

## 12. Task 1 2 Investigation and Study of Innovation and Leading Technology

### 12.1. Research and Development Goals

The WE-NET is a project worked out from a long-range point of view. In the process of promoting this project, it is conceivable that the innovative and leading technologies which are promising in the future but not covered at present by the project would ripen into maturity. Conventional technologies may also have to be introduced as part of the technologies which constitute the WE-NET, depending on the trend of their improvements. It is aimed at giving valuable suggestions and proposals to the direction of the WE-NET project and contributing to the research and development through feasibility study, as well as further research if necessary, of such innovative, leading and conventional technologies.

### 12.2. Results of FY2001 Research and Development

#### 12.2.1 Search for and Assessment of Innovative and Leading Technologies

In FY2001, we received three new technology proposals. The last meeting of the committee in FY2000 reported on assessment results indicating that, of the feasibility studies carried out during the year, it is desirable to continue studies on three topics. In FY2001, therefore, feasibility studies were conducted on six topics in all.

**Table 12.2.1-1 Names of Proposed Feasibility Studies in FY2001**

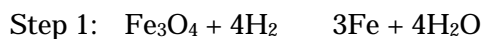
Names of Proposed Feasibility Studies	Contractors
A study on the storage of hydrogen using an iron oxide as a medium	Tokyo Institute of Technology
A study on a hydrogen production system by partial oxidation of biomass and waste used as raw materials	Ebara Corporation
Search for new hydrogen-storing inorganic and organic composite materials	Yamanashi University
A study on gas turbine systems coupled with non-equilibrated methane reforming process	Toshiba Corporation
A technical study on a hydrogen storage system using new decalin/naphthalene hydrogenation and dehydrogenation processes based on a superheated liquid membrane method	Nisseki Technologies Co., Ltd.
A study on the method of producing hydrogen without generating carbon dioxide, using natural gas as raw materials, and an assessment of by-products	Osaka Gas Co., Ltd.

#### 12.2.2 Study on Innovative and Leading Technologies

##### (1) Assessment of FY2001 Feasibility Study Results

A study on the storage of hydrogen using an iron oxide as a medium

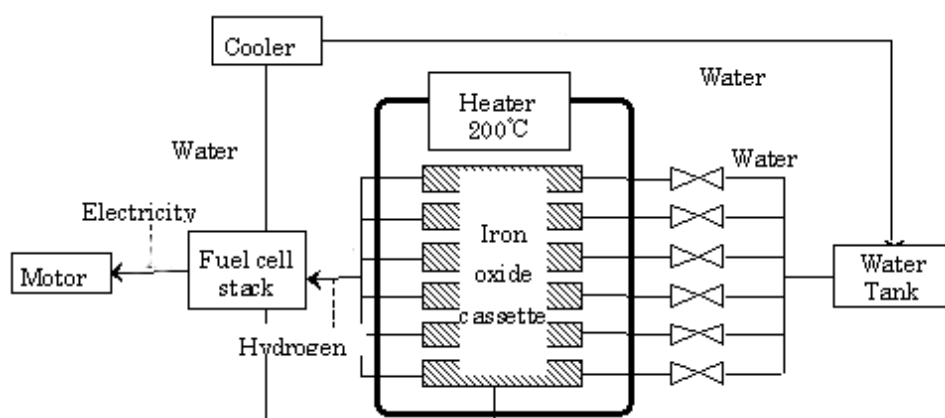
A study was conducted on a hydrogen storage and transport method using the oxidation-reduction of an iron oxide as described in the following formula:



This method first produces metallic iron by reduction of an iron oxide (Step 1 - hydrogen storage) and then produces hydrogen by contacting the metallic iron with steam (Step 2 - hydrogen recovery). In the FY2001 study, we added a very small quantity (3 ~ 5 mole percent) of various metallic ions to the metallic iron to accelerate the decomposition of water at a low temperature not exceeding 400 °C (Step 2) and examined the effects of the ion addition. A proposed Iron Oxide system for Fuel Cell Vehicle is shown in Fig. 12.2.2-1

From alternately repeated reduction and oxidation of the iron oxide with different metallic ions added to it, we found that when Al, Sc, Ti, V, Cr, Ga, Zr or Mo ion was added to the iron oxide, it was more quickly reduced by hydrogen in Step 1 reaction and more efficiently produced hydrogen in Step 2 reaction than when no metallic ion was added to it. We also found that the iron oxide with these metallic ions added to it declined only slowly in activity for hydrogen production even if it was used repeatedly.

Of all research activities on various hydrogen storage technologies, the topic of this study is the sole example of hydrogen storage system using the chemical reaction characteristics of inorganic solid substance. When we consider the performance of the proposed system as installed in a fuel cell vehicle, however, it has a theoretical hydrogen storage capacity of only 4.8wt% and, if water weight and added alloys are taken into account, its storage capacity would further decrease. This implies that the system can hardly be applied to fuel cell vehicles at the present stage. We decided to watch the progress of the study and temporarily discontinue the examination of this study within the framework of the Task 12 in the next fiscal year (FY2002) partly because of a plan to conduct a part of this study in the next fiscal year under other development project than WE-NET for industrial technology commercialization sponsored by the New Energy and Industrial Technology Development Organization (NEDO).



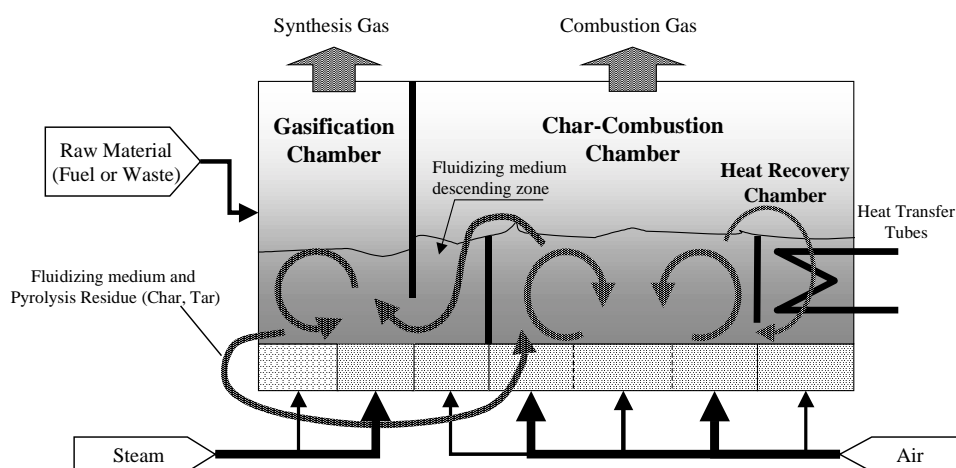
**Fig. 12.2.2-1 Conceptual Diagram of a Fuel Cell Vehicle System Using an Iron Oxide Cassette**

A study on a hydrogen production system by partial oxidation of biomass and waste used as raw materials

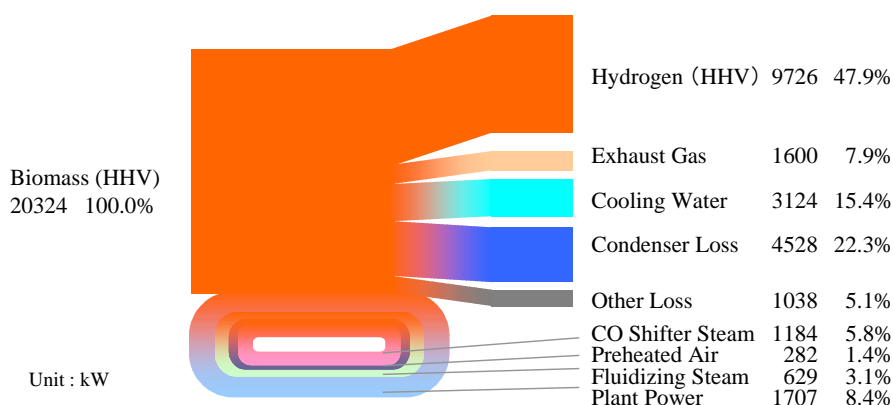
Envisaging the use of hydrogen produced by partial oxidation of biomass and waste as fuel for motor vehicles powered by fuel cells, we carried out a survey on the hydrogen production and supply potential of biomass and waste in Japan. As a case study, we also conducted a feasibility study on a hydrogen production system with the gasification of wood chips used as a raw material.

It is estimated that the hydrogen supply potential of biomass in Japan will reach approximately 7.4 billion Nm<sup>3</sup>/y in FY2010. From a feasibility study on a hydrogen production system with an internal circulation fluidized bed gasifier (ICFG) applied to forest biomass (wood chips), we found that as a development target for the proposed system, its energy recovery efficiency could be set as high as some 50%.

Since the production of hydrogen from biomass is important from the viewpoint of effectively utilizing new energy sources, we believe that a study should be continued on the proposed technology in the next fiscal year to make it economically viable. The feasibility study in fiscal year 2001 found that the technology could hardly be made economically viable unless it is used under very special conditions. To solve this problem, steps were taken to make a more accurate economic assessment of this technology and coordinate the matters involved so that a study on the technology could be continued in the next fiscal year, with the achievement of its economic viability set as a primary goal.



**Fig. 12.2.2-2 Conceptual Diagram of an Internal Circulation Fluidized Bed Gasifier (ICFG)**



Estimating conditions: Wood biomass (HHV: 17.6 MJ/kg-W.B.) x 100 t/d  
65,700 m<sup>3</sup>/d (NTP) of high-pressure hydrogen (20 MPa)

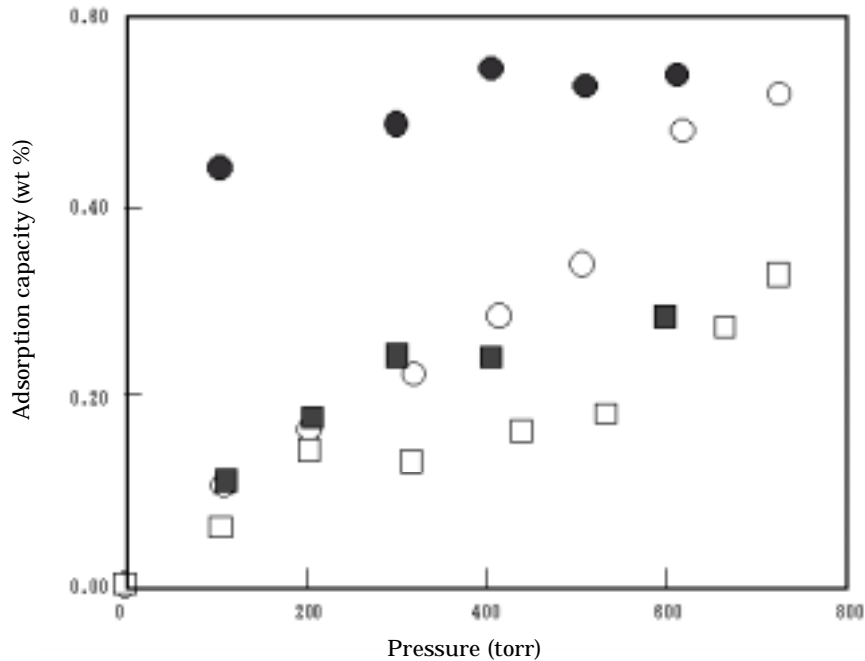
Fig. 12.2.2-3 Heat Balance Chart of the Proposed Hydrogen Production System

#### Search for new hydrogen-storing inorganic and organic composite materials

This study was carried out in a bid to develop new hydrogen-storing materials with far larger storage capacity than conventional materials, based on the concept of nanopore materials design.

The findings indicate it is possible that new materials having a greater hydrogen adsorption capacity than activated charcoal at the room temperature will appear from such lightweight materials as silica modified with an organic substance and partially carbonized ion-exchange resin. These materials are quite different from any of the conventional substance categories which have been considered to serve as hydrogen absorption materials. It is expected that the new materials will bring forth new developments of the situation in this field.

It is a topic on which a study should be continued in the next fiscal year in the hope of achieving a technical breakthrough. The topic covers many types of materials and also a method of increasing their hydrogen storage capacities through the application of higher pressure. Apparently the sintering temperature and many other parameters will have to be examined but we desire to grasp the trend of hydrogen storage data on the proposed method by experiments under typical conditions. Action was taken to coordinate the matters involved toward the continuance of a study on this topic in the next fiscal year.



- : Adsorption measured at 100 torr in vacuum after one-hour pretreatment
- : Desorption measured at 100 torr in vacuum after one-hour pretreatment
- : Adsorption measured at 25 torr in vacuum after one-hour pretreatment
- : Desorption measured at 25 torr in vacuum after one-hour pretreatment

**Fig.12.2.2-4 Changes in Hydrogen Adsorption Capacity of a partially carbonized ion-exchange resin at Room Temperature in Response to Variations in Pretreatment Conditions**

A study on gas turbine systems coupled with non-equilibrated methane reforming process

Methane, the main component of natural gas, reforms catalytically into a hydrogen-rich gas in the presence of steam. This process is an endothermic reaction and accordingly if a methane steam reforming process is coupled with gas turbine, the efficiency of power generation can be improved by chemical recovery of exhaust heat from gas turbines.

Based on the results of a study in the preceding year, an attempt was made in FY2001 to assess the viability of the proposed gas turbine system by studying the specifications of the membrane reactor-type reformer and preparing its detail design. A conceptual design of the reformer was drawn up based on calculations of a non-equilibrated methane reforming gas turbine system using a 4-MW simple cycle turbine available on the current market. The findings indicate that the system can hardly be realized because the reformer offers only a negligible effect of non-equilibrium when the hydrogen separation membrane has a permeability of  $10^{-7}$  mol/s/m<sup>2</sup>/Pa.

An equilibrated methane reforming gas turbine system has sufficient advantages to reach the stage where it can be commercialized by further efforts of equipment manufacturers. Meanwhile, the non-equilibrated methane reforming system has no significant advantage unless some technical innovations are made for the membrane.

The module designed during the study had little effect in total because, although higher efficiency could be attained by its non-equilibrated methane reforming configuration, the back pressure of the gas turbine rises in a corresponding degree. This does not mean that the membrane reactor itself is defective. In the next fiscal year, we will watch the technical trend of hydrogen separation membranes instead of continuing a study on the proposed system.

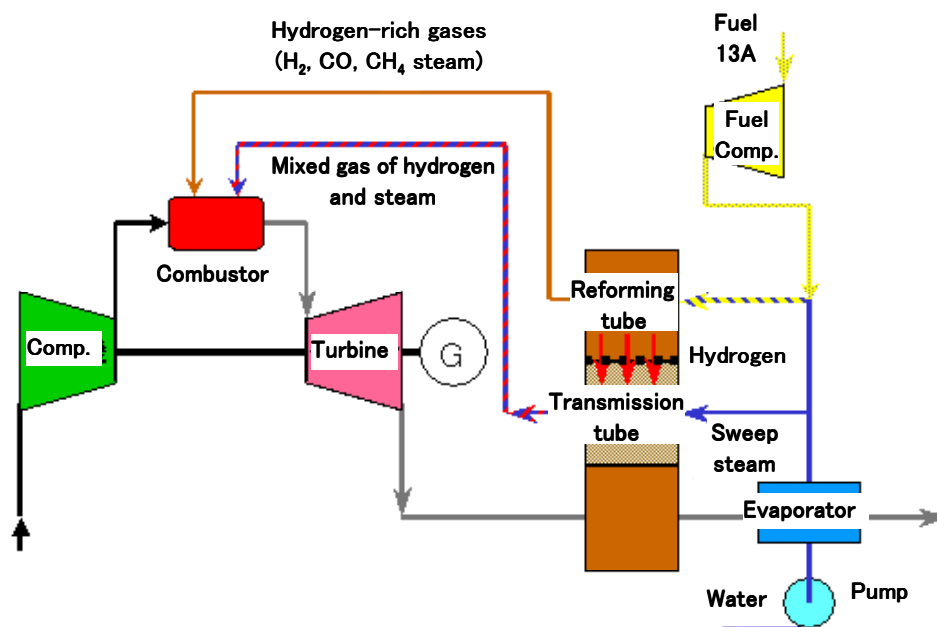
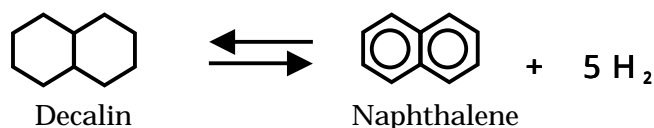


Fig. 12.2.2-5 gas turbine systems coupled with non-equilibrated methane reforming process

A technical study on a hydrogen storage system using new decalin/naphthalene hydrogenation and dehydrogenation processes based on a superheated liquid membrane method

Aromatic hydrocarbons such as naphthalene have been considered to be promising hydrogen carriers for installation of hydrogen fuel tank in fuel cell vehicles because they can be handled as easily as gasoline due to its hydrogen content and liquid form.

The catalytic reaction couple of decalin dehydrogenation and naphthalene hydrogenation has hydrogen storage density as high as 7.3 wt %.

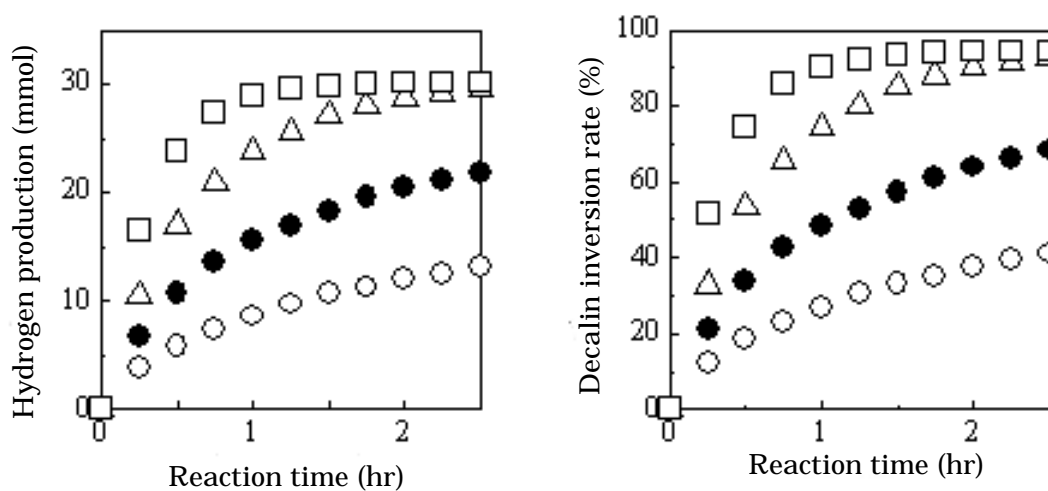


A study in FY2000 led to the discovery of a “superheated liquid membrane method” as a new non-equilibrated process in decalin dehydrogenation, indicating the possibility of more quantitatively assessing the characteristics of the proposed reaction method, depending on future progress of study on this topic. In FY2001, we made an experiment with a superheated liquid

membrane dehydrogenator aiming at further improvement of the conversion ratio. In parallel with the experiment, a series of surveys and studies was conducted to successfully deal with more realistic tasks necessary to design a total system for fuel cell vehicles using a decalin/naphthalene hydrogen storage and transport system.

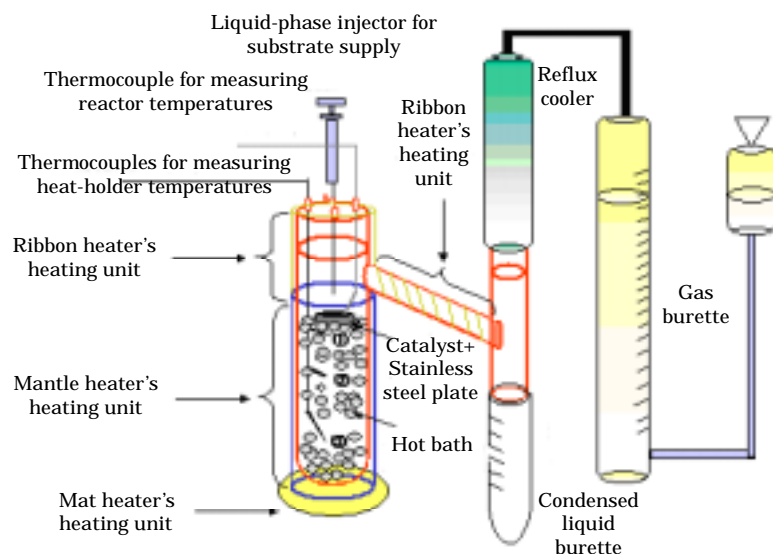
As a typical result, a hydrogen evolution of around 7.3 wt % (100% of theoretical value) was attained under an external heating condition of 280 °C during a test on the production of hydrogen from decalin by a Pt-Re composite catalyst.

In the next fiscal year, we are planning to step up the study from feasibility study level to a basic study level and install and operate a bench-scale testing apparatus (with a reactor capacity of 5L) on continuous dehydrogenation with a superheated liquid membrane to find scale up effects and make reaction engineering and chemical engineering analyses. The cost of the proposed system should be assessed under two conditions, one for hydrogen fueling stations and the other for fuel cell vehicles. Considering the recent climate for fuel cell vehicles (FCVs), we made arrangements for coordinating the matters involved to continue a study on the system in the next fiscal year with priority on engineering examinations (e.g., a system design and performance evaluation), holding in view the application of the system to hydrogen tanks to be installed in FCVs.



Catalyst: Pt/C (5 wt-metal %), Ratio of catalyst quantity to substrate quantity: 300 mg/1.0 ml  
 Reaction conditions: Boiling reflux (cooling at 5 °C and external heating at 210 °C (□), 240 °C (△), 260 °C (●), 280 °C (○))

**Fig. 12.2.2-6 Heating Temperature Dependence of Hydrogen Evolution from Decalin by Carbon-Supported Platinum Catalyst**



**Fig. 12.2.2-7 Continuous Decalin Dehydrogenation Test Apparatus**

A study on the method of producing hydrogen without generating carbon dioxide, using natural gas as raw materials, and an assessment of by-products

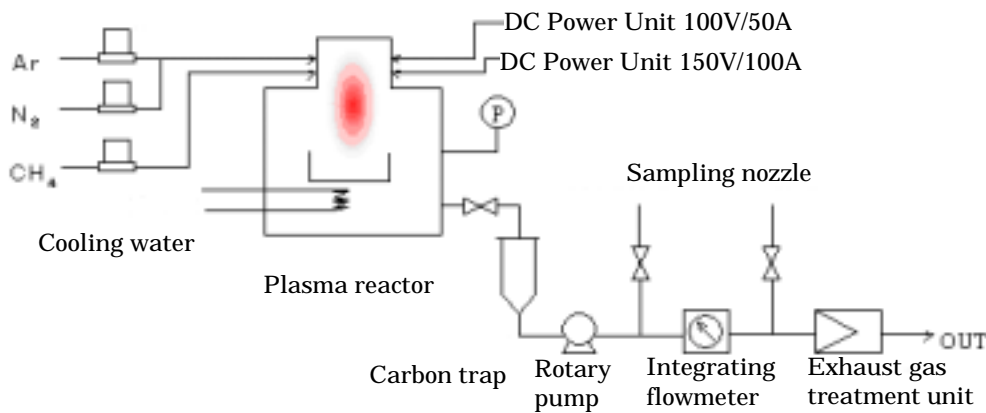
A study was conducted in FY2000 on the method of producing hydrogen from methane by a plasma process. It was found that the plasma hydrogen reformer technology developed by Kvaerner, a Norwegian corporation, is a notable technology already at the commercialization stage. In the practical application of the technology, however, it appears that no significant progress has been achieved in using produced carbon for high-value-added products as it is used mainly as a raw material for tires and some other rubber products. In FY2001, we carried out a study including a verification test on the feasibility of a technology for high-value-added uses of carbon materials obtained during the production of hydrogen from methane by a plasma process. The study also aimed at systematic formulation of a natural gas-based hydrogen production process that involves low CO<sub>2</sub> emissions. Major results of the study are summarized below:

- An attempt was made to determine the quantity of hydrogen produced by injecting methane into plasma whose working gas were Ar or N<sub>2</sub> or a mixed gas of Ar and N<sub>2</sub>. It was found that this process could achieve a methane conversion ratio of 96% or more.
- Carbon produced by plasma reaction showed a hydrophobic property in the case of Ar plasma, while in the case of N<sub>2</sub> plasma or Ar-N<sub>2</sub> plasma, it had a hydrophilic property. This indicates the possibility of utilizing it as carbon for ink.
- The electric energy required by the proposed process to produce 1 Nm<sup>3</sup> of hydrogen using natural gas ranged from 16 kWh to 70 kWh, which is far larger than 1.3 kWh required by Kvaerner's technology.



It is a good idea to store a by-product of the process as carbon instead of generating carbon dioxide but, if the by-product is used as a raw material as in this study, it would be finally disposed in an incineration system resulting in an emission of CO<sub>2</sub>. It is unlikely, therefore, that this process will lead to any reduction of CO<sub>2</sub> emissions.

The output of carbon as a by-product involves a significant consumption of energy. If the cost of producing hydrogen from methane is found to be lower than the cost of separating carbon dioxide from the combustion gas of methane and sequestering it in the sea by a comparison between them, a further study should be conducted on the proposed process. We decided to temporarily discontinue the study in the current fiscal year and reassess the cost of the process later if and when the introduction of a carbon tax, for instance, leads to the realization of CO<sub>2</sub> separation and storage technologies.



**Fig. 12.2.2-8 A Flowchart of the Plasma Reactor Used for the Experiment**

(2) Assessment of Basic Study Results Obtained in Fiscal 2001

A Basic study on hydrogen liquefaction technology with a magnetic refrigeration method

We started a basic study on this topic in FY2000. In the current fiscal year, we examined the realizability of hydrogen liquefaction based on a magnetic refrigeration method by carrying out a survey on elemental technologies that would serve as the key point of hydrogen liquefaction in a magnetic refrigeration type hydrogen liquefaction system with a throughput of 10 kg/day.

The study comprised a system analysis relating to preliminary drawings of series-and parallel-type AMRL (Active Magnetic Regenerative Liquefier) for a prototype hydrogen liquefaction system based on the magnetic refrigeration method with a throughput of 10 kg/day, the design and manufacture of an active magnetic regenerative refrigerator (AMRR) for Stage 1 of AMRL, the measurement of its pressure drop and thermal conductivity characteristics, and the design, manufacture and testing of a flow subsystem of heating fluid that connects AMR with heat sinks and thermal loads.

In taking specific measures for this purpose, we first selected Stage 1 for AMR experimental

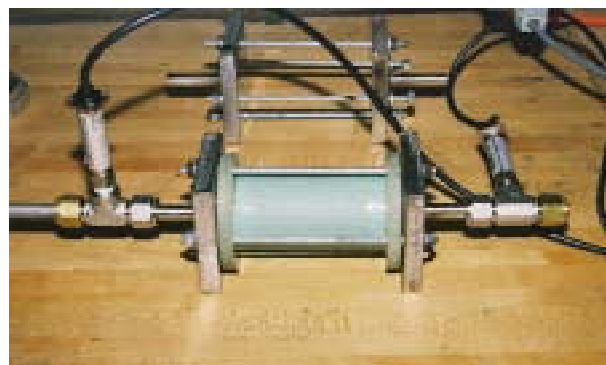
measurement. The temperature at Stage 1 is supposed to range from 200 K to 300 K. Then we decided on the parts, size and assembling method of the AMR. From heat transfer calculations, we adopted fine particle with a diameter of 250  $\mu$ m for the magnetic material and experimentally manufactured a monolithic AMR for stage 1 by an epoxy coating process. Three kinds of magnetic materials gadolinium and three  $Gd_{1-x}Dy_x$  alloys were used for the 1<sup>st</sup> stage AMR. Evaluating the performance of the 1st stage AMR in terms of Reynolds Number derived from nitrogen flow and a pressure drop through AMR, we verified the AMR had the specified performance.

During the FY2001 study, the design of the AMRL was changed from a rotary type to a stationary type for the following reasons: The aim of this basic study was to experimentally build a prototype hydrogen liquefaction system based on the magnetic refrigeration method with a throughput of 10 kg/day and verify the realizability of the proposed system from operational data on the experimental system. So far, no solution has been found to problems involved in sealing helium gas resulting from the use of an AMRL system. Accordingly we decided to evade tackling these problems by changing the AMRL from a rotary type to a stationary type. The alteration of the system does not cause any essential assessment problem to the “basic study on hydrogen liquefaction technology with a magnetic refrigeration method.” A study will be continued on necessary improvements and countermeasures to successfully cope with the helium-sealing problems and the results will be reflected in a large-capacity hydrogen liquefaction system that will be built in the years ahead.

The magnetic refrigeration type hydrogen liquefaction system is capable of significantly reducing liquid hydrogen production costs because of its advantage in such aspects as efficiency, initial investment and installation space. It is of great significance that a prototype testing unit will be built in FY2002 to assess the realizability of the magnetic refrigeration type hydrogen liquefaction system. Steps were taken to coordinate the matters involved so that a study will be continued on the proposed system in the next fiscal year.



**Fig. 12.2.2-9**



**Fig. 12.2.2-10**

Experimentally Made AMR for Stage 1

Measurement of Pressure Drop Data

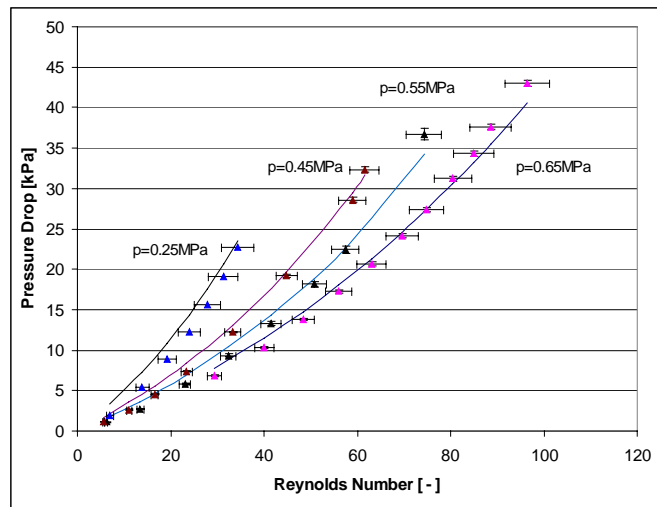
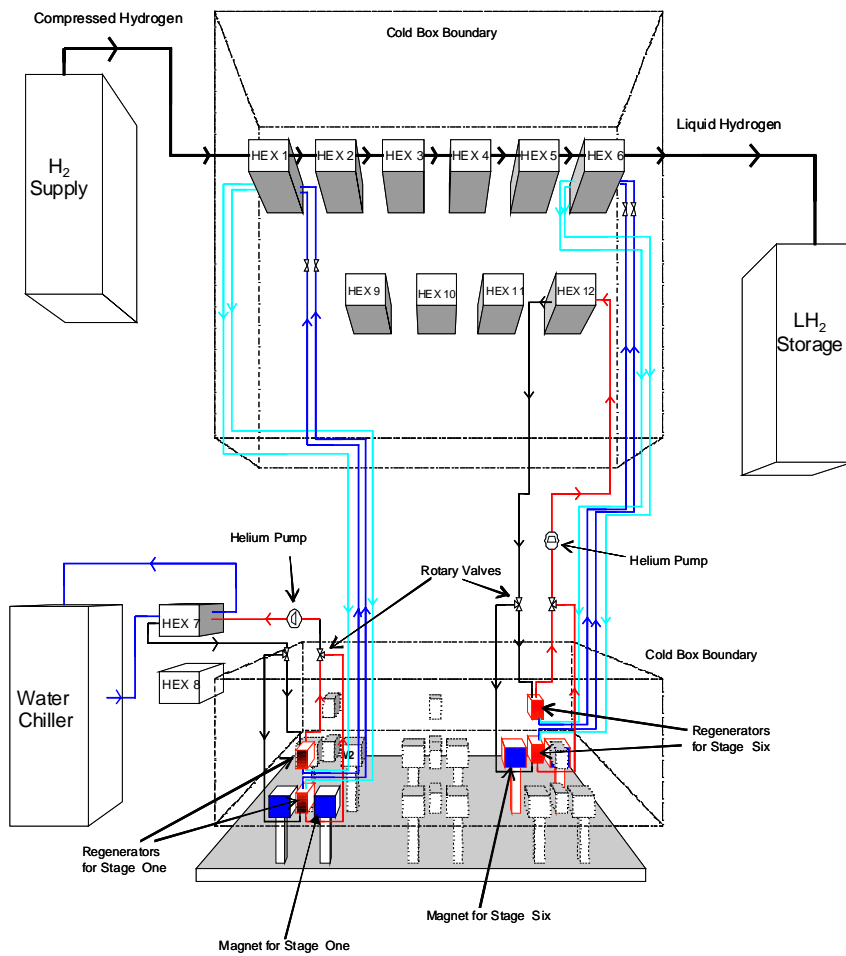


Fig. 12.2-11 Pressure Drop Data on the 1<sup>st</sup> stage AMR (as Adjusted by Reynolds Number)



### **Fig. 12.2.2-12 Flow System of Prototype Magnetic Liquefier**

A study on materials for magnetic liquefier of hydrogen

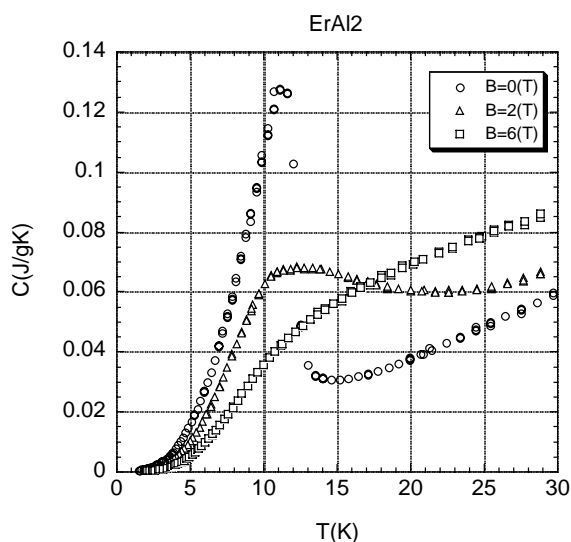
This study is based on a committee comment of FY2000, "Material data have to be verified in Japan as part of a basic study on hydrogen liquefaction technology with a magnetic refrigeration method."

The concept which serves as an essential element of performance in magnetic refrigeration relates to a calorific effect (a magnetic calorific effect) induced by variations in the magnetic entropy of a magnetic substance in response to an external magnetic field. However, entropy has to be converted on the basis of measured or calculated values of other physical properties because it is not a directly observable physical quantity. In this study, basic data on the refrigeration cycle were obtained by determining the temperature and magnetic field dependence curves of entropy from the measurement of magnetization and specific heat. The grades of magnetic materials were assessed by examining their magnetic structure and magnetic transition temperature. Concerning the thermal properties of magnetic materials, the study included the measurement of their thermal conductivity and thermal expansion coefficients and an assessment of their thermophysical properties.

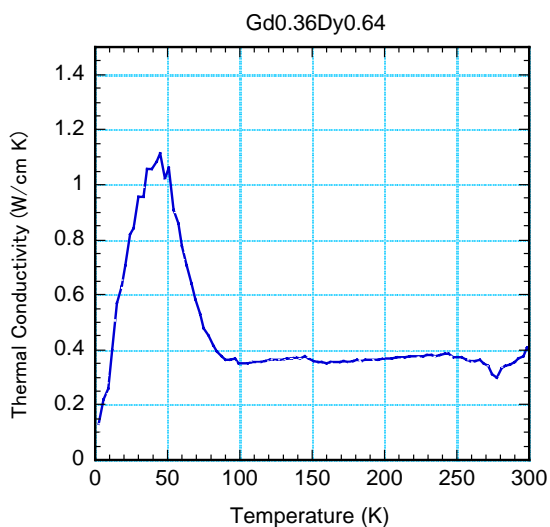
- Er-Dy-Al materials: Measured values concerning these materials are approximately equal to the relevant data in literature and they have desirable properties.
- Gd (SiGe) materials: These materials have a composite structure consisting of complex primary and secondary transitions. It is difficult to make entropy conversion from magnetization.
- Dy-Gd materials: The materials are subject to competitive magnetism between Dy and Gd in the vicinity of 200 K but probably no serious problem will occur in a high magnetic field above 1T and at >200 K, where the materials are expected to be used.
- Thermal conductivity: Presumably these materials are equal to SUS.
- Samples in general: Intermetallic Compounds of rare-earth are generally brittle and liable to oxidation. This tendency can be found from their cut surfaces.
- Thermal expansion coefficient: The thermal expansion coefficients of the materials, which will be measured later on, are predicted to vary at the magnetic transition temperature. Depending on the degree of such variation, it is necessary to consider the possibility of cracks resulting from a magnetization in cycle.

The assessment of magnetic materials is an important factor in building a prototype hydrogen liquefaction testing unit. In FY2001, some of the planned surveys on magnetic materials could not be carried out due to financing and time-frame limitations, and it is desirable to continue a study on these materials in the next fiscal year. Accordingly we have decided to properly

coordinate the matters involved so that the study will be continued in the next fiscal year.



**Fig. 12.2.2-13 Results of Measuring Specific Heat in ErAl<sub>2</sub>**



**Fig. 12.2.2-14 Results of Measuring Thermal Conductivity of Gd<sub>x</sub>Dy<sub>1-x</sub> (X = 0.36)**

### 2.3 A Search for New Areas and Items of Research and Development

The aim of the search is to examine promising technologies to be reflected in the WE-NET Project and to propose new areas and items of research and development. Since the study in FY2001 found that it is important to develop substitute catalyst materials for platinum group metals, Task 12 calls for conducting a study on this topic in FY2002.

#### (1) Necessity of Developing Substitute Catalyst Materials for Platinum Group Metals

It is pointed out that the market for platinum group metals (platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir) and osmium (Os)) may be seriously affected by the varying amounts of consumption because of such factors as the rarity of available resources, uneven distribution of production areas (with South Africa and Russia supplying more than 90% of platinum, palladium and rhodium) and oligopoly (80% of the market held by four major companies).

**Table 12.2.3-1 World Annual Supply of Major Platinum Group Metals (t/y)**

Platinum group metals	1999	2000	2001
Pt	151.5	164.6	173.5
Pd	250.7	242.6	234.2
Rh	15.6	23.8	17.6
Ru	12.8	13.7	N/A
Ir	2.89	3.86	N/A

**Table 12.2.3-2 Annual Supply of Major Platinum Group Metals by Region (t/y)**

	South Africa	Russia	North America	Others	Total
Pt	121.3	16.8	8.4	5	151.5
Pd	58.2	167.9	19.6	5	250.7
Ph	12.8	2	0.6	0.2	15.6

(2) A Survey on Trends in the Research and Development of Substitute Catalysts for Platinum  
As a preliminary examination, we conducted a survey on trends in the research and development of substitute catalysts for platinum.

The low-temperature fuel cells now under development use precious metals, particularly platinum, and their alloys as electrode catalysts. The survey found that research efforts are needed to research and develop a new, high-activity, oxygen-reduction catalyst.

### **12.3. Future Plan**

In order to attain the goal of making suggestions and proposals useful for the future of the WE-NET Project, we will, during this study, push forward with research activities on all technologies which are not covered by ongoing research and development under the WE-NET Project.

In the area of hydrogen liquefaction, we set about a “basic study on hydrogen liquefaction technology with a magnetic refrigeration method” in FY2000 and are planning to experimentally build the world first prototype hydrogen liquefaction unit based on the magnetic refrigeration method in the next fiscal year.

Concerning hydrogen storage technology, we carried out a study on a “new dehydrogenation process for a naphthene-base hydrogen storage system” in FY2000 and found some promising seeds. In FY2001, the phase of the study shifted to a “technical study on a hydrogen storage and transport system using new decalin/naphthalene hydrogenation and dehydrogenation processes based on a superheated liquid membrane method. At the laboratory level, the study verified the superiority of the proposed system in producing hydrogen in a superheated liquid membrane reactor. In the next fiscal year, we will increase the size of the experimental system and experimentally build a continuous dehydrogenation system using the superheated liquid membrane method on a scale of 1/ 20 of a supposed commercial plant.

Some of the technologies which we consider it unnecessary to study under the WE-NET Project at present may prove promising later on, depending on the future progress of research and development activities. In a bid to maintain the effectiveness of the WE-NET Project in the years ahead, we think we will have to keep watch over the trend of related technologies.