Tessier: "Catalyzed reactive milling," Ibid. [PR+PU] (Proj. 9)
- R.A. Zidan, S. Takara, A.G Hee and C.M. Jensen: "Hydrogen cycling behavior of zirconium and titanium-zirconium doped sodium aluminum hydride," Ibid. [PR+PU] (Proj. 10)
- K. Yvon: "New metal hydrides," Ibid. [PR+PU] (Proj. 11)
- G. Sandrock: "Metal hydrides and carbon for hydrogen storage: international R&D program under IEA Task 12," Ibid. [PR] (Proj. 7)
- E. Rönnebro, J.O. Jensen, D. Noréus and N. Bjerrum: "Distorted Mg₂NiH₄ formed by mechanical grinding," Ibid. [PR+PU] (Proj. 1)

H. Tanaka, D. Noréus, H.T. Takeshita, N. Kuriyama, T. Sakai and I. Uehara: "Crystal structure and hydrogenation characteristics of Ca-Al-Si alloys," Ibid. [PR+PU] (Proj. 4)

H. Enoki, P. Tessier and E. Akiba: "Ball milling of Mg₂Ni under hydrogen," Ibid. [PR+PU] (Proj. 9)

M. Bortz, B. Bertheville, K. Yvon, E.R. Movlaev, N. Verbetsky and F.Fauth: "Mg₃MnH₇, Containing the First Known Hexahydridomanganese(I) Complex," J. Alloys and Compounds, **279** (1998) L8-L10 [PU] (Proj.11)

K. Yvon: "Complex Transition Metal Hydrides," in Advanced Materials in Switzerland, Chimia **52** (1998) 613-619 [PU] (Proj. 11)

S.F. Parker, U.A. Jayasooriya, J.C. Sprunt, M. Bortz and K. Yvon: "Inelastic Neutron Scattering, Infrared and Raman Spectroscopic Studies of Mg₂CoH₅ and Mg₂CoD₅," J. Chem. Soc., Faraday Trans., **94** (1998) 2595-2599 [PU] (Proj.11)

R. Cerny, J.-M. Joubert and K. Yvon: "Mg₃IrH₅, Another Example of Hydrogen Induced Anisotropic Line Broadening due to Microtwinning," Proceedings of the Fifth European Powder Diffraction Conference, EPDIC 5, Parma, Italy, May 1997, R. Delhez and E.J. Mittemeijer, Eds., Mater. Sci. Forum, **278-281** (1998) 121-126 [PR+PU] (Proj.11)

M. Bortz, A. Hewat and K. Yvon: "The Crystal Structure of Rb₂MgH₄ and Rb₃MgH₅ by Neutron Powder Diffraction," J. Alloys and Compounds **268** (1998) 173-176 [PU] (Proj.11)

L. Zaluski, A. Zaluska and J.O. Ström-Olsen: "Synergy of hydrogen sorption in ball milled hydrides of Mg and Mg₂Ni," to be published in J. Alloys Comp. [PU] (Proj. 8)

Meetings Held in 1998

- North American Carbon-Experts' Organizational Meeting, West Palm Beach, FL, USA, January 26, 1998
- Experts' Workshop, Davos, Switzerland, March 9-10, 1998
- Experts' Workshop, Tokyo, Japan, September 30-October 1, 1998
- Extensive Task participation in Spring 98 Meeting of the Materials Research Society, San Francisco, CA, USA, April 13-17, 1998
- IEA Task 12 sponsorship and extensive Task participation in International Symposium on Metal-Hydrogen Systems, Fundamentals and Applications, Hangzhou, Zhejiang, China, Oct. 4-9, 1998

Meeting Schedule for 1999

- # Experts' Workshop, Henniker, NH, USA, July 19-20, 1998
- # Possible Task 12 sponsorship and extensive Task participation in Gordon Research Conference on Hydrogen-Metal Systems, Henniker, NH, USA, July 18-23, 1998

Hydrogen in Material Science and Technology: State of the Art and New Tendencies

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Editor's Note: The following is a discussant paper prepared for the Executive Committee of the IEA Hydrogen Agreement for the purposes of reviewing research and development opportunities that could lead to increased market share for hydrogen in the area of material science and technology. The goal of research and development efforts within the IEA Hydrogen Agreement is to advance hydrogen energy related technologies. Although use in the material science field is not strictly energy related, advancement of non-energy uses of hydrogen could result in improved infrastructure development, which, in turn, would facilitate the commercialization of energy-related technologies. This paper forms a basis for the task development efforts of the proposed annex on Industrial Uses of Hydrogen.

INTRODUCTION

Today the bulk of hydrogen is used in the production of ammonia, methanol and other organic chemicals and for hydrotreating of crudes in refineries. Consumption figures for hydrogen show that applications in materials technology consume less than 5% of the hydrogen produced world-wide. This share rises significantly if one looks at the merchant hydrogen market. More significant, though, is the *value* of the hydrogen consumed by the materials industries, since high-purity hydrogen is required. Because of the growth and revenue potential for hydrogen in these markets, materials production may play a key role in the stimulation of advancements in hydrogen transport, purification and analysis, as well as in the development of efficient small-scale hydrogen production units. In recent years, hydrogen consumption in the production of metals and electronic equipment has grown at a faster rate than overall hydrogen consumption. Materials production continues to show the highest growth rates of all applications for hydrogen in industry. Thus, the success of hydrogen energy technologies can be closely linked to materials science and technology, since hydrogen is a key substance for a vast range of processes in the material science field.

SUPPLY

Economics of Hydrogen Supply

The nature of the hydrogen supply will vary greatly from one materials producing industry to another, depending on the quantity, quality and continuity of the hydrogen demand.

! Bottled hydrogen

Bottled hydrogen is the most expensive means for purchasing hydrogen. In western Europe only 5% of merchant hydrogen is sold bottled, yet this 5% contributes 35% of the market revenue. Small- to medium-sized companies, laboratories, and so forth, often require small amounts of hydrogen for a variety of applications, but generally on a limited or temporary basis.

! Compressed bulk hydrogen

For somewhat larger consumers of hydrogen, compressed bulk gas may be an interesting alternative. Bulk gaseous hydrogen is transported in tube trailers containing 1000 to 4000 cubic meters of hydrogen.

! Liquid hydrogen

Liquid hydrogen is typically transported in truck trailers containing 35,000 to 55,000 liters (equivalent to 30,000 to 45,000 cubic meters of gas). When transported by rail, tank cars containing 115,000 liters (90,000 cubic meters) are typically used. For distances of up to 50 km, a pipeline for liquid hydrogen may be economically attractive. Customer facilities usually store between 6000 and 75,000 liters (or 5000 and 60,000 cubic meters gas) of liquid hydrogen. For most applications liquid hydrogen is revaporized to the gaseous state.

Many consumers choose to purchase liquid rather than gaseous hydrogen because of the savings in handling costs resulting from the tenfold increase in density for liquid compared to gaseous storage. Bulk liquid hydrogen is often less expensive to store and transport than the equivalent quantity of bulk gas. This is particularly true for transport distances beyond 200 km. For consumers using less than 1500 cubic meters of hydrogen per month, bulk gas and liquid costs are roughly equivalent. For larger purchases, gas is generally more expensive. A drawback of liquid hydrogen storage is that it is subject to significant losses due to evaporation. It is generally not recommended for locations where less than 2500 cubic meters per month of hydrogen are consumed.

! Gas pipeline

Gas pipeline as a transport mechanism is less expensive than bulk liquid hydrogen, since there are essentially little or no costs associated with liquefaction, transportation or storage. However, the hydrogen can only be delivered where a pipeline exists. For most large consumers of hydrogen, costs of pipelined hydrogen will be nearly the same as operation of an on-site hydrogen production plant.

! On-site production

On-site hydrogen production costs are strongly dependant on use. As a rule of thumb, costs are usually equivalent for liquid hydrogen and on-site production for plants consuming between 150,000 and 250,000 cubic meters of hydrogen per month. Above 250,000 cubic meters per month, on-site production is less expensive in cost per unit of hydrogen. However, on-site production may have some disadvantages: 1) strong changes in hydrogen demand may leave the company with a hydrogen plant that will no longer be of use; 2) an on-site plant requires maintenance and intense care for its reliability, especially if needed flow rates of hydrogen are not continuous; and 3) an on-site production plant requires capital investment or a long-term leasing contract.

Means of Supply for Specific Industries

Since materials industries generally require much smaller amounts of hydrogen than do major users like refineries and the fertilizer industry, their supply is often covered by liquid or compressed gaseous hydrogen.

! Electronics

Because of the high purity required for electronics applications, the industry usually purchases hydrogen in its liquid form or as ultra-pure gas in cylinder bottles.

! Flat glass

Today, flat glass production is mainly served by liquid hydrogen. In areas with significantly rising demand for flat glass, on-site production is being considered by more producers, especially as small hydrogen producing units become more cost effective.

! Metals

The metal industry is the largest consumer of hydrogen in the materials processing industry. Hydrogen is purchased as liquid or gas through pipelines, or is produced by a variety of on-site methods, particularly dissociation of methanol and ammonia. Heat treaters are estimated to dissociate approximately 600,000 short tons of ammonia to produce an atmosphere that is 75% hydrogen and 25% nitrogen.

Materials Technology as a Source for Hydrogen

As well as a consumer of hydrogen, the materials industry is an important source hydrogen. Several processes within this field, namely the coke oven process, produce hydrogen that can be utilized for other purposes. All of these processes have historically been based on the use of fossil fuels. Recently, though, some new processes have been developed that allow for hydrogen production using renewable energy.

! Coke oven gas

The production of coke results in a by-product gas that contains substantial amounts of hydrogen. This, along with other coal refining processes, accounts for 18% of the world's annual hydrogen production. Coke is usually consumed in various metal and alloy producing processes. Since much of the hydrogen produced by this means is burned for fuel purposes, in most cases the oven gas does not contribute to the world hydrogen supply. However, there are a number of coke oven plants, especially in Japan, that feed this hydrogen to pipelines to serve the needs of other companies. This means of production could make a greater contribution to world hydrogen supplies than it does today.

! Metal/metal-oxide processes

Organizations, such as the Swiss Paul-Scherrer-Institute, the Weitzmann Institute in Israel and the U.S. National Renewable Energy Laboratory, have been developing solar concentrator-based chemical cycles for metal/metal oxides processes. Solar thermal energy is used to drive the following simplified reaction:



Although not yet commercially viable, more efficient and low-cost methods to focus the solar radiation could lead to a practical method to produce high purity hydrogen. Regions with high solar radiation input could especially benefit from this approach.

METALLURGY

Hydrogen is used in both primary metal production and secondary metal processing. Primary operations that consume hydrogen include the production of a vast range of pure metals, such as tungsten, tungsten carbide and molybdenum metal powder production. Secondary operations that consume hydrogen include heat treating, sintering, casting and brazing. The majority of hydrogen used in the metals industry is for secondary operations rather than primary metal production, though this ratio may be subject to change in the future.

In secondary operations hydrogen is commonly used in furnaces that require a reducing atmosphere or improved thermal conductivity. Small quantities of hydrogen are sometimes used as backfill gas in vacuum furnaces. Hydrogen is used in large quantities for heat treating. Specific heat treating operations that consume hydrogen include normalizing low-carbon steel prior to galvanizing, annealing of steel strip and coil, bright annealing of stainless steel and decarburizing. Types of companies likely to consume hydrogen for heat treating include steelworks, finishing mills and in-house and commercial heat treaters.

Hydrogen Use in the Metals Industry

<u>Year</u>	<u>Country</u>	<u>Gas</u>	<u>Liquid</u>	<u>Merchant</u>	<u>Captive</u>	<u>Total</u>
[thousand standard cubic meter]						
1987	Western Europe	-	-	-	-	1,800,000
	Japan	-	-	20,000	-	-
1990	Western Europe	-	-	-	-	1,880,000
	Japan	-	-	40,000	-	-
1993	USA	38,700	85,200	123,900	14,800	138,700
	Western Europe	-	-	-	-	2,000,000
	Japan	-	-	35,000	-	-
1996	USA	59,200	124,900	184,100	14,900	99,000
	Western Europe	-	-	-	-	2,100,000
	Japan	-	-	42,000	-	-
1997	USA	77,600	133,300	210,900	14,900	225,800

Processes

! Annealing

Much of the hydrogen consumption growth in metals can be attributed to increased demand in annealing furnaces. Historically, annealing furnaces used an atmosphere that was mostly nitrogen and approximately 6% hydrogen. Over the past five years pure hydrogen atmospheres have become increasingly common. Industry sources estimate that about 500 work bases for annealing furnaces with 100% hydrogen atmospheres have been installed at about 50 locations in the U.S. Substantial growth opportunities still exist. Several thousand work bases could potentially be converted to 100% hydrogen atmosphere furnaces at existing facilities and about 50 new locations.

! Brazing

Brazing is largely used in the aerospace and electronics industries to join parts. Brazing joins solid materials together by heating them to a suitable temperature and by using a filler metal having a liquidus above 1544°C and below the solidus of the base materials. Hydrogen flames are used to provide the necessary heat (up to 2800°C) for certain brazing applications. Also, when used as the atmosphere for the brazing furnace, hydrogen minimizes oxide surface contamination on some treated metals. [Note, hydrogen atmospheres are not effective for metals that form stable oxides, such as aluminum, silicon and chromium.]

! Casting

When metals are melted and run into molds, a specific protective atmosphere is often needed to prevent corrosion. Hydrogen is not only very useful in this kind of operation, but it is also lighter than other gases. In the U.S. for example, this is a growing business of more than 60 millions U.S. dollars per year.

! Corrosion prevention

In nuclear power reactors, primary systems measures have to be taken to suppress intergranular stress corrosion cracking (IGSCC). Hydrogen is applied for this purpose in a growing number of power plants. The average hydrogen consumption for IGSCC prevention is about 1400 standard cubic meters per day per plant. [This may be lowered by up to 75% through application of a noble metal catalyst.] In the coming years, many U.S. facilities are expected to start using hydrogen, which is considered, by many, to be a superior method for preventing IGSCC.

! Direct reduction

One primary steel production process that is receiving increased attention is the direct reduction of iron ore or scrap metal. This technology has been demonstrated at several locations throughout the world. Currently some demonstration plants are still under operation. It has long been known that iron can be produced in a direct reduction process from its ores by using hydrogen or a mixture of hydrogen and carbon monoxide. This process affords far lower temperatures than the conventional blast-furnace process and, thus, saves energy. The resulting iron sponge still contains lots of other minerals as admixture, so further treatment is necessary.

! Sintering

Loose or compressed powders are bonded by heating at temperatures below the melting point of the major constituents. Because powdered metals undergoing sintering have such a large exposed surface area, hydrogen atmospheres are commonly used to prevent oxidation. Metal compacts that are typically sintered in a hydrogen atmosphere include tool steel, stainless steel and nickel- and cobalt-based alloys, as well as alloys of tungsten carbide with cobalt, solid tungsten and molybdenum metal.

Special Metals

! Boron

Volatile boron compounds like BBr_3 or other halogenides are reduced by hydrogen at a heated tantalum contact. This is the most effective way to synthesize ultra pure (>99.9%) boron.

! Germanium

At 530°C , the oxide of germanium is reduced by hydrogen into its elemental form. This is the last step in the complex procedure to produce germanium via the industrial standard process.

! Iron

A small share of the world's iron production is in the form of pure iron metal. One of the common processes to get pure iron is the reduction of purified iron oxide or hydroxide with hydrogen.

! Molybdenum

An important share of the world's molybdenum is used as a pure metal. The commercially applied process synthesizes pure molybdenum by reducing ammonium molybdate with hydrogen. A fine metal powder results that is then sintered to solid metal in a hydrogen atmosphere.

! Nickel

Nickel oxide is reduced to pure nickel metal either through use of pure hydrogen or by the Mond process, which utilizes steam and a mixture of hydrogen and carbon monoxide.

! Osmium, Ruthenium, Rhodium and Iridium

The final step to produce osmium, ruthenium, rhodium or iridium is the burning of precursor compounds that contain the respective metals in a pure hydrogen atmosphere.

! Rhenium

Pure rhenium is produced by reducing $(\text{NH}_4)\text{ReO}_4$ at elevated temperatures with hydrogen.

! Selenium

Very pure selenium is produced through heating of raw selenium with hydrogen. The resulting compound, H_2Se , is decomposed into its elements in a quartz tube at 1000°C .

! Silicon

Silicon is a semi-metallic element that can be produced similarly to boron through thermal decomposition of a mixture of hydrogen and its tetra iodide at a heated tungsten contact. Another method is the epitactic growth of single crystal layers by decomposition of silicon hydride. These are both standard methods for the production of very pure silicon.

! Technetium

Pure technetium is produced through reduction of a precursor compound (e.g. Tc_2S_7) with hydrogen at high temperatures.

! Tungsten

The final step of the industrial production of pure tungsten is the reduction of tungsten trioxide at 850°C using hydrogen. A fine metal powder results, which must then be sintered under hydrogen atmosphere to produce the solid metal.

! Vanadium

One of the more common methods to produce pure vanadium is the reduction of vanadium pentachloride with hydrogen.

Developments in Metallurgy

Recently, the consumption of hydrogen for metal treatment has grown at about double the rate of growth for the overall hydrogen market. In the U.S., hydrogen consumption in the metals industry has increased even more rapidly, with steel annealing being one of the fastest growing applications. As previously mentioned, atmospheres of about 10% hydrogen and 90% nitrogen have traditionally been used during the annealing process. The current trend towards utilizing pure hydrogen atmospheres is expected to continue over the next five years, as there are still a lot of work bases that could be converted to the use of 100% hydrogen. Additional reasons for these high growth rates are the increasing focus on higher-value-added products and, especially in Europe, a needed increase in competitiveness through application of new process technologies.

Some of the recently developed processes to produce metals may have a strong impact on the mid-term hydrogen market. First is the direct reduction of metal ores, which demands for large (captive) amounts of hydrogen, assuming the currently operating pilot plants demonstrate superior performance. Until now, this process has only been applied to iron oxides (pilot plants are under operation), copper silicates, zinc silicate and nickel oxides, but the ores of other metals may also be accessible through reduction with hydrogen.

The synthesizing, handling and modifying of finely dispersed metals and alloys, as well as that of solid alloys and ceramics, steadily advances upward on the technology ladder. With the demand for more pure and reliable compositions of these materials, the need grows for controlled, oxygen-free atmospheres in processing. Hydrogen is the gas most commonly used for these purposes.

The scenarios for future uses of materials show a large rise in the use of tools, catalysts, etc., made of rare metals. The necessary amounts of raw material supplied from natural ore mines may not be sufficient to satisfy industries demands. A solution for this deficit could be found in a more intense retrieval of rare metals from scrap materials. Here hydrogen will play an important role, since many rare metals are refined through reduction of precursors by hydrogen.

ELECTRONICS AND CERAMICS

Hydrogen is commonly used during the production and modification of ceramics and during integrated circuit, optical fibers, and fused quartz manufacturing for electronics. Because of the high purity requirements for these applications, bulk hydrogen sold to electronics or ceramics companies is usually liquid or gas vaporized from liquid. Contamination by moisture, other gases, hydrocarbons or metals in concentrations as low as one part per million can adversely affect semiconductor device performance.

Hydrogen Used in the Electronics Industry

<u>Year</u>	<u>Country</u>	<u>Gas</u>	<u>Liquid</u>	<u>Merchant</u>	<u>Captive</u>	<u>Total</u>
		[thousand standard cubic meter]				
1987	Japan	-	-	41,000	-	-
1990	Japan	-	-	49,000	-	-
1993	USA	13,700	57,800	71,500	0	71,500
	Japan	-	-	40,000	-	-
1996	USA	13,700	89,300	103,000	0	103,000
	Western Europe	-	-	-	-	25,000
	Japan	-	-	62,000	-	-
1997	USA	13,700	99,800	113,500	0	113,500

Processes

Numerous methods in electronics and ceramics need hydrogen either as a reagent in chemical reactions or to form a protective atmosphere against oxidation.

! Annealing

Crystals are slowly regrown from amorphous material through the application of heat in a controlled atmosphere. This process is commonly used to relieve stress after the substrate has been bombarded by accelerated ions.

! Bonding

The electrical circuits of integrated circuits are attached to the external environment, while under a controlled atmosphere.

! Chemical Vapor Deposition

A thin film is formed on a substrate by the chemical reaction of a gaseous species. Epitaxy is a special form of chemical vapor deposition. Hydrogen serves as a carrier gas and additionally as a reducing agent if the substrate is polycrystalline silicon or one of the group III to V elements.

! Clean-burning

Controlled combustion of hydrogen is used to remove impurities from the materials used. Significant amounts of hydrogen are used for this purpose in the manufacturing of quartz and glass fiber.

! Crystal Growth

Single crystals, usually silicon, are produced from a melt of polycrystalline starting material. The two most common crystal growth methods are the Czochralski method and the Float Zone method, both of which require a controlled hydrogen atmosphere.

! Diffusion

Diffusion is a high-temperature process in which dopants are introduced into the surface layer of the semiconductor material to change its electrical characteristics. Hydrogen serves as carrier gas in this process.

! Epitaxy

Epitaxy is the process by which a crystalline layer having the same structure as the substrate is deposited. Impurities, such as diborane or phosphine, are often added to the epitaxial layers to change the electrical conductivity of the crystalline silicon. This approach is used for the growth of semi-conductor layers and for diamond epitaxy. Hydrogen is used as a reducing medium and/or carrier gas.

! Etching

During etching, unwanted material are removed from a highly defined surface under a reducing atmosphere, such as hydrogen.

! Ion Implantation

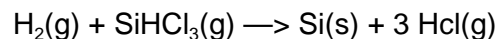
Ion implantation is a technique for doping impurity atoms into an underlying substrate by accelerating the selected dopant ion toward the silicon target through an electrical field. Hydrogen dilutes the dopant-bearing gases.

! Oxidation

Through oxidation a layer of silicon dioxide is grown on a silicon surface. Hydrogen and oxygen are combined to make pyrogenic steam.

! Polysilicon Production

Silicon is produced by the pyrolytic decomposition of trichlorosilane or silicon tetrachloride through the reaction:



Hydrogen is needed as a reducing agent in this process.

Developments for Electronics and Ceramics

In recent years growth rates of hydrogen consumption in the electronics and ceramics industries have been as much as triple that of overall hydrogen production. This trend is expected to continue, particularly in countries with a non-mature semiconductor industry or with high demand for glass fibers.

The demand for hydrogen in electronics and ceramics industries is definitely focused on small quantities of very pure hydrogen. Changing requirements of quantities will not have a major impact on the overall hydrogen market in the next years, if ever. However, there are three areas where hydrogen supply may be influenced by these industries. First, the distribution network for bulk gaseous or liquid hydrogen will become more dense. Second, the demand for small-scale hydrogen producing units might significantly increase if companies from the electronics industry prefer to have more control over the raw material inputs to their production process. Finally, the growing demand for very pure hydrogen affords more activities in the analysis and purification of hydrogen.

HIGH TEMPERATURE PROCESSES

Many processes require temperatures on the order of those seen during the combustion of hydrogen and oxygen. Most of these processes are still at the research and development stage, as their basic mechanisms are not yet fully understood. Nevertheless, some of these processes will be used for advanced materials production in the coming years.

! Diamonds

The standard method to produce diamonds from graphite works by applying high pressures. A new process utilizes very low pressure on the order of 0.05 atmospheres. Diamonds are formed in a plasma fed by a mixture of 99% hydrogen and 1% methane. This technique enables large areas to be covered with pure flat diamond layers. A new generation of superior flat panel displays may be produced using this method.

! Other precious stones

Like diamonds, other precious stones, such as sapphires, are usually produced by applying high pressure to selected raw materials. More recent methods utilize the high temperature of the hydrogen combustion reaction to improve efficiency. This method requires very pure hydrogen, absent of any traces of carbon.

! Plasma reduction

The general method of reduction in a hydrogen plasma opens the opportunity to selectively treat materials, such as ceramics, under extreme conditions. This might allow for new pathways to produce metastable materials, not accessible by other means. Currently, a lot of basic research is being done in this field.

! Welding

Welding and hot cutting of metals may be performed with a hydrogen-oxygen flame in the same way as with the current oxygen-acetylene method. This is already the standard method in the processing of special carbon-free materials. If it is to be applied in other, more robust technical applications, the existing technical equipment would first have to be adapted for this purpose.

Developments for High Temperature Processes

The expected developments mentioned previously for electronics are also valid for high temperature processes using hydrogen, to a lesser extent. Very high purity hydrogen is required and the quantities of hydrogen needed are similar. Increased market share for hydrogen for these processes will not have dramatic effects on the hydrogen production market, but could have prove beneficial for distribution networks and the development of small-scale production units and analysis and purification equipment. Progress in the use of high temperature processes may also enhance the use of hydrogen by the ceramics industry.

GLASS

Hydrogen is the standard gas in the production of a number of high quality glass products, from flat glass to glass fibers to glass ceramics.

Hydrogen Used in the Glass Industry

<u>Year</u>	<u>Country</u>	<u>Gas</u>	<u>Liquid</u>	<u>Merchant</u>	<u>Captive</u>	<u>Total</u>
[thousand standard cubic meters]						
1987	Japan	-	-	9,000	-	-
1990	Japan	-	-	18,000	-	-
1993	USA	0	17,100	17,100	0	17,100
	Japan	-	-	29,000	-	-
1996	USA	0	21,000	21,000	0	21,000
	Western Europe	-	-	30,000	-	-
	Japan	-	-	46,000	-	-
1997	USA	0	22,300	22,300	0	22,300

Materials

! Flat glass

Flat glass is almost always produced using the float glass process, which requires hydrogen as an inerting gas (4.5 standard cubic meter per ton of glass). In this process, a continuous ribbon of glass is floated on a bed of molten tin. The glass is held in a controlled atmosphere of roughly 94-95% nitrogen and 5-6% hydrogen, while irregularities in the glass even out and the glass becomes flat. The glass is then cooled while it advances across the molten tin until the glass surface is hard enough for the glass to be removed.

The hydrogen in the controlled atmosphere acts as a scavenging agent to ensure an oxygen-free environment. Molten tin is highly sensitive to oxidation. Even trace oxygen can cause problems. Glass quality is also affected by oxygen, since oxygen can cause a residue to form on the glass and make it hazy.

Flat glass production requires reliable and pure hydrogen supply. Generally liquid hydrogen is used, but on-site production may be used in the future.

! Quartz and glass fibers

Hydrogen is used in a controlled combustion process to remove impurities from the raw materials. Even more important than in flat glass production, the absolute high performance of the products has to be guaranteed. The mentioned cleaning process and the protective measurements must be very precise.

! Glass ceramics

Aside from the usual cleaning by hydrogen combustion, hydrogen is needed for inerting purposes.

Developments for Glass

Like in most other materials applications, growth rates for hydrogen consumption have been much higher than the overall market growth for hydrogen in recent years. The further development of hydrogen demand in the glass industry is chiefly determined by the expansion of float glass and glass fiber production. While the first will account for more hydrogen demand in Europe and the U.S., the second will stimulate the merchant hydrogen market, especially in Japan where an ambitious optical fiber project to connect every household is still under construction.

The supply sources for hydrogen to the glass industry is expected to change to some degree in the near future, as glass in its various modifications becomes more important as an industrial material. Aside from a rise in demand for more small-scale captive production plants, the future will see more use of larger on-site hydrogen plants.

OTHER USES

Storage media

Various materials are currently under intense research regarding their hydrogen storage capacity. Currently, the IEA Hydrogen Agreement has an active Annex examining various hydrogen storage materials. For this reason, only a short summary of known methods is given below, along with other potential applications.

! Cryo-Adsorption

Gaseous hydrogen at low temperatures (60-150 K) is physically adsorbed on porous material, mostly activated carbon. The storage densities achievable lie between those of liquid storage systems and high pressure systems. At 3.5 MPa, approximately 25 g H₂/ liter can be stored

at 77 K, which is about 30% of the density of liquid hydrogen, and is equivalent to 30 MPa pressurized storage.

! Metal Hydrides

Metal hydrides are usually charged with pressurized hydrogen of between 3 and 6 MPa. Suitable metal alloys provide spaces in their lattice where hydrogen atoms can be accommodated. The hydriding heat set free when absorption of hydrogen occurs has to be removed from the system in order to avoid damage to the storage containers. Currently available high-temperature hydrides (based on the temperature at which the hydrogen discharging process takes place) have higher storage capacities than low-temperature hydrides. In automobile applications, waste heat is available from engine cooling, favoring low-temperature hydrides. More recently, though, experiments with medium-temperature hydrides have begun. Metal hydride storage systems are also regarded as a very safe way to store hydrogen for domestic/residential applications.

! Organic Hydrides

Hydrogen can be stored in liquid organic commodities, such as methylcyclohexene, which is transformed into toluene through the addition of hydrogen. Processes have already been optimized on a laboratory scale. Pilot plants are still in the planning phase. This may be an option for seasonal or short-term storage of excess hydrogen.

! Sponge Iron

During the charging process, sponge iron storage makes use of the reduction of Fe_3O_4 by hydrogen or carbon monoxide, liberating water vapor or carbon dioxide and leaving Fe as a product. In the discharging process, water vapor is added, resulting in clean moist hydrogen gas from the oxidation reaction. The advantage of this process is that the hydrogen-rich gases obtained from the hydrocarbon source and used for charging the storage medium do not require a shift reaction or selective oxidation down-stream. Furthermore, this storage concept has been estimated to be an order of magnitude cheaper than its competitors and falls into the acceptable weight range for vehicle applications (half that of hydrides, double that of pressurized hydrogen storage) at atmospheric operational pressure levels.

! Carbon nanotubes

Carbon nanotubes are tube-like structures made entirely of carbon. They have very large surface areas in comparison to their volume, which allows them to adsorb more hydrogen than previously studied materials, such as activated carbon. The nanotubes pack together easily for more efficient hydrogen storage and transport. The production of this material seems possible at reasonable cost levels, although work in this area is still at the research stage. The promise of these materials for on-board hydrogen storage has resulted in cooperation between research institutions and large automobile manufacturers.

! Glass microspheres

Engineered microspheres, tiny bubbles made of glass, are loaded by exposing the heated microspheres to heated hydrogen. The increased permeability of the glass permits rapid loading of the spheres to the external pressure. When the temperature is reduced to room temperature, the permeability decrease traps the hydrogen in the spheres. The microspheres

are about 25 to 500 microns in diameter and the walls are about 1 micron thick. Current research is focused on optimization of design parameters to allow for better control of the loading and discharging process. Assuming optimization of these microspheres leads to a cost-competitive means of hydrogen storage, large-scale production should not be a problem, since the production technology has been in place for decades.

Carrier gas

Hydrogen is an interesting carrier gas, due to its light weight and thermodynamic and heat conductivity properties. Several applications are already taking advantage of the unique characteristics of gaseous hydrogen. One of the commercially important applications, for example, is the utilization of hydrogen in aerospace paint shops.

Coolant

Gaseous hydrogen has greater conductivity than air and can provide more efficient cooling. At many electric utilities, hydrogen is circulated through heat exchangers in the shell of the generator to cool the rotor. Although this is a closed recirculating system, some hydrogen is lost through leakage. Additionally, a complete flushing with fresh hydrogen is periodically required for system maintenance. As a rule of thumb, about one standard cubic foot of hydrogen has to be replaced each day per megawatt of generating capacity.

CONCLUSIONS/RECOMMENDATIONS

A task for internationally coordinated research concerning hydrogen and materials science could prove beneficial for the advancement of hydrogen energy technologies. Increased market penetration of hydrogen in the materials science industries could lead to improved infrastructure for storage and distribution, as well as development of cost-effective small-scale hydrogen production units, and purification and analysis equipment. The main issue in defining a task of this nature is the diverse materials and processes that might be included into such a program. Despite these difficulties, four recommendations are made here:

- ! A data bank for hydrogen-related processes in materials science should be set up. This type of information is not currently centralized. Issues in different hydrogen research programs are often closely related or may be solved easily with better access to related research areas.
- ! Research efforts should be initiated to improve the cost-effectiveness of purification and analyses methods, as well as small-scale hydrogen production units. This becomes more and more important with the growing demand for hydrogen, especially for very high purity hydrogen. This can be accomplished through one or more specially dedicated tasks and/or coordinated governmental interaction to strengthen latent market potentials.
- ! The current collaborative activities focused on metal hydrides and carbon materials for hydrogen storage should continue to be supported. Furthermore, if other materials are found to show similar promise for hydrogen storage, they should also be incorporated into the international cooperative effort.

- ! The need for better coordination of thermal and other production methods should be assessed. Production of hydrogen is expected to remain a long-term issue. There is a need to assess different supply paths for a future hydrogen economy. This could be achieved through a more cooperative strategy in the evaluation of possible technologies and approaches.

In conclusion, improvements to some of the hydrogen utilization methods available, but not widely practiced, could lead to increased market share for hydrogen in materials science. Although not a major factor in overall hydrogen consumption figures, this increased demand for hydrogen in materials science could lead to better hydrogen storage materials, construction of distribution infrastructure, and development of improved purification and analysis equipment, all of which will prove important for the advancement of hydrogen energy technologies as they mature.