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HTTR WORKSHOP (WORKSHOP ON HYDROGEN PRODUCTION TECHNOLOGY)

July 5-6, 2004, JAERI, Oarai, Japan

December 2004

Department of HTTR Project
and
Department of Advanced Nuclear Heat Technology

日本原子力研究所
Japan Atomic Energy Research Institute

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HTTR Workshop (Workshop on Hydrogen Production Technology)
July 5-6, 2004, JAERI, Oarai, Japan

Department of HTTR Project
and
Department of Advanced Nuclear Heat Technology

Oarai Research Establishment
Japan Atomic Energy Research Institute
Oarai-machi, Higashiibaraki-gun, Ibaraki-ken

(Received October 15, 2004)

Various research and development efforts have been performed to solve the global energy and environmental problems caused by large consumption of fossil fuels. Research activities on advanced hydrogen production technology by the use of nuclear heat from high temperature gas cooled reactors, for example, have been flourished in universities, research institutes and companies in many countries.

The Department of HTTR Project and the Department of Advanced Nuclear Heat Technology of JAERI held The HTTR Workshop (Workshop on Hydrogen Production Technology) on July 5 and 6, 2004 to grasp the present status of R&D about the technology of HTGR and the nuclear hydrogen production in the world and to discuss about necessity of the nuclear hydrogen production and technical problems for the future development of the technology.

More than 110 participants attended the Workshop including foreign participants from USA, France, Korea, Germany, Canada and United Kingdom.

In the Workshop, the presentations were made on such topics as R&D programs for nuclear hydrogen production, heat utilization of nuclear energy and hydrogen production technologies by thermo-chemical or other processes. Also, the possibility of the nuclear hydrogen production in the future society was discussed. The workshop showed that the R&D for the hydrogen production by the thermo-chemical process has been performed in many countries.

The workshop affirmed that nuclear hydrogen production could be one of the competitive supplier of hydrogen in the future. The second HTTR Workshop will be held in the autumn next year.

Keywords: Hydrogen, HTGR, HTTR, Nuclear Heat, Thermo-chemical Process, IS Method Electrolysis

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(Eds.) Yasuaki SHIINA, Takakazu TAKIZUKA (Department of Advanced Nuclear Heat Technology)

JAERI-Review 2004-026

ＨＴＴＲワークショップ（水素製造技術に関するワークショップ）報告
2004年7月5日～6日、大洗研究所、大洗町

日本原子力研究所大洗研究所
高温工学試験研究炉開発部・核熱利用研究部

（2004年　10月15日受理）

現在、化石燃料の大量消費に起因する地球環境・エネルギー問題に対処するためにさまざまな研究開発が行われており、高温ガス炉等の核熱を利用した新しい水素製造システムの実現に向けた研究開発が各国の大学、研究機関、企業等において盛んに行われている。

日本原子力研究所、高温工学試験研究炉開発部及び核熱利用研究部は、高温ガス炉の実用化を目指した高温ガス炉技術、及び未だ多くの技術的課題があると考えられる核熱を利用した水素製造技術の研究開発に関して、現状把握及び将来技術としての位置づけと技術的課題に関する討論を目的として、2004年7月5日-6日に大洗研究所においてHTTRワークショップ（水素製造技術に関するワークショップ）を行った。

本ワークショップでは、国外からは米国、フランス、韓国、ドイツ、カナダ、イギリスの研究者を含む国内外合わせて110名を超える参加者により活発な討論が行われた。

会議では各国の研究開発の現状と方向、高温ガス炉と核熱利用システムの接続技術開発、熱化学法等による水素製造に関する研究の現段階に関する発表及び将来社会における核熱を利用した水素製造の可能性についての討論が行われたが、特に熱化学法による水素製造の研究が各国において盛んに行われていることが示された。

会議は、将来の水素社会において核熱による水素製造が有力な水素供給手段になりうることを確認し、来年秋に第2回のワークショップを行うことが報告されて終了した。

大洗研究所: 〒311-1394　茨城県東茨城郡大洗町成田町新堀3607
（編）椎名保顕・滝塚貴和（核熱利用研究部）

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1. Preface

Various research and development efforts have been performed to solve the global energy and environmental problems caused by large consumption of fossil fuels. Research activities on advanced hydrogen production technology by the use of high temperature gas cooled reactors have been flourished in universities, research institutes and companies in many countries. There still remain many technical problems, however, to be solved before application of future systems for hydrogen production.

The 15th World Hydrogen Energy Conference was held on June 27－July 2, 2004 in Yokohama, Japan. Taking this opportunity, we planned to invite the worldwide experts and held a workshop (HTTR workshop－Workshop on Hydrogen Production Technologies) at the Oarai Research Establishment of the Japan Atomic Energy Research Institute (JAERI) on July 5 and 6.

The objective of the workshop was to bring together experts in HTGR technology and advanced hydrogen production technology to encourage the exchange of information on state-of-the-art technology, to identify major R&D issues, to assess its feasibility and to explore the future development. More than one hundred participants attended the workshop including 21 foreign attendants from USA, France, Korea, Germany, Canada and United Kingdom.

At the beginning of the workshop, Dr. S.Shiozawa, Director general of the Oarai Research Establishment presented opening remark and Treasurer of Oarai Town presented welcome remark on behalf of the Mayer of Oarai Town.

Technical sessions followed the opening and welcome remarks. The technical sessions consisted of the following five sessions:

(1) Session 1: Country reports
(2) Session 2: Discussion about Hydrogen Production Technologies by Nuclear Energy
(3) Session 3: Heat Utilization of Nuclear Energy
(4) Session 4: Hydrogen Production Technologies
(5) Session 5: Thermo-Chemical Process

The presentations and discussions in each session are as follows.

(1) Session 1: Country report of R&D program for hydrogen production technologies

Dr. T.Iyoku(JAERI, Japan) made a presentation about the achievement of 950℃ high temperature operation of HTTR and success in the hydrogen production operation by Iodine-Sulfur(IS) method and future R&D program of HTGR and hydrogen production.

Dr. D.Henderson(DOE, USA) presented the hydrogen production program by nuclear energy including the Nuclear Energy Research Initiative(NERI) in USA. The hydrogen production program by nuclear energy in the USA has three phases such as laboratory scale, pilot plant scale and engineering scale, and the thermo-chemical process and high temperature electrolysis have higher priority in USA.

Dr. F.Werkof (CEA, France) presented the outline of the research on the hydrogen production by IS method progressed in France. In the presentation, a flow-sheet of the Bunsen reaction, liquid-vapor equilibrium measurements of HI-I_2-H_2O solution and research on a hydrogen separation membrane in the HI reaction are introduced. He also presented that Westinghouse process and high temperature vapor electrolysis are regarded as second candidate of the hydrogen production.

Dr. Y-J. Shin (KAERI, Korea) presented the research program of hydrogen production in KOREA. The high priority hydrogen production processes are the IS process, high temperature electrolysis and MMI (Methane – Methanol – Methyl-Iodine) cycle. Discussion was made about the selection of reactions in MMI cycle and the situation of steam reforming in Korea.

Dr. K. Verfondern (FZJ, Germany) reported the hydrogen and fuel cell program in the sixth frame work program of EC(European Commission) as the hydrogen production program by nuclear energy in EU. He introduced the projects on thermo-chemical process, high temperature electrolysis and biomass heat as hydrogen production method. He also reported that the VHTR-Integrated Program was now under negotiation in EC.

Dr. A.Miller (AECL, Canada) introduced analytical results of the opening the market of hydrogen and cost estimation about hydrogen produced by nuclear heat. He also reported that electrolysis of water has an advantage in the flexibility on hydrogen production and that hydrogen production by the use of the off-peak electric power of Generation Ⅲ nuclear energy is the most promising.

After the session 1, technical tour was performed to visit the HTTR and the test facilities of nuclear heat utilization including the experimental apparatus of IS process.

(2) Session 2 : Discussion about Hydrogen Production Technologies by Nuclear Energy

At the beginning of the Session 2, Dr. Takeda (JAERI, Japan) presented comparison of the estimated cost of hydrogen produced by a thermo-chemical method with that produced by other methods such as reforming of fossil resources, electrolysis of water and solar or wind power. He concluded that hydrogen produced by nuclear energy would be able to compete with that produced by other energy in future Japan. After the presentation, subsistent possibility of the hydrogen production by nuclear energy from the economical viewpoint in the future society was discussed among the attendants. Many opinions were presented such that energy price depends on political affairs because renewable energy receives financial support from the government or that construction cost of HTGR plant would be the limiting hurdle to reduce nuclear hydrogen price for such countries as the USA where the price of the electricity is cheap. Finally, attendants affirmed that nuclear hydrogen would be one of the dominant source of hydrogen supply among the several hydrogen supplies in the future.

(3) Session 3: Heat Utilization of Nuclear Energy

Dr. Y.Kato (TITech, Japan) presented a conception of hydrogen production system which produces hydrogen and circulates carbon by the use of CaO. This system aims zero emission cycle of CO_2 such that a car is driven by the hydrogen produced by the reaction between methane and CaO and generated CO_2 in the reaction is adsorbed by CaO, and such that the CO_2 is recycled by the use of nuclear energy. He presented the experimental results of the cycle.

Dr. K.Kunitomi (JAERI, Japan) presented a nuclear system GTHTR300C which generates hydrogen and electricity simultaneously. The system is based on the proposed gas turbine HTR plant, GTHTR300. He also presented design of an intermediate heat exchanger, total reactor system and conception of co-generation of hydrogen and electricity.

Dr. Y.Inagaki (JAERI, Japan) presented the development of interface technology between an HTGR and a nuclear heat application system. He presented the results of performance test of out-of-pile test facility. The test facility includes a steam generator which is the steam supplier of the system and also used to isolate thermal load generated in the hydrogen production process from the reactor. He introduced a mock-up model of a high temperature isolation valve.

(4) Session 4 : Hydrogen Production Technologies

Dr. K.Verfondern (FZJ, Germany) presented evaluation of the safety concept of the combined nuclear/chemical complex for hydrogen production with HTTR. He presented the experimental results of the flame propagation velocity and the safety distance between the reactor and LNG tank. He compared the guideline of the safety distance in USA, Germany and Japan. He suggested that machinery in the reactor building would be protected more safely from LNG explosion by improved design of reactor building.

Dr. M.Richard (GA, USA) presented a concept of the 600-MW Modular High Temperature Reactor(MHR). He reported that the exit temperature of the reactor would be about 950-1000°C to use for hydrogen production and also he explained the design concept of the reactor, fuel configuration in the reactor core, coolant flow distribution and its control method.

Dr. J.S.Herring (INEEL, USA) presented the R&D for hydrogen production by the high temperature electrolysis with solid oxide membrane by the use of nuclear energy in the USA. He reported the electric voltage-current characteristics of a button cell, hydrogen production test results of cell stack experiment and a concept of a high temperature electrolysis plant.

(5) Session 5 : Thermo-Chemical Process

Dr. M.Kawaji (Tronto Univ., Canada) presented hydrogen production using thermo-chemical process and biomass heat from the combustion of wood waste in Canada.

Conceptual design of the hydrogen production system and the estimated amount of hydrogen production using the biomass heat in Canada were presented. He also reported that main subject of the research is improving efficiency, which could be improved up to near 50% theoretically.

Dr. G-J Hwang (KIER, Korea) presented hydrogen production using thermo-chemical process in Korea. He presented research phase of IS process in Korea and the research subjects in the first stage. He introduced experimental apparatus of bunzen reaction, method for improving efficiency using membrane and outline of the material corrosion test.

Dr. T.Nakagiri (JNC, Japan) presented hybrid hydrogen production using thermo-chemical process and electrolysis with the heat from a fast breeding reactor(FBR). In the presentation, experiment of electrolytic SO_3 with solid electrolyte, thermal efficiency estimation and a plant concept of the hybrid hydrogen production using a FBR were explained. He also reported the recent experimental results of the hybrid process.

Dr. H.Kawamura (CRIEPI, Japan) presented development of electrode material with high electrical conductivity for sulfur-cycle hybrid hydrogen production system. He presented the effects of electrical conductivity and corrosion resistance of ceramics with pyrochlore structure on hydrogen production by electrolysis of H_2SO_4.

2.Agenda

HTTR Workshop
Workshop on Hydrogen Production Technologies
July 5－6, 2004

Department of Advanced Nuclear Heat Technology
Japan Atomic Energy Research Institute

(Workshop Chairman Dr. Yasuaki Shiina/ JAERI/ Japan)

AGENDA

Topic		Name/Organization/Country	Time
Monday, July 5, 2004			
Auditorium, Safety Information Exchange building			
1. Opening Remarks			13:20-13:30
Director General of Oarai Research Establishment		Dr. Shusaku Shiozawa	
Treasurer of Oarai town (on behalf of town mayer)		Mr. Shin'ichi Haga	
2. Session 1			13:30-14:45
Country Report of R/D Program for Hydrogen Production Technologies			
Chairman		Dr.Alister Miller/ AECL/ Canada	
Presenter	Japan	Dr.Tatsuo Iyoku/ JAERI/ Japan	
	USA	Dr.David Henderson/ DOE/ USA	
	France	Dr.Francois Werkoff/ CEA/ France	
COFFEE BREAK			14:45-15:05
3.Continue with Session 1			15:05-16:20
Chairman		Dr. Alister Miller	
	Korea	Dr.Young Joon Shin/ KAERI/ Korea	
	EU	Dr. Karl Verfondern/ FZ-Juelich/ Germany	
	Canada	Dr. Alister Miller/ AECL/ Canada	
WORKSHOP PHOTOGRAPH			
TOUR (HTTR and Heat Utilization Experimental Facilities)			16:30-18:00
BUFFET BANQUET (Asahi-Bunshitsu)			18:30-20:00
Tuesday, July 6, 2004			
Conference room, Fourth floor, HTTR Research Building			

Topic	Name/Organization/Country	Time
4. Session 2		9:20-10:25
Discussion about Hydrogen Production Technologies by Nuclear Energy		
Chairman	Dr.Kazuhiko Kunitomi/ JAERI/ Japan	
	Dr.David Henderson/ DOE/ USA	
Presenter	Dr.Tetsuaki Takeda/ JAERI/ Japan	
COFFEE BREAK		10:25-10:45
5. Session 3		
Heat Utilization of Nuclear Energy		10:45-12:00
Chairman	Dr.David Henderson/ DOE/ USA	
Presenter	Dr.Yukitaka Kato/ TITech/ Japan	
	Dr.Kazuhiko Kunitomi/ JAERI/ Japan	
	Dr.Yoshiyuki Inagaki/ JAERI/ Japan	
LUNCH (Cafeteria)		12:00-13:30
6.Session 4		13:30-14:45
Hydrogen Production Technologies		
Chairman	Dr.Francois Werkoff/ CEA/ France	
Presenter	Dr.Karl Verfondern/ FZ-Juelich/ Germany	
	Dr.Matthew.B.Richards/ GA/ USA	
	Dr.James S.Herring/ INEEL/ USA	
COFFEE BREAK		14:45-15:05
7. Session 5		15:05-16:45
Thermo-Chemical Process		
Chairman	Prof.Ray W.K.Allen/ Shefield Uiv./ UK	
Presenter	Prof.Masahiro Kawaji/ Toronto Univ./ Canada	
	Dr.Gab Jin Hwang/ KIER/ Korea	
	Dr.Toshio Nakagiri/ JNC/ Japan	
	Dr.Hirotaka Kawamura/ CRIEPI/ Japan	
8. Concluding Remarks		
Director of HTTR Dept. Dr.Seigou Fujikawa		

3. Opening Remarks

Shusaku SHIOZAWA

Director General of Oarai Research Establishment of JAERI

Good afternoon, ladies and gentlemen,

I am Shusaku Shiozawa,
Director General of Oarai Research Establishment, JAERI.

On behalf of JAERI, I would like to extend a cordial welcome to all of you gathering here at the Oarai site for the HTTR Workshop.
I am especially grateful to the participants from overseas' countries.

As we have well understood, the hydrogen age is coming up soon to give one of the solutions against the global environmental issues of the emission of greenhouse effect gases such as carbon dioxide, as well as to secure the global energy supply.

It is also widely recognized that the nuclear energy would make a significant contribution to produce hydrogen without emitting carbon dioxide. Among the nuclear energy, the high temperature gas-cooled reactor is thought to be most promising tool for the future application to produce hydrogen because of its capability of high temperature supply to the production systems.
On the basis of this recognition, Japan Atomic Energy Research Institute, JAERI is proceeding with the HTTR Project. The HTTR Project is a national project to commercially develop the hydrogen production systems using high temperature gas-cooled reactors, including nuclear reactor technology and its heat application technology of hydrogen production.
Regarding the nuclear reactor technology, the HTTR, which is the first high temperature gas-cooled reactor in Japan, was built here at the Oarai site. In the HTTR, 950 degree centigrade of high temperature helium gas was successfully taken out from the rector. This was the first achievement in the world and I think that with this success we have passed the first step toward the hydrogen production using high temperature gas-cooled reactor.
JAERI will continue the HTTR operation and testing to setup the database regarding the nuclear reactor technologies.

On the other hand, regarding the hydrogen production technology, the Iodine – Sulfur process (so-called IS process) was selected as one of the most promising systems to be coupled with high temperature gas cooled reactor. In the development of the IS Process, we have recently succeeded in the continuous loop operation of the system.
The latest fruits from the HTTR Project are introduced in the workshop later.

Under this situation, it is our pleasure to have the workshop on hydrogen production technologies at this timing and at this area of Oarai site.
The objectives of the workshop are:
・ Firstly to make information exchange on the latest status of research and development on

hydrogen production technologies, and

- Secondary to identify important and necessary research and development subjects to be done in the future to produce hydrogen.

Furthermore, as far as I understand, in the workshop strategic discussion is to be done for suggesting the direction of the future worldwide research and development.
I hope that the workshop will be successful and useful for the worldwide activities towards the hydrogen society.

Finally I would like all of you to enjoy the stay here today and tomorrow.
Also I hope that you will be refreshed with the nice climate and atmosphere of Oarai area as well as hospitality of the nice people in Oarai.

Thank you very much.

4. Welcome Message from the Mayor of Oarai Town

Sin'ichi HAGA

Tresurer of Oarai Town (on behalf of the Mayor of Oarai Town)

Ladies and gentlemen,

As Mayor of the town of Oarai, I am pleased to welcome you to Oarai town.
Oarai is facing the Pacific Ocean that blesses us with mild climate and gentle natural features. The town has been developed as a spot of sightseeing and a base of fishery industry.

In 1967, the Oarai Research Establishment of the Japan Atomic Energy Research Institute was set up here. Since then, nearly 40 years have passed and our town has also been characterized as a center of nuclear power.

In recent years, it is expected to realize the hydrogen energy society in the course of this century. Hydrogen energy is clean in the sense that it burns without discharging greenhouse gases, which are suspected of causing global warming.

We are looking forward to your efforts to lead the hydrogen energy society to come through the research and development of high temperature gas cooled reactors and heat utilization technologies.

We hope you enjoy your stay in Oarai even though for only two days, and we wish you make this workshop a great success.

Thank you very much.

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5. Technical Sessions

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5.1 Session1: Country Report for Hydrogen Production Technologies

5.1.1 Present Status of HTTR Project

Tatsuo Iyoku
Department of HTTR Project, Japan Atomic Energy Research Institute
Narita-cho, Oarai-machi, Ibaraki-ken, 311-1394, Japan

The High Temperature Gas-cooled Reactor (HTGR) is particularly attractive due to its capability of producing high temperature helium gas as well as its inherent safety characteristics. Hence, perspective of HTGR as possible future nuclear energy source was discussed in the review of "Long-term Program for Research, Development and Utilization of Nuclear Energy" by the Atomic Energy Commission of Japan, and the High Temperature Engineering Test Reactor (HTTR), which is the first HTGR in Japan, was successfully constructed at the Oarai Research Establishment of the Japan Atomic Energy Research Institute.

The HTTR attained the first criticality on November 10, 1998 and achieved the full power of 30MW and the reactor outlet coolant temperature of 950°C on April 19, 2004. The hydrogen production was demonstrated over one week with the IS process bench plant using newly developed control method and devices. The purpose of the HTTR project is to establish and upgrade HTGR technologies. It is widely recognized to the nuclear community that the timely and successful operation and tests of the HTTR are major milestones in development of the HTGR and high temperature nuclear process heat application. Extensive tests such as safety demonstration tests are now performing using the HTTR and a process heat application system will be coupled to the HTTR, where hydrogen will be produced directly from the nuclear energy.

KEYWORDS: *HTGR, HTTR, Full power operation, Rise-to-power test, Safety demonstration test, Nuclear heat utilization, IS process, Hydrogen production*

Present status of HTTR project

Tatsuo Iyoku
Department of HTTR Project
Oarai Research Establishment, JAERI

Presented at the HTTR Workshop.
Workshop on Hydrogen Production Technologies
July 5-6, 2004

1

Toward the Hydrogen Energy Utilization

Current Society depends on fossil energy

- Exhaustion of fossil energy
- Effects on global environment; acid rain, global warming, etc.

Activities on Hydrogen in Japan

"Basic Plan for Energy Supply and Demand"
based on "Basic Law on Energy Policy Making"
(Decided upon by the Cabinet on 6 October, 2003)

Effort for Hydrogen Energy Utilization (Chapter 2, section 6.3)

- Hydrogen is a clean energy carrier without CO_2 emission.
- Commercialization of hydrogen production system using nuclear, solar and biomass, not fossil fuels, is desired.

2

Features of HTGR

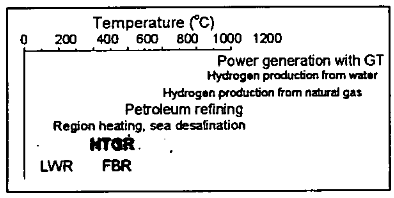
Inherent safety

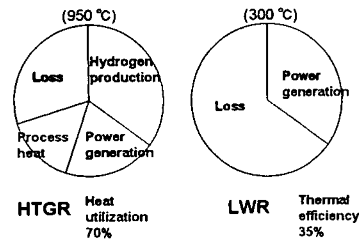
- Fuel (TRISO coated fuel particles)
  : High thermal integrity,
  High FP retention capability
- Core components (graphite)
  : No meltdown
  Slow temperature transient
- Coolant (helium-gas)
  : No phase change
  No chemical reaction

⇩

•No accidents causing large scale fuel failure or core meltdown

Extension of nuclear heat utilization



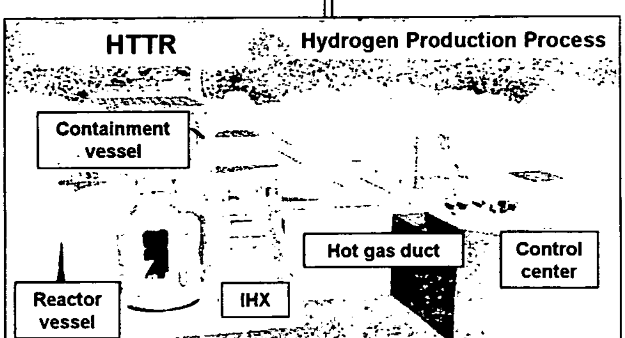


3

HTTR Project

Objective: **Establishment of HTGR technology**
Establishment of heat utilization technology

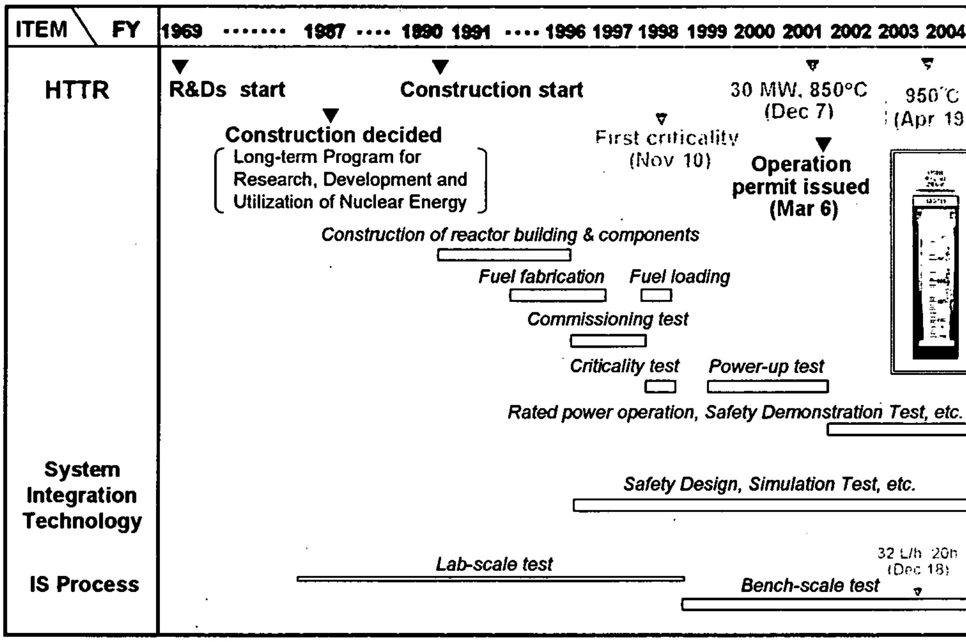
Reactor Technology	System Integration Technology	Hydrogen Production Technology



Bench-scale apparatus of IS Process

4

History of HTTR Project



5

HTTR: Major Technical Achievements

"Establishment of major technological basis for HTGR"

Metallic Materials

- ***Heat and corrosion resistant super alloy Hastelloy XR*** (~1000°C, Corrosion resistance)

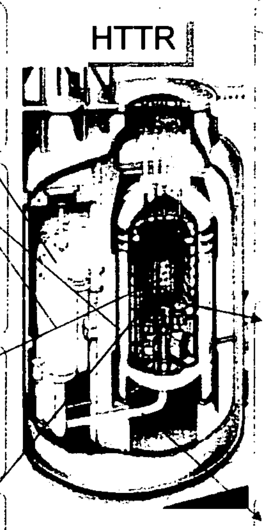
Design Guideline for High Temperature Components

- ***High temperature structural design guideline*** (~1000°C for Hastelloy XR)

Reactor Physics

- ***R&D using VHTRC*** (Critical mass, Neutron flux distribution, Control rod worth, etc)

Seismic Design of Multi Layered Structure of Graphite Blocks



Fuel

- ***Fabrication technology*** (Low as-fabricated failure fractions; 2×10^{-6} (Through coatings failure fraction), 8×10^{-5} (SiC failure fr.))
- ***Irradiation tests at OGL-1*** (Irradiation temp.: 1350~1500 °C, Burnup: 3.9 %FIMA(max.))
- ***Design Guideline for fuel***

Graphite

- ***High grade graphite IG-110*** (Irradiation temp.: ~1300°C, Neutron fluence: ~ 3.8×10^{26} n/m^2)
- ***Design Guideline for graphite components***

Thermal Hydraulics

- ***R&D using HENDEL***

6

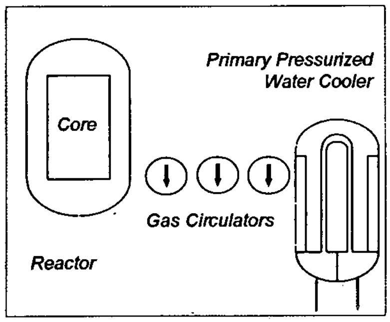
Safety Demonstration Test using HTTR

Objective

To demonstrate Inherent Safety Features of HTGRs under conditions simulated:

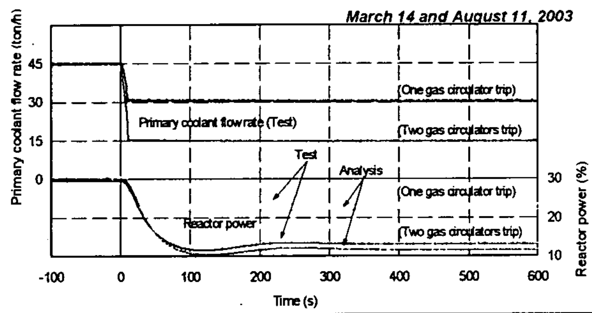
- ***Malfunction of Cooling System and***
- ***Malfunction of Reactivity Control System***

- ***Improve safety evaluation technologies of HTGRs***
- ***Contribute to VHTR System (Gen IV)***



An Example of Test Result
(Coolant Flow Reduction Test)

- *Test result;*
  Reactor power decreased to a stable level only by negative reactivity feedback.

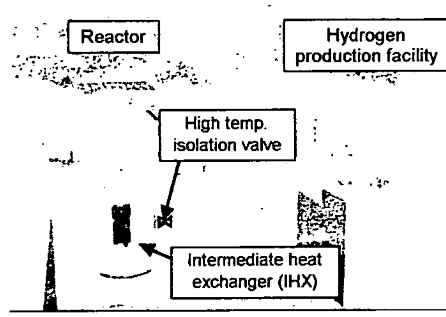


[This study is entrusted from MEXT of Japan.]

7

System Integration Technology

- **Objective**
  - Development of technology for safe and economical connection between reactor and hydrogen production facility
- **R&D Items**
  - Safety technology against explosion
    - Design for protection and mitigation against combustible gas release: underway
    - Estimation of damage on nuclear plant by blast waves from explosion: underway
  - Safety technology against radioactive materials release
    - Development of high temp. isolation valve: underway
    - Estimation of tritium permeation passing through IHX: finished
  - Control technology
    - Prevention of thermal disturbance from hydrogen production facility to reactor by steam generator : finished
  - Plant simulation code
    - Verification by simulation test: underway



[This study is entrusted from MEXT of Japan.]

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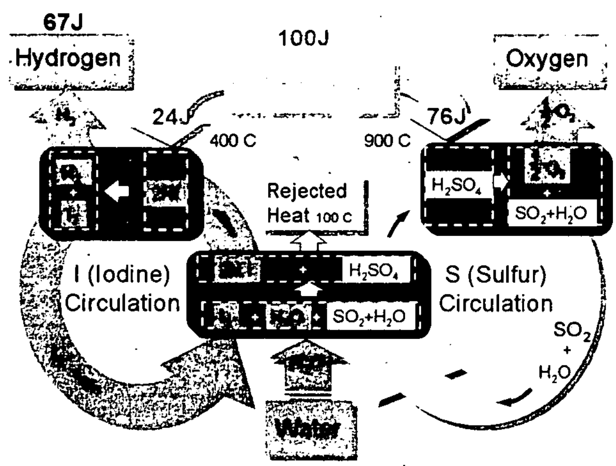
Hydrogen Production Technology



IS Process

- ***Hydrogen from water and nuclear heat (CO_2 free)***
- ***Thermochemical cycle***
- ***Iodine- and Sulfur-compounds are used as recycling materials***

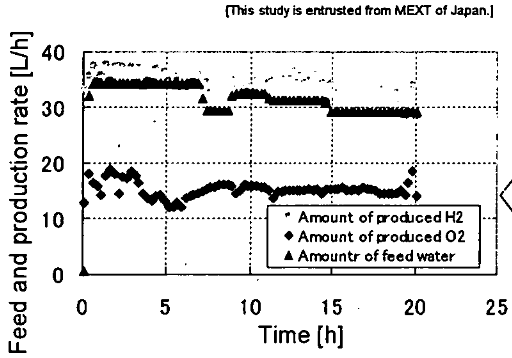
9

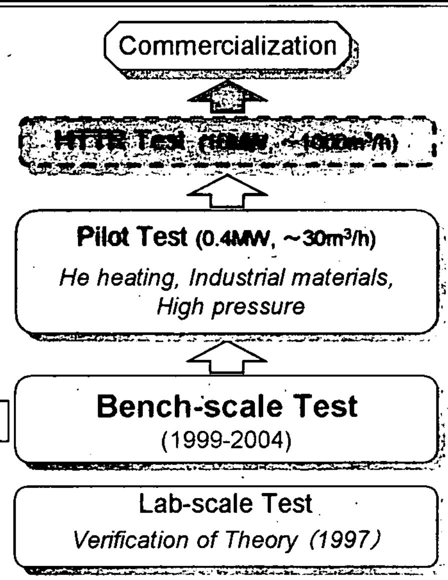
R&D on IS Process

Completion of Hydrogen Production (Dec. 2003)

Continuous hydrogen production was successfully achieved at the hydrogen production rate of 32 NL/h for 20 hours.

[This study is entrusted from MEXT of Japan.]





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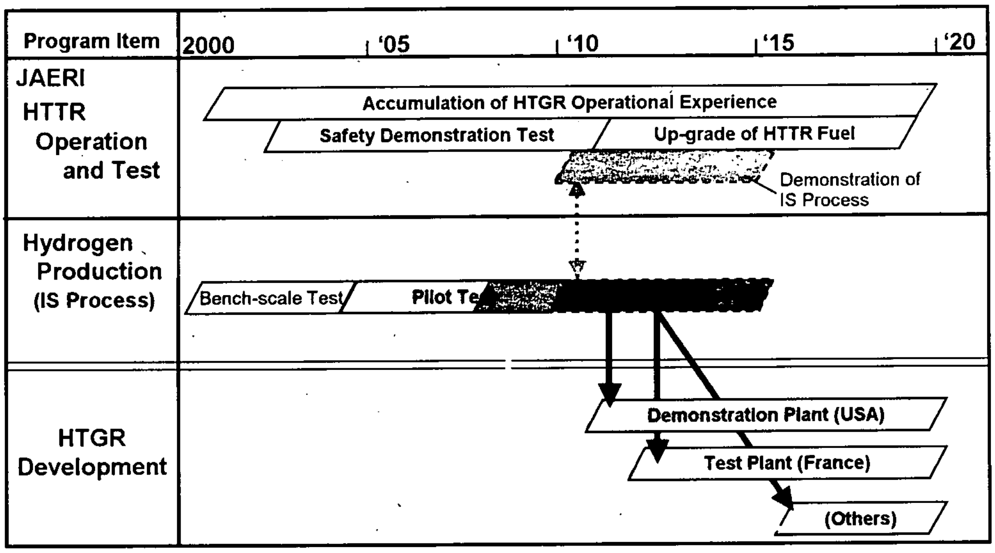
International Collaboration on HTGR and Hydrogen Production System (JAERI's Proposal)



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Summary

JAERI is conducting HTTR Project on HTGR and hydrogen production system.

HTTR has demonstrated the reactor outlet temperature of 950°C. Safety demonstration test is underway.

System integration technology is under development for safe and economical connection between reactor and hydrogen production facility.

Bench-scale test is underway on IS process for hydrogen production from water.

The pilot test is planned.

JAERI proposes an international collaboration on HTTR project.

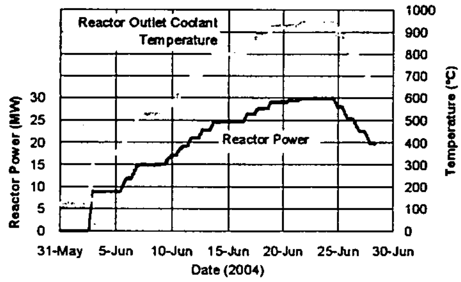
12

Latest Topics

Reactor Technology

Performance tests at 950°C were completed, and JAERI received an operation permit for the high-temperature test operation (950°C operation) from the government.

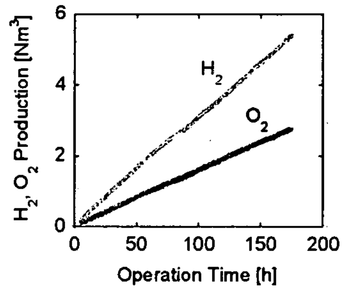
(June 24, 2004)



Hydrogen Production Technology

H_2 production was demonstrated over 1 week with the IS process bench plant using newly developed control method and devices, which will be applied to the pilot plant. [This study is entrusted from MEXT of Japan.]

(June, 2004)



5.1.2 Nuclear Hydrogen Initiative

Ashley David Henderson
DOE. USA

Clean forms of energy are needed to support sustainable global economic growth while mitigating greenhouse gas emissions and impacts on air quality. To address these challenges, the U.S. President's National Energy Policy and the U.S. Department of Energy's (DOE's) Strategic Plan call for expanding the development of diverse domestic energy supplies. Working with industry, the Department developed a national vision and roadmap for moving toward a hydrogen economy—a solution that holds the potential to provide sustainable clean, safe, secure, affordable, and reliable energy. DOE has examined and organized its hydrogen activities in pursuit of this national vision. This includes the development of fossil and renewable sources, as well as nuclear technologies capable of economically producing large quantities of hydrogen.

Nuclear Hydrogen Initiative

David Henderson

Office of Nuclear Energy, Science and Technology

Workshop on Hydrogen Production Technologies

Oarai, Japan

July 5, 2004

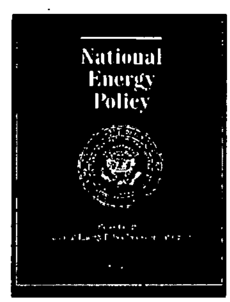
Office of Nuclear Energy, Science and Technology

The National Energy Policy Recommends:

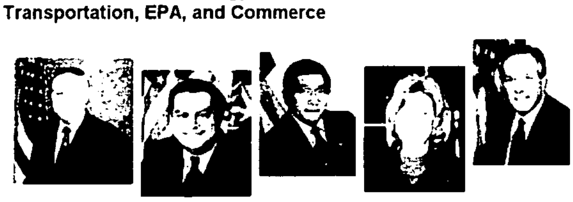
"The expansion of nuclear energy in the U.S."

Development of "next generation technology – including hydrogen," and that

"The U.S. should consider technologies...to develop reprocessing and fuel treatment...that are cleaner, more efficient, less waste-intensive, and more proliferation-resistant"



– Vice President Cheney, and the Secretaries of State, Energy, Transportation, EPA, and Commerce



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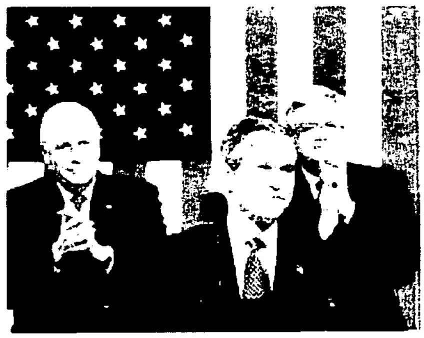
The Hydrogen Economy

"A single chemical reaction between hydrogen and oxygen generates energy, which can be used to power a car -- producing only water, not exhaust fumes. With a new national commitment, our scientists and engineers will overcome obstacles to taking these cars from laboratory to showroom, so that the first car driven by a child born today could be powered by hydrogen, and pollution-free... Join me in this important innovation to make our air significantly cleaner, and our country much less dependent on foreign sources of energy."



President Bush's 2003 "State of the Union Address"

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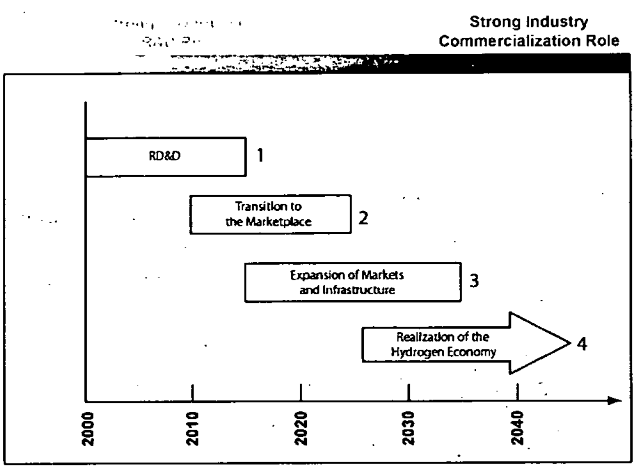
Development of the Hydrogen Economy



Transitional Phases

1. **Technology Development Phase**
   H_2 power and transport systems available in select locations; limited infrastructure
2. **Initial Market Penetraion Phase**
   H_2 power and transport systems begin commercialization; infrastructure investment begins with governmental policies
3. **Infrastructure Investment Phase**
   H_2 power and transport systems commercially available; infrastructure business case realized
4. **Fully Developed Market and Infrastructure Phase**
   H_2 power and transport systems commercially available in all regions, national infrastructure

03-GA51038-14

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DOE Hydrogen Program

- $1.2 Billion over five years (FY 2004-2008)
- Production goal - provide multiple feedstock options to fuel hydrogen economy
- Significant cooperation between offices
  - Energy Efficiency & Renewable Energy (EE)
  - Fossil Energy (FE)
  - Nuclear Energy, Science & Technology (NE)
  - Science (SC)
  - Management, Budget & Evaluation (ME)
- EE has responsibility for coordinating overall DOE Hydrogen Program and R&D on delivery and infrastructure issues
- NE has responsibility for R&D on production processes most suited for nuclear applications

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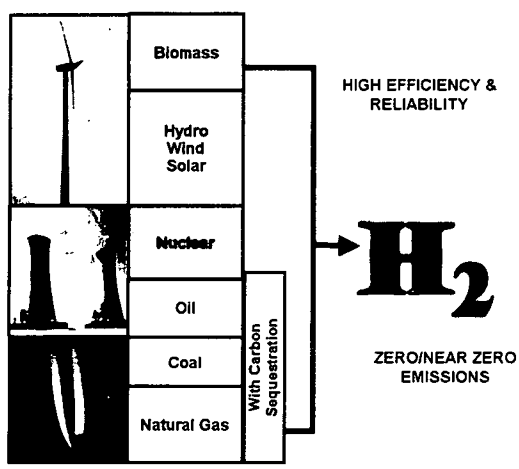
Why Nuclear?

- Currently is, and should stay, part of the overall energy mix
- Does not produce greenhouse gases or other air-borne pollutants
- Potential to produce H2 competitive with gasoline
- Utilizes domestically-based resources



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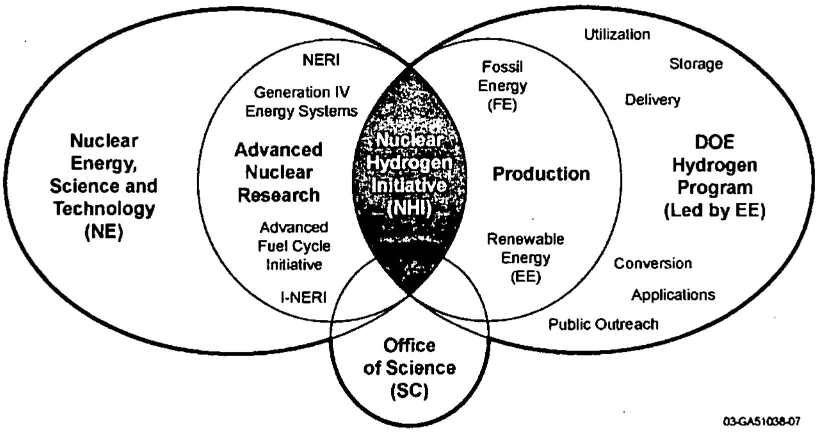
Nuclear Hydrogen Initiative

- **The goal of the Nuclear Hydrogen Initiative (NHI) is to demonstrate the commercial-scale production of hydrogen using nuclear energy by 2017.**



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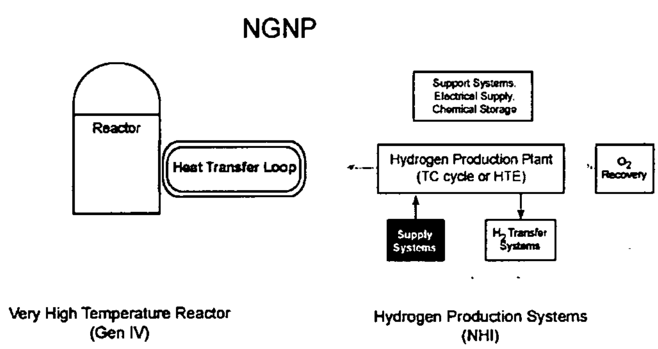
Coupled Nuclear-Hydrogen System



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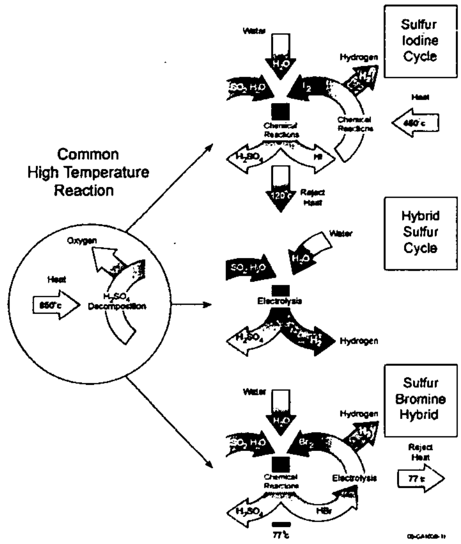
Methods for Nuclear Hydrogen Production

- **Steam-Methane Reforming - Heat from a nuclear reactor would replace fossil heat source used in commercial process**
- **Electrolytic - Existing electric generation efficiencies of 33% in today's light water reactors will be improved to 40-50% through advanced and next-generation (Gen IV) reactors, plus opportunity for high-temperature electrolysis**
- **Thermochemical (TC) Cycles - Use high-temperature heat from an advanced reactor to drive chemical reactions which break down water into H_2 & O_2**
- **Hybrid Cycles – Use electricity to electrolyze a chemical product using high temperatures from an advanced reactor.**



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Nuclear Hydrogen R&D Plan

- **Research Priorities**
  - Sulfur-based Thermochemical Processes
  - High-Temperature Electrolysis
  - Alternative Methods – primarily thermochemical
  - High-payoff Process Improvements (e.g., membranes)
- **Two-tiered approach to reduce development risk**
  - Baseline process development
  - Alternate process research
- **Three-phased scaling approach**
  - Laboratory-scale (<5 kW)
  - Pilot plant (500 kW – 1 MW)
  - Engineering-scale (20-50 MW)

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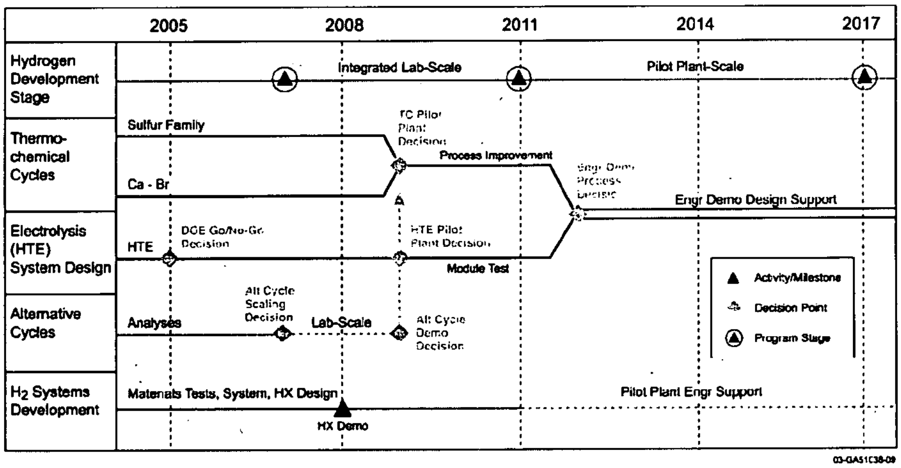
Major R&D in the NHI



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Principal Technical Barriers

- **High-temperature, corrosion resistant materials - R&D will be required to develop, test, and verify materials capable of performing at high temperatures (400-950° C) in the presence of corrosive chemicals to ensure the safety and economics of the facility.**
- **High-temperature heat exchangers – Research is needed to design heat exchangers to transfer heat from an intermediate heat loop to the process at high temperatures, high pressures, and in harsh chemical environments**
- **Chemical reaction data - Research is needed on basic chemical reaction data (equilibrium constants, reaction rates, etc.) to better determine the operating parameters of the thermochemical system**
- **System design – Studies are needed to study the hydrogen plant and its relationship to the reactor, including configuration options and operating conditions, system isolation issues, and intermediate heat transfer loop design.**

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NHI Program Funding

Fiscal Year	FY 2004 Appropriation*	FY 2005 Request
Thermochemical Cycles	$3.0	$5.0
High-Temperature Electrolysis	$2.0	$2.5
Systems Interface / Other	$1.1	$1.5
Total NHI R&D	$6.1**	$9.0

* $2 million earmark to University of Nevada, Las Vegas

**After Budget Reductions and SBIR

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Conclusions

- Technical challenges are significant, but the development of emission-free hydrogen production technologies is essential to the long-term viability of a hydrogen economy
- Nuclear energy has the potential to play a major role as a secure and environmentally-sound source of transportation fuels
- Sulfur-based cycles and high-temperature electrolysis were identified as most promising hydrogen production technologies for coupling with nuclear reactors
- Multi-phase scale-up of baseline technologies ensures successful demonstration of process(es)

5.1.3 The CEA Program for Massive Hydrogen Production from Nuclear

A. Le Duigou[1]*, P. Anzieu[1], P. Lucchese[2], F. Le Naour[2], X. Vitart[1], P.Mauchien[1], P. Aujollet[1], J.M. Borgard[1*], S. Colette[1], J. De Lamare[1], D.Doizi[1], C. Eysseric[1], J. Leybros [1], A. Terlain[1], F. Werkoff[1]

[1]CEA/Direction de l'Energie Nucléaire
[2]CEA/Direction de la Recherche Technologique
**to whom correspondence must be addressed: aleduigou@cea.fr or borgard@cea.fr*
DEN/DPC/SCP, Bât. 450N, CEA-Saclay, 91191 Gif-Sur-Yvette Cedex. France

The French Commissariat à l'Énergie Atomique (CEA) has done, since mid 2001, a preliminary evaluation of different methods to produce hydrogen. The objective is to compare the hydrogen production processes, including both technical and economical points of view.

The present CEA program for massive hydrogen production from Nuclear Energy, consists mainly of the assessment of the S/I thermochemical cycle and of alternative solutions such as the High Temperature Electrolysis (HTE) or the hybrid Westinghouse cycle.

1. **Theoretical and experimental program, related to the assessment of the S/I thermochemical cycle:**
- optimisation of the process : thermodynamics, flow-sheet;
- parametric tests for the Bunsen reaction ; materials evaluations;
- construction of a laboratory demonstration loop, in order to test the key features of a full scale system, able to deliver 100 l H_2/h (CEA : Bunsen section);
- Liquid/Vapour equilibrium of HI-I_2-H_2O, liquid and vapour phases diagnosis;
- search for advanced innovative solutions, such as membranes.

2. **Accompaning an alternative R&D works**
- evaluation of the alternative Westinghouse cycle;
- evaluation of HTE processes.

3. **Techno Economical studies and coupling with a VHTR**
- costs evaluation of the HTE ;
- costs evaluation of the S/I cycle;
- HTR coupling evaluation.

3. **International collaborations**:

With US, Japan, EC, Iceland....

- *CEA, General Atomics, Sandia National Laboratory and the University of Kentucky.* Demonstration of the key technology elements of the S/I: efficient operation of the Bunsen Reaction, successful operation of the HI reactive distillation column, and the heat exchanger materials technology in the corrosive H_2SO_4 environment ability.
- *Cooperation agreement with JAERI* consisting in information exchanges on the S/I cycle.
- *European Research Program* : Innovative medium-long term Routes for Hydrogen Production (INNOHYP and HYTHEC).
- *Iceland, Norway and CEA* are attending to develop a 5 kWh_e HTE demonstrator.

THE CEA PROGRAM FOR MASSIVE HYDROGEN PRODUCTION FROM NUCLEAR

by

Le Duigou[1*], P. Anzieu[1], P. Lucchese[2], F. Le Naour[2], X. Vitart[1], P. Mauchien[1], P. Aujollet[1], J.M. Borgard[1*], S. Colette[1], J. De Lamare[1], D. Doizi[1], C. Eysseric[1], J. Leybros [1], A. Terlain[1], F. Werkoff[1]

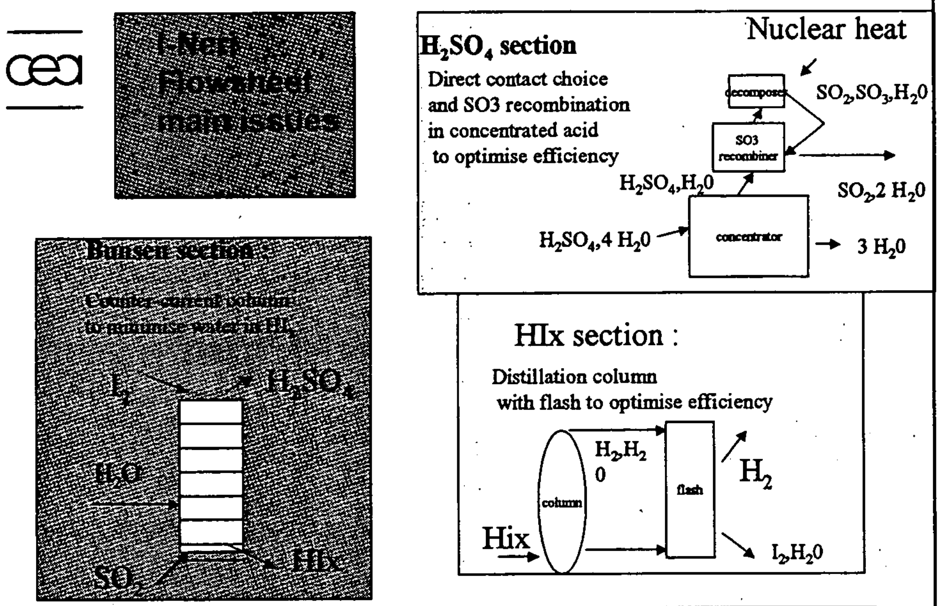
[1]CEA/Nuclear Energy Division
[2]CEA/Research & Technology Division

**to whom correspondence must be addressed*

Contents

1. Theoretical and experimental program, related to the assessment of the S/I thermochemical cycle:
   - *Flow-sheet assessment*
   - *Bunsen studies : fundamental and corrosion tests, demonstration loop*
   - *HI / I_2 / H_2O system fundamental study – use of membranes*
2. Alternative R&D work : *Westinghouse cycle, HTE.*
3. Techno Economical studies and coupling with a HTR.
4. International collaborations.

1. Towards a reference (US-French) FlowSheet for S/I



1. Experimental study of Bunsen reaction

General objectives

Thermodynamic study from final products (B1 step)
Thermodynamic and Kinetic study from initial reactants (B2 step) in order to optimise (lowest amounts of H_2O and I_2, HIx recycling) and to control (no side reaction) Bunsen reaction

Experiments

Design of new devices appropriate for very concentrated and corrosive media (B1 and B2 steps)
Design of original analytical diagnostics
Ex situ for B1 and B2_version 1 (UV-visible for I and ICP-AES for S)
In situ for B2_version 2 (UV-visible with ATR probe)

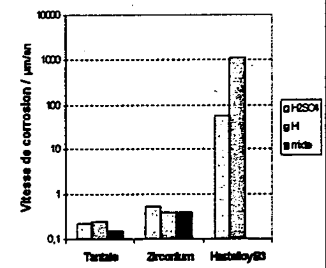
1. Corrosion Studies - :Methodology CEA approach is based on :

1> Overview of the available bibliography (thermodynamics and corrosion kinetics data...)

2> Selection Tests : Corrosion modes (ex : localized corrosion->not acceptable)

3> Determination of acceptable ranges of use and corrosion rates

4> Study of associated mechanisms



Bibliography GA, JAERI, Ispra Studies
- screening tests
- no locking point
- material behaviour very dependant on conditions

> First Experimental Studies :
- **focused on Bunsen part of the IS Cycle**

→ Zr,Ta, Hastelloy, ceramics, coated-materials...)

-Testing methods:
- electrochemistry : corrosion modes for metallic materials and reactions
- immersion tests : long time experiments in representative T, P and concentration ranges

- First results with metallic materials: Ta is well corrosion resistant, the sensitivity of Zr to localised corrosion could limit its use

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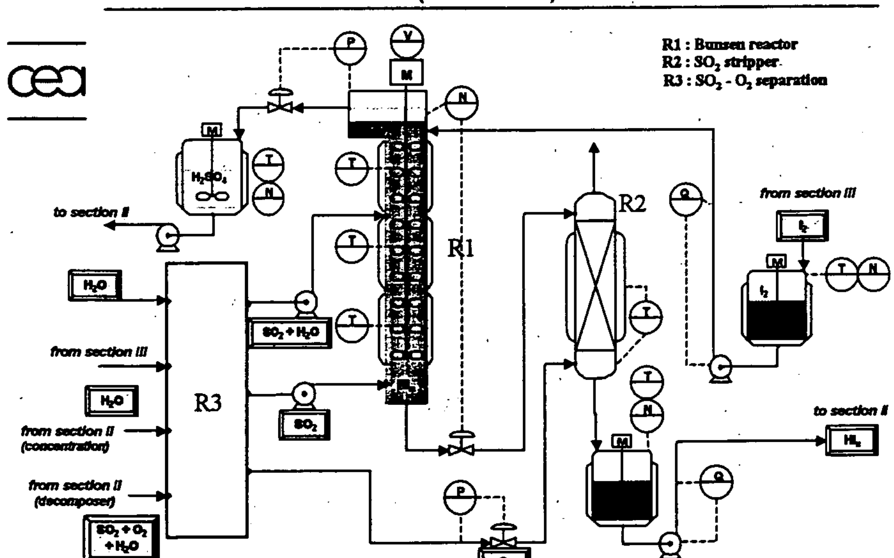
1. Schematic Flow Diagram of Section I of the I-NERI loop (100 l/h H2)



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1. Experimental study of the liquid vapor equilibrium $HI - I_2 - H_2O$

- Main objective of the work
  - **The complete knowledge (nature and partial pressure measurements of the species in the vapor phase) of the ternary system $HI - I_2 - H_2O$ around 600 K and 50 bars necessary to calculate the HI distillation column.**
- Analytical diagnostics
  - **Choice of optical « *in situ* » techniques to characterize this very concentrated medium**
    - FTIR for H_2O and HI
    - UV/Visible spectrophotometry for I_2 and HI
    - Raman techniques for all species.

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1. Research Program on I/S Membranes

1) H_2 extraction from $HI-H_20-H_2-I_2$ vapors (HI decomposition section) :

   1.1. Zeolitic film/Alumina substrate composite membranes [screening tests of zeolitic materials, films elaboration and membranes test, PhD thesis in collaboration with *Laboratoire des Matériaux Minéraux (Mulhouse, France)]*
   1.2. Silica film/Alumina substrate composite membranes, in collaboration with *Institut Européen des Membranes de Montpellier (France).*

2) HI decomposition heterogeneous catalysis.

3) Development of models and numerical simulations of HI and H2 sorption phenomena on zeolitic materials in collaboration with *laboratoire de modélisation de thermochimie et thermodynamique (CEA saclay, france).*

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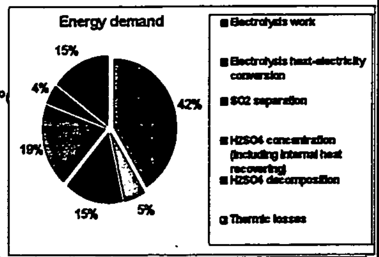
2. Westinghouse cycle evaluation for H_2 production coupled to nuclear heat source

➢**Process principle**

$SO_2 + H_2O + H_2O \rightarrow H_2 + H_2SO_4$ Electrolysis

$H_2SO_4 \rightarrow H_2O + SO_2 + ½ O_2$ Heat (~ 900°



➢**Flowsheet definition** : mass and enthalpy balances using PROSIM calculations

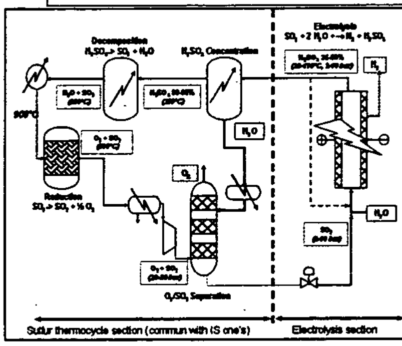
➢**Thermal efficiency first calculations**

$\eta_{thermic} \sim 38\ \%$

with principle hypothesis

$E_{cell} = 0{,}60\ V$

$\eta_{heat\ to\ electricity} = 45\ \%$



➢**Next studies**

- **TE evaluation after flowsheet optimization commun with IS studies**
- **Partial electrolysis data confirmation**

2. High Temperature Electrolysis (HTE)

➢Improvement of the theoretical models : cells, stack systems, heat exchanger networks, ...

➢Design of cells and stacks (1- 5kW) (2004-2008)

➢Study of a pilot device to be coupled to a geothermal heat source (200 Nℓ H_2/h), in collaboration with Iceland (→ 2009)

➢Coupling studies to a VHTR reactor : comparisons between exothermal and endothermal operation processes

➢Techno-economical studies for a H_2 production plant coupled to a VHTR, comparisons with the S/I cycle

3. Techno Economic study on High Temperature electrolysis (HTE)

Process	Cost of production for 1kg of H_2 [€-2001]	Contribution due to the electrolyser investment [%]	Contribution due to electricity consumption [%]
exothermal	2.1	34.	56.
isothermal	2.2	35.	55.
endothermal	3.2	52.	35.

HTE would be competitive with alkaline electrolysis (between 2.5 and 3.5 €/kg)

- Key points:
- ➢ Electrolyser (life expectancy and unit cost) *progress expected from current R&D works on SOFC*
- ➢ High temperature heat exchangers
- For the heat source, an alternative to HTR is geothermics. The *Jules Verne* French-Icelandic project is devoted to the assessment of H_2 production by Géothermics+ HTE.

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3. Techno Economic study on S/I termochemical cycle

- The energy consumption and the recovery of the iodine are key points of the S/I cycle.
- The reduction of the energy consumption is possible but should begin with the elaboration of improved FlowSheets with regard to the current ones.
- For the recovery of the iodine, it should be necessary to reach a recovery rate better than those of the traditional chemical industry.

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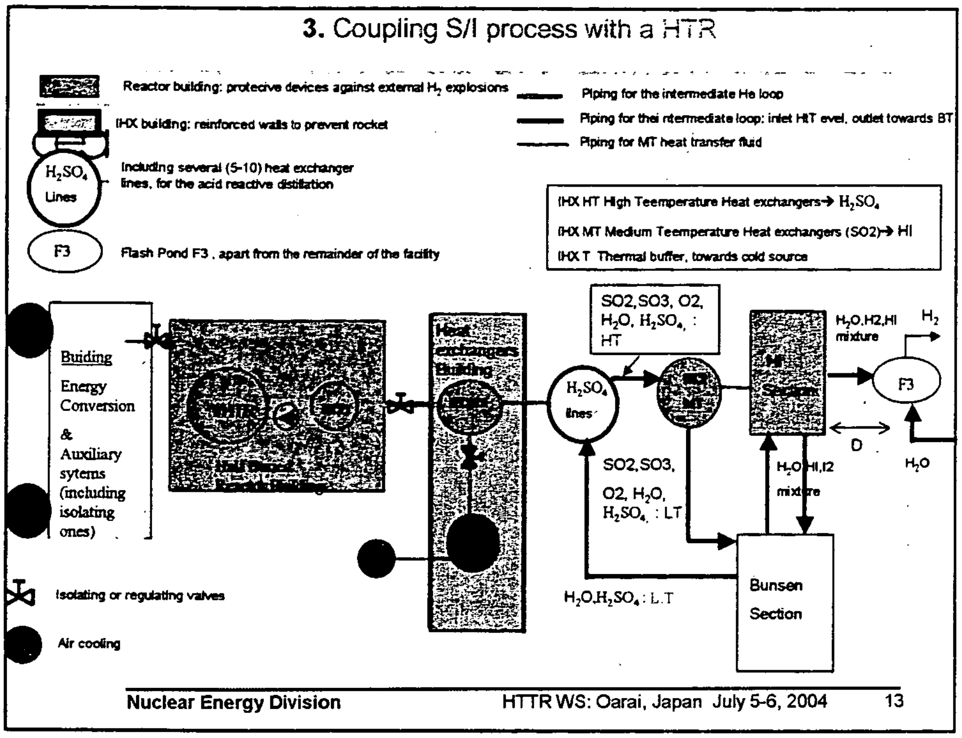
3. Coupling S/I process with a HTR
Reactor building: protective devices against external H2 explosions
IHX building: reinforced walls to prevent rocket
Including several (5-10) heat exchanger lines, for the acid reactive distillation
Flash Pond F3, apart from the remainder of the facility
Piping for the intermediate He loop
Piping for MT heat transfer fluid
IHX HT High Teemperature Heat exchangers→ H2SO4
IHX MT Medium Teemperature Heat exchangers (SO2)→ HI
IHX T Thermal buffer, towards cold source
Buiding Energy Conversion & Auxiliary sytems (including isolating ones)
SO2, SO3, O2, H2O, H2SO4 : HT
H2SO4 lines
SO2, SO3, O2, H2O, H2SO4 : LT
H2O, H2, HI mixture
H2
F3
D
H2O
Bunsen Section
H2O, H2SO4 : LT
Isolating or regulating valves
Air cooling
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HTTR WS: Oarai, Japan July 5-6, 2004
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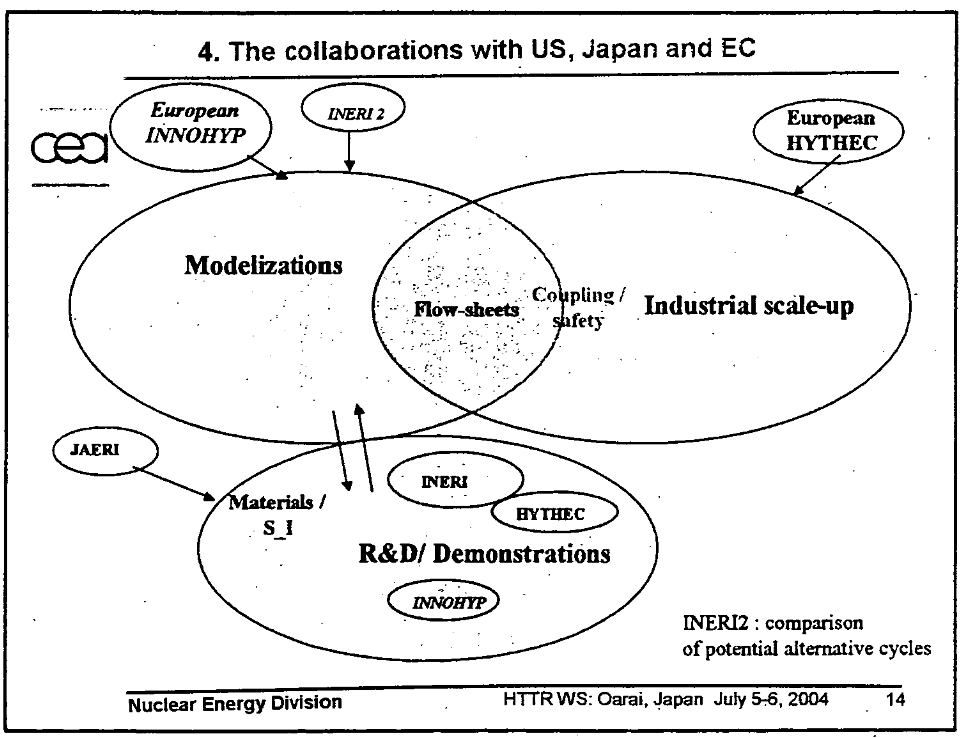
4. The collaborations with US, Japan and EC
European INNOHYP
INERI 2
European HYTHEC
Modelizations
Flow-sheets
Coupling / safety
Industrial scale-up
JAERI
Materials / S_I
INERI
HYTHEC
R&D/ Demonstrations
INNOHYP
INERI2 : comparison of potential alternative cycles
Nuclear Energy Division
HTTR WS: Oarai, Japan July 5-6, 2004
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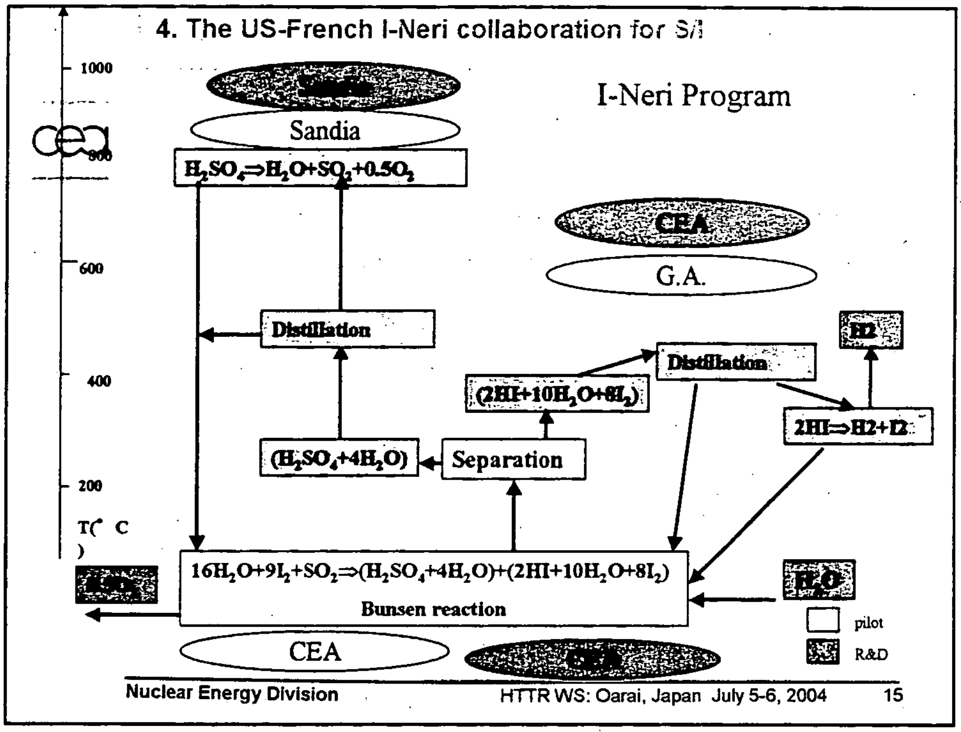
4. The US-French I-Neri collaboration for S/I
I-Neri Program
1000
600
400
200
T(° C)
Sandia
$H_2SO_4 \Rightarrow H_2O+SO_2+0.5O_2$
G.A.
Distillation
Distillation
$(2HI+10H_2O+8I_2)$
$2HI \Rightarrow H2+I2$
$(H_2SO_4+4H_2O)$
Separation
$16H_2O+9I_2+SO_2 \Rightarrow (H_2SO_4+4H_2O)+(2HI+10H_2O+8I_2)$
Bunsen reaction
CEA
pilot
R&D
Nuclear Energy Division
HTTR WS: Oarai, Japan July 5-6, 2004
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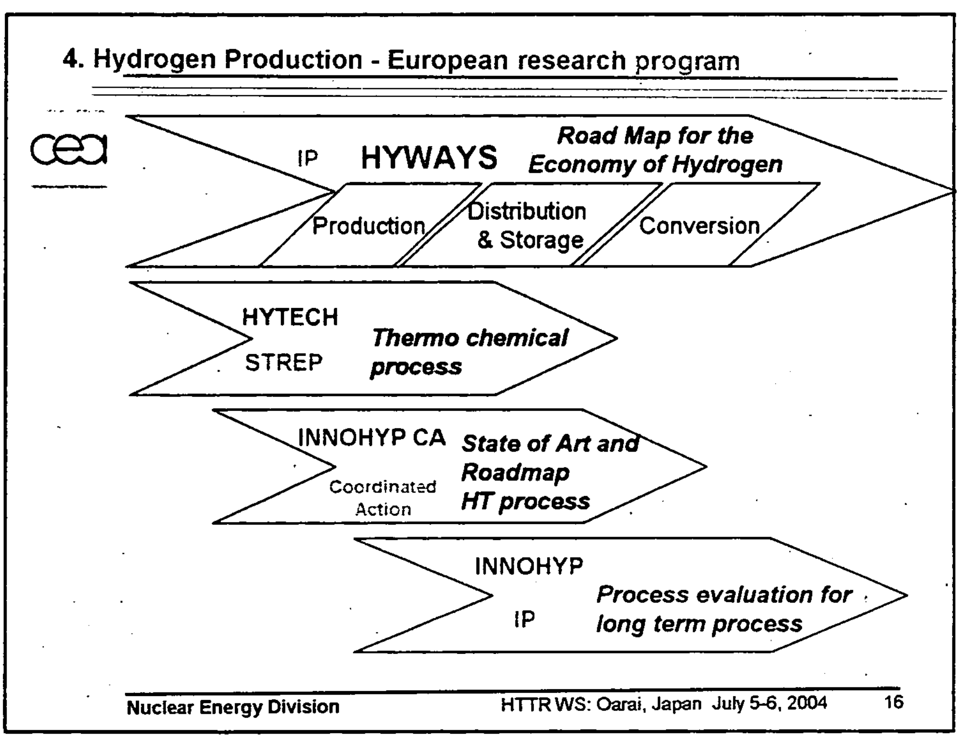
4. Hydrogen Production - European research program
IP HYWAYS
Road Map for the Economy of Hydrogen
Production
Distribution & Storage
Conversion
HYTECH
STREP
Thermo chemical process
INNOHYP CA
Coordinated Action
State of Art and Roadmap HT process
INNOHYP
IP
Process evaluation for long term process
Nuclear Energy Division
HTTR WS: Oarai, Japan July 5-6, 2004
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5.1.4 Development of VHTR-Assisted Hydrogen Production Technology in Korea

Youngjoon Shin*, Jonghwa Chang*, Changkue Park*
Taehwan Kim, Byunggwon Lee*****

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***Korea Institute of Energy Research, 71-2 Jang-dong, Yuseong-gu, Daejeon, Korea 305-343, E-mail; thkim@kier.re.kr, Tel; +82 42 860 3115*
****Korea Institute of Science and Technology, P.O.Box 131,Cheongryang, Seoul, Korea 130-650, E-mail; bglee@kist.re.kr, Tel; +82 2 958 5857*

The new worldwide task presented to us since the Kyoto Protocol for the UN Framework Convention on Climate Change in December 1997 is how to overcome the energy imbalance for the future well-being of humans.

It has been suggested that hydrogen should partly replace gasoline for fueling automobiles within the next decade and its economical competitives should be obtained by the 2020s.

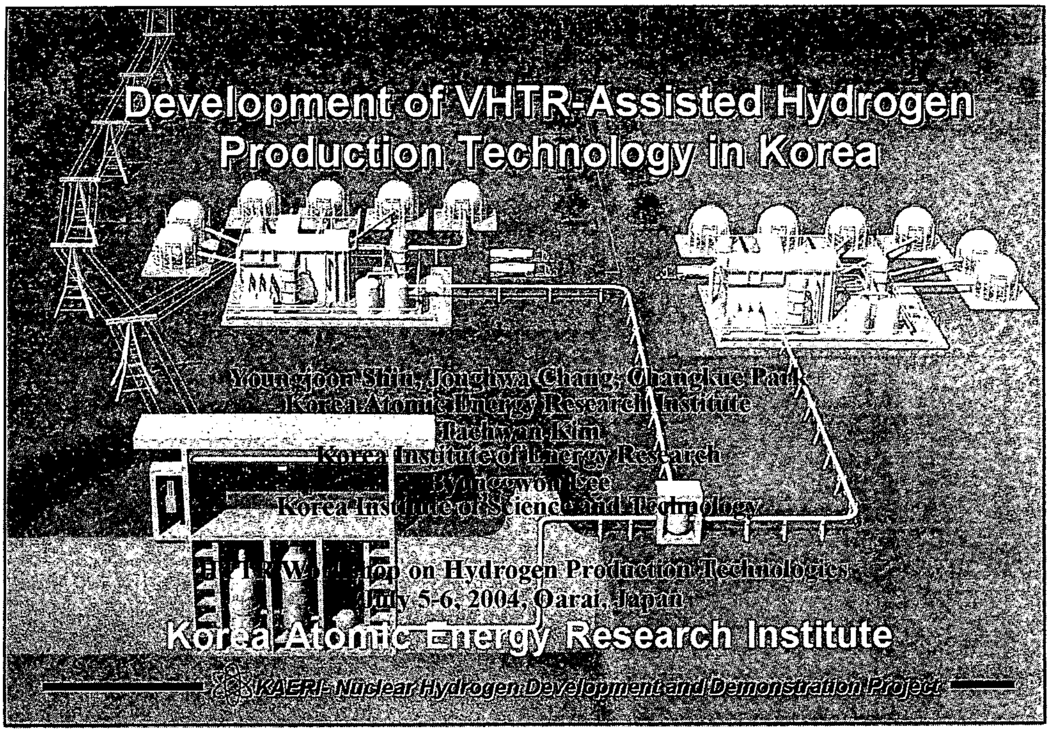
A Very High Temerature Gas-Cooled Reactor(VHTR) can be used for hydrogen production through several CO_2-free alternative technologies, such as thermochemical or electrochemical cycles having a total chemical reaction of water splitting.

Most countries including Korea are very interested in the Sulfur-Iodine(SI) cycle, the High Temperature Electrolysis of Steam(HTES), and the Steam Methane Reforming(SMR) cycle with zero CO_2 emissions.

JAERI-Oarai already achieved the integrated test of the SI cycle with a 50 NL·H_2/h capacity in 2003. The HTES using ceramic electrolysis cells is gradually being developed according to the vigorous development of the solid oxide fuel cell(SOFC) technology.

Based on this background, the Korea Atomic Energy Research Institute(KAERI) has prepared a R&D proposal for the development of the nuclear hydrogen production technology in 2003, in cooperation with the Korea Institute of Energy Research(KIER) and Korea Institute of Science and Technology(KIST). This R&D has been launched this year.

In our current presentation the final R&D target and schedule are introduced and more detailed R&D activities for the development of the VHTR-assisted hydrogen production technology are described.



Korean Plan

❑ **Purpose**

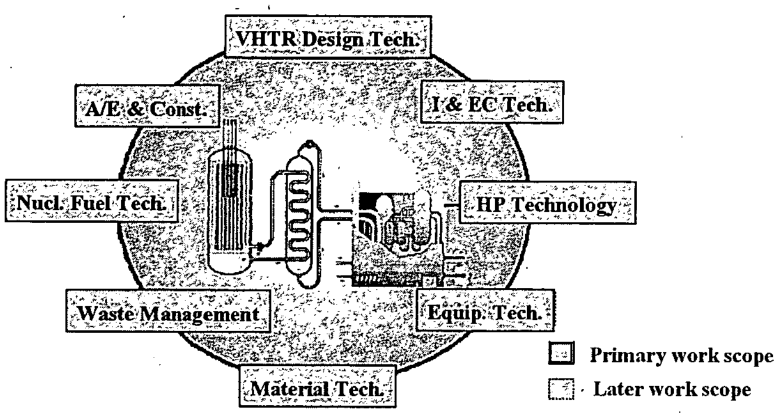
Development and Demonstration of Nuclear Hydrogen Production Technology

- ❑ **Nuclear Hydrogen will cover 20% of the total vehicle fuel demand for the 2020s.**
  - ➢ **Equivalent to crude oil of 85,000,000 barrels**
  - ➢ **Equivalent to 3,300,000 t•H_2**
- ❑ **The capacity of the demonstration facilities ; 7,800~30,000 t•H_2/y⇒40,000~150,000 H_2 Cars' Fuel**

KAERI - NHDD Project

- 1 -

❑ Key Technologies for the NHP Demonstration



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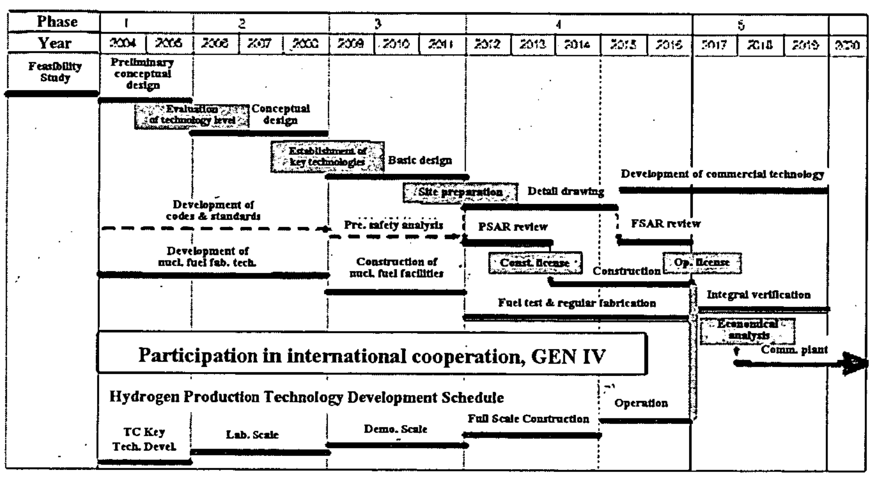
- 2 -

Project Plan



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- 3 -

Nuclear Hydrogen Production Technology

Development of the NHPT

☞ Evaluation of the Hydrogen Cycles

- **Three top-ranked cycles to be evaluated;**
  - *Sulfur Iodine(SI) Cycle*
  - *High Temperature Electrolysis(HTE)*
  - *Methane-Methanol-Iodomethane(MMI) Cycle*
- **Evaluation Activities**
  - *Collection and production of technical data*
  - *Development of the MMI cycle flowsheet*
  - *Comparison of thermal pathway and efficiency*

☞ Development of the Advanced SI Cycle

- **Membrane-based high technology**
  - *HI concentration by electrodialysis*
  - *Membrane reactor for hydrogen separation*
- **High temperature materials**
  - *Screening test for equipment material selection*
  - *Coatings and fabrication technology*
- **Scale-up and engineering**
  - *Key technology closed-loop test(5L/hr)*
  - *Lab.-scale test (0.1Nm³/hr)*
  - *Pilot-scale test (30-100Nm³/hr)*
  - *Demonstration facilities (10,000Nm³/hr)*

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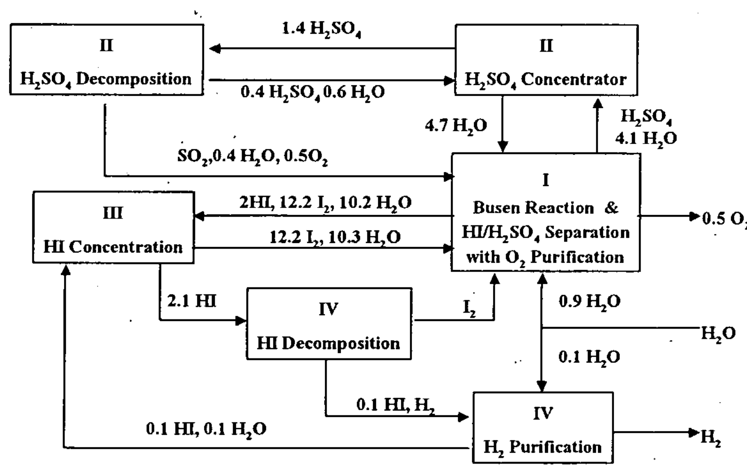
Flow Diagram of the 1981 Version SI Cycle



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Long-Term Challenges for the SI Cycle

Field	Purpose	Contents
Reaction & Unit Process Tech.	➢ Design of a chemical reactor and unit process operation ■ Separation/Purification ■ Closed-cycle operation	- Loop design for H_2SO_4 decomposition - An experiment on the Bunsen reaction and a basic design - An experiment on the HIx decomposition - Side-reaction control - Separation/Purification of HIx from H_2SO_4 obtained by the Bunsen Rx. - Separation/Purification of H_2SO_4 from HIx obtained by the Bunsen Rx. - Closed-cycle operation
Advanced Process Tech. for a High Efficiency	■ Two membrane technologies (electrodialysis & membrane reactor) ■ Distillation/Vacuum distillation	- Vacuum distillation of HIx - Vacuum distillation coupled with electrodialysis - HI concentration by electrodialysis only - Hydrogen separation by using a special membrane reactor
Materials for Equipment Fabrication	■ Screen test of candidate materials to withstand at operating conditions ■ Corrosion and integrity test of welding and fabricated parts at real operating conditions ■ Establishment of procurement specification on pump head materials	- Materials for the H_2SO_4 decomposition process - Materials for the HIx decomposition process - Materials for the Bunsen reaction process - Design/Fabrication of reactors and modules using selected materials
Process Analysis and Design	- Analysis of heat & mass balance and fluid mechanics - Process design	-Analysis of heat & Mass balance in the unit process -Determination of the total thermal efficiency -Up-date for heat recovery -Design of the Korean peculiar demonstration facilities

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- 6 -

The 1st Phase R&D on the SI Cycle Technology

Objective : Basic Technology Establishment for the Hydrogen Production Plant Construction [Lab.-Scale (5ℓ/hr H_2) Design Study]

Work Scope	Contents
Reaction & Unit process tech.	■ An experiment on the Bunsen reaction unit process and basic design ■ Development of the HI decomposition ■ Design of the test loop for the H_2SO_4 decomposition reaction process
Process tech. for a high efficiency	■ HI concentration by electrodialysis ■ An experiment on the membrane reactor for hydrogen separation ■ Hydrogen production from HI by vacuum distillation ■ Preparation of the experimental apparatus and its scale-up design
Equipment materials	■ Corrosion test and selection of the materials for each unit process
Process analysis and design	■ Modification and up-date of the published process data and the process design by using the modified process data

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Thermal Dissociation of H_2SO_4 in the SI Cycle

❖ **Catalyst Development by using nano-tech.**

- ✓ Thermodynamic analysis (T-P-Concn.)
- ✓ Highly active catalyst (non-noble catalyst)
- ✓ Highly thermal stable catalyst
- ✓ Catalyst with a high thermal coefficient
- ✓ Non-corrosive catalyst for acids

❖ **Reaction Kinetics**

- ✓ Intrinsic kinetics for homogeneous reaction
- ✓ Intrinsic kinetics for heterogeneous reaction
- ✓ Derivation of the overall kinetic equation
- ✓ Thiele modulus

❖ **Establishment of the Reactor Design Concept**

❖ **Thermodynamic properties establishment**

- ✓ Phase equilibria
  - Liq./Gas ; H_2SO_4-SO_2/O_2, SO_2-O_2, H_2O-SO_2
  - Liq./Liq. ; H_2O-H_2SO_4
- ✓ Multicomponent equilibrium modeling
- ✓ Selelection of separation unit for purifying O_2

❖ **Separation process**

- ✓ Lab.- scale O_2 purification unit installation
- ✓ Collection of the operation data
- ✓ Simulation of the O_2 purification unit
- ✓ Modification of the O_2 purification unit

❖ **Development of the new O_2 purification unit**

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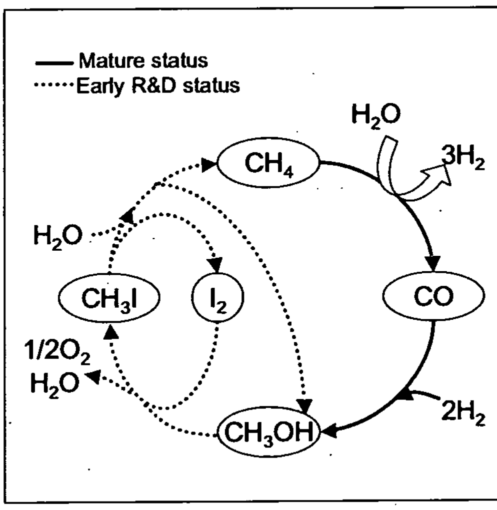
Near-Term Challenges for the MMI Cycle



- **Minimization of the shift reaction in the steam methane reforming.** $CO + H_2O = CO_2 + H_2$
- **Realization of the iodization of methanol.**
- **Determination of the iodization method; electrochemical or catalytic reactions.**
- **Suppression of the by-products(HI, CH_2O)**
- **Prevention of the carbon oxides and iodine release from the closed cycle.**
- **Development of the flowsheet with the optimized thermal pathway.**

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Several CH_3I Synthesis Routes

(1) MeOH + P + I_2

(2) KI + methyl sulfonate

(3) I_2 + Metals + Alcohols etc

- Metals : H,Li,Na,K,Rb,Cs,Fr, (Ia) Be,Mg,Ca,Sr,Ba,Ra (IIa)
B,Al,Ga, In, Tl (IIIa) Cu,Ag,Au (Ib)
Zn,Cd,Hg (IIb)
Sc, Y, La, Ce, Pr, Nd,... (Lantanides)
Ti,Zr,Hf,Rf & Ac,Th,Pa,U,Np.. (Actinides)

- Alcohols etc.: alcohols, esters,dialkyl ethers, diallyl ethers)

(4) I_2+ H_2+MeOH over Rh, Ir, Ru as catalysts

(5) I_2 +H_2+CH_3COOCH_3 (or DME) under Pd, Rh, Pt, Ru (or Ni)
(Disadvantage : Expensive catalyst)

- Key Factors : molar ratio (Halide / Metals or Catalysts),
temperature, etc.

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Experiment for the Optimum CH_3I Synthesis

- Overall Reaction: $CH_3OH + I_2 \rightarrow CH_3I$

- CH_3OH + Catalysts + I_2 (as Precursor) to CH_3I

- Operating Variables:
  Promoters (d-, f-orbital electron containing group IV compound)
  molar ratio, rxn. temp, distill. temp, RPM, rate of MeOH addition

- Expected Optimum Conditions:
  molar ratio (MeOH/Catalyst) 1.0
  molar ratio (I_2/Catalyst) 0.5
  Temp. range 53 ~ 109 ℃,
  (= optimum formation temp. of Catalyst-I)

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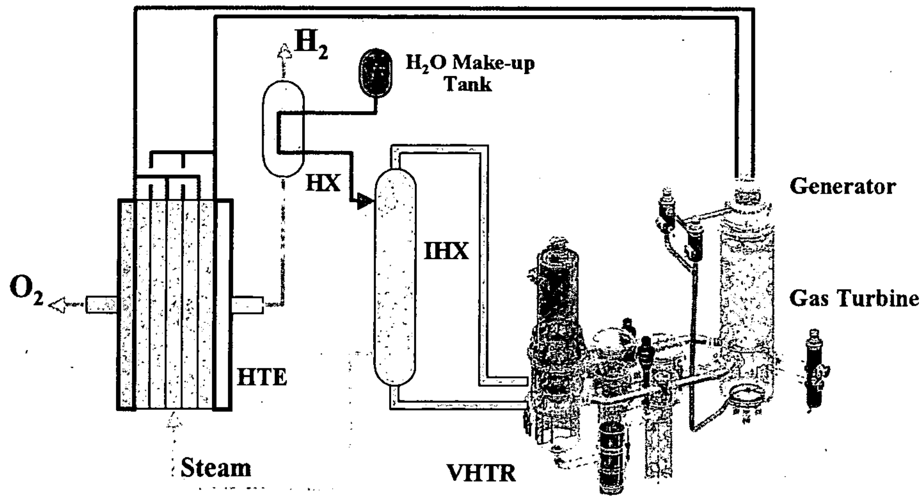
HTES Coupled with the VHTR



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Assessment of the HTES' Thermal Efficiency

Advantages of the HTES coupled with the VHTR
- *Higher overall thermal-to-hydrogen heat conversion efficiency*
- *Favorable electrode activity and lower over-voltages*
- *Incentive from the thermodynamic and kinetic aspects*

Short-term work scopes
- *Theoretical evaluation of the thermal efficiency based on the parallel paths of electricity generation and heat supply for HTES;*
  - *1)Total Energy Demand = Electricity for HTES + Heat for HTES*
  - *2) Applying a high efficiency power conversion cycle from heat to electricity*
  - *3) Effect of the electrolysis efficiency of the HTES on the total thermal efficiency*
- *Comparison of the total thermal efficiency among SI, HTES, and MMI*

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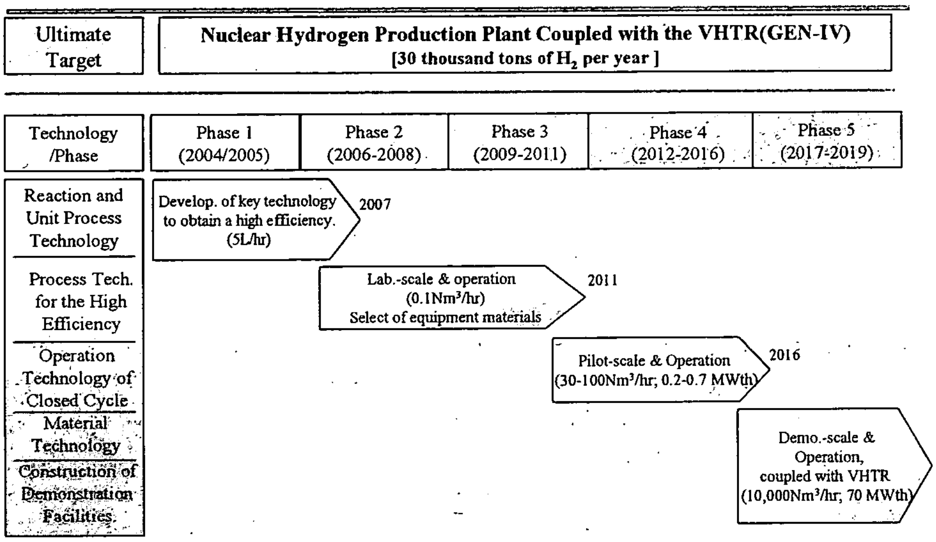
Technological Roadmap for the NHPT



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-14-

Thank You.

http://www.hydrogen.re.kr/

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5.1.5 R&D Activities on Nuclear Hydrogen Production in the European Union

K. Verfondern, W. von Lensa

Research Center Jülich, 52425 Jülich, GERMANY

With the worldwide increasing interest in hydrogen as a clean energy carrier and potential fuel of the future, Europe has embarked on comprehensive research, development, and demonstration activities to pave the way for the transition from a fossil towards a CO_2 emission free energy structure. Policy groups such as the "High Level Group on Hydrogen and Fuel Cells" (HLG) or the "European Hydrogen and Fuel Cell Technology Platform" have been created recently in the European Union to develop European consensus on the introduction of hydrogen energy and to define a strategy for a European roadmap.

A "Quick Start" initiative launched by the European Commission resulted in 16 contracts (as of March 2004) covering various technologies of hydrogen and fuel cells with approx. 100 million Euro of EU funding within the Framework Programme (FP) 6 (2002-2006) to be matched by corresponding private funding. Another 150 million Euro of EU funding are planned to be awarded in later calls.

Hydrogen production technologies are strongly focusing on CO_2-neutral or CO_2-free methods as represented by, e.g., biomass conversion or thermo-chemical water splitting processes or reforming of fossil fuels plus CO_2 sequestration. Primary energy sources include nuclear and renewable energies.

With EURATOM as a new member of the "Generation-IV International Forum" (GIF), R&D activities in different European countries have been starting to develop the design of a GenIV nuclear reactor with the potential of providing both electricity and process heat for the production of hydrogen.

The presentation will describe some of the European FP activities in more detail.

R&D Activities on Nuclear Hydrogen Production in the European Union

by
Karl VERFONDERN and Werner VON LENSA
Research Center Jülich, Germany

Research Center Juelich
Institute for Safety Research and Reactor Technology (ISR)

Creation of Policy Groups

- **High Level Group on Hydrogen and Fuel Cells (HLG)**
  to develop European consensus on the introduction of hydrogen energy
- **European Hydrogen and Fuel Cell Technology Platform** (Jan. 04)
  to develop coherent hydrogen research and deployment strategy for Europe

Research Center Juelich
Institute for Safety Research and Reactor Technology (ISR)

„Quick Start" Initiative by EC

- First call for proposals of FP6 (March 2004)

  EC awarded 10 contracts in H_2 with 62 M E
  EC awarded 6 contracts in FC with 30 M E
  (to be matched by private funding)

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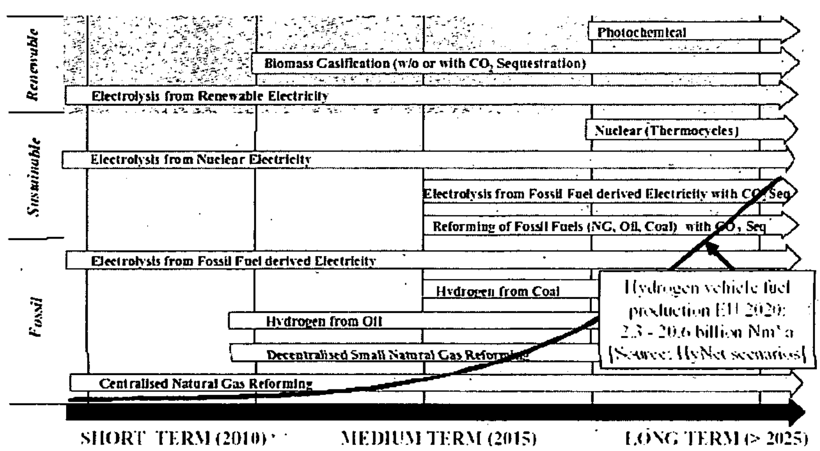
Institute for Safety Research and Reactor Technology (ISR)

Timeline for H_2 production technologies



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Institute for Safety Research and Reactor Technology (ISR)

EU Contracts on Hydrogen in FP-6 (First Call)

Project	Topic	Coordinator	EU Funding [M E]
HYTHEC-STREP	Thermochemical cycles	CEA (F)	1.9
CHRISGAS-IP	H_2 rich gas from biomass	Växjo Uni (S)	9.5
Hi2H2-STREP	HT electrolysis	EDF (F)	0.9
HYWAYS-IP	European hydrogen roadmap	LBST (G)	4.0
NATURALHY-IP	Infrastructure H_2-Nat. Gas mixes	Gasunie (NL)	11.0
STORHY-IP	Storage for on-board applications	Magna Steyr (A)	10.0
HYSAFE-NE	Research in safety issues	FZK (G)	7.0
ZEROREGIO-IP	H_2 fuel cell fleet demonstration	Infraserv (G)	7.5
PREMIA-SSA	Effectiveness of demo initiatives	VITO (B)	1.0
HYICE-IP	Internal combustion engines	BMW (G)	9.0

Workshop on Technical Issues and Feasibility of Advanced Hydrogen Production Systems, July 5-6, 2004, Oarai, JAPAN 5

Research Center Juelich
Institute for Safety Research and Reactor Technology (ISR)

INNOHYP-IP (March 2003)

- 30 M Euro IP on innovative hydrogen production processes (incl. nuclear)
- Evaluate and compare different processes of H_2 production with focus on thermochemical cycles, but includes also steam reforming as well as "very innovative" ways
- Not accepted (July 2003)
  Modified version to be relaunched as CA

Workshop on Technical Issues and Feasibility of Advanced Hydrogen Production Systems, July 5-6, 2004, Oarai, JAPAN 6

Research Center Juelich
Institute for Safety Research and Reactor Technology (ISR)

HYSAFE-NE (March 2003)

- EU Network of Excellence
- Strengthening capacities to implement new technological solutions for H_2 as energy carrier
- Harmonize methodologies for safety assessment
- Focus on studies of fire and explosion safety, mitigation techniques, detection devices
- Promote use of H_2
- Establish a European Hydrogen Safety Center

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Research Center Juelich
Institute for Safety Research and Reactor Technology (ISR)

V/HTR-IP (under negotiation)

Overall Objectives

- to study 1st generation of advanced gas reactor technologies with R&D support to existing demonstrator projects;
- to explore options for 2nd generation by developing systems for very high temperature (950 - 1000 °C) applications.

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V/HTR-IP: Breakdown Structure

1. Coupled Reactor Physics and Core Fluid Dynamics
2. Fuel Technology
3. Back-End of the Fuel Cycle
4. Materials Development
5. Component Development
6. Safety
7. System Integration
8. Education & Training

Research Center Juelich
Institute for Safety Research and Reactor Technology (ISR)

V/HTR-IP

- 35 partners, coordinated by Framatome-ANP (D. Hittner)
- Facilitates and supports the EURATOM contribution to the GenIV International Forum (GIF)
  [at present technically represented by MICANET]
- Complements national efforts on HTR/VHTR
- Is connected to hydrogen activities in FP6 by sub-projects „System Integration" and „Safety"
- Currently under negotiation with EC
  [evaluation process: 26.5 out of 30 points]

Workshop on Technical Issues and Feasibility of Advanced Hydrogen Production Systems, July 5-6, 2004, Oarai, JAPAN

GenIV nuclear reactor: VHTR

- 400-600 MW(th) for electricity and process heat production;
- Helium-cooled, graphite-moderated, thermal neutron spectrum;
- Gas outlet temperature of 900-1000 °C;
- IHX for heat transfer to H_2 production plant or gas turbine.

R&D program plan for VHTR by 2010

- Long-term technology improvement by making use of knowhow from HTGR development;
- HTTR and HTR-10 to demonstrate VHTR capabilities in pilot scale and in near term;
- INEEL co-generation project as full-scale demonstration of VHTR objectives with H_2 production system.

VHTR hydrogen R&D program

- Developing and optimizing thermo-chemical water splitting processes of the sulfur family (reference: S/I, special focus on HT step);
- Evaluating alternatives;
- Advancing the high temperature electrolysis process.

Thank you for your attention !

私の話を聞いていただいて
ありがとうございました。

5.1.6 Opening the Market: What Precedes Advanced Hydrogen Production

Alistair I. Miller

Atomic Energy of Canada Limited, Canada

Hydrogen is becoming the reference fuel for future transportation and, in the USA in particular, a vision for its production from advanced nuclear reactors has been formulated. Fulfillment of this vision will depend on its economics in 2020 or later. It is now widely recognized that hydrogen needs to gain a substantial foothold long before then. It must do so without incurring excessive costs for the establishment of the distribution network for the new fuel. Provided electricity is produced at costs expected for nuclear reactors of near-term design, electrolysis appears to offer superior economics over the costs of SMR production when costs of distribution and sequestration are included. This paper shows this to hold at least until several percentage points of road transport have been converted to hydrogen.

Electrolysis has large advantages over SMRs in being almost scale-independent and allowing local production. Scale independence allows this approach to launch the hydrogen market in an affordable appropriately way without incurring large capital commitments for centralized facilities and distribution networks. The key requirements for affordable electrolysis are low capital cost and relatively high utilization, although the paper shows that it should be advantageous to avoid the peaks of electricity demand and cost. The electricity source must enable high utilization as well as being itself low-cost and emissions-free. By using off-peak electricity, no extra costs for enhanced electricity distribution should occur.

The longer-term supply of hydrogen may ultimately evolve away from low-temperature water electrolysis but it appears to be an excellent technology for early deployment and capable of supplying hydrogen at prices not dissimilar from today's costs for gasoline and diesel provided the vehicle's power unit is a fuel cell.

Opening the market: what precedes advanced hydrogen production?

Alistair I. Miller

Workshop on Hydrogen Production Technologies
Oarai, Japan
2004 July 5 & 6

Canada

AECL Atomic Energy of Canada Limited EACL Énergie atomique du Canada limitée

Why Hydrogen?

- The answer is "hydrogen"
- But what is the question?
- It really has to be:
  "How do we severely curtail CO_2 emissions, worldwide?"
- If what we propose doesn't do that, then it does not address the real question and becomes part of the problem.

Page 2

AECL Atomic Energy of Canada Limited EACL Énergie atomique du Canada limitée

Launching the Hydrogen Age

✓ Objective is non-polluting transport
- Eliminate local pollution
- Eliminate CO_2 emissions

✗ Avoid CH_4-consuming, CO_2-producing SMRs

✓ Two new visions of H_2 production
- Centralized (SMRs, thermochemical or high-temperature electrolysis with high-temperature nuclear reactors)
- Distributed (low-temperature electrolysis using electricity from sources that do not emit CO_2)

Page 3

Why not by SMR?

✓ Cost of natural gas is bearable, even at 5 $/GJ

✓ SMR H_2 is cheap for large units with local, industrial markets

✓ CO_2 sequestration, where available, is a bearable extra
- But recovery from the 30% produced as flue gas will be costly.

✗ Problem is with scale: SMRs scale with about a 0.66 power
- A smallish industrial SMR (250 tonne/d) could fuel 600 000 cars
- Reducing size by factor of 1000, raises unit cost by a factor of 10
- The unit cost of CO_2 sequestration probably becomes prohibitive

✗ Or, alternatively, with large distribution costs

✗ Unthinkable for on-board reforming

➢ Overall, an archaic way to make hydrogen

Page 4

AECL EACL
Atomic Energy of Canada Limited
Énergie atomique du Canada limitée

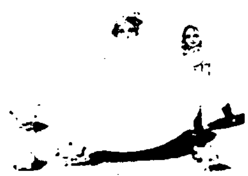
Hydrogen's Introduction - Chicken Or Egg?

Eggs predate chickens by hundreds of millions of years.
It took that long to hatch?
And what poor creature had to sit on it that long?
And precisely when did the chicken suddenly appear? Was it's mother not a chicken?

Page 5

How to Hatch the Egg?

- The problem is the size of the egg
  - Large centralized installations make too much H_2
  - Dependency on one or two large installation is a problem
  - Small distribution pipelines are uneconomic
  - Big nuclear "eggs" won't be even be available till after 2025
- Initially scattered, small chickens
  - Can nibble electrolytic H_2
    - Using cheap off-peak nuclear power
      - Over existing electricity grids
    - Using low-cost electrolysers
  - Supply expands smoothly in small increments



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EACL Énergie atomique du Canada limitée

A 2000 MW(th) reactor can supply ...

- At 50% thermal efficiency, a 2000 MW(th) HTR reactor can fuel 1.1 million cars using H_2 and PEM fuel cells
- A typical city has 1 to 2 million light vehicles
  - 1.5 to 3 million equivalent in all vehicles
- Needs substantial market penetration before reactor is needed
  - > one-third of transportation switched to H_2
  - Inter-city pipelines to cover down-time

A Generation III+ reactor can supply ...

- Either electricity or hydrogen, flexibly
- A 700 MW(e) ACR™ making H_2 85% of the time can fuel 0.46 million cars

Page 7

Making Hydrogen by Electrolysis

- Always important to keep the capital cost of the electrolysis low
  - Particularly true if not run continuously
- Essential that the electricity by low-cost
  - Significant cost reduction if one avoids demand peaks
  - Peak-average difference is likely to grow if coal replaced by nuclear
- Electrolysis is flexible and avoids need to build distribution networks before the demand is extensive (i.e. > 5 to 10 percent)
- Allows conversion to begin in the relatively near future
  - Electricity at 3 US¢/kW.h from Gen III+ reactors such as AECL's ACR™ will be available in a few years
  - Fuel cells would be desirable (and may well be available) but could use ICEs in short term and still gain significant efficiency of conversion

Page 8

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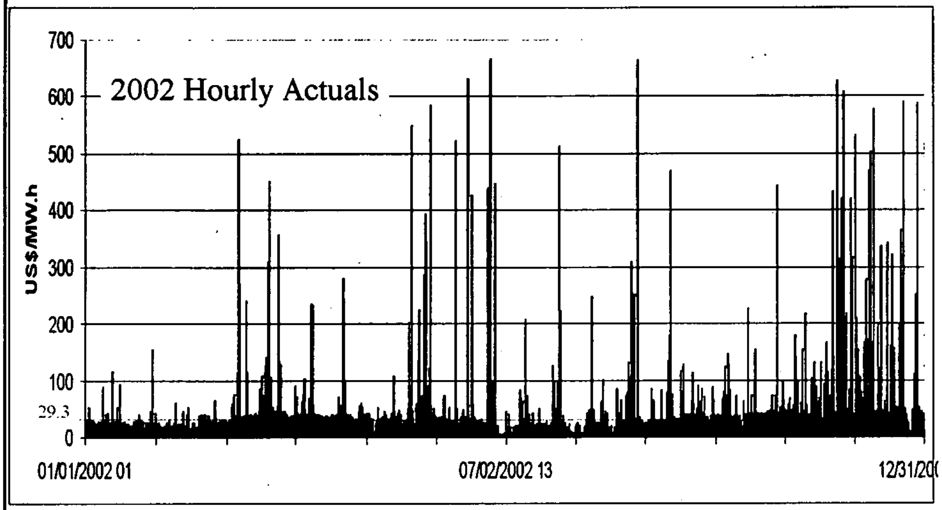
Énergie atomique du Canada limitée

Alberta Pool Electricity Price (US$/MW.h)



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Details of 2002 Alberta Electricity Prices

- Average value was 29.3 US$/MW.h
- Only 35.5% of power cost > 30 US$/MW.h
  - The other 64.5% had an average value of 14.6 US$/MW.h
- At below 60 US$/MW.h
  - Average cost was 22.4 US$/MW.h
  - Using that, electrolysis would have been on-line for 95% of time
  - The other 5% sold for an average of 157.8 US$/MW.h
  - Interestingly, the fuel cell can produce 1 kW.h from each 3 kW.h of input
    - Some limited scope for re-selling electricity

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Typical Car Density in Major Cities

City	Approx. diameter (km)	Population (millions)	Cars per 1000 people	Density (cars/km^2)
Toronto	40	2.2	430	753
Atlanta	35	3.5	475	1729
Paris	48	11	425	2585
Stockholm	27	1.9	390	1295
Delhi	44	9.4	200	1237
Rio de Janeiro	50	9	180	825
Tokyo	53	12.3	190	1070
Typical major city	**40**			**1200**

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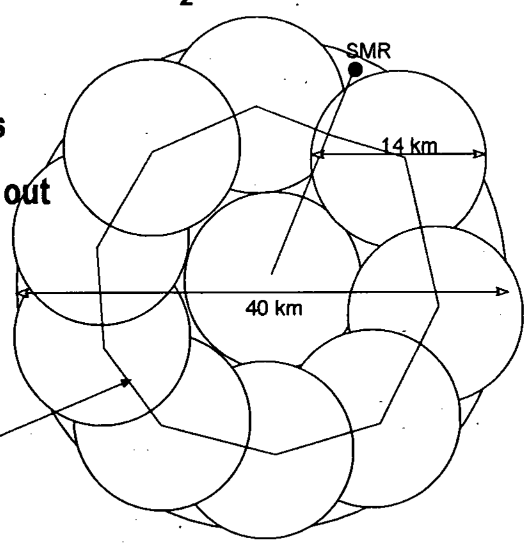
Hypothetical Urban H_2 Distribution

10 service stations @ 1 tonne/d for 340 fuelings

Supply 24 000 vehicles out of 1 million

133 km of pipeline
or
540 km of truck route



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Electrolytic Hydrogen

- Focus on low-cost electrolysis
  - 300 US$/kW
  - Penalty on electricity use (total equivalent to 2.1 volts)
- Storage
  - Use 400 000 US$/tonne H_2 for tube-trailers
  - Store at least 12-hours of average demand
- Optimize
  - Cheaper power
    - = Less time on-line
    - = More electrolysis cells
    - = More storage
  - Add 10 $/MW.h for distribution over existing grid (since off-peak)

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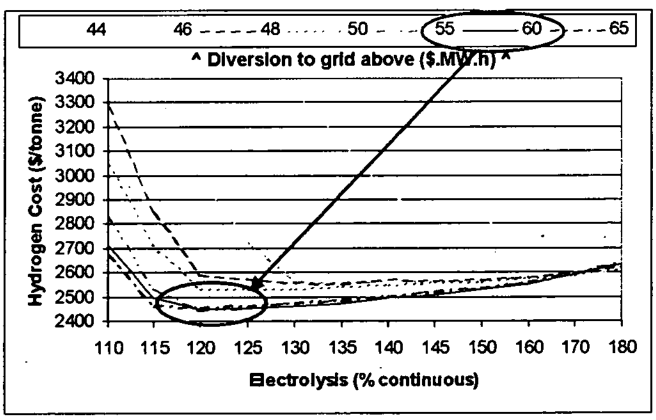
Optimum

- Lowest cost of 2447 US$/tonne H_2
  - ~ 60 US$/MW.h cut-off
  - 125% electrolysis installation
  - ~ 15 hours storage



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Can do somewhat better

- 2447 US$/tonne comes from a rigid scheme
  - The electricity price is known one week in advance
  - So, if the H_2 storage level is low, can occasionally accept higher power costs
  - Can then install less electrolysis and only 12-h storage
  - Simple scheme with a normal ceiling 55 US$/MW.h and an upper ceiling of 125 US$/MW.h *used only when storage levels are less than four hour's production*

  ⇒ 2412 US$/tonne H_2
- This still relatively rigid
  - One should be able to do a little better

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GEN III+ ⇒ INPEL

- At 29.3 US$/MW.h, Alberta Power Pool in 2002 had unusually low cost electricity
  - Average in 2003 was 45.0 US$/MW.h (partly weaker US dollar)
  - Average in 2003 in Ontario was 38.6 US$/MW.h
- The important consideration is the cost of generating power
  - Generate at about 30 US$/MW.h using Gen III+ nuclear
  - Make hydrogen when grid price drops
    - avoid large-scale additions of base-loaded nuclear plants causing a seriously depressed price
  - And use nuclear to supply peaking power at prices that exceed the average required overall for return on investment
- INPEL = Intermittently Protonated Electrons
  - Affordable hydrogen where you need it

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Costs for Production Alternatives

	SMR + pipeline	SMR + trucks	Local SMR	Local E off-peak	Local E continuous
Prod'n capital ($/GJ H_2)	4.6	4.6	8.5	4.2	3.5
Energy ($/GJ H_2)	8.4	8.4	7.3	12.8	>15.6
H_2 Distrib'n ($/GJ H_2)	13.3	4.6	0.0	0.0	0.0
CO_2 charge ($/GJ H_2)	1.6	1.6	>>1.6	0.0	0.0
TOTAL ($/GJ H_2)	27.9	19.2	>>17.4	17.0	>19.1
TOTAL ($/tonne H_2)	4000	2753	>>2470	2414	>2712

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Affordable – Adding up to

Costs are for systems supplying 10 tonnes H_2/day

Option	1	2	3	4	5
Concept	Remote SMR + Pipeline	Remote SMR + Trucks	10 Local SMRs	10 Local Electrolysis with off-peak power	10 Local Electrolysis running full-time
Total ($/GJ)	27.9	19.2	>>17.4	17.0	>19.1
Total ($/tonne H_2)	4000*	2753*	>>2470	2414	>2712
Total ($/tonne H_2)	With 600 $/kW cells			2870	3010
Total ($/tonne H_2)	If electricity is +1 $/MW.h				2765

*CO_2 sequestration cost is 37 $/t CO_2

Page 18 A change of 10 $/t CO_2 = 61 $/t H_2

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Cost Relative to Gasoline

- Based on energy content (LHVs)
  - 1 tonne hydrogen = 2.68 tonnes gasoline
  - 2.68 tonnes gasoline (968 US gal) before taxes = ~1600 US$
    - (Before recent spike in oil prices)
  - On energy content, gasoline is one-third cheaper
- Based on equal distance travelled
  - For 16 090 km
    - Gasoline at 11.3 L/100 km = 793 US$
    - Hydrogen in a 55%-efficient fuel cell = 589 US$
    - Of course, a gasoline-electric hybrid would undercut the fuel cell
    - However, the point is that hydrogen does not cause fuel price shock
    - All before tax: governments can taxes adjust to promote clean fuel

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Deeper into the Hydrogen Age

- This is the starting pathway
  - By 5 to 10% of the vehicle market, pipelines start to become affordable for city supply
  - Centralized, perhaps thermochemical, hydrogen production can be deployed economically
    - Electrolytic systems relocate to less densely populated areas
- Even then, electrolysis could prove persistent
  - Producing electrolytic H_2 is very flexible for load-leveling and as a way of storing electricity
  - Will depend on the economics
    - Of nuclear thermochemical processes
    - Of carbon-based sources with sequestration

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Available – Is the Technology Ready?

- Generation III+ nuclear can displace open-exhaust coal-fired electricity
  - Coal can compete but *MUST INCLUDE SEQUESTRATION*
  - Wind and solar can contribute
    - Shouldn't be excessively subsidized
    - Likely will provide only a small percentage of total
    - Electrolysis with nuclear+wind may work where wind alone doesn't
- Nuclear is proven technology
  - Economics are best with baseloading, so balance peak electric demand by ...
  - Generating hydrogen off-peak using electrolysis
    - Cheaper electricity
  - Distributed H_2 generation is the lowest-cost start-up technology
- In 20+ years, the option will exist to begin switch to Gen IV reactors
  - Produce additional hydrogen centrally in bulk
    - Demand will then justify pipeline networks and distribution

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GHG build-up is the biggest challenge ever faced by humanity

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Unless we are prepared to meet the challenge with scores of EJ/a (i.e. hundreds of millions of tonnes of H_2 per annum), we are not a solution and we deserve to be ignored.

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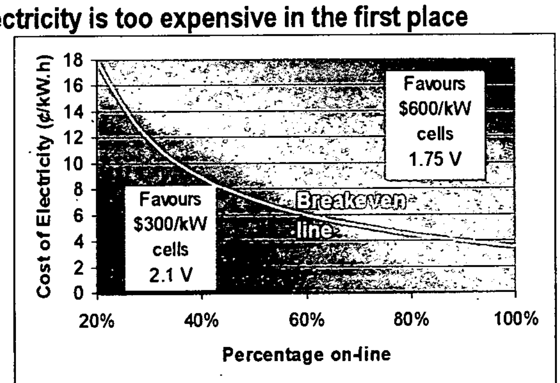
Electrolysis: High Cost vs Low Voltage

- **Focus on low-cost electrolysers**
  - **Both electricity and equipment need to be cheap**
    - **Electricity will be cheaper if it can be interrupted**
  - **Higher-cost electrolysers cost more than the electricity they save or the electricity is too expensive in the first place**



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Realistic?

- Depends on low-cost electrolysis equipment
  - 300 $/kW
- Depends on low-cost electricity
  - ~ 3 ¢/kW.h at generation
  - The target for AECL's ACR™
    - Based on Qinshan experience
    - Saving 7.5% on less D_2O; 6% with smaller core size; 11.5% on simplification, elimination, better materials; 5% on BOP optimization; and 10% with modularization, construction advances, engineering tools
  - Distributed off-peak
    - So not encumbered with heavy distribution costs
    - Helps to keep new nuclear stations running continuously
    - ... and so able to displace coal-fired peaking plants
    - We benefit from a mix

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5.2 Session2: Discussion about Hydrogen Production Technologies by Nuclear Technologies

5.2.1 Competitive Economy of Nuclear Hydrogen in the Marketplace

Tetsuaki TAKEDA

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Abstract

So far, hydrogen is being used as raw material of chemical products such as nitrogenous fertilizer. In the near future, hydrogen will be used as clean energy in the world. Various countries are carrying out the development of the fuel cell which generates electricity with hydrogen as fuel actively. For a fuel cell vehicle (FCV) in Japan, the target number of the FCV is 50000 in 2010, 5 million in 2020, and 15 million in 2030. Therefore, the amount of demand for hydrogen is 7.3 Gm^3/y in 2010, 38.7 Gm^3/y in 2020, and 54.4 Gm^3/y in 2030. One HTGR can produce hydrogen about 80000m^3/h for 0.8 to 0.9 million FCVs, as assumption of the computation is 600MW thermal power, 90% rate of operation, and 55% of thermal efficiency.

This presentation will provide a subject for discussion which is "Can nuclear hydrogen compete with hydrogen produced by other energy sources in the market?" General questions are as follows.

- Who is the competitor of nuclear (HTGR) hydrogen?
- Can nuclear (HTGR) hydrogen coexist with hydrogen produced by other energy sources?
- Can nuclear (HTGR) hydrogen compete economically with hydrogen produced by other energy sources in the market?

We believe nuclear (HTGR) hydrogen can coexist and compete economically with hydrogen produced by other energy sources in the marketplace. Everyone in the industrial, academic, and government should cooperate and let us do our best for development of nuclear hydrogen technology.

KEYWORDS: HTGR, Electricity, Nuclear hydrogen, Fuel cell vehicle, Hydrogen production

Competitive economy of nuclear hydrogen in the marketplace

- Can nuclear hydrogen compete with hydrogen produced by other energy sources in the market ? -

Presented by T. TAKEDA

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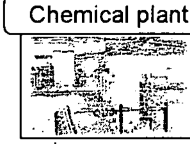
Oarai, Ibaraki, 311-1394, Japan

HTTR-WS, July 6, 2004, Oarai Research Establishment of JAERI, JAPAN

What do we use hydrogen for ?

Chemical plant



- So far, hydrogen is being used as raw material of chemical products such as nitrogenous fertilizer.

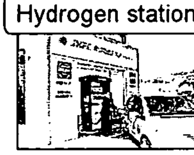
- Hydrogen will be used as clean energy in the near future !

$2H_2 + O_2 \rightarrow 2H_2O$ + Energy

- Fuel cell: generate electricity with hydrogen as fuel
  - <u>Fuel cell vehicle</u>: A kind of electric vehicle
  - <u>Fuel cell for household, business</u>: co-generate electricity and heat

Fuel cell for household, business

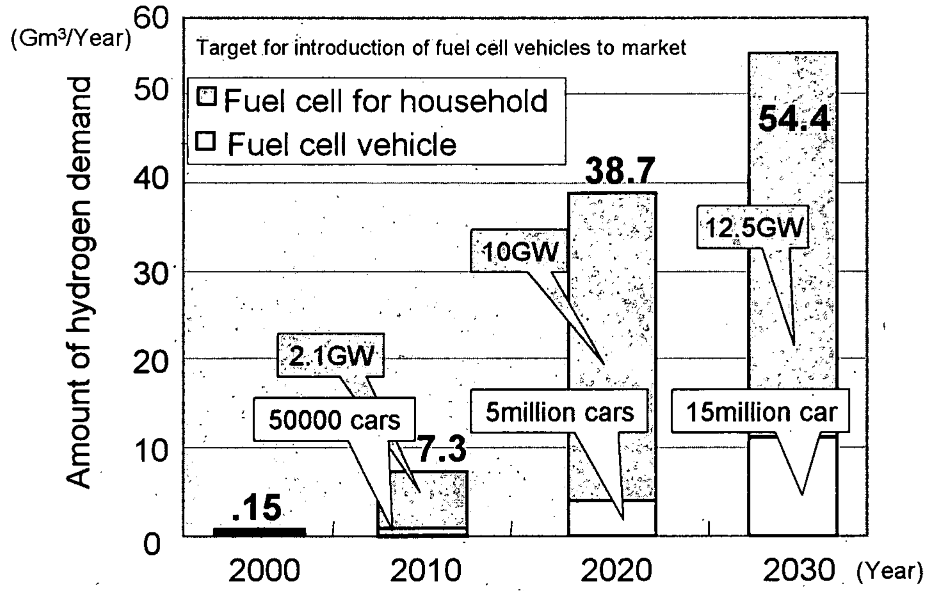
Hydrogen station



Fuel cell vehicle

1

How much hydrogen do we need ?



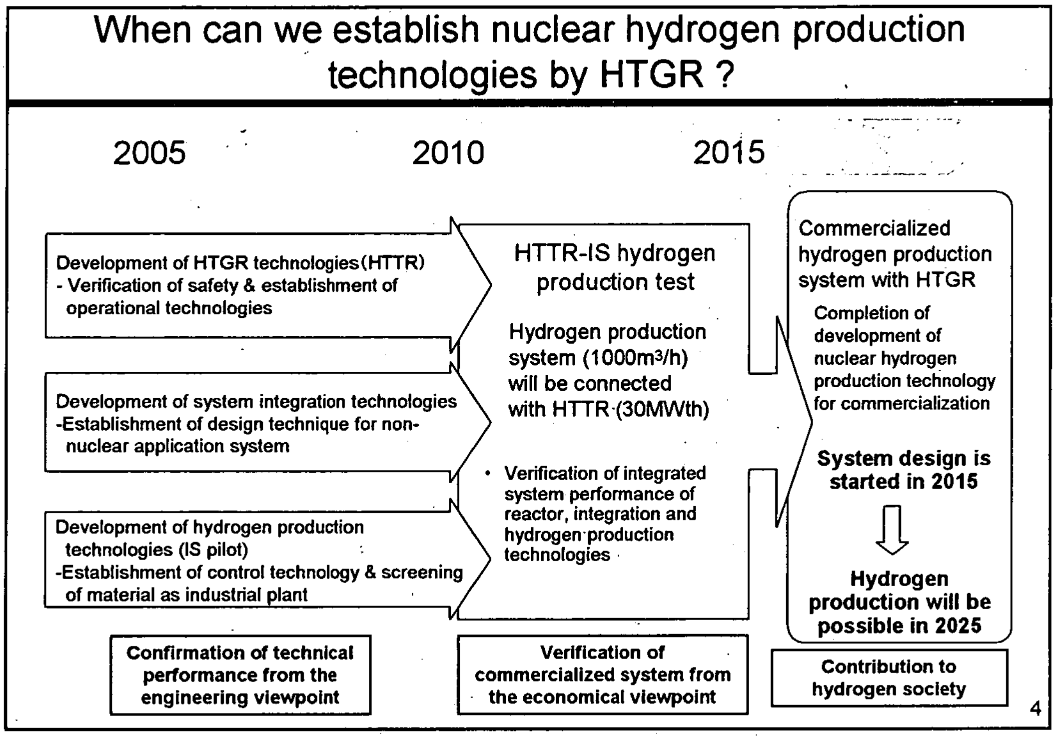
(Source: WE-NET Report & MEXT home page)

2

How much hydrogen can be produced by a HTGR ?

- To supply hydrogen to the 5 million FCVs, for example, several High Temperature Gas-cooled Reactors (HTGRs) are necessary. (It is about 6 HTGRs)
  Thermal power; 600MW
  Rate of operation; 90%
  Thermal efficiency; 55%
- One HTGR can produce hydrogen about 80000m³/h for 0.8 to 0.9 million FCVs.
- 5 million FCVs are about only 7% of all cars in Japan.
- A large quantity of hydrogen will be consumed in the near future.

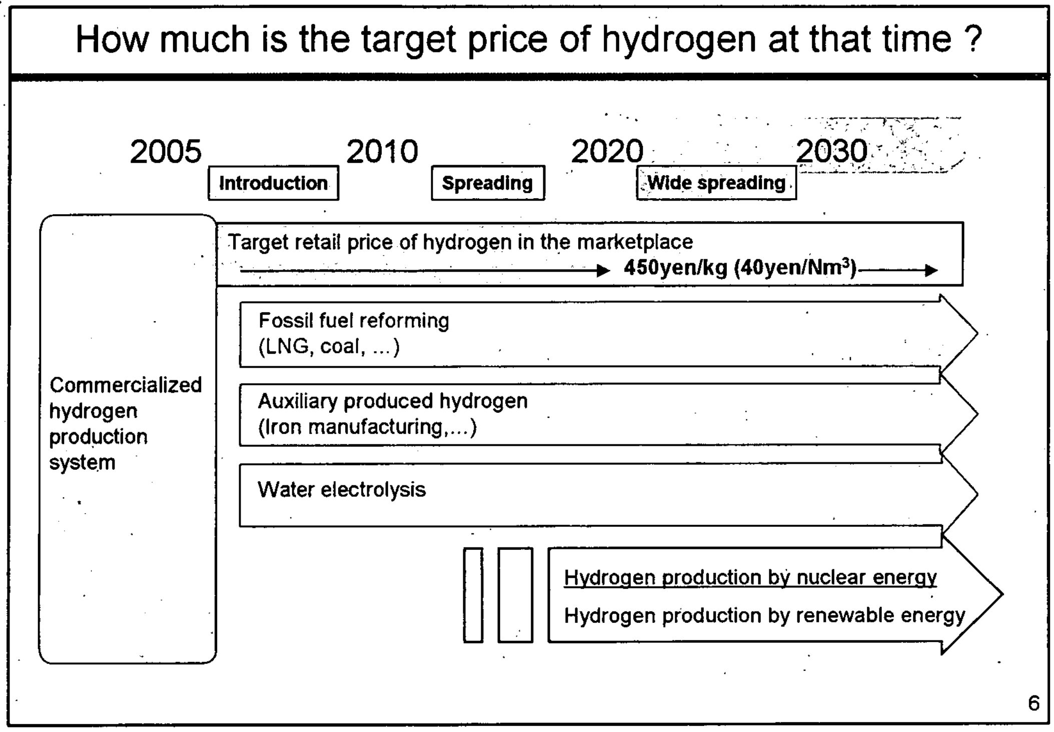
3

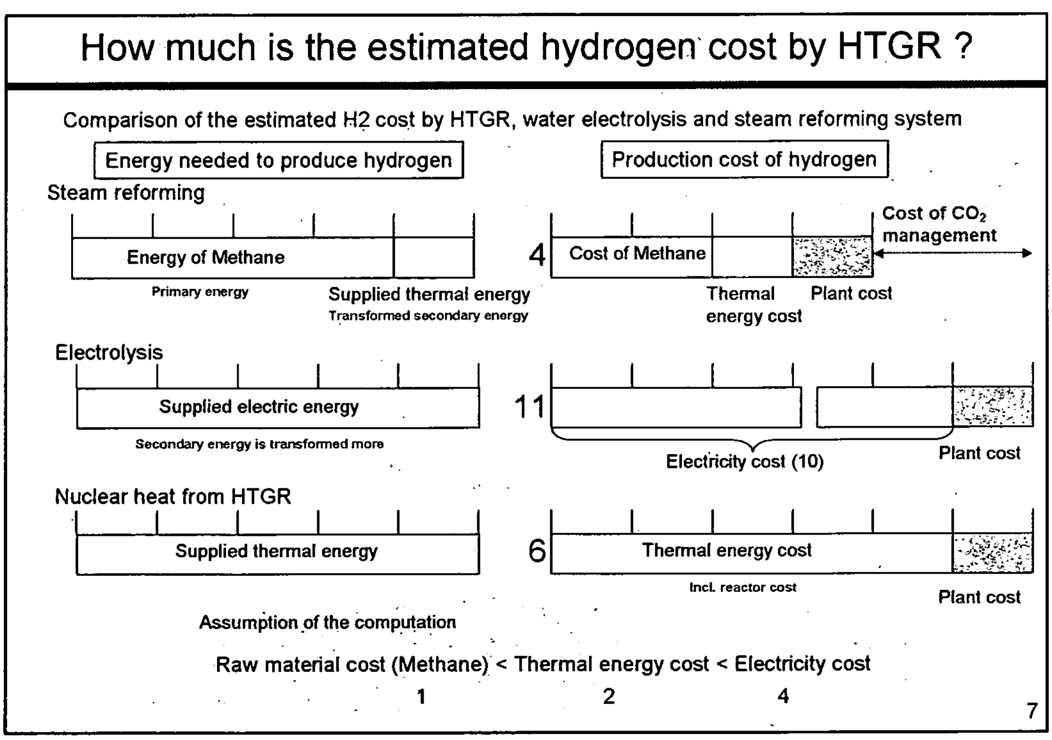


Who is the competitor of nuclear (HTGR) hydrogen ?

- Hydrogen which has already distributed in the market before 2025
  - Auxiliary produced hydrogen(Iron and glass manufacturing, etc.)
  - Off-site production system
    - Methane (Naphtha) steam reforming
  - On-site production system
    - Town gas reforming
    - Gasoline reforming
    - Water electrolysis
- Hydrogen which distributes in the market in about 2025
  - Nuclear hydrogen from HTGR
  - Coal reforming with carbon capture and sequestration
  - Renewable energy (Solar, Wind, etc.)

5


How much is the target price of hydrogen at that time ?
2005
2010
2020
2030
Introduction
Spreading
Wide spreading
Target retail price of hydrogen in the marketplace
450yen/kg (40yen/Nm3)
Commercialized hydrogen production system
Fossil fuel reforming
(LNG, coal, ...)
Auxiliary produced hydrogen
(Iron manufacturing,...)
Water electrolysis
Hydrogen production by nuclear energy
Hydrogen production by renewable energy
6


How much is the estimated hydrogen cost by HTGR ?
Comparison of the estimated H2 cost by HTGR, water electrolysis and steam reforming system
Energy needed to produce hydrogen
Production cost of hydrogen
Steam reforming
Energy of Methane
Primary energy
Supplied thermal energy
Transformed secondary energy
4
Cost of Methane
Thermal energy cost
Plant cost
Cost of CO2 management
Electrolysis
Supplied electric energy
Secondary energy is transformed more
11
Electricity cost (10)
Plant cost
Nuclear heat from HTGR
Supplied thermal energy
6
Thermal energy cost
Incl. reactor cost
Plant cost
Assumption of the computation
Raw material cost (Methane) < Thermal energy cost < Electricity cost
1
2
4
7

Reference: Estimation of thermal energy cost

Comparison with each cost per unit energy

Incl. fossil fuel boiler cost — Incl. reactor cost

Raw material cost (Methane) < Thermal energy cost < Electricity cost

1 : 2 : 4

LNG import price : 1.56yen/kWh (1999) : **1**

Electricity price : 5.3 – 5.6yen/kWh (retail price : 27yen/kWh) : **4**

Assumption of the thermal energy cost :

Thermal energy cost = electricity cost x conversion efficiency

1 : 2

For example : Thermal energy cost by HTGR — 2yen/kWh = 4yen/kWh x 50%

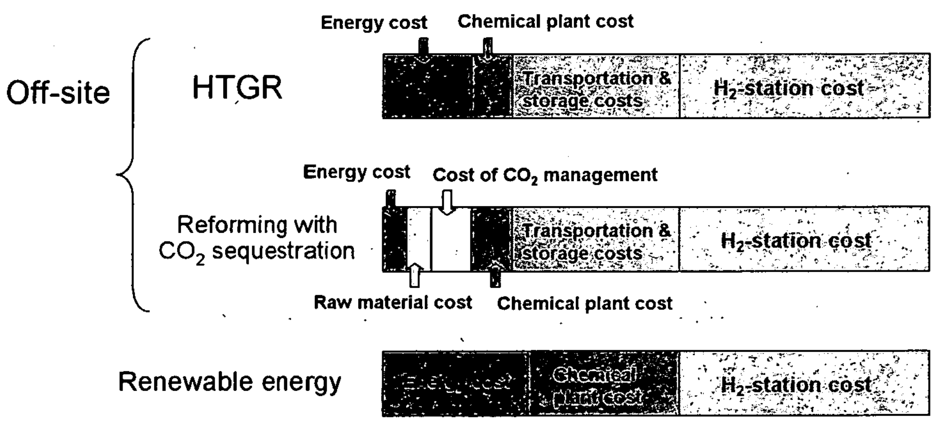
Thermal energy cost by LNG power plant — 3yen/kWh = 6yen/kWh x 50%

If you have a good idea to evaluate the thermal energy cost, please let us know !

8

How are the items of future total hydrogen cost?

- HTGR : Thermochemical water splitting IS process
- Fossil fuel reforming : Cost of CO_2 management is needed
- Renewable energy : On-site water electrolysis by solar or wind energy



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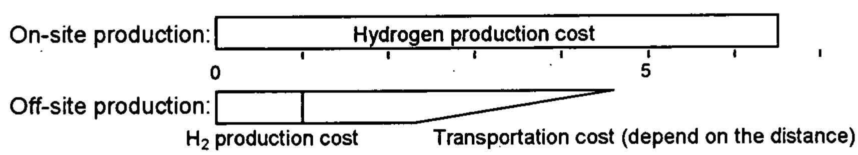
Comparison with on-site and off-site production of hydrogen

- In the on-site production system
  - H_2 production plant cost becomes high because the plant scale is small, however, the transportation cost becomes low.
- In the off-site production system
  - H_2 transportation cost becomes high, however, the plant cost is low because it is advantageous to construct the plant by scale merit.
- If both are compared, it is the following.
  - H_2 production cost with the on-site production system in the H_2-station (200m³/h) is about 6.5 times of that with the off-site mass production system (100000m³/h).
  - In the off-site mass production system, the transportation cost in a city or suburbs is about 1.3 to 3.6 times of the production cost.



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How much is the area which is necessary for the nuclear and renewable energy systems?

Scales of photovoltaic cells and windmills to provide energy to one residential house and one H_2-station

	One family	One H_2-station
	1.0 kW electricity	1300 kW electricity
■ Area of Photovoltaic cells	45-77 m^2	60-100 x10^3 m^2
■ Number of Windmills	One small windmill (3.1-4.6 m blade-diameter)	Two large windmills (75-88 m blade-diameter)
One HTGR with 600MW-th	About 0.27 million families	About 270 H_2-stations

11

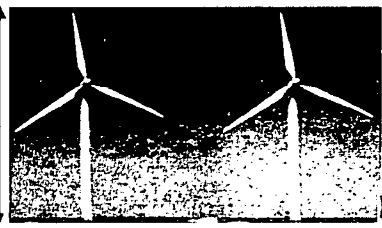
Site areas necessary for photovoltaic cell and windmill

- Site area necessary for one H_2-station (1300 kWe; 300m³/h) -

Electricity output: 2MW x 2 windmills, 75-88 m blade-diameter

- Photovoltaic cell; 60-100 times of H_2-station

Height; 100 m



H_2-station (0.1 ha 40m x 25m)

Area: About 30 ha (=(diameter)²x30x2)

H_2-station

Area; 6-10 ha

40m x 25m

- Windmill; About 300 times of H_2-station

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Site area necessary for HTGR

- Site area necessary for 270 H_2-station (300 x 270 m³/h) -

- One 600 MWth HTGR 250 m x 250 m

1000 times smaller in area than the renewable energy system

- Renewable energy can be used for a residential house.
- However, there will be a limit to use renewable energy for many H2-stations.

13

Questions to the audience

- Who is the competitor of nuclear (HTGR) hydrogen ?
- Can nuclear (HTGR) hydrogen coexist with hydrogen produced by other energy sources ?
- Can nuclear (HTGR) hydrogen compete economically with hydrogen produced by other energy sources in the market ?

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5.3 Session3: Heat Utilization of Nuclear Energy

5.3.1 Nuclear Power Utilization for Carbon Dioxide Zero-emission Hydrogen System

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Fuel cell (FC) offers the possibility of expanding the electricity utilization market. One of the key technologies that will make the widespread use of fuel cells possible is a hydrogen supply system. The possibility of a hydrogen production system for FC vehicles, which utilized chemical reactants and capable to realize carbon dioxide zero-emission, was discussed in this study. The system uses a portable thermally regenerative fuel reformer of carbon dioxide fixation type and is based on nuclear power. The concept is applicable also on unstable energy sources such as renewable energy, surplus industrial process heat and so forth. The reactivity of metal oxide to carbon dioxide was used for the carbon dioxide fixation and also for heat source of fuel reforming. In this study, calcium oxide was used as the first candidate. Methane was chosen as a candidate reactant for steam reforming, because it is the most popular natural fuel resource and has a simple hydrocarbon fuel structure. The methane steam reforming process consists of the two gas phase reactions of methane reforming and carbon monoxide shifting with various catalysts. This study attempts to use calcium oxide carbonation to remove carbon dioxide from the reformed gas and fix it. Then, the study aims to cause the reforming and shifting and carbonation reactions in the same reactor at once. The reaction realizes high-purity hydrogen production under mild operation conditions, and is regenerative thermally by consuming high-temperature thermal energy produced form nuclear power plants and so forth. To estimate the efficiency of the fuel reforming system using the reaction system, the reactivity of hydrogen production was examined experimentally. The contribution of nuclear power on the zero-emission hydrogen career system was evaluated based on the experimental results. The proposed system was expected to develop new market of nuclear power utilization.

Nuclear Power Utilization for Carbon Dioxide Zero-Emission Hydrogen System

Yukitaka Kato
Research Laboratory for Nuclear Reactors
Tokyo Institute of Technology, Japan

HTTR Workshop on Hydrogen Production Technologies
July 5-6, 2004
Department of Advanced Nuclear Heat Technology
Japan Atomic Energy Research Institute

Y. Kato, Tokyo Tech

Contents

- Back ground
- Hydrogen supply based on nuclear system for fuel cell vehicles
- Regenerative reformer for CO_2 zero-emission FC system
- Experimental demonstration
- Evaluation of the zero emission system

2

Y. Kato, Tokyo Tech

Unstable Operation

-Load leveling for Economical Plant Operation-

- Load change and unstable operation
  - Low-annual operation rate
  - Uneconomic
- Load leveling for 100% operation
  - Energy storage
  - Energy conversion

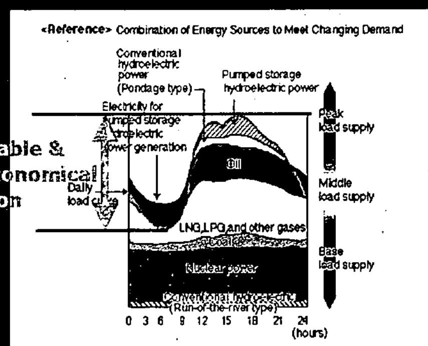

Fig. A daily load change in a summer day in Japan
Tokyo Electric Power Co. http://www.tepco.co.jp/

Peak Electric Load (2001)
Japan=181 GW
Tokyo area=64 GW (24 Jul.), 51 GW (15 Jan.)

3

Y. Kato, Tokyo Tech

Diversification of energy supply and demand

	Supply		Demand
Present	Stable	→	Stable
Future	Diversified	→ Storage →	Instable
	Decentralization/ Renewable energy		Daily and Seasonal change

Fig. Forecast of the change of energy flow pattern

- Future society needs high-efficient tech. of,
  - Energy storage
  - Energy transportation → **Use of chemical reaction**
  - Energy conversion

4

Y. Kato, Tokyo Tech

Hydrogen for FC
-A fuel cell is environmental friendly?-

Problems of H_2 supply to a conventional fuel cell vehicle

- Compressed H_2 fuel : high-energy consumptions for production and pressurization, and explosiveness

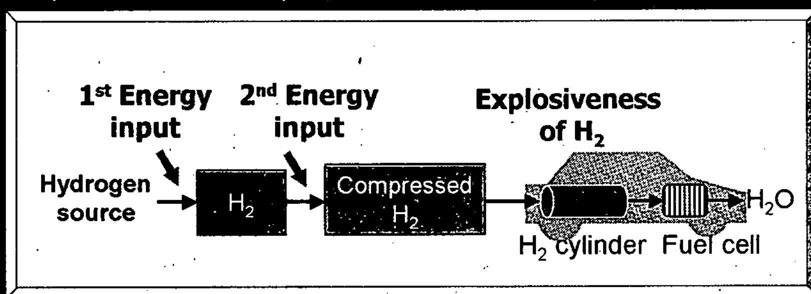

Fig. Subjects for hydrogen supply to a fuel cell vehicle

5

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Fuel reforming for hydrogen supply to a fuel cell vehicle

Problems of H_2 supply to a conventional fuel cell vehicle

- Fuel Reforming: complex structure, and CO_2 emission

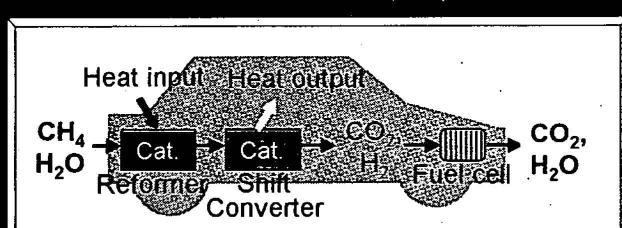

Fig. Conventional reforming system for a FC vehicle

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Regenerative Reforming

-Use of chemical absorption-

- Fuel reforming for methane
  - $CH_4 + H_2O \leftrightarrow 3H_2 + CO$, $\Delta H°_1 = +205.6$ kJ/mol
  - $CO + H_2O \leftrightarrow H_2 + CO_2$, $\Delta H°_2 = -41.1$ kJ/mol
- CaO carbonation
  - $CaO(s) + CO_2(g) \leftrightarrow CaCO_3(s)$, $\Delta H°_3 = -178.3$ kJ/mol
- Regenerative reforming (CO_2 absorption reforming, self-heating)
  - $CaO(s) + CH_4(g) + 2H_2O(g) \leftrightarrow 4H_2(g) + CaCO_3(s)$, $\Delta H°_4 = -13.3$ kJ/mol

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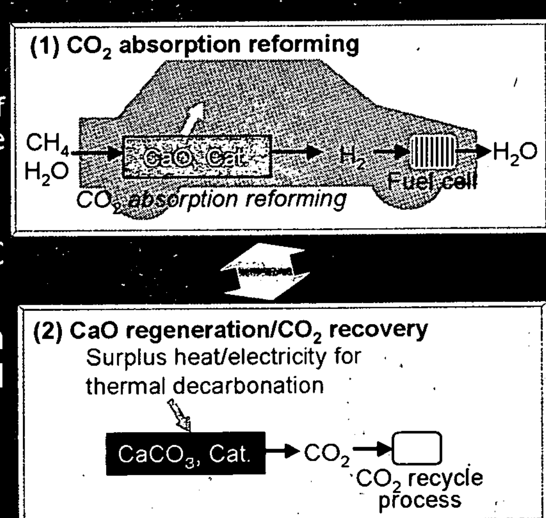
Y. Kato, Tokyo Tech

CO_2 zero-emission FC vehicle

- Regenerative reforming
  - CO_2 recoverable, self heating, and simple reforming system
  - thermally regenerative
- CO_2 zero-emission FC vehicle
- Safety H_2 carrier system under low-pressure and high-density



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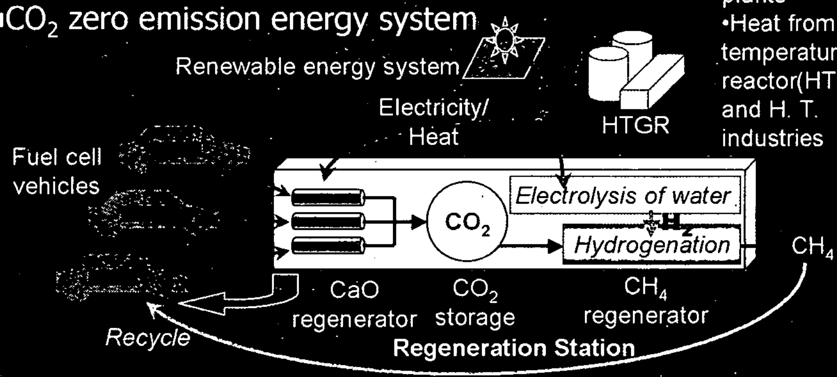
CO_2 zero-emission hydrogen system

- Hydrogen system driven by surplus electricity and heat from nuclear power plants, and unstable energy.
- Safe and compact hydrogen transportation
- CO_2 zero emission energy system

•Electricity from nuclear power plants
•Heat from high-temperature gas reactor(HTGR) and H. T. industries

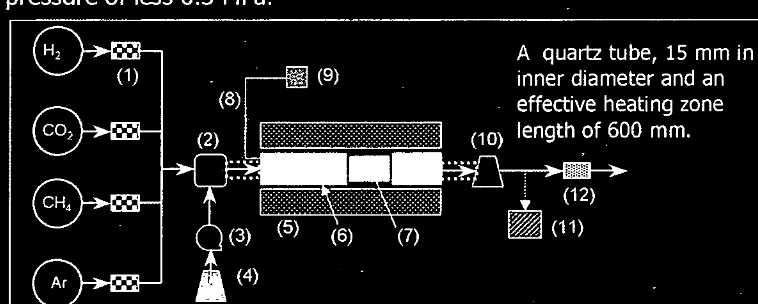


9

Y. Kato, Tokyo Tech

Experiment of the regenerative reformer

- Demonstration of the possibility of the regenerative reforming system
- For polymer electrolyte fuel cell (PEFC) operated at a hydrogen pressure of less 0.3 MPa.



(1) flow meter, (2) evaporator, (3) micro-feeder, (4) water reservoir, (5) electric furnace, (6) reactor tube, (7) reactor bed, (8) thermocouple, (9) furnace heating controller, (10) liquid-gas separator, (11) gas chromatograph, (12) soap flow meter

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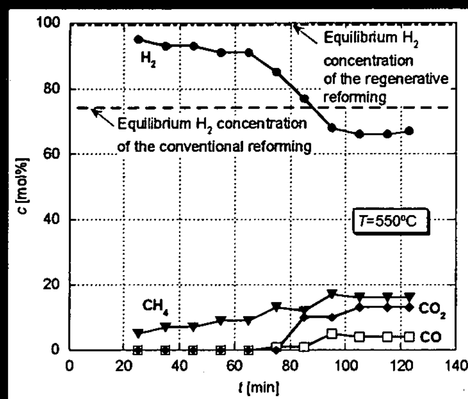
CO_2 absorption reforming

- During the initial 60 min, hydrogen production was higher than the equilibrium concentration of conventional reforming.
- Charged CaO absorbed well CO_2 by carbonation. CO_2 <1%
- CO was removed, <1%
- Low-temperature reforming (conventional reform. temp. > 700°C)



(a) regenerative reformer (RGR)

Fig. Temporal change of effluent composition of the regenerative reformer at 550°C

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CO_2 removal from reforming gas

- Effluent CO_2 concentration from RGR at 550°C was less than 1%.

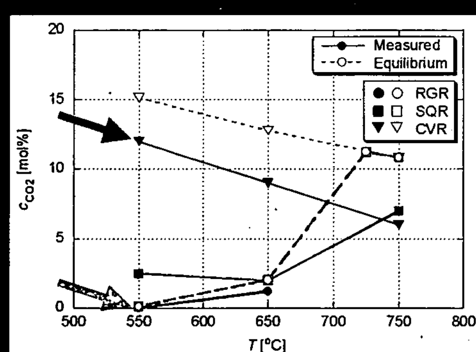

Fig. Effect of bed temperature on effluent carbon dioxide concentration of the reformer comparing with other type reformers.

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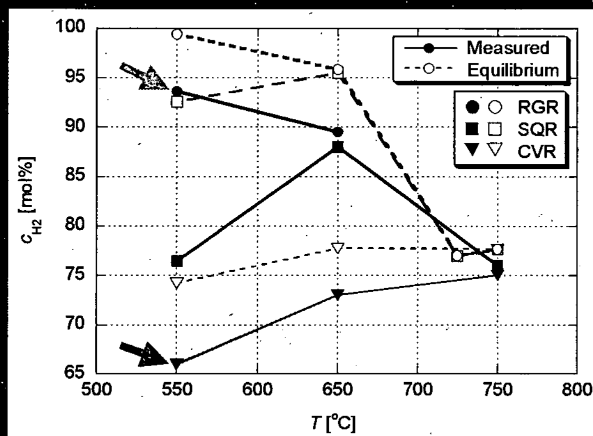
H_2 productivity

- 94% of H_2 production was measured by the RGR at 550°C.



Effect of bed temperature on hydrogen production concentration of the reformers.

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Y. Kato, Tokyo Tech

Estimation of a zero emission vehicle

- 1 kg of H_2 in order to drive for 100 km
- 7.46 kg (9.04 liters) of CaO was required for the RGR.

SSR-FC Vehicle		
Viehcle mileage	km	100
Hydrogen requirement	kg	1.0
Hydrogen production conc	mol%	94
CaO requirement mass	kg	7.94
CaO requirement volume	liter	9.62
Recovered CO_2	kg	5.5

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Y. Kato, Tokyo Tech

Estimation of zero emission energy system

- Nighttime surplus electricity of **1 GW for 8 hours** was used for the regeneration at the regeneration stations.
- The RGR packages of **1.3 million pieces/day** are able to be regenerated in the stations.
- **CO_2 of 7.1×10^3 ton/day** is expected to be recovered from the stations.

Power plant		
Power plant output	GW	1
Night time operation duratio	h	8
Total Electricity amount	GWh	8
	GW	2.88E+04
FC Vehicle		
Viehcle mileage	km	100
Hydrogen requirement	kg	1
Hydrogen production conc	mol%	94
CaO requirement mass	kg	7.94
CaO requirement volume	liter	9.62
CO2	kg	5.5
CO2	mol	125
dH for regeneration	kJ/mol-CO_2	178
Regeneration station		
Requirement reaction heat	kJ/piece	2.23E+04
Cell piece	pieces	1.29E+06
CO2 amount	kg	7.12E+06
	m3(STP)	3.62E+06

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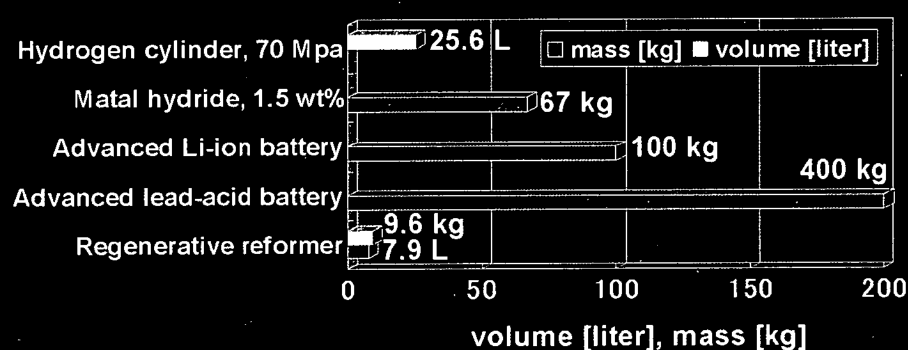
Comparison between H_2 system

Table: Scale of energy storage facilities for 100 km mileage, 14.7 kWh, 500 mol-H_2 (= Petroleum of 4 L, 2.8 kg)



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Y. Kato, Tokyo Tech

Conclusions

- A CO_2 zero-emission fuel cell system using a regenerative fuel reformer based on a nuclear power plant was proposed
- The regenerative reformer was applicable at a lower temperature than common reformer was. At 550°C, the reformer demonstrated 94% hydrogen production and concentrations of less than 1% each of CO and CO_2.
- The system can utilize surplus electricity generated from commercial nuclear power plant. Electricity of 1 GW for 8 h can regenerate 1.3 million of reforming packages.
- The required amount of CaO for the reformer was expected to be similar to the total weight of methane and water as fuel resources.
- The fuel cell system contributes to load leveling of nuclear power plant operation, and improvement of the value of nuclear power system.

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Y. Kato, Tokyo Tech

COE-INES

Tokyo Institute of Technology

COE-INES Project

The 21st Century **COE** Program "**I**nnovative **N**uclear **E**nergy **S**ystems for Sustainable Development of the World" (**COE-INES**)

Organized by Dep. of Nuclear Eng. and Dep. of Energy Sciences, Tokyo Inst. of Technology

COE (Center Of Excellence) program is adopted by the Japanese Ministry of Education and Science (MEXT) to reinforce university education and research functions for study at a higher level and cultivation of creative, internationally competitive talent.

Our proposal, COE-INES, was the only chosen one for the Nuclear Science and Technology Category

Duration: 2003-2008, 196 million JPY for 2003 (=1.4 million Euro)

Invitation to

COE-INES International Workshop on "Toward Hydrogen Economy; What Nuclear can contribute and how"

5 - 6 November, 2004

The Centennial Hall, Tokyo Institute of Technology,
O-okayama, Tokyo

東京工業大学 21世紀COEプログラム
世界の持続的発展を支える革新的原子力
Innovative Nuclear Energy Systems for Sustainable Development of the World
COE-INES

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5.3.2 GTHTR300 for Hydrogen Cogeneration

Kazuhiko KUNITOMI and Xing YAN

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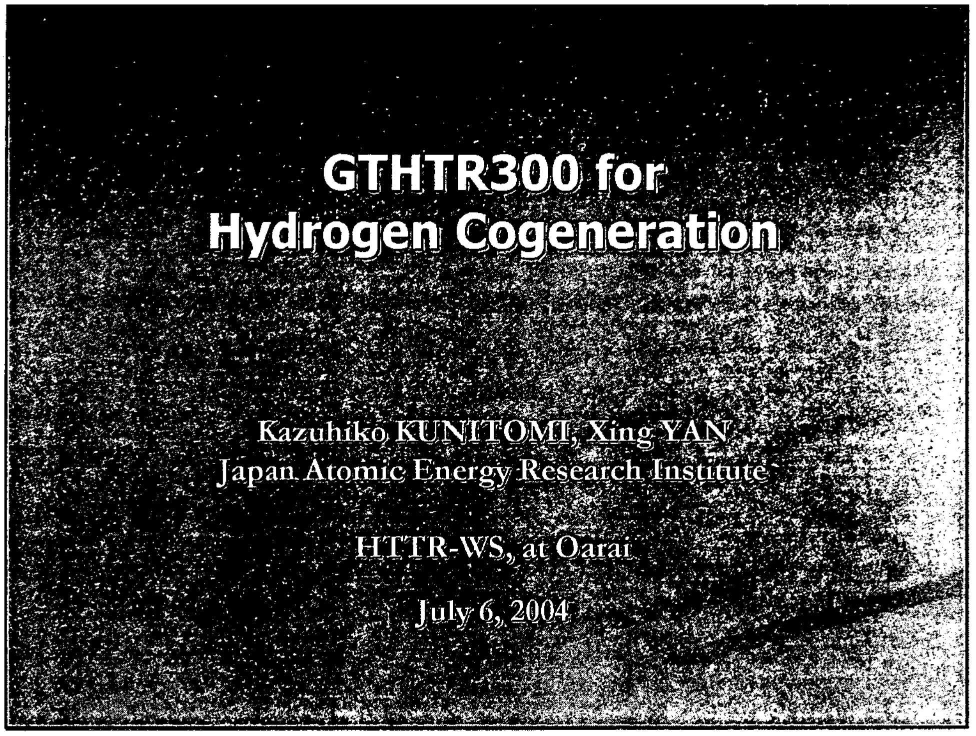
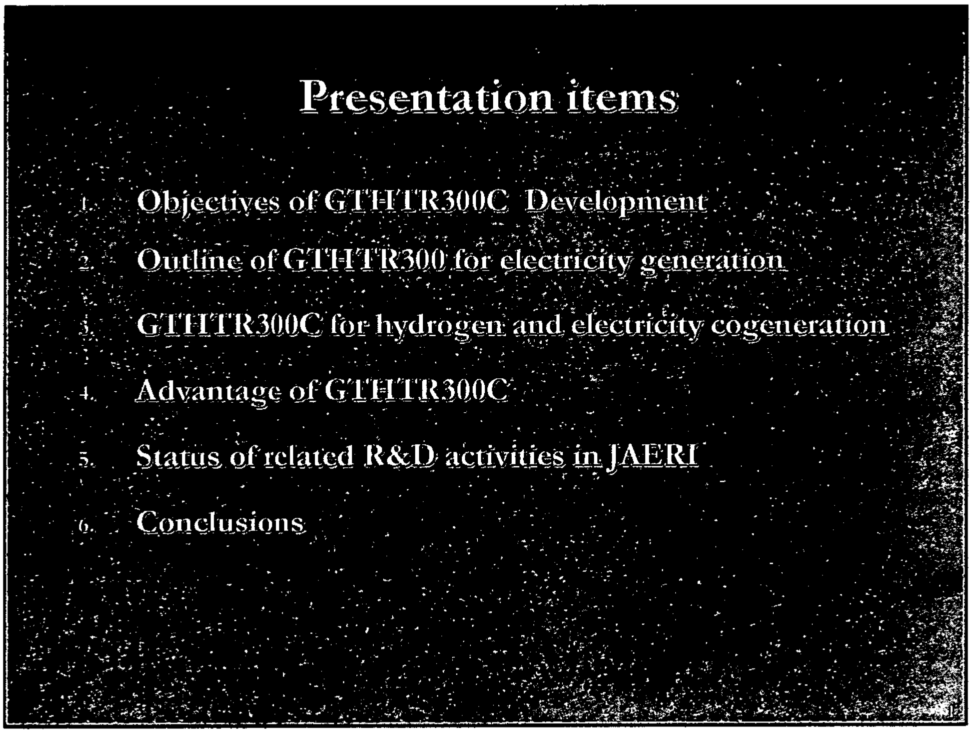
kunitomi@httr.oarai.jaeri.go.jp

Design study on the GTHTR300-cogeneration (GTHTR300C) aiming at producing both electricity by a gas turbine and hydrogen by a thermochemical water splitting method (IS process method) was conducted. The GTHTR300C is a block type High Temperature Gas-cooled Reactor (HTGR) with its reactor thermal power of 600MW and outlet coolant temperature of 950°C. An intermediate heat exchanger (IHX) is located between the reactor pressure vessel (RPV) and the gas turbine system. The heat capacity of the IHX is 170MW and is used for hydrogen production. The balance of the reactor thermal power is used for electric generation. The GTHTR300C is designed based on existing technologies for the High Temperature Engineering Test Reactor (HTTR) and the helium turbine power conversion technology under development for the Gas Turbine High Temperature Reactor (GTHTR300) so as to minimize cost and risk of deployment.

This presentation explains the original design features focusing on the plant layout and plant cycle of the GTHTR300C together with present development status of the GTHTR300, IHX, etc. Also, the advantage of the GTHTR300C is presented.

Keyword *: HTGR, HTTR, Gas Turbine, Intermediate Heat Exchanger, Hydrogen Production*


GTHTR300 for
Hydrogen Cogeneration
Kazuhiko KUNITOMI, Xing YAN
Japan Atomic Energy Research Institute
HTTR-WS, at Oarai
July 6, 2004


Presentation items
1. Objectives of GTHTR300C Development
2. Outline of GTHTR300 for electricity generation
3. GTHTR300C for hydrogen and electricity cogeneration
4. Advantage of GTHTR300C
5. Status of related R&D activities in JAERI
6. Conclusions

Objectives of GTHTR300C Development

JAERI

将来型高温ガス炉システム開発グループ

Objectives

Deployment of economical HTGR system providing hydrogen and electricity in 2030s in Japan

Development condition

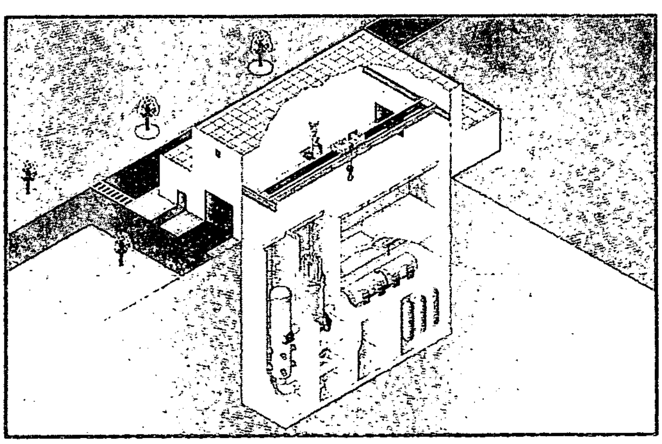
- Design and development under practical condition in Japan(considering anti-nuclear movement, sluggish economic growth in Japan)
- Economical competitiveness with other systems
- Avoid development of new cutting edge technology. Design and development based on existing technology

2

Outline of GTHTR300

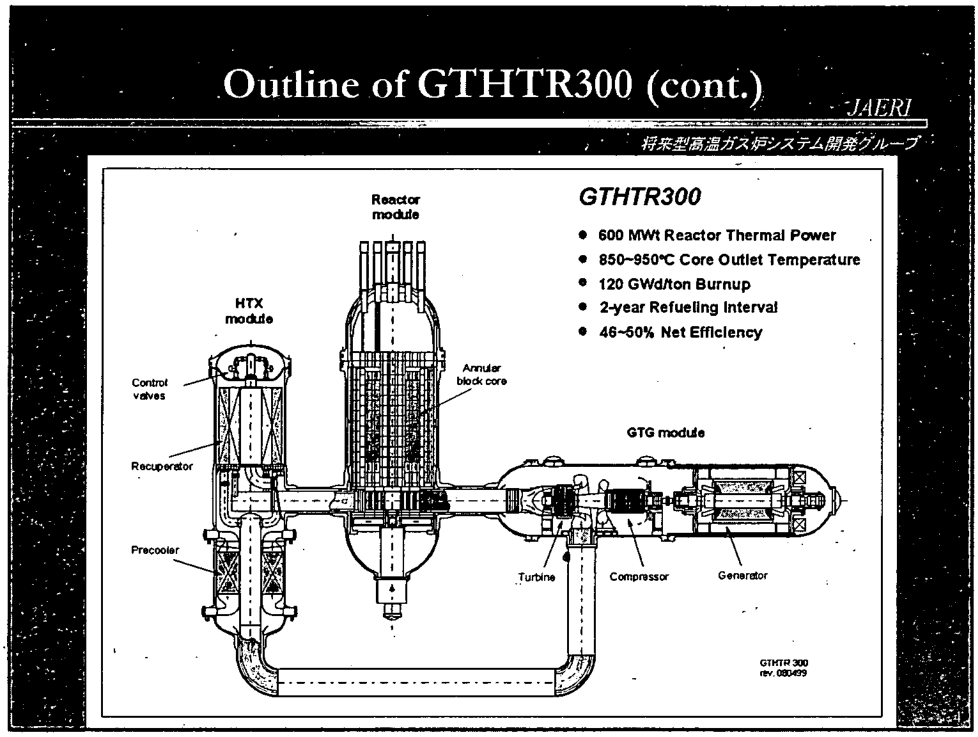
JAERI

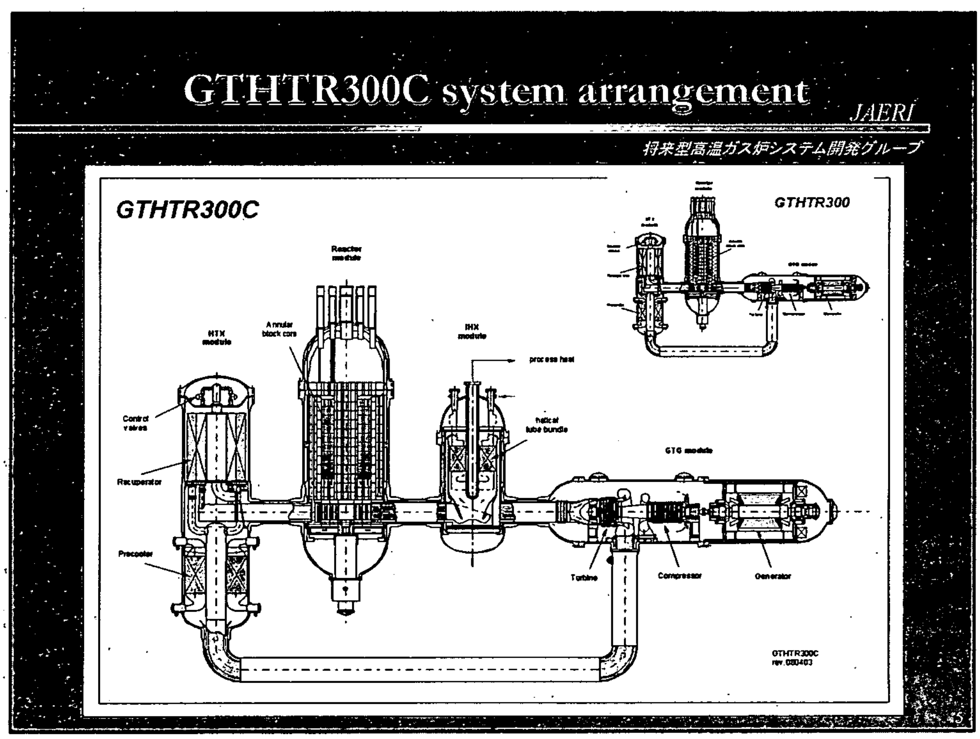
将来型高温ガス炉システム開発グループ



GTHTR300 Plant Arrangement

3

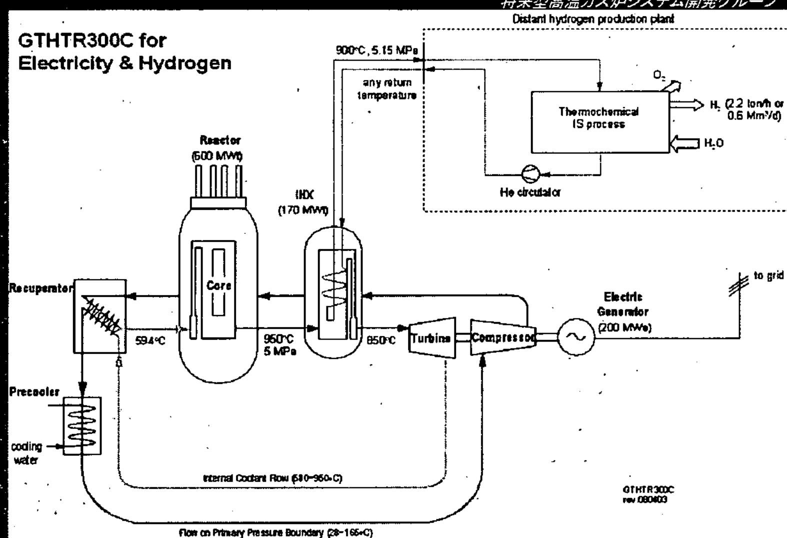

Outline of GTHTR300 (cont.)
JAERI
将来型高温ガス炉システム開発グループ
GTHTR300
600 MWt Reactor Thermal Power
850~950℃ Core Outlet Temperature
120 GWd/ton Burnup
2-year Refueling Interval
46~50% Net Efficiency
Reactor module
HTX module
Control valves
Recuperator
Precooler
Annular block core
GTG module
Turbine
Compressor
Generator
GTHTR 300
rev. 080499


GTHTR300C system arrangement
JAERI
将来型高温ガス炉システム開発グループ
GTHTR300C
GTHTR300
Reactor module
HTX module
Annular block core
IHX module
process heat
helical tube bundle
Control valves
Recuperator
Precooler
GTG module
Turbine
Compressor
Generator

GTHTR300C system

JAERI

将来型高温ガス炉システム開発グループ



6

Major specification of GTHTR300C and GTHTR30(

JAERI

将来型高温ガス炉システム開発グループ

Items	GTHTR300C	GTHTR300
Reactor power	600MW	600MW
(Hydrogen／Electricity)	170/430MW	600MW
Outlet gas temperature	950°C	850°C
Inlet gas temperature	594°C	587°C
Primary flow rate	324kg/s	439kg/s
Primary pressure	5.1MPa	6.9 MPa
Operational cycle	1.5 year	2 year
Burnup rate	120GWd/t	120GWd/t
Electricity generation	202MWe	274MWe
Hydrogen production	1.9～2.4t/h	-
Efficiency of electric generation	45.7%	45%
Efficiency of hydrogen production	45～55%	-

Advantage in deployment of GTHTR300C

JAERI
将来型高温ガス炉システム開発グループ

Site

- Design as replacement of LWR . Supply electric and hydrogen demand in 2030. New site is not necessary.

Economics

- Design based on JAERI's technology development such as reactor technology, hydrogen production technology and gas turbine technology. R&Ds only for this system are limited.
- Economical advantage of this system can be proved by the GTHTR300 deployment.

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Technical advantage of GTHTR300C

JAERI
将来型高温ガス炉システム開発グループ

Reactor design

- Reactor design for the GTHTR300 is basically applicable. Reactor core size, fuel design, etc. are almost the same as those of the GTHTR300.

Intermediate Heat Exchanger

- The IHX for the GTHTR300C is designed based on the IHX in the HTTR. Development of an innovative intermediate heat exchanger is not necessary.

Circulators in primary circuit

- Gas turbine is used as circulator for primary helium gas. Development of large scale circulator in primary circuit is not necessary.

Electric generation system

- The GT system for the GTHTR300 is directly applicable.

Hydrogen production system

- JAERI is developing IS process technologies. These technologies are applicable.

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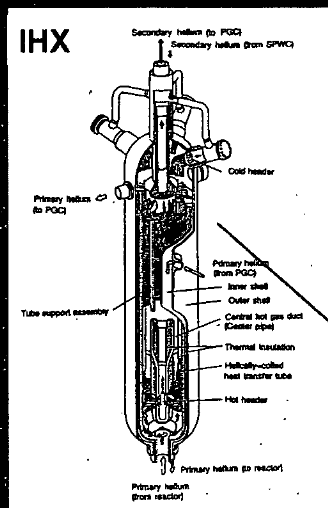
950°C capable helical He/He IHX in HTTR

JAERI

将来型高温ガス炉システム開発グループ

IHX developed technologies and experience:

- Heat and corrosion resistant super alloy Hastelloy-XR (helium ~950°C)
- High temperature structural design guideline (IHX design limits and rules)
- Licensing experience
- Operations experience



10

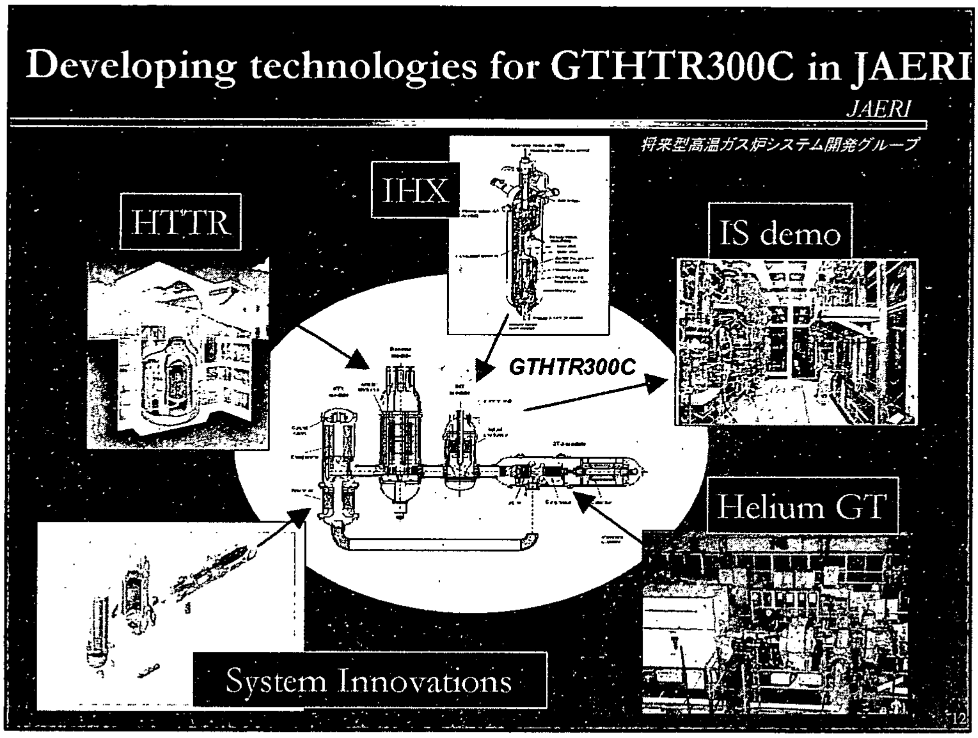
IHX for GTHTR300C and HTTR

JAERI

将来型高温ガス炉システム開発グループ

Items	GTHTR300C	HTTR
Heat capacity	168MW	10MW
Primary He temp.(in/out)	950/850°C	950°C/389°C
Secondary He temp. (in/out)	500/900°C	237/869°C
Primary coolant flowrate	324kg/s	3.4kg/s
Primary coolant pressure	5.02MPa	4.06MPa
Secondary coolant flowrate	81/kg/s	3.0kg/s
Secondary coolant pressure	5.15MPa	4.21MPa
Legalistic average temp.	154°C	113°C
Heat transfer tube		
Material	Hastelloy XR	
Dimension	31.75mm × 3.5t	
Manifold		
Material	Hastelloy XR	
Dimension	1.056m(O.D.)	0.827m(O.D.)

11



Conclusions

JAERI

将来型高温ガス炉システム開発グループ

Major features of GTHTR300C

- The GTHTR300C can supply hydrogen and electricity in 2030.
- The GTHTR300 is designed as replacement of LWRs. No new site is necessary.
- Economical advantage can be proven by the deployment of GTHTR300.
- Reactor technology, IS process technology and gas turbine technology developed or to be developed in JAERI will be directly applicable to this system.

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5.3.3 Research and Development on HTTR Hydrogen Production System

Y. Inagaki

Department of Advanced Nuclear Heat Technology
Oarai Research Establishment
Japan Atomic Energy Research Institute

Research and Development (R&D) on the system integration technology has been carried out for safe and economical connection between a nuclear reactor and a hydrogen production facility.

The R&D items are as follows;

1) Safety technology against explosion of combustible gas
   - Design for protection and mitigation against combustible gas release
   - Estimation of damage on a nuclear plant by blast waves from explosion
2) Safety technology against radioactive materials release
   - Development of a high temperature isolation valve
   - Estimation of tritium permeation
3) Control technology
   - Prevention of thermal disturbance from a hydrogen production facility

This presentation explains the results on the control technology and the high temperature isolation valve. As for the control technology, the simulation test showed that a steam generator was able to mitigate the thermal disturbance, namely fluctuation of the helium temperature caused by a chemical reactor, within the allowable limit. As for the high temperature isolation valve, a new coating material was developed to keep hardness in a high temperature environment, and a mock-up model test is underway.

Research and Development Program on HTTR Hydrogen Production System

Yoshiyuki INAGAKI
Department of Advanced Nuclear Heat Technology
Oarai Research Establishment
Japan Atomic Energy Research Institute

Workshop on
Hydrogen Production Technology
JAERI, Oarai, Japan
July 5-6, 2004

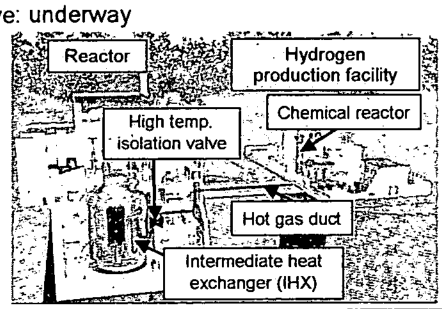
System Integration Technology

■ Objective

- Development of technology for safe and economical connection between reactor and hydrogen production facility

■ R&D Items

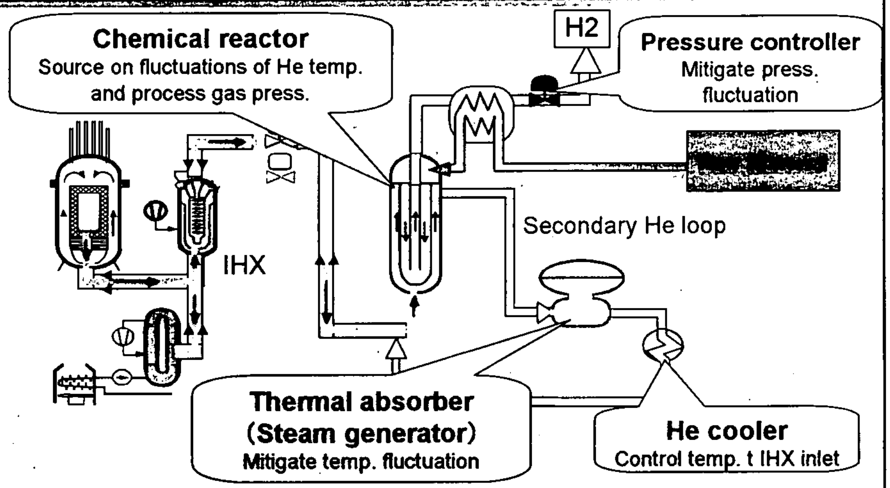
- Safety technology against explosion
  - Design for protection and mitigation against combustible gas release: underway
  - Estimation of damage on nuclear plant by blast waves from explosion: underway
- Safety technology against radioactive materials release
  - Development of high temp. isolation valve: underway
  - Estimation of tritium permeation passing through IHX: finished
- Control technology
  - Prevention of thermal disturbance from hydrogen production facility to reactor by steam generator : finished
- Plant simulation code
  - Verification by simulation test: underway



Controllability

Concept

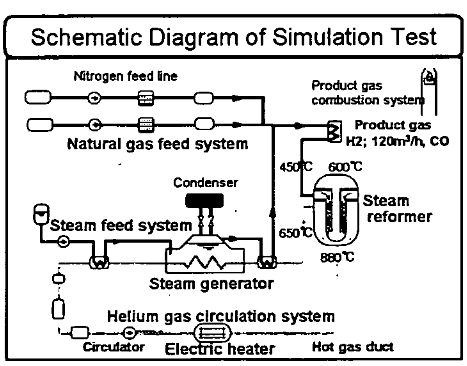
- Operation of the nuclear reactor will not be affected by transient behavior of hydrogen production facility, such as fluctuations of helium temperature and process gas pressure.

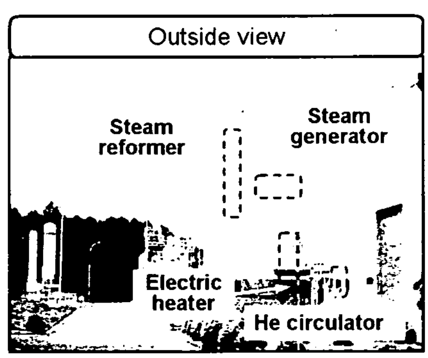


Simulation Test

Feature of test facility

- Simulate key components downstream from IHX
- Heat helium with electric heater instead of nuclear reactor
- Perform test as the same temp. and press. conditions as those of HTTR, and 1/30 flow rate





Simulation Test on Controllability

➢ Experimental condition

- Helium gas temperature at steam reformer (SR) inlet : 840°C
- Helium gas pressure at SR inlet : 4.1MPa

➢ Experimental procedure

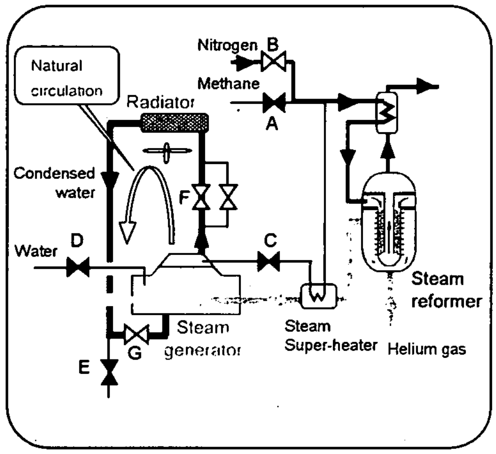
(1) Stop methane feed to SR
: close stop valve A

(2) Start nitrogen feed to SR
: open stop valve B

(3) Stop steam feed to SR
: close stop valve C

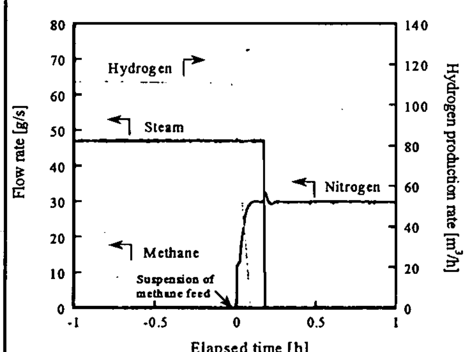
(4) Stop water feed to SG
: close stop valve D

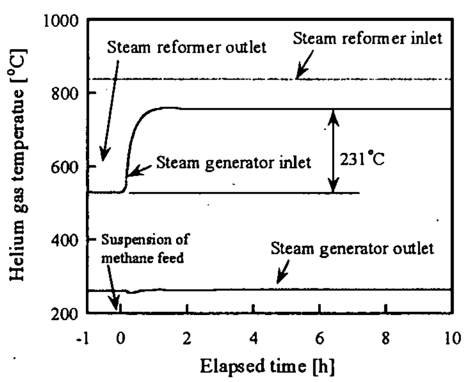
(5) Start natural circulation of steam and condensed water between SG and radiator
: close stop valve E
and open stop valve F and G



Simulation Test on Controllability

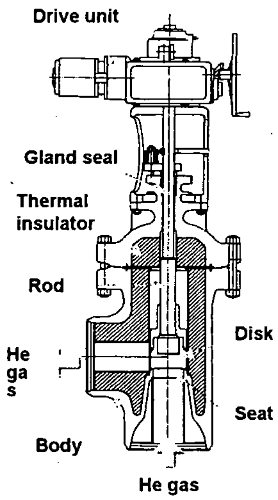
➢ Experimental results





Fluctuation range of helium gas temperature at SG outlet
: -5.5 ~ +4.0°C

High temperature isolation valve



Objective

Development of high temperature isolation valve

Technical issues to be developed

Structure

- Mitigation of thermal deformation
- Details of valve seat and disk

Material

- New coating material for seat and rod

Long-term operation

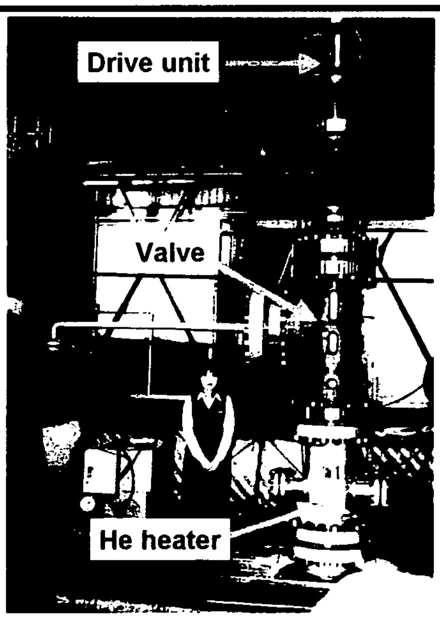
Current status

Design on structure and development of the new coating material was finished.

Mock-up test is under way

FY	2002	2003	2004	2005	2006
	Design & Fabrication		Standalone Test	Long-term Operation	

Mock-up Model



Main Specifications
- Type : Angle valve
- Scale : 1/2
- Pressure : 4.5MPa
- Temperature : 900℃
- Inner diameter of seat : 100mm
- Thickness of internal thermal insulator : 117～129.5mm

Remarks

- Hydrogen Production with a High Temperature Gas-cooled Reactor can considerably contribute to reduction of CO_2 emission.
- The HTTR project is a very important milestone to commercialize the hydrogen production with a HTGR.
- R&D and design required for connection of hydrogen production facility to the HTTR will be finished in FY2009.
- The licensing and construction are scheduled after FY 2010.

5.4 Session4: Hydrogen Production Technologies

5.4.1 Valuation of the Safety Concept of the Combined Nuclear/Chemical Complex for Hydrogen Production with HTTR

K. Verfondern, T. Nishihara*

Research Center Jülich, 52425 Jülich, GERMANY
** Japan Atomic Energy Research Institute, Oarai, Ibaraki-ken, JAPAN*

The High-Temperature Engineering Test Reactor (HTTR) in Oarai, Japan, will be worldwide the first plant to demonstrate the production of hydrogen by applying the steam reforming process as one of the most promising candidates and using nuclear process heat as primary energy. Particular safety aspects for such a combined nuclear/chemical complex have to be investigated to further detail. One of these special aspects is the fire and explosion hazard associated with the presence of flammable gases including a large LNG storage tank in close vicinity to the reactor building. A special focus is laid upon the conceivable development of a detonation pressure wave and its damaging effect on the reactor building. A literature study has shown that methane is a comparatively slow reacting gas and that a methane vapor cloud in the open atmosphere or partially obstructed areas is highly unlikely to result in a detonation if inadvertently released and ignited. Various theoretical assessments and experimental studies, which have been conducted in the past and which are of significance for the HTTR-steam reforming system, include the spreading and combustion behavior of cryogenic liquids and flammable gas mixtures providing the basis of a comprehensive safety analysis of the combined nuclear/chemical facility.

Research Center Juelich
Institute for Safety Research and Reactor Technology (ISR)

Valuation of the Safety Concept of the Combined Nuclear/Chemical Complex for Hydrogen Production with HTTR

by
Karl VERFONDERN* and Tetsuo NISHIHARA**
*) Research Center Jülich, Germany
**) JAERI Oarai, Japan

Research Center Juelich
Institute for Safety Research and Reactor Technology (ISR)

Objectives

- Description of the HTTR/SR system for H_2 production by steam reforming;
- Examination of safety aspects of the combined nuclear/chemical complex;
- Summary of status of knowledge on vapor cloud explosions.

Research Center Juelich
Institute for Safety Research and Reactor Technology (ISR)

Guidance

GUIDANCE ON THE PREPARATION
OF A SAFETY REPORT
TO MEET THE REQUIREMENTS
OF COUNCIL DIRECTIVE 96/82/EC
(SEVESO II)

G.A. Papadakis, A. Amendola

(Editors)

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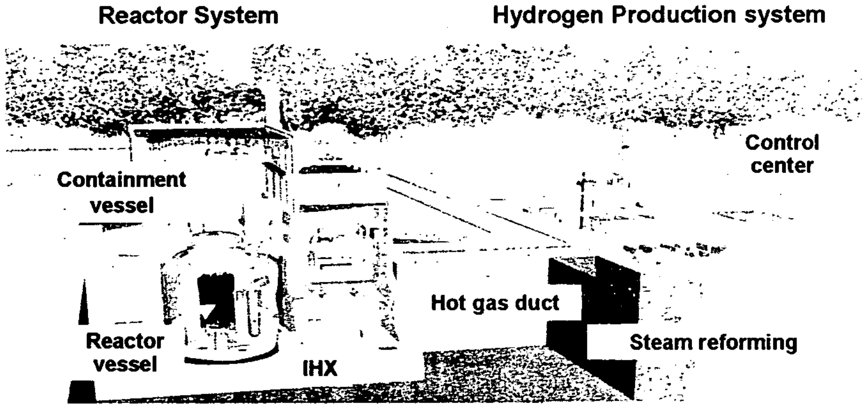
Workshop on Technical Issues and Feasibility of Advanced Hydrogen Production Systems, July 5-6, 2004, Oarai, JAPAN 3

Research Center Juelich
Institute for Safety Research and Reactor Technology (ISR)

Combined HTTR/SR Complex

Reactor System **Hydrogen Production system**



$CH_4 + H_2O \rightarrow 3H_2 + CO$

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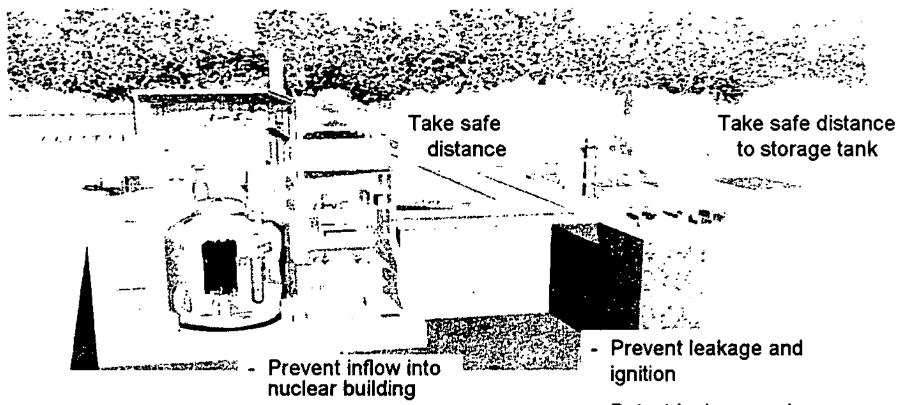
Institute for Safety Research and Reactor Technology (ISR)

Safety design against fire and explosion

Reactor System **Hydrogen Production system**



- Detect leakage and shut off natural gas line

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Institute for Safety Research and Reactor Technology (ISR)

Potential hazards in HTTR/SR complex

- Tritium transportation from core to product gases;
- Thermal turbulences induced by problems in steam reforming system;
- Fire and explosion of flammable mixtures with process gases.

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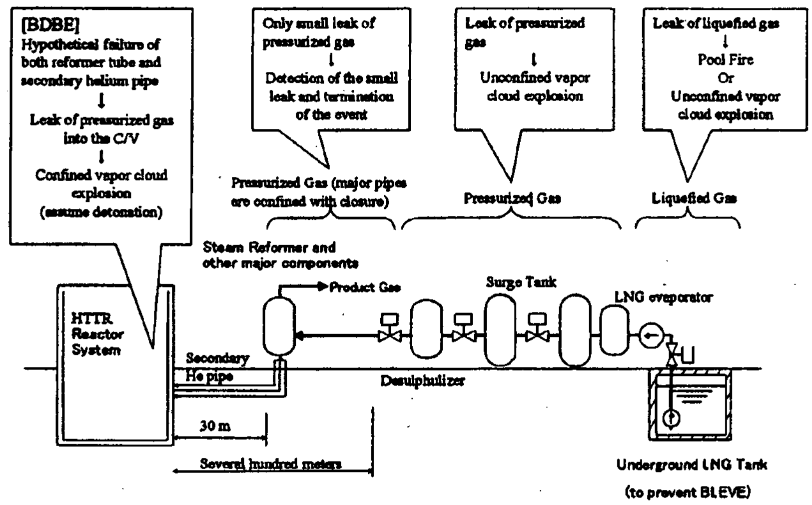
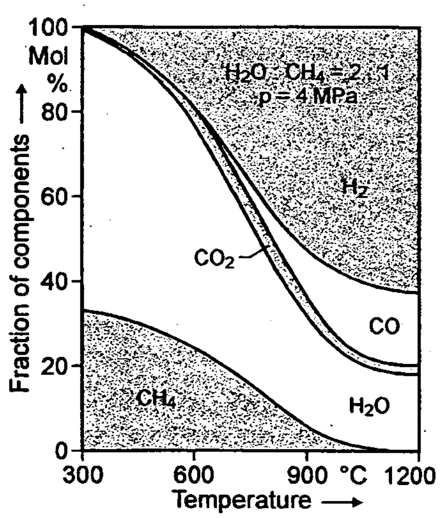
Research Center Juelich
Institute for Safety Research and Reactor Technology (ISR)

Possible effects of fire/explosion accidents

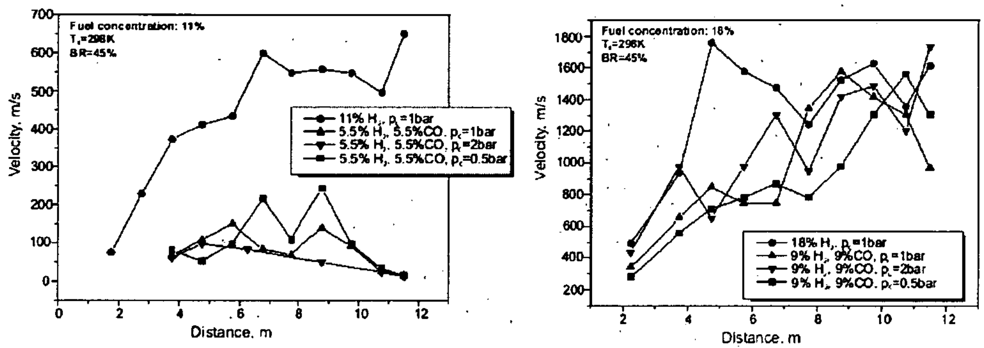


Research Center Juelich
Institute for Safety Research and Reactor Technology (ISR)

Equilibrium process gas distribution



Flame velocities of H2-CO-air mixtures



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Institute for Safety Research and Reactor Technology (ISR)

Potential hazards of LNG storage

- Boil-off;
- Tank „roll-over" (e.g., by ageing, heat input)
- Change of material properties at cryo temp.;
- BLEVE type catastrophic failure of storage tank
  (Boiling Liquid Expansion Vapor Cloud Explosion);
- Rupture of tank or pipeline;
- Cryogenic burns of personnel.

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Safety Distance

$$R = k * M^{1/3}$$

With R: safety distance [m]

M: mass of flammable substance [kg]

k: factor 2.5-8 for working building

22 for residential building

200 for no damage

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Institute for Safety Research and Reactor Technology (ISR)

German BMI Guideline (1974) for the Protection of NPP against External Explosions

Protection by means of safety distance

$$R = 8 * M^{1/3}$$

100% for unsaturated HC and non-liquefied gases
50% for gases liquefied under pressure
10% for gases liquefied at low temperatures
0.3% for combustible liquids
TNT equivalent for explosives

Minimum Distance: $R \geq 100$ m

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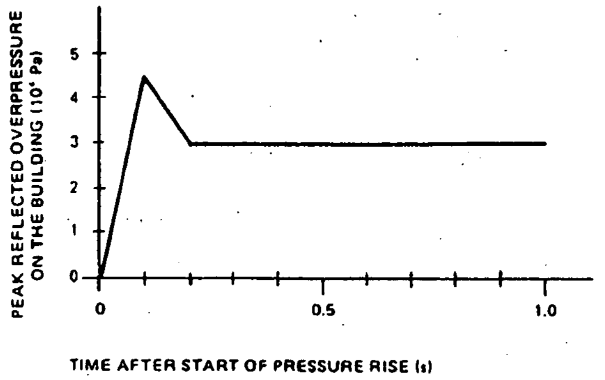
Institute for Safety Research and Reactor Technology (ISR)

German BMI Guideline (1974)

Protection by means of design against pressure wave



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German BMI Guideline (1976)

- Guideline was the result of experts' opinion.
- Guideline was confirmed by PNP gas cloud program that gas mixtures typical for PNP cannot generate pressures beyond the design curve.
- However, Guideline is not to be applied to process heat HTGRs.
- If applied to HTTR/SR:
  k = 3.7 → R = 205 m for LNG storage tank
  (not considered: inventory in steam reformer)

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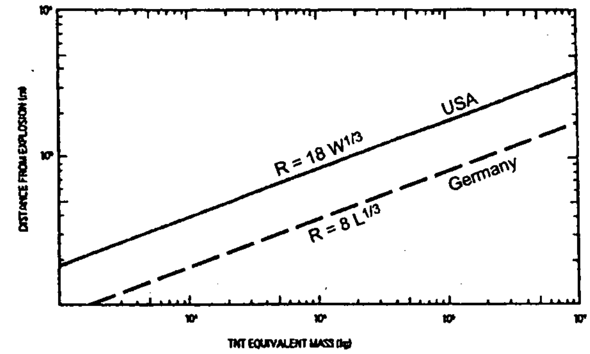
US Regulatory Guide 1.91 (1975)



LNG: 400 m^3 → 169 t → 1859 t TNT

R = 2.2 km

(or show that attendant risk be sufficiently low)

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Conclusions

- Methane combustion occurs most certainly as flash fire with insignificant pressure wave.
- Detonantion of methane-air vapor cloud has never been observed in field trials nor accidents.
- Only for more reactive gases, overpressures > 30 kPa could be measured. Here partial detonations may not be excluded (IAEA).
- BLEVE type combustion has never been reported
to have occurred in an LNG storage vessel. Cannot occur in underground container.

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Conclusions

- Safety distance of „more than 300 m" between HTTR and LNG tank would meet German BMI Guideline, but not the US Regulatory Guide 1.91.
- If reactor building is well designed to withstand pressure wave from outside, impact on components inside is covered by resp. design against airplane crash and earthquake.

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Thank you for your attention !

私の話を聞いていただいて
ありがとうございました。

5.4.2 High Temperature Operation of the Modular Helium Reactor for Hydrogen Production

Matt Richards, Arkal Shenoy*, Futoshi Okamoto, Yoshihiro Kiso**, Nobumasa Tsuji****

**General Atomics*
P.O. Box 85608, San Diego, CA, USA, 92186-5608
***Fuji Electric Systems,*
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High-temperature, helium-cooled nuclear reactor designs have been developed since the middle 1960s for electricity production and a variety of process heat applications, including the production of hydrogen. A goal for continuing the development of this technology is to increase the thermal efficiency in order to reduce the costs of electricity production and/or commodities produced using the process heat. This can be accomplished by operating the reactor with a higher coolant outlet temperature. Commercial-scale, gas-cooled reactor designs currently being developed in the U.S. Japan, and Russia operate with a coolant outlet temperature of about 850° C. We discuss potential modifications to the thermal hydraulic design of a modular helium reactor (MHR) core in order to produce helium at temperatures up to 1000° C while maintaining acceptable fuel performance and operating temperatures for the reactor vessel and other components. These modifications include using lateral restraint and sealing mechanisms to reduce the amount of coolant flow that bypasses the fuel block cooling holes, alternative paths for routing the inlet flow to the top of the reactor vessel, and optimizing the flow distribution to increase the amount of coolant flow in the hotter channels. Preliminary results show it should be possible to operate the MHR with a coolant outlet temperature of up to 1000° C using nuclear-grade graphite fuel blocks, carbon-carbon (CC) composite materials for control rods and other internal reactor components, and existing coated-particle fuel technology with silicon carbide (SiC) and pyrolytic carbon coatings. A fallback position would be to develop and qualify advanced coated-particle fuels with higher temperature capability.

High Temperature Operation of the Modular Helium Reactor for Hydrogen Production

by
Matt Richards, Arkal Shenoy
General Atomics
and
Yoshihiro Kiso, Nobumas Tsuji, Futoshi Okamoto,
Fuji Electric Systems

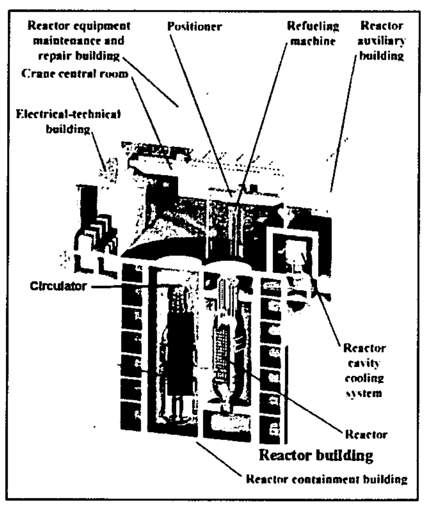
Japan Atomic Energy Research Institute
Workshop on Hydrogen Production Technologies

July 5-6, 2004 • Oarai Research Establishment • Oarai, Japan

GENERAL ATOMICS

GT-MHR Provides Springboard to H2-MHR

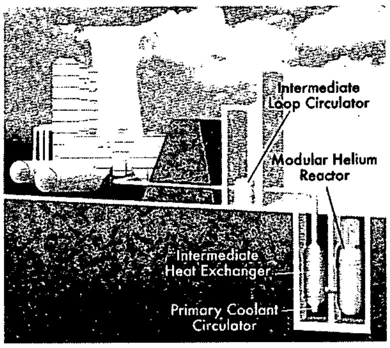
- **Module includes Reactor System and Heat Transport System (HTS)**
- **Reactor system 600 MW(t), 102 column, annular core, prismatic blocks**
- **Heat Transport system includes a Circulator and Intermediate Heat Exchanger (IHX)**

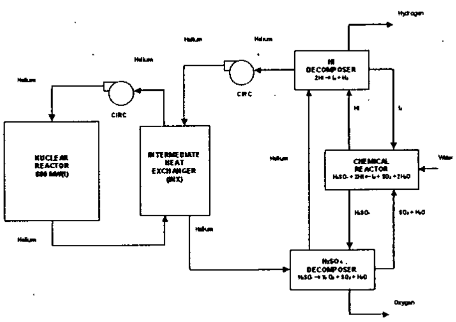


Slide 2

GENERAL ATOMICS

SI-Based H2-MHR Concept Using Helium-to-Helium IHX





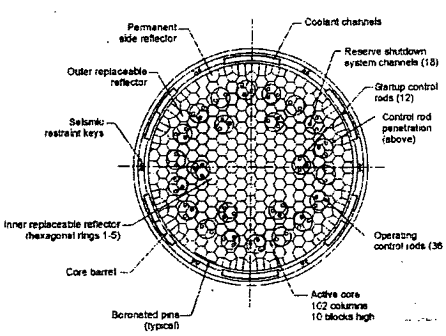
Slide 3

GENERAL ATOMICS

GT-MHR Core Design Parameters

Core thermal power (MW)	600
Number of fuel columns	102
Number of fuel blocks per column	10
Thermal power density (MW/m^3)	6.6
Effective inner diameter of active core (m)	2.96
Effective outer diameter of active core (m)	4.83
Active core height (m)	7.93
Fissile fuel (19.8% enriched in U-235)	$UC_{0.5}O_{1.5}$
Fertile Fuel (natural U)	$UC_{0.5}O_{1.5}$
Equilibrium fuel cycle length (full-power days)	425
Number of columns per refueling segment	51
Mass of heavy metal per refueling segment (kg)	1748 (fissile fuel)
	514 (fertile fuel)
Core inlet temperature (°C)	490
Core outlet temperature (°C)	850
Core upper plenum inlet pressure (MPa)	7.1
Core pressure drop (MPa)	0.05
Coolant flow rate (kg/s)	320
Heat loss to RCCS during normal operation (MW)	3.3

Annular Core Layout



Slide 4

GENERAL ATOMICS

Reactor System Design Issues

- To improve thermal efficiency, we need to increase coolant outlet temperature from 850°C to 950°C - 1000°C
- Desirable to maintain cycle-averaged peak fuel temperature below about 1250°C during normal operation and 1600°C during accidents
  - Negative impacts of high temperatures on fuel performance and fission product release
- Desirable to keep coolant inlet temperature below 500°C
  - Impacts selection of reactor vessel materials and vessel performance
- Minimize coolant "hot streaks"

Slide 5

GENERAL ATOMICS

H2-MHR Point Design Options

	GT-MHR	H2-MHR Orificed Core	Proposed H2-MHR Baseline
Power Level (MW_t)	600	600	600
Helium Inlet Temperature (°C)	490	490	590
Helium Outlet Temperature (°C)	850	1000	950
Coolant Flow Rate (kg/s)	320	226	320
Core Pressure Drop (kPa)	~50	~50	>50

Slide 6

GENERAL ATOMICS

Design Approach for Higher Temperature Operation

- Optimize Core Physics / Thermal Hydraulic Design
  - Reduce Power Peaking Factors
    - + *Fuel placement refueling scheme to reduce "age" component of power peaking*
    - + *Improved zoning of fissile/fertile fuel ratio and burnable poison*
    - + *Use C-C composite control rods in inner reflector (reduce "radial" component of power peaking)*
  - Reduce Bypass Flow
    - + *Core restraint and sealing devices to minimize gaps*
    - + *Reduce or eliminate flow in control-rod channels using C-C rods*
    - + *Goal is to reduce bypass flow fraction from about 0.2 to about 0.1*
- Use Higher Temperature Materials, Modify Reactor Internal Design as Needed

Slide 7 GENERAL ATOMICS

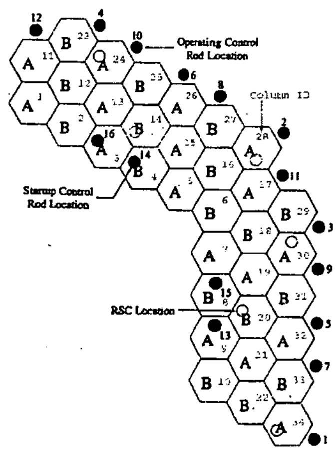
Other Available Design Options

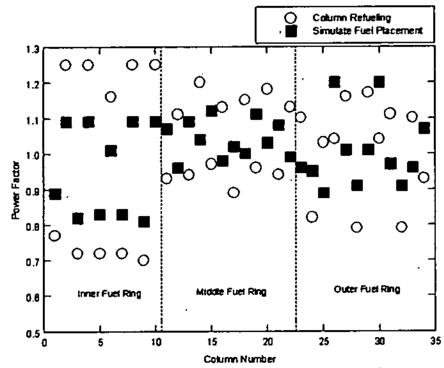
- Reduce power density
  - Lower overall power level
  - Maintain overall power level, add one layer of fuel blocks
    - + *Potential impacts on axial power stability*
- Incorporate fixed orifices in upper and/or lower reflector to force more flow to hotter columns
  - Increases lateral pressure gradients
    - + *Increases cross flow and bypass flow*
    - + *Potential impacts on column movement / oscillations*
- Adopt ZrC-TRISO fuel
  - Much smaller data base relative to SiC-TRISO fuel
  - Potential impacts on schedule
- Alternative inlet flow configurations
  - Flow through inner / side reflectors
  - Use helium purification flow for vessel cooling

Slide 8 GENERAL ATOMICS

Fuel Placement Refueling Scheme Reduces Age Component of Power Peaking Factor

1/3 Core Symmetry





JAERI "sandwich shuffling" scheme also merits evaluation

GENERAL ATOMICS

Slide 9

Effects of Sealing and Restraint Devices on Core Flow Distribution

- **A significant bypass flow occurs in the gaps between PSR blocks, unless a restraint mechanism is used to maintain gap widths at approximately 0.5 mm (compare Cases 1 and 2).**
- **An increase in cross flow generally results in an increase in bypass flow (compare Cases 3 and 4).**
- **Graphite sealing keys below the core can significantly reduce bypass flow (compare Cases 2 and 3)**

Flownet calculations performed by Fuji Electric Systems

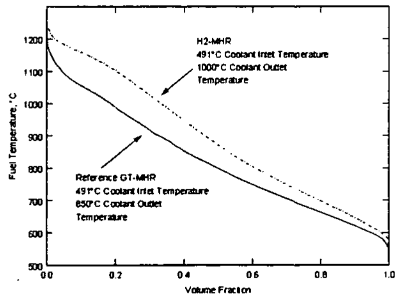
Case	Parameter							Fuel Coolant Hole Flow Rate			Core Pressure Drop
	Gap width between replaceable columns (mm)	Gap width between PSR blocks (mm)	Graphite sealing keys below core	Cross flow gap width (mm)	Sealing device between PSR blocks and CB	Metallic restraint block gap width (mm)	Coolant inlet temperature (°C)	Ave. (%)	Min. (%)	Max. (%)	ΔP (kPa)
1	3	3	No	0.25	No	3	490	56.4	56.1	56.8	14.7
2	3	0.5	No	0.25	No	3	490	79.5	79.2	80.0	23.8
3	3	0.5	Yes	0.25	No	3	490	91.0	89.5	92.9	30.3
4	3	0.5	Yes	1	Yes	1	490	82.0	80.2	86.3	26.0
5	3	0.5	Yes	1	Yes	1	550	82.3	80.5	86.7	33.2
6	3	0.5	Yes	1	Yes	1	600	82.5	80.7	87.0	41.8
7	3	0.5	Yes	0	No	3	490	95.0	95.0	95.0	31.9

GENERAL ATOMICS

Slide 10

Effect of Using Fixed Orifices to Control Flow Distribution

	Flow Control Scheme		
	None	Optimized by POKE	Optimized by POKE
Inlet Coolant Temperature (°C)	640	640	490
Coolant Flow Rate (kg/s)	320	320	226
Average Outlet Coolant Temperature (°C)	1000	1000	1000
Maximum Fuel Temperature (°C)	1309	1204	1239
Maximum Outlet Coolant Temperature (°C)	1124	1030	1042
Core Pressure Drop (kPa)	69	100	48



Potential negative impacts of increased lateral pressure gradients have not been assessed

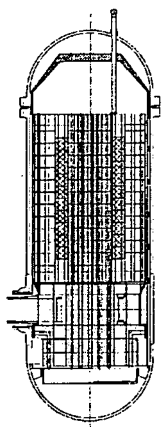
GENERAL ATOMICS

Slide 11

Assessment of Routing Inlet Flow Through Inner Reflector

- **Significantly reduces vessel temperatures during normal operation (confirmed by OKBM)**
- **Loss of heat capacity results in somewhat higher temperatures during conduction cooldown accident**
- **However:**
  - **Cross flow from inner reflector increases bypass flow**
  - **Total pressure drop is higher because of smaller flow area / higher coolant velocities**

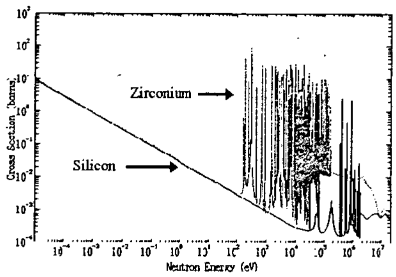
FES ANSYS Model



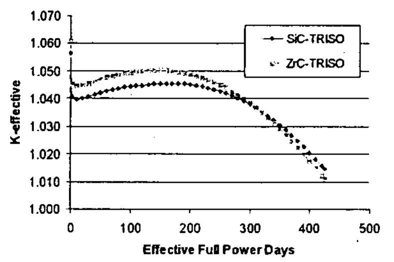
GENERAL ATOMICS

Slide 12

Potential Use of ZrC-TRISO Fuel



Zr has cross section resonances at higher neutron energies.



Effect on core reactivity is compensated for by loading less fixed burnable poison at beginning of core life.

Conclusion: ***Use of ZrC-TRISO fuel is a viable option from a core physics perspective. However, considerable fuel development and qualification is required.***

GENERAL ATOMICS

Slide 13

CONCLUSIONS

- **MHR is well suited for hydrogen production**
  - **Produces high temperature heat needed for thermochemical water splitting and high-temperature electrolysis**
- **Technical challenges for higher temperature operation are being addressed**
  - **Reactor physics / fuel cycle optimization**
  - **Thermal hydraulic optimization**
  - **Modifications to reactor internals design**
    - + *Use of carbon-carbon composites and other higher temperature materials*
    - + *Alternative inlet flow configurations*

GENERAL ATOMICS

Slide 14

5.4.3 Hydrogen Production Using High-temperature Electrolysis

J. Stephen Herring, James E. O'Brien, Carl M. Stoots, Paul A. Lessing, Joseph Hartvigsen*, S.Elangovan*

Idaho National Engineering and Environmental Laboratory
Idaho Falls, ID 83415
**Ceramatec Inc.*
Tel: 208-526-9497, Fax: 208-526-2930, Email: sth@inel.gov

An experimental research program is being conducted by the INEEL and Ceramatec, Inc., Salt Lake City, Utah, to test the high-temperature, electrolytic production of hydrogen from steam using a solid oxide cell. The research team is designing and testing solid oxide cells for operation in the electrolysis mode, producing hydrogen using high-temperature heat and electrical energy. The high-temperature heat and the electrical power would be supplied simultaneously by a high-temperature nuclear reactor. Operation at high temperature reduces the electrical energy requirement for electrolysis, besides increasing the thermal efficiency of the power-generating cycle. The high-temperature electrolysis process will utilize heat from a specialized secondary loop carrying a steam/hydrogen mixture. It is expected that, through the combination of a high-temperature reactor and high temperature electrolysis, the process will achieve an overall thermal conversion efficiency of 40 to 50% while avoiding the challenging chemistry and corrosion issues associated with the thermochemical processes. Planar solid oxide cell technology is being utilized because it has the best potential for high efficiency due to minimized voltage and current losses. These losses also decrease with increasing temperature.

Initial testing has determined the performance of single "button" cells. Subsequent testing will investigate the performance of multiple-cell stacks operating in the electrolysis mode. Testing is being performed both at Ceramatec and at INEEL. The first cells to be tested were single cells based on existing materials and fabrication technology developed at Ceramatec for production of solid oxide fuel cells. These cells use a relatively thick (~175 μm) electrolyte of yttria- or scandia-stabilized zirconia, with nickel-zirconia cermet anodes and strontium-doped lanthanum manganite cathodes. Additional custom cells with lanthanum gallate electrolyte have been developed and tested. Results to date have shown an area specific resistance (ASR) of 0.45 ohm-cm^2 at 850 °C, and produced 73% H_2:27%H_2O from an 50:50 input stream. Our most recent results from a six-cell stack show a production of 32 normal liters/hr for a duration of 800 hours. The critical parameters for a 300-$MW_{hydrogen}$ commercial electrolysis plant have been determined, based on these experimental results.

Idaho National Engineering and Environmental Laboratory

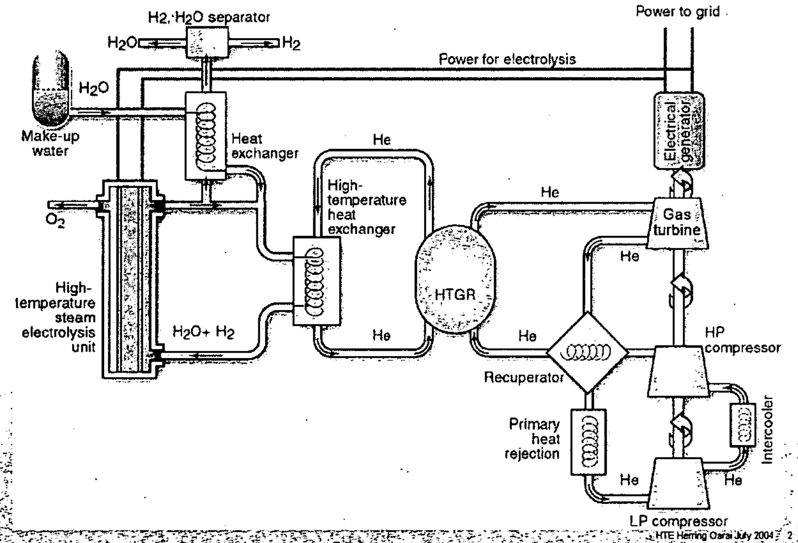
Hydrogen Production using High-Temperature Electrolysis

J. Stephen Herring, James E. O'Brien, Carl M. Stoots, Paul A. Lessing, INEEL
Joseph Hartvigsen, S. Elangovan, Ceramatec, Inc.

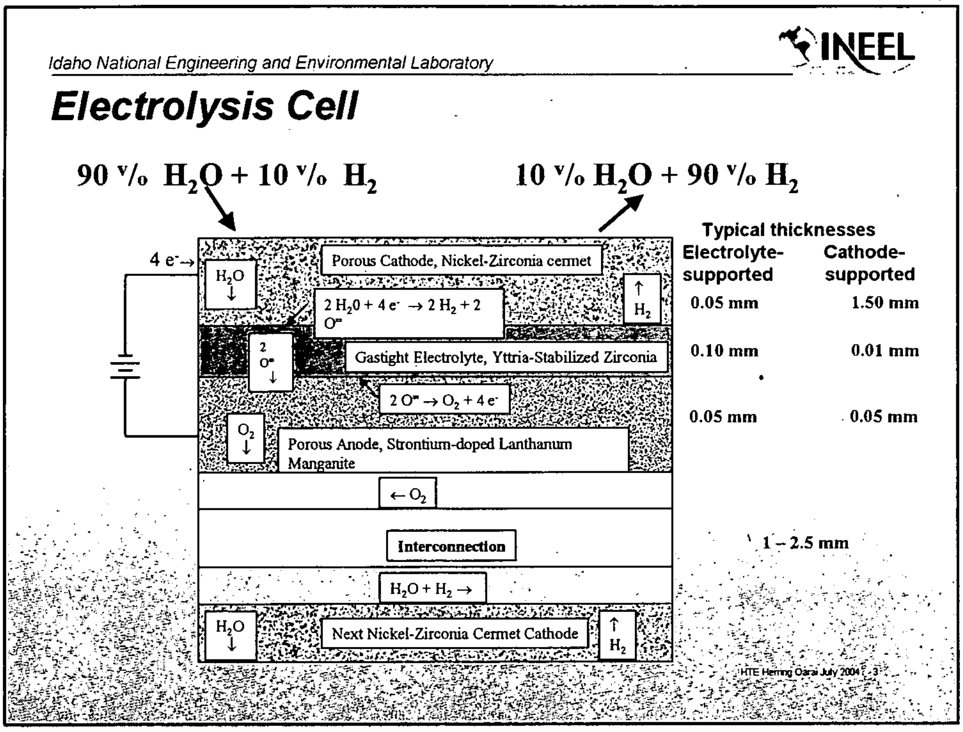
Workshop on Hydrogen Production Technologies
July 5-6, 2004 Oarai, Japan

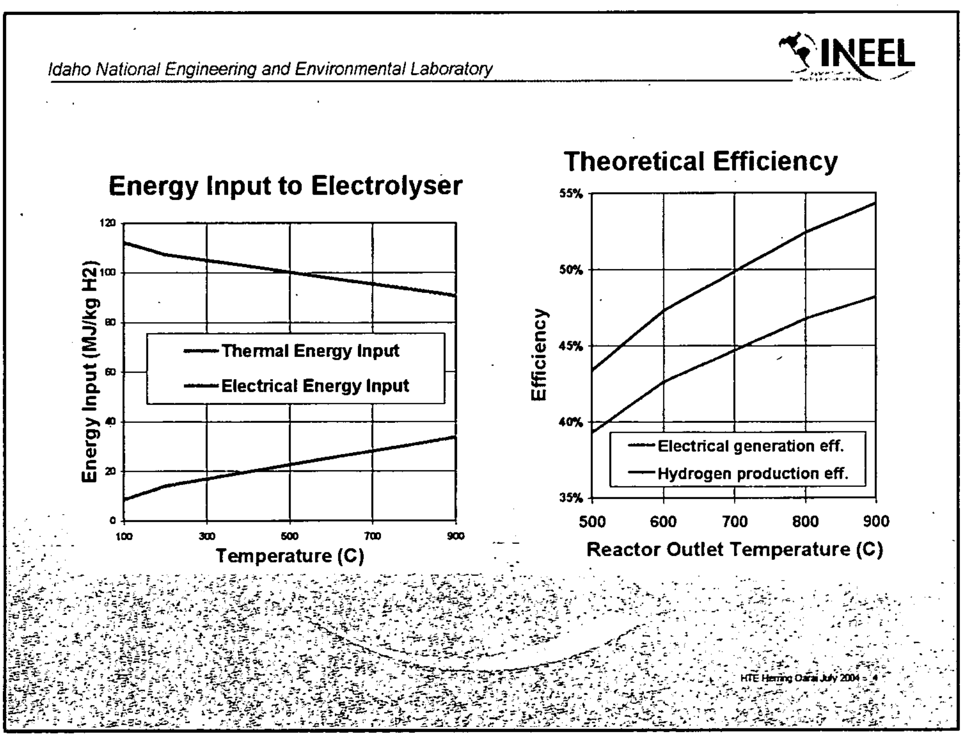
Idaho National Engineering and Environmental Laboratory INEEL

High Temperature Electrolysis Plant



HTE Herring Oarai July 2004 2


Idaho National Engineering and Environmental Laboratory
INEEL
Electrolysis Cell
90 v/o H2O + 10 v/o H2
10 v/o H2O + 90 v/o H2
4 e-→
H2O ↓
Porous Cathode, Nickel-Zirconia cermet
↑ H2
2 H2O + 4 e- → 2 H2 + 2 O=
2 O= ↓
Gastight Electrolyte, Yttria-Stabilized Zirconia
2 O= → O2 + 4 e-
O2 ↓
Porous Anode, Strontium-doped Lanthanum Manganite
← O2
Interconnection
H2O + H2 →
Next Nickel-Zirconia Cermet Cathode
Typical thicknesses
Electrolyte-supported
Cathode-supported
0.05 mm
1.50 mm
0.10 mm
0.01 mm
0.05 mm
0.05 mm
1 - 2.5 mm


Idaho National Engineering and Environmental Laboratory
INEEL
Energy Input to Electrolyser
Energy Input (MJ/kg H2)
Thermal Energy Input
Electrical Energy Input
Temperature (C)
Theoretical Efficiency
Efficiency
55%
50%
45%
40%
35%
Electrical generation eff.
Hydrogen production eff.
500
600
700
800
900
Reactor Outlet Temperature (C)

Idaho National Engineering and Environmental Laboratory INEEL

Thermal Water Splitting Efficiencies, from Yildiz and Kazimi (MIT)

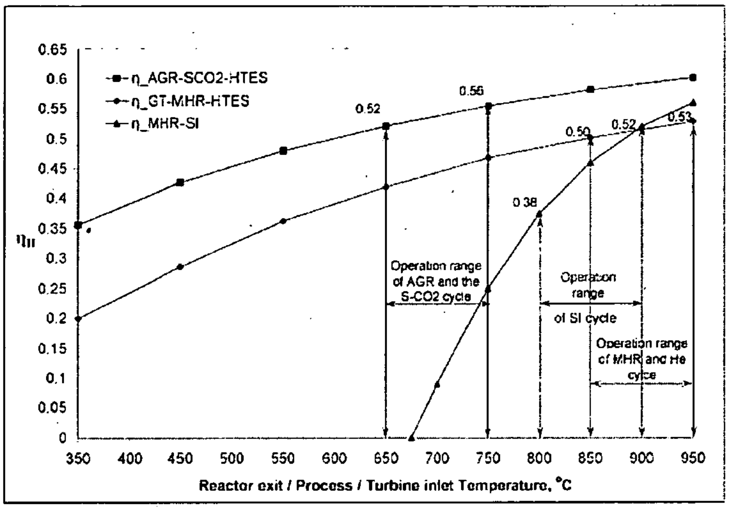


Figure 14: Comparison of the thermal-to-hydrogen efficiency of the HTES and SI related technologies as a function of temperature

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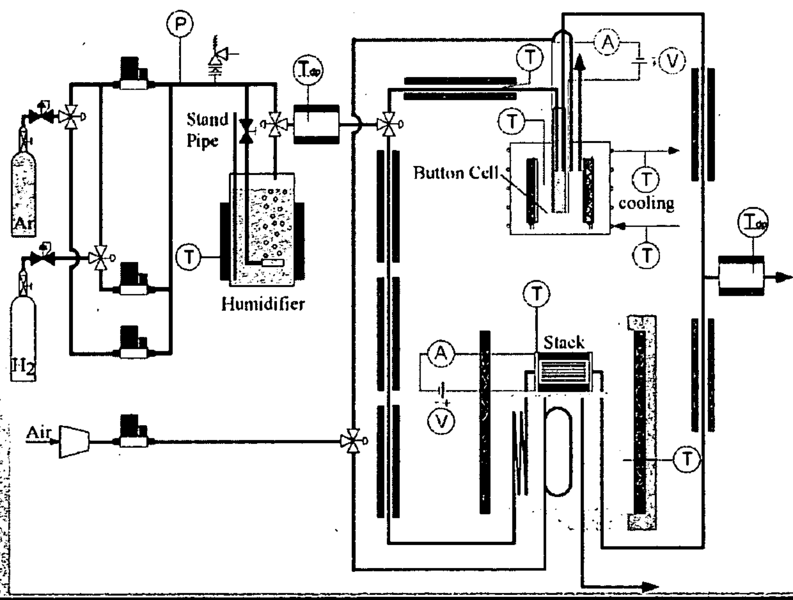
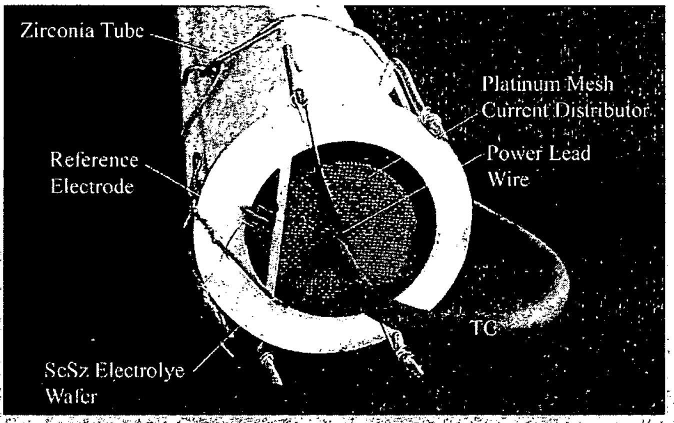
Simultaneous Button Cell and Stack Testing

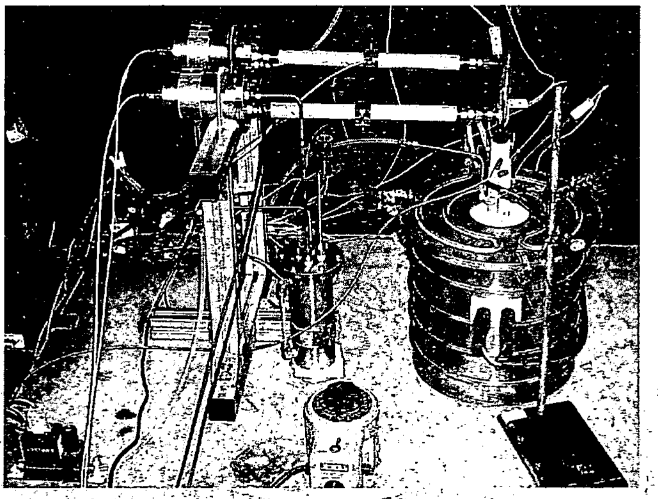


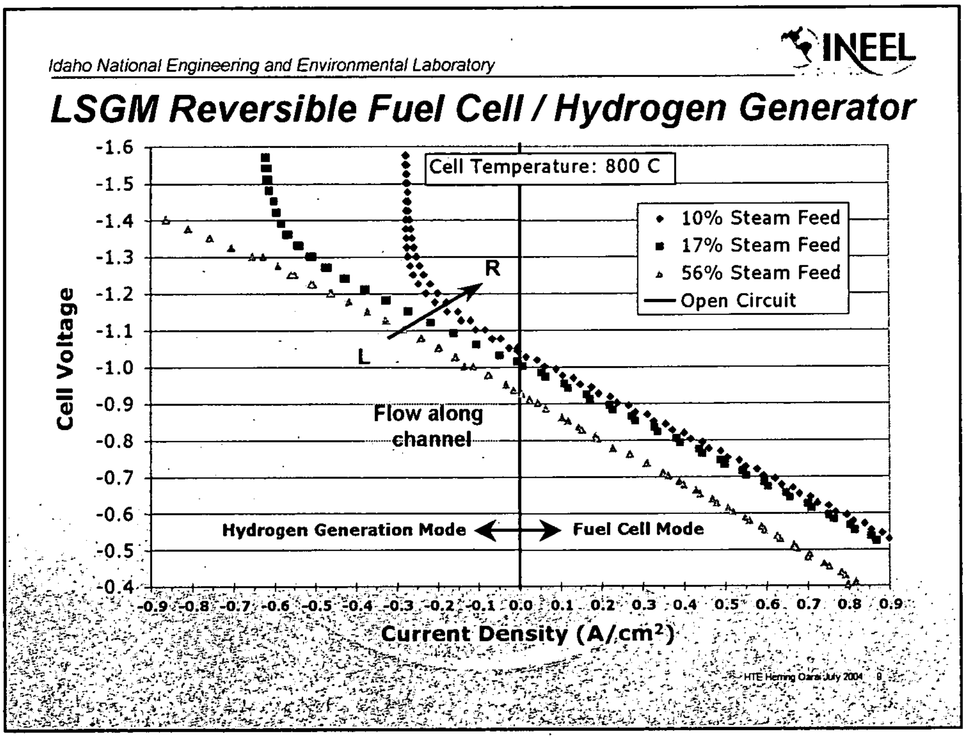
Button Cell for Single-cell Tests

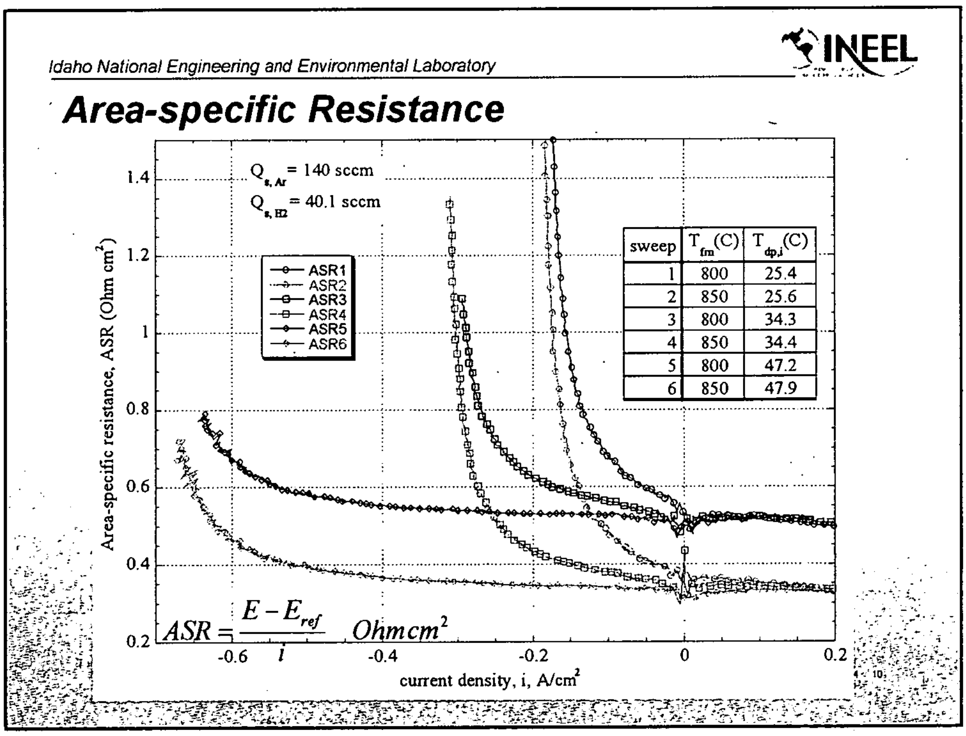
- Steam/hydrogen electrode: Nickel zirconia cermet
- Oxygen electrode: Strontium-doped lanthanum manganite (LSM)
- Electrolyte: YSZ or ScSZ, ~ 100 - 150 μm thickness
- Active cell area: 2.5 cm^2



Test Loop Components




Idaho National Engineering and Environmental Laboratory
INEEL
LSGM Reversible Fuel Cell / Hydrogen Generator
Cell Temperature: 800 C
10% Steam Feed
17% Steam Feed
56% Steam Feed
Open Circuit
R
L
Flow along channel
Hydrogen Generation Mode
Fuel Cell Mode
Cell Voltage
Current Density (A/cm²)
-1.6
-1.5
-1.4
-1.3
-1.2
-1.1
-1.0
-0.9
-0.8
-0.7
-0.6
-0.5
-0.4
-0.9 -0.8 -0.7 -0.6 -0.5 -0.4 -0.3 -0.2 -0.1 0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9


Idaho National Engineering and Environmental Laboratory
INEEL
Area-specific Resistance
Q_s,Ar = 140 sccm
Q_s,H2 = 40.1 sccm
ASR1
ASR2
ASR3
ASR4
ASR5
ASR6
sweep | T_fm(C) | T_dp,i(C)
1 | 800 | 25.4
2 | 850 | 25.6
3 | 800 | 34.3
4 | 850 | 34.4
5 | 800 | 47.2
6 | 850 | 47.9
ASR = (E − E_ref) / i Ohm cm²
Area-specific resistance, ASR (Ohm cm²)
current density, i, A/cm²
1.4
1.2
1
0.8
0.6
0.4
0.2
-0.6
-0.4
-0.2
0
0.2

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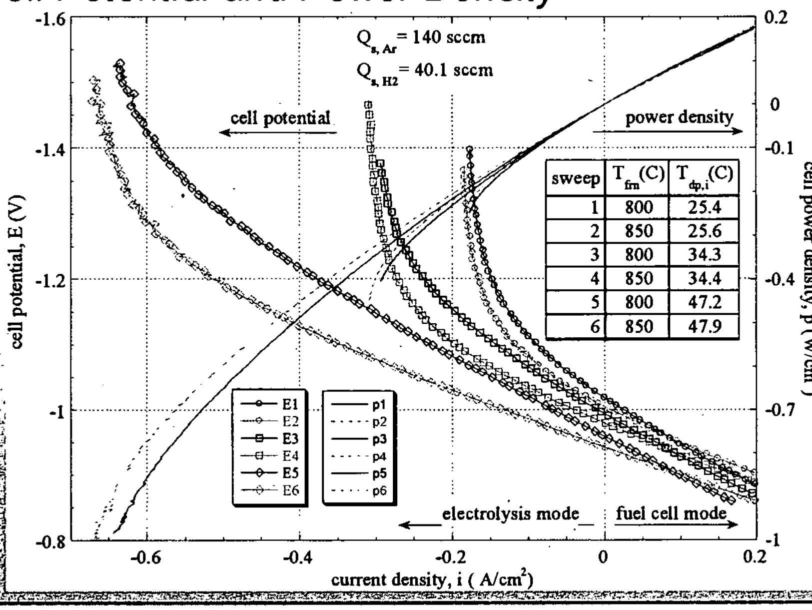
Cell Potential and Power Density



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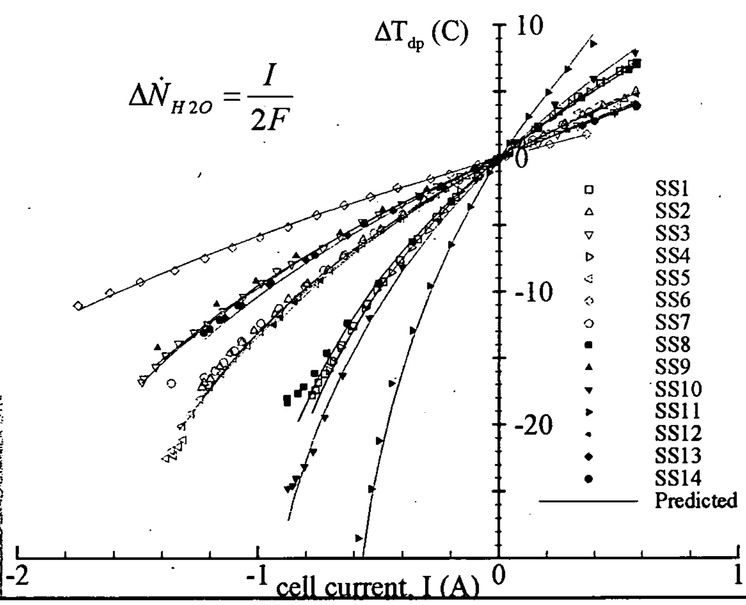
Dewpoint temperature change across cell. . .



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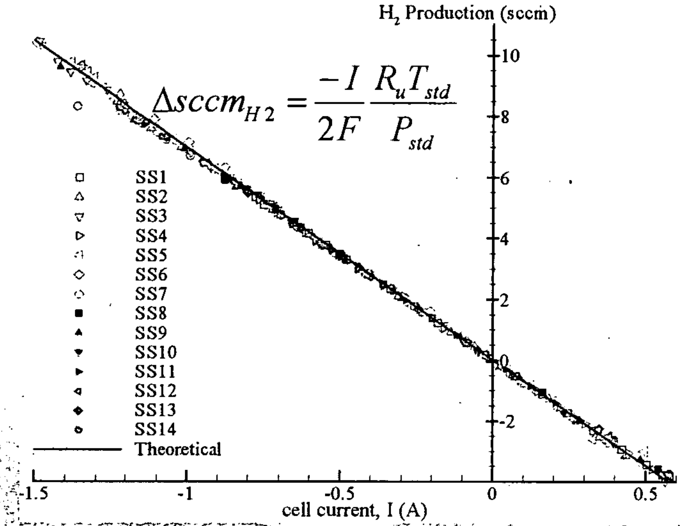
Hydrogen Production Rates



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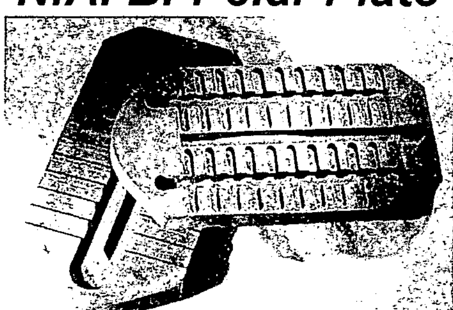
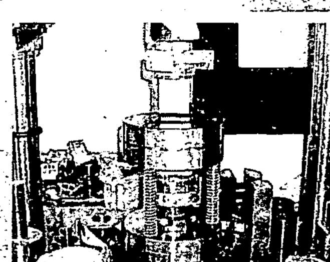
NiAl Bi-Polar Plate Development



NiAl Bipolar Plates



Die Set in Press

- Near net shape design for low cost commercial production
- Ceramic filler formula's to match the CTE of anode, cathode, & electrolyte
- Fiber/binder additions for controlled porosity
- Combustion synthesis reaction rate control through composition
- Punch, die and support fixture design for plate pressing

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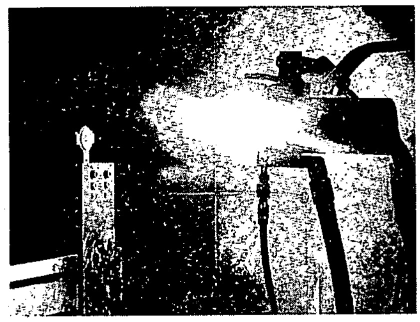
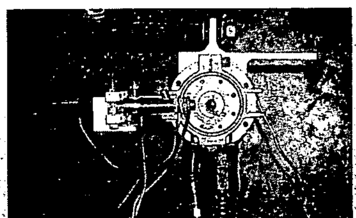
Liquid Injected Plasma Coatings

New injection techniques were developed

- Allows ultra-fine particle size coating
- Allows graded porosity coatings
- Allows direct coating of chemical compounds





Invention disclosures have been submitted on these new processes

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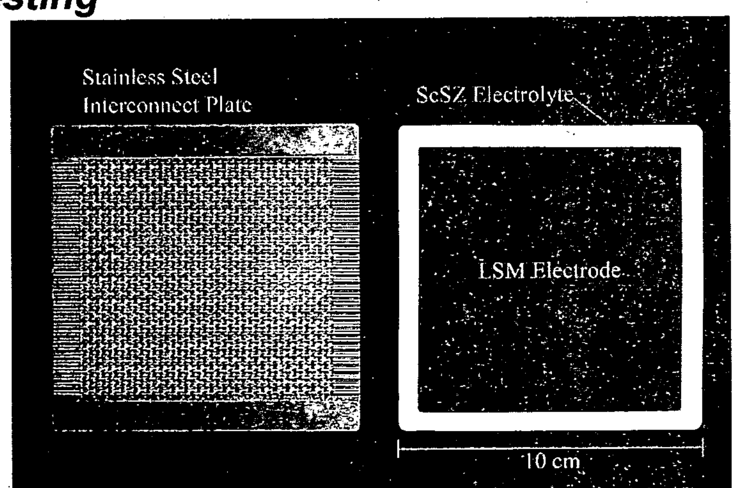
Interconnect Plate and Electrolyte for Stack Testing



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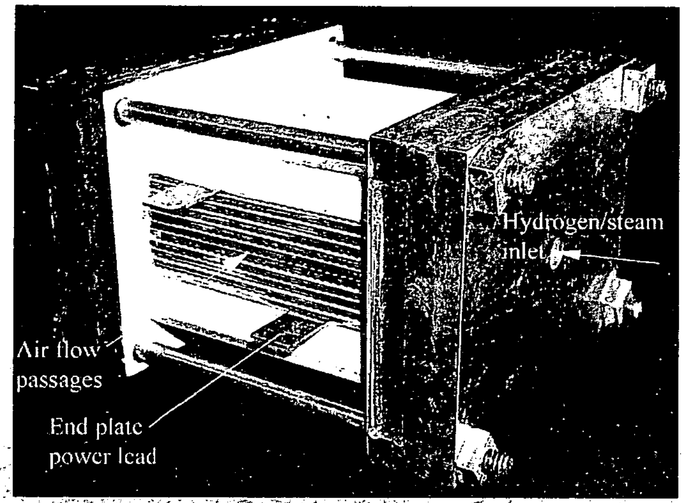
Ten-cell Stack Experiment



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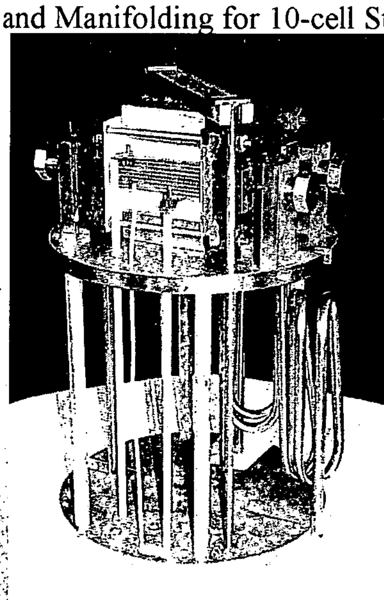
Fixture and Manifolding for 10-cell Stack Tests



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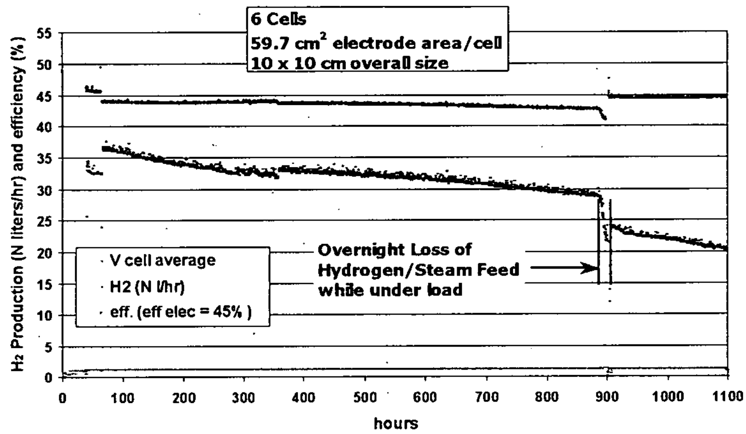
Ceramatec Test

Hydrogen Production in 6-cell stack



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Conceptual HTE Plant

Reactor Power	600 MW thermal	
H_2 Production		
Overall process efficiency	50%	
Rate based on LHV	2.5 kg/s	238 ton/day
	1667 x 10^6 sccm	84.8 x 10^6 scf/day
Water Consumption	22.3 kg/s	354 gpm
Electrolysis Cell Conditions		
Temperature	850° C	1560°F
Pressure	5 MPa	702.5 psi
Inlet mole fractions, H_2O/H_2	0.9/0.1	
Outlet mole fraction, H_2O/H_2	0.1/0.9	
Volumetric H_2+H_2O flow rate	2.90 m³/s	
Volumetric O_2 flow rate (generated)	1.16 m³/s	
Current Density	0.2 A/cm²	
Cell Operating Voltage	1.1 V	

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Table 4. Cell Configuration.

Cell Area	
Individual Cell Width	10 cm
Individual Cell Active Area	100 cm^2
Total Number of Cells	12×10^6
Total Active Cell Area	120,000 m^2
Cell Layer Thickness	
Electrolyte	10 μm
Anode	1500 μm
Cathode	50 μm
Bipolar Plate	2.5 mm
Total Cell Thickness	4.06 mm
Stack Dimensions	
Cells/stack	1000
Stack Height	4.06 m
Stack Volume	0.041 m^3
Stack Volume with Manifolding	0.162 m^3
Number of Stacks	12000
Total volume of all stacks	486 m^3
Hot volume	1944 m^3
Stacks per Row	75
Number of Rows	160
Hot Volume Height	5 m
Hot Volume Width	15 m
Hot Volume Length	25.9 m

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Conclusions

- High temperature electrolysis using solid oxide technology appears to be a viable means for producing hydrogen using nuclear energy
- Laboratory experiments indicate this technology can produce hydrogen at close to theoretical parameters
- A conceptual design of an electrolytic plant to be attached to a 600 MWth reactor has been developed suggesting the plant would be of moderate size and parameters of cells would be reasonable
- Electrolysis shows promise particularly in the near-term
- Thermochemical cycles may have moderately higher efficiency but under more daunting operating conditions

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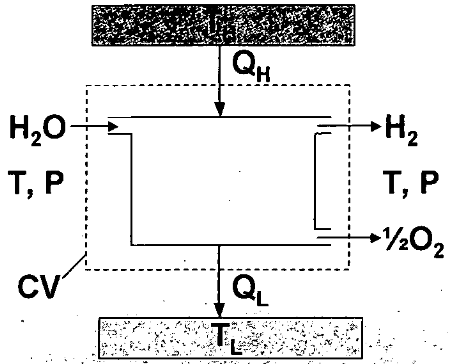
Thermodynamics 101 for Hydrogen Production from Water and Heat (thermal water splitting)



1st Law: $Q_H - Q_L = \Delta H_R$

2nd Law: $\Delta S_R \geq \frac{Q_H}{T_H} - \frac{Q_L}{T_L}$

Process Efficiency: $\eta_T = \frac{\Delta H_R}{Q_H}$

$$\eta_T = \left(1 - \frac{T_L}{T_H}\right)\left(\frac{HHV}{-\Delta G^o_{f,H2O}}\right) = \left(1 - \frac{T_L}{T_H}\right)\frac{1}{.83}$$

Maximum possible efficiency for ANY thermal water-splitting process operating between T_L and T_H.

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5.5 Session5: Thermochemical Process

5.5.1 Hydrogen Production Using a Thermochemical Cycle and Biomass Heat

M. Kawaji[1] and K. Mori[2]

1. Department of Chemical Engineering and Applied Chemistry, University of Toronto Toronto, Ontario M5S 3E5, Canada

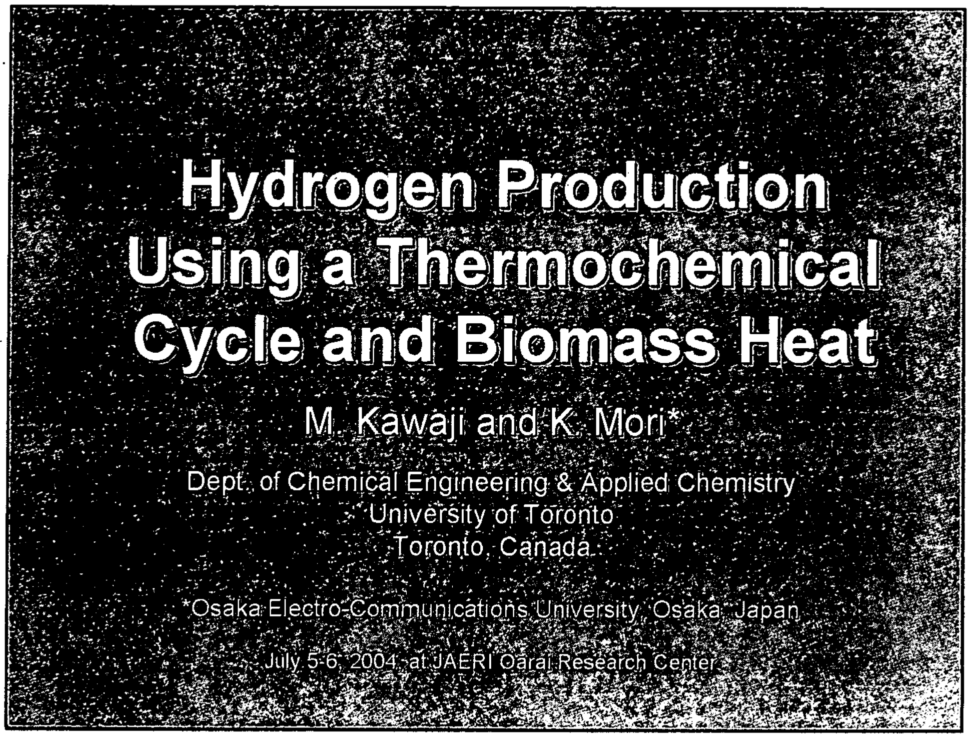
2. Department of Mechanical Engineering, Osaka Electro-communication University, Osaka, Japan

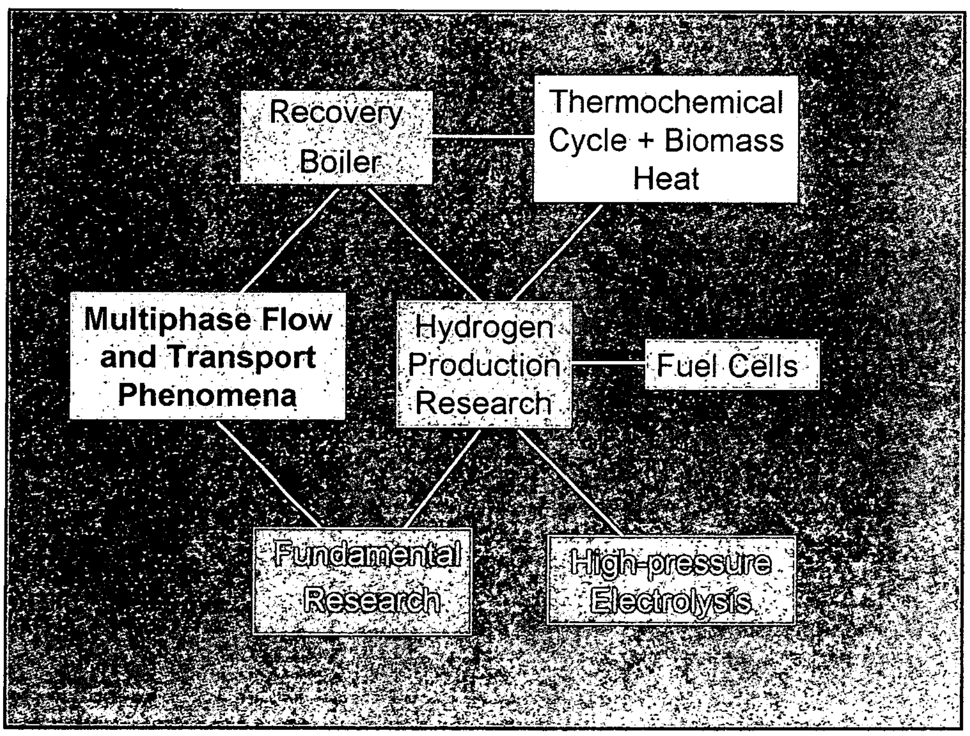
It is proposed to conduct research on the development of the S-I thermochemical cycle for hydrogen production using high-temperature heat produced by combustion of biomass, in particular wood wastes and residues from various forest operations such as pulp and paper mills and saw mills which are abundant in Canada. The development of a promising thermochemical cycle for hydrogen production is important in itself, and a combination of this technology with combustion of wood wastes and other biomass would offer even greater long term benefits to Canada and the world in reducing greenhouse gas emissions and better utilization of a renewable resource. Energy derived from biomass is regarded as "green" energy because biomass fuels are infinitely renewable, and bio-energy is neutral in terms of CO_2 emissions.

The short-term objectives of the proposed project are to investigate the technical problems associated with scaling up the S-I cycle-based hydrogen production process, such as the improvement in thermal efficiency and the method of effectively coupling the S-I cycle to a biomass incinerator used as a source of high-temperature process heat. In the longer term, certain key aspects of a large scale thermochemical cycle-based system will be investigated with the goal of building a pilot plant in 5 ~ 10 years, and improving the operational reliability and economic viability of a commercial hydrogen production plant in 10 ~ 15 years.

The forest industry in Canada converts large volumes of wood into value added products that are exported, contributing significantly to Canada's export trade balance. However, large quantities of clean-burning wood residues or wastes (up to 30-50 % of the volume of wood processed) are also generated in many pulp and paper mills, saw mills, and other forest operations. For example, more than 6.1 million dry tons of wood residue are generated annually in the mainland region of BC. A significant fraction is incinerated in beehive burners with no energy recovery. Using this wood residue as fuel for cogeneration and power plants would provide about 200 MW of additional power. An additional 1.5 million tons of non-forest industry wood residue is another potential source of fuel in B.C., along with other biomass resources, such as demolition and land clearing waste, municipal solid waste and landfill gas.

The incinerators and boilers burning wood can generate a flue gas at temperatures exceeding 900°C. Small power plants have been built to generate electricity from the wood wastes, for example, the Williams Lake Power Plant in B.C. Thus, proven technologies already exist to cleanly burn wood wastes and recover energy in the form of heat and/or electricity. The use of high-temperature heat source from combustion of wood wastes and other biomass will be investigated for incorporation into a thermochemical cycle-based hydrogen production system. Assuming an overall thermal efficiency of 40%, heat from combustion of one kg of wood waste is expected to yield 0.56 Nm^3 or 0.05 kg of hydrogen gas. The incineration of 5 million tons of wood wastes will be able to generate 250,000 tons of hydrogen gas annually. Assuming the energy efficiency of fuel cell-powered cars to be twice as high as that of gasoline-powered vehicles, this quantity of hydrogen gas would be equivalent to 2 billion L of gasoline. This would reduce CO_2 emission by 3.7 million tons, which amounts to 6 % of the GHG emission reduction target (*Action Plan 2000)* for Canada under the Kyoto protocol. An even greater production of hydrogen gas is possible with the same plant, if other fuels such as fast growing wood harvested for fuel and agricultural biomass are used.


Hydrogen Production
Using a Thermochemical
Cycle and Biomass Heat
M. Kawaji and K. Mori*
Dept. of Chemical Engineering & Applied Chemistry
University of Toronto
Toronto, Canada
*Osaka Electro-Communications University, Osaka, Japan
July 5-6, 2004 at JAERI Oarai Research Center

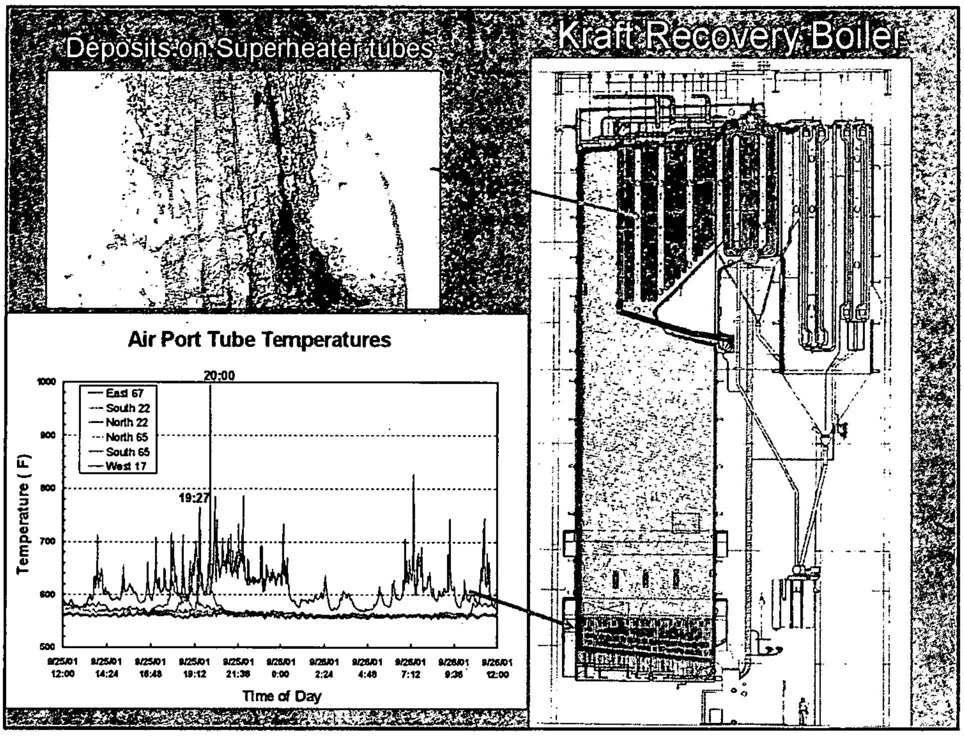

Recovery Boiler
Thermochemical Cycle + Biomass Heat
Multiphase Flow and Transport Phenomena
Hydrogen Production Research
Fuel Cells
Fundamental Research
High-pressure Electrolysis

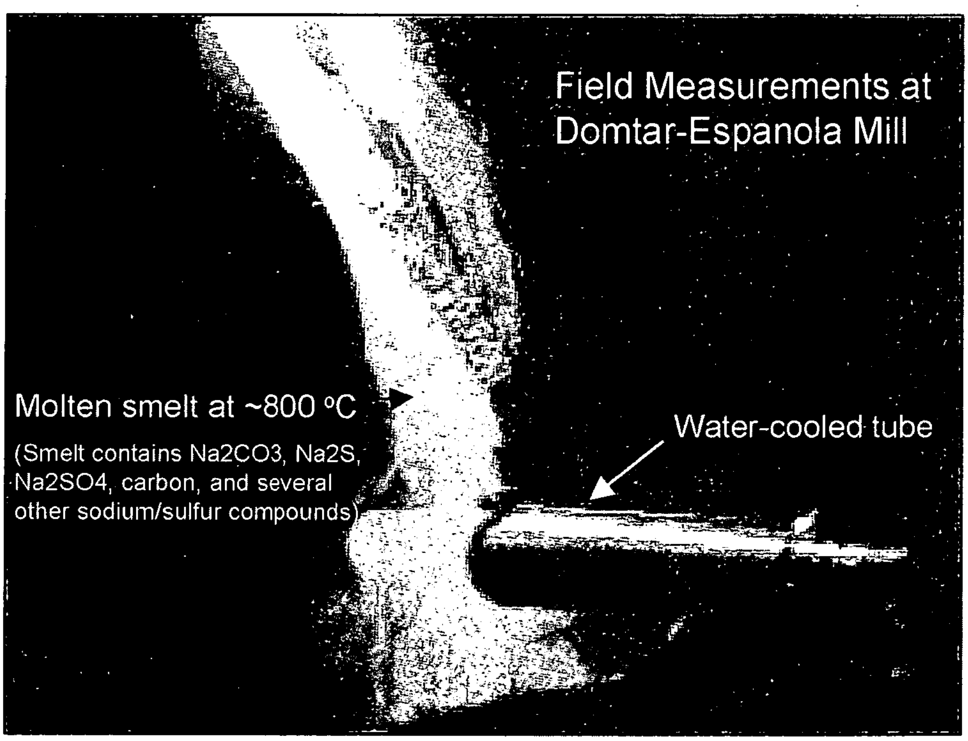
New Hydrogen Production Technology

- NSERC Strategic Grant Proposal
  - Greenhouse Gas Mitigation (GHGM) project
- A novel technology that can produce hydrogen gas from water without emitting any greenhouse gases
  - Thermochemical cycle
  - Biomass heat
- Will start in the next Recovery Boiler Research Consortium

Recovery Boiler Research Consortium

- NSERC Research Network Grant Application
  "Development of Strategies and Technologies for Effective Energy and Chemical Recovery in the Kraft Pulping Process"
  - Five Year project with a budget of \$1.1~1.5 million/year
  - > 15 Pulp & Paper Companies and Boiler Manufacturers, 5 Universities
- Theme: to increase the efficiency of energy and chemical recovery, and improve overall productivity of kraft pulp mills
  - evaporator operation, chemical and energy balances, sensor development, process control and new technologies
- Heat transfer research will focus on
  - Evaporator operation and performance
  - New technologies, e.g. syngas and hydrogen production


Deposits on Superheater tubes
Kraft Recovery Boiler
Air Port Tube Temperatures
20:00
19:27
East 67
South 22
North 22
North 65
South 65
West 17
Temperature (F)
Time of Day


Field Measurements at
Domtar-Espanola Mill
Molten smelt at ~800 °C
(Smelt contains Na2CO3, Na2S,
Na2SO4, carbon, and several
other sodium/sulfur compounds)
Water-cooled tube

Thermochemical Cycle

- Over 100 thermochemical water-splitting cycles have been identified
- Two most advanced thermochemical processes are the sulphur-iodine (S-I) cycle and the calcium-bromine (UT-3) cycle
- Thermochemical hydrogen production enjoys high overall heat-to-hydrogen efficiencies (up to 50%) vs. electrolysis (up to 35%)

Status of Non-Fossil Hydrogen Production Technologies

	Process Temperature (°C)	Heat-to-Hydrogen Efficiency (%)	Status
Electrolysis	-	20-25 (up to 35)	Commercial
Sulphur-Iodine cycle	850	45-49 (up to 51)	Bench scale
Calcium-Bromine cycle	760	36-40	Laboratory scale
Copper-Chlorine cycle	550	41	R&D begun at ANL

Sulphur-Iodine Thermochemical Cycle

- Consists of three chemical reactions in which water is dissociated into H_2 and O_2 without using any fossil fuels and causing emissions of CO_2 gas

- Reaction II: $H_2SO_4 \rightarrow SO_2 + H_2O + \frac{1}{2}O_2$
- Reaction I: $I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4$
- Reaction III: $2HI \rightarrow I_2 + H_2$

Non-Fossil Sources of High Temperature Heat (> 850°C)

- Nuclear power: High Temperature Gas Reactor
- Solar heat
- Biomass heat

Biomass Heat

- Combustion of wood wastes from various forest operations such as pulp & paper and saw mills
- A thermochemical cycle with biomass heat would offer long term benefits to Canada and the world – a novel concept
- Reduction in greenhouse gas emission and better utilization of a renewable resource
- Biomass energy is "green" energy because biomass fuels are infinitely renewable and carbon neutral in terms of CO_2 emissions

Wood Wastes

- Up to 30-50 % of the volume of wood processed end up as clean-burning wastes such as sawdust, bark, trim, sort-yard debris, chip fines and shavings
- More than 6.1 million dry tons of wood wastes are generated annually in the mainland region of B.C. alone
- 1.5 million tons are incinerated in beehive burners with no energy recovery, causing air pollution. It would provide about 700 MW of heat for a year

- Proven technologies already exist to cleanly burn wood wastes and generate a flue gas at > 900°C
- e.g., the Williams Lake Power Plant in B.C. annually converts over 600,000 tons of wood wastes into 65 MW of electricity without polluting the atmosphere

Hydrogen Production by S-I Cycle and Biomass Heat

- At an overall thermal efficiency of 40%, heat from 1.0 kg of wood waste should yield 0.56 Nm^3 or 0.05 kg of hydrogen gas
- 5 million tons of wood wastes can generate 250,000 tons of hydrogen gas, equivalent to 2 billion L of gasoline
- This would reduce CO_2 emission by 3.7 million tons, amounting to 6 % of the GHG emission reduction target *(Action Plan 2000)* for Canada
- More production of hydrogen possible if fast growing wood is harvested for fuel and agricultural biomass is used

Research Needs

1) Thermodynamics and kinetics of thermochemical reactions

2) Increasing the thermal efficiency and utilization of biomass heat

3) Material durability

Thermal Efficiency

Current thermal efficiency achieved so far is ~20% rather than the optimal 45 ~ 50%

- use electrodialysis method to concentrate the HI solution before heating to form I_2-H_2?
- Vaporization of sulphuric acid and heating its vapour to 850°C need to be carried out efficiently with minimum heat loss

Utilization of Biomass Heat

- utilization of a flue gas from wood waste combustion
- a fluidized bed incinerator for complete gasification and combustion of moist wood
- use a plate-fin type heat exchanger to heat sulfuric acid vapour but it may be severely fouled due to entrained particulates on the flue gas side

Thermodynamics and Kinetics

- Thermodynamics and reaction kinetics parameters: temperature dependence needs to be known for achieving optimum process control

Material Durability

- Durable materials need to be used in high-temperature parts: ceramics and alloys
- High temperature flue gas-to-sulphuric acid vapour heat exchanger
- Sulphuric acid evaporator and superheater

Concluding Remarks

We will begin our research soon, collaborate internationally and wish to contribute to the development of a commercially feasible hydrogen production technology based on an S-I cycle

Thank You!

5.5.2 Nuclear Hydrogen Production by IS (Iodine-Sulfur) Process in Korea

Gab-Jin Hwang, Chu-Sik Park, Sang-Ho Lee and Tae-Hwan Kim

Hydrogen Energy Research Center, Korea Institute of Energy Research, Daejeon, 305-343, Korea

e-mail : gjhwang@kier.re.kr Tel :+82 42 860 3227

With the advent of the 21st century, concern about environmental problems such as depletion of fossil energy resources and global warming has increased dramatically.

Hydrogen is spotlight as one of the future clean energy to solve those problems. It is an attractive fuel for the future because it is renewable resource and also flexible as an energy carrier. One of the promising methods for large-scale hydrogen production is thermochemical water decomposition using heat energy from nuclear.

In March 2004, the nuclear hydrogen production program which is led by the Ministry of Science and Technology (MOST) in Korea was started. The target of this program is covering the 20% of fuel in transportation by the hydrogen energy after 20 years in Korea. In this program, KIER (Korea Institute of Energy Research) carry out the research for hydrogen production by IS (Iodine-sulfur) process.

In this presentation, it is presented for the nuclear hydrogen production plan by IS process in KIER.

한국에너지기술연구원
KOREA INSTITUTE OF ENERGY RESEARCH

Nuclear hydrogen production by IS (iodine-sulfur) process in Korea

2004. 7. 5-6

Workshop on Hydrogen Production Technologies

Gab-Jin Hwang, Chu-Sik Park, Sang-Ho Lee and Tae-Hwan Kim

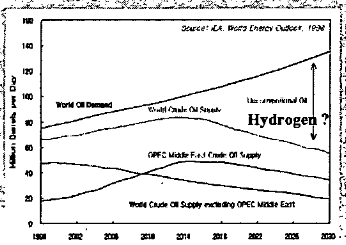
Hydrogen Energy Research Center, Korea Institute of Energy research

Hydrogen Energy Research Center

한국에너지기술연구원
KOREA INSTITUTE OF ENERGY RESEARCH

Why need hydrogen energy in Korea?

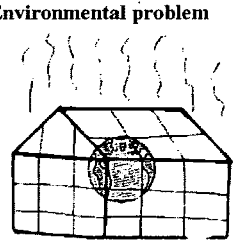
○ Energy problem



(Source:IEA, World Energy Outlook, 1998)

- **The demand quantity of first energy (in 2000) : 192.9 MTOE (dependence to import : 97%, 24.2 billion US$), 311.8 MTOE (in 2020)**
  → estimate continuously dependence to petroleum oil
- **Need a security of the new energy for the future than security of a fossil fuel (solve the energy and environment problem at the same time)**
- **A view of the stable supply and demand of energy by independence to import**

○ Environmental problem



- **Dependence to a fossil fuel : 84% of overall energy**
  → Serious environment pollution by emission of SO_2 and CO_2 gas etc.
  → Increase of the energy cost by introduce a carbon tax (20$/carbon-ton)
- **Overall emission quantity of CO_2 gas : 120 MTC (10[th] in world)**
  Population : 2.7 TC (10[th] in world)
  Area : 1,200TC/km² (1[st] in world)

→ Hydrogen Energy for clean energy in the future

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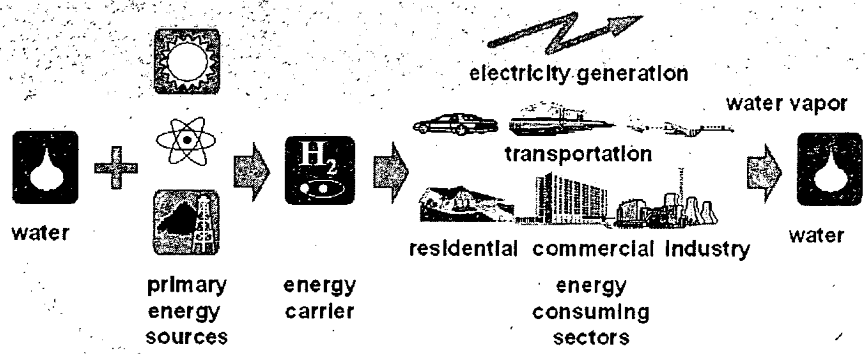
Hydrogen Society in 21st C

○ Hydrogen: 2ry energy source (clean energy, energy carrier)

- Using for fuel: no SO_2 and CO_2 emission
- Product by combustion → Water



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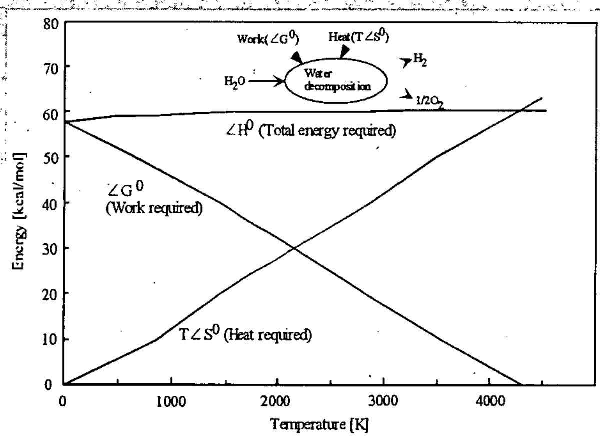
What is thermochemical hydrogen production ?

○ Need heat for hydrogen production by direct water-splitting (about 4000K)



* J.E.Funk and R.M.Reinstrom, I&EC Process Design and Development, 5 (1966) 336.

→ Thermochemical water-splitting method by chemical cycle consist of endothermic and exothermic reaction using solar or nuclear heat in low temperature *

1) Hydrogen production method using high temperature of HTGR

2) Hydrogen production method using high temperature of the concentrated solar radiation

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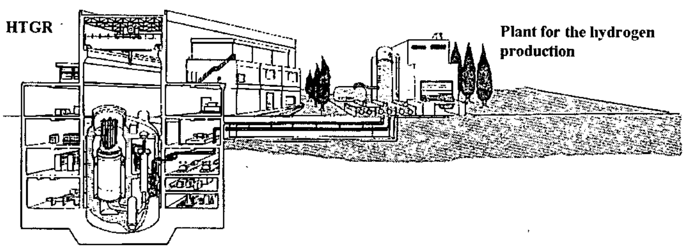
Hydrogen production using the high temperature of VHTR

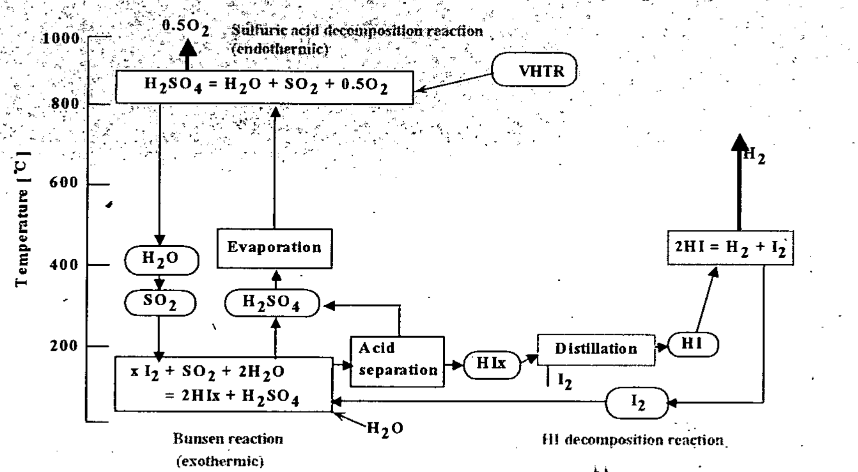
○ Thermochemical hydrogen production process using nuclear heat

- UT-3 cycle (Tokyo Unv.)
  - $CaBr_2 + H_2O \xrightarrow{700\sim750℃} CaO + 2HBr$ (endothermic)
  - $CaO + Br_2 \xrightarrow{550\sim600℃} CaBr_2 + (1/2)\,O_2$ (exothermic)
  - $Fe_3O_4 + 8HBr \xrightarrow{200\sim300℃} 3FeSO_4 + 4H_2O + Br_2$ (exothermic)
  - $3FeBr_2 + 4H_2O \xrightarrow{570\sim620℃} Fe_3O_4 + 6HBr + H_2$ (endothermic)
- IS cycle (JAERI)
  - $2H_2O + I_2 + SO_2 \xrightarrow{약\ 100℃} 2HI + H_2SO_4$ (exothermic)
  - $2HI \xrightarrow{200\sim500℃} H_2 + I_2$
  - $H_2SO_4 \xrightarrow{약\ 800℃} H_2O + SO_2 + (1/2)O_2$ (endothermic)



IS (Iodine-Sulfur) Process

○ Water-splitting process by chemical materials under 1000℃
○ Re-cycle of the reaction materials exclusion water (closed-cycle process)



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Long-Term Challenges for the IS Cycle

Field	Purpose	Contents
Reaction & Unit Process Tech.	➤ Design of chemical reactor and unit process operation • Separation/Purification • Closed-cycle operation	- Loop design for H_2SO_4 decomposition - An experiment on the Bunsen reaction and basic design - An experiment on the HIx decomposition - Side-reaction control - Separation/Purification of HIx from H_2SO_4 obtained by Bunsen reaction - Separation/Purification of H_2SO_4 from HIx obtained by Bunsen reaction - Closed-cycle operation
Advanced Process Tech. for High Efficiency	• Two membrane technologies (electrodialysis & membrane reactor) • Distillation/Vacuum distillation	- Vacuum distillation of HIx - Vacuum distillation coupled with electrodialysis - HI concentration by electrodialysis only - Hydrogen separation by using a special membrane reactor
Materials for Equipment Fabrication	• Screen test of candidate materials to withstand at operating conditions • Corrosion and integrity test of welding and fabricated parts at real operating conditions • Establishment of procurement specification on pump head materials	- Materials for the H_2SO_4 decomposition process - Materials for the HIx decomposition process - Materials for the Bunsen reaction process - Design/Fabrication of reactors and modules using selected materials
Process Analysis and Design	- Analysis of heat & mass balance and fluid mechanics - Process design	-Analysis of heat & Mass balance in the unit process -Determination of total thermal efficiency -Research for advanced heat recovery method -Design of the Korean peculiar demonstration facilities

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The 1st Phase R&D on the IS Cycle Technology

Objective : Basic Technology Establishment for the Hydrogen Production Plant Construction [Lab.-Scale (5ℓ/hr H_2) Design Study]

Work Scope	Contents
Reaction & Unit process tech.	• An experiment on the Bunsen reaction unit process and basic design • Development of HI decomposition • Design of the test loop on the H_2SO_4 decomposition reaction process
Process tech. for high efficiency	• HI concentration by electrodialysis • An experiment on the membrane reactor for hydrogen separation • Hydrogen production from HI by the vacuum distillation • Preparation of experimental apparatus and its scale-up design
Equipment materials	• Corrosion test and selection of the materials for each unit process
Process analysis and design	• Modification and up-date of the published process data and the process design by using the modified process data

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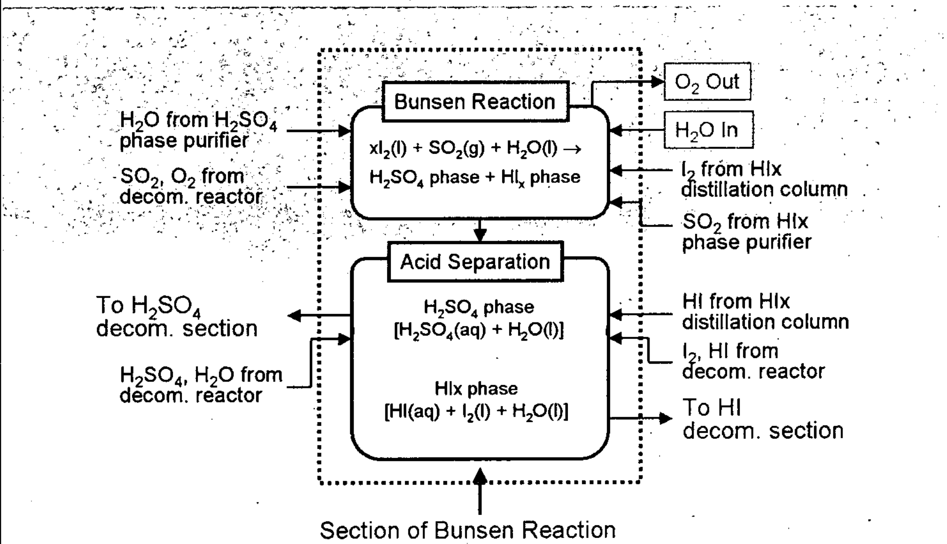
Bunsen reaction



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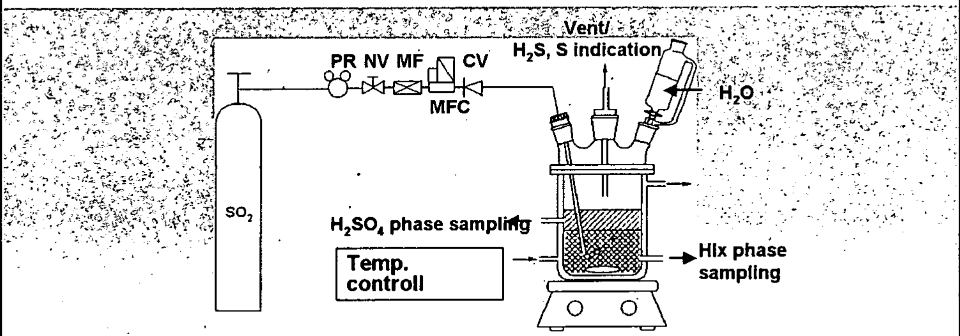
Concept and research contents



- Basic research for the process parameters in Bunsen reaction (temperature, pressure, concentration etc.)
- Side-reaction control in HI / H_2SO_4 / I_2 / H_2O
- Acid separation of 2-phase (H_2SO_4 phase/ HIx phase)
- Purification of each phase
- Loop design to connect with H_2SO_4 decomposition process

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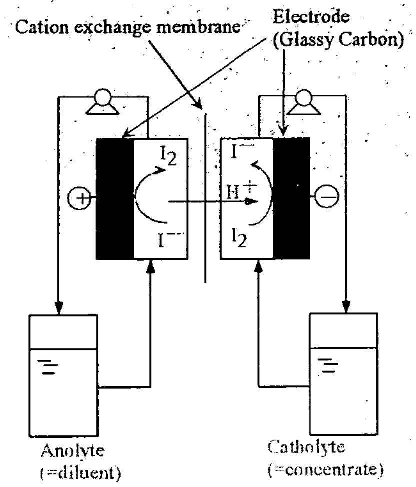
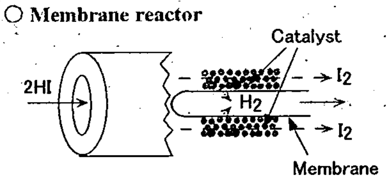
Advanced process technology for high efficiency

○ **Electro-electrodialysis**



○ **Membrane reactor**



○ **Coupling system with electro-electrodialysis and distillation column (or vacuum distillation)**

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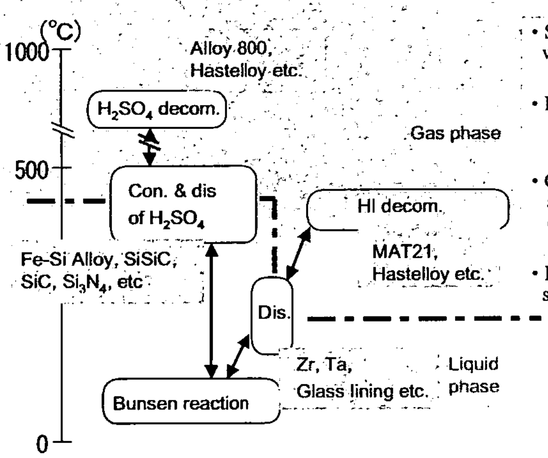
Materials for equipment fabrication



* Onuki et al., 14th World Hydrogen Energy Conf., June, Montreal, Canada (2002).

- Screen test of candidate materials to withstand at operating conditions
- Possibility test for the fabrication
- Corrosion and integrity test of welding and fabricated parts at real operating conditions
- Establishment of procurement specification on pump head materials

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Process analysis & design

■ Analysis of heat & mass balance and fluid mechanics

- Analysis of heat & Mass balance in the unit process
- Determination of total thermal efficiency
- Research for advanced heat recovery method

■ Process design

- Design of the Korean peculiar demonstration facilities

■ Evaluation of the hydrogen production cost

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KOREA INSTITUTE OF ENERGY RESEARCH

Technological Roadmap for NHPT

Ultimate Target	Nuclear Hydrogen Production Plant Coupled with VHTR(GEN-IV) [30 thousand tons H_2 per year]

Technology /Phase	Phase 1 (2004/2005)	Phase 2 (2006-2008)	Phase 3 (2009-2011)	Phase 4 (2012-2016)	Phase 5 (2017-2019)
Reaction and Unit Process Technology	Develop. of key technology to obtain the high efficiency. (5L/hr) → 2007				
Process Tech. for High Efficiency		Lab.-scale & operation ($0.1Nm^3/hr$) Select of equipment materials → 2011			
Operation Technology of Closed Cycle				Pilot-scale & Operation ($30\text{-}100Nm^3/hr$; 1 MWth) → 2016	
Material Technology					
Construction of Demonstration Facilities					Demo.-scale & Operation, coupled with VHTR ($10,000Nm^3/hr$; 100 MWth)

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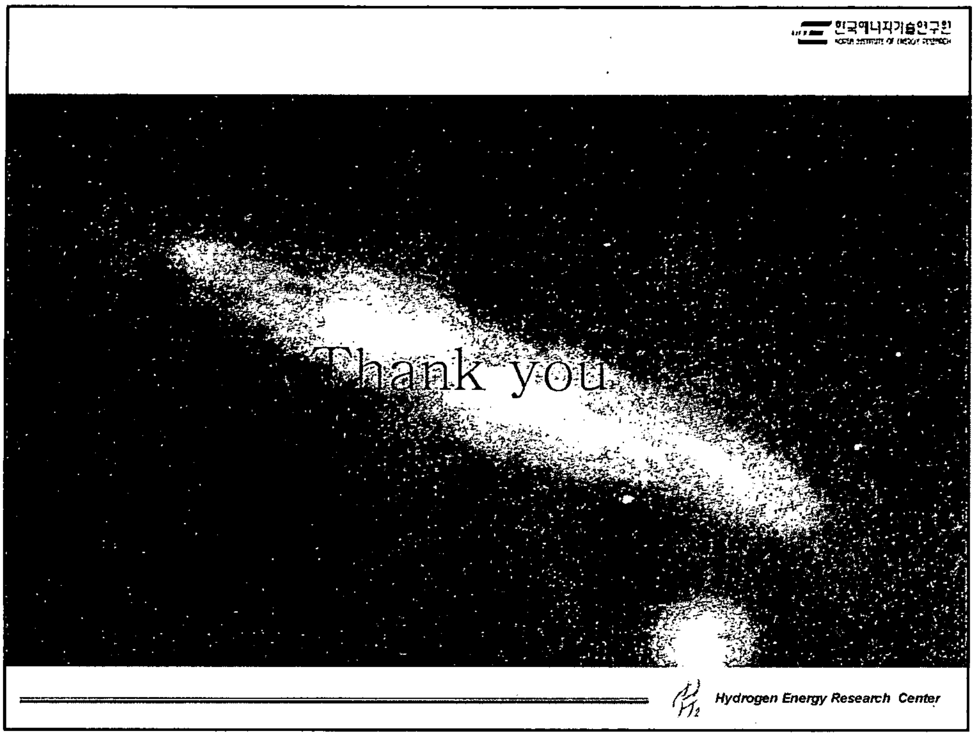

Thank you.
Hydrogen Energy Research Center

5.5.3 Development of a New Thermochemical and Electrolytic Hybrid Hydrogen Production System for FBR

Toshio Nakagiri[1*]
[1]*Japan Nuclear Cycle Development Institute, O-Arai, Higashi-Ibaraki, Ibaraki, 311-1393, Japan*

A new thermochemical and electrolytic hybrid hydrogen production process to realize the hydrogen production from water using the heat generation of coolant in Fast Breeding Reactor (FBR).

The process is consists of sulfuric acid (H_2SO_4) synthesis and the decomposition reactions, and sulfur trioxide (SO_3) decomposition process at about 500° C is facilitated by electrolysis with ionic oxygen conductive solid electrolyte.

Hydrogen production experiment was performed in laboratory scale using yttria stabilized zirconia (YSZ) for electrolytic SO_3 splitting, and hydrogen and oxygen generation continued for two hour in the experiment. (Hydrogen generation rate was about 0.1 ml/min).

System design study of hydrogen production plants with sodium cooled FBR was performed, and investigation to confirm the possible efficiency of the electrolysis cells and durability of structural materials are under performed.

KEYWORDS: *hydrogen, hydrogen production, thermochemical hybrid process, sodium cooled FBR, solid electrolyte, electrolysis, sulfuric acid*

15th WHEC 30J-07

Development of a new thermochemical and electrolytic hybrid hydrogen production system for FBR

6 July 2004

HTTR, JAERI O-arai, Japan

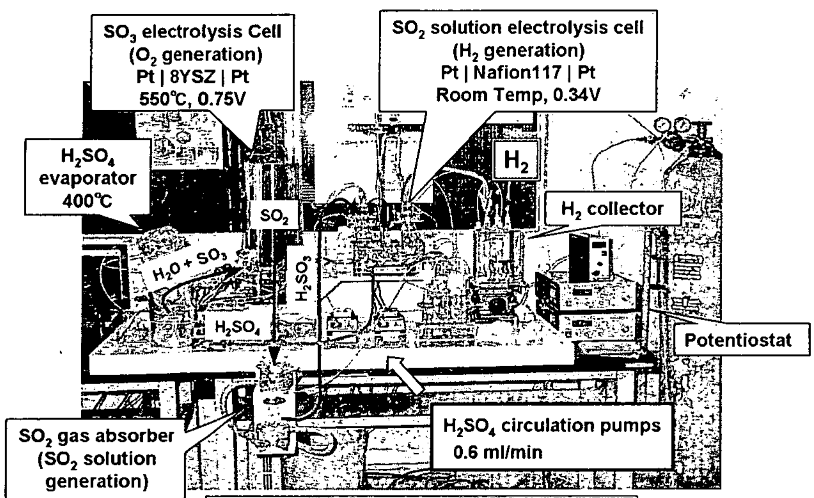
Toshio NAKAGIRI, Yoshitaka CHIKAZAWA

O-arai engineering Center,
Japan Nuclear Cycle Development Institute

JNC

Experiment to substantiate the hybrid hydrogen production process

- The hydrogen production experiment with the hybrid process was performed on June 24th.



Test apparatus and test conditions

JNC 1

Contents

- Background
- Principle and characteristics of new hybrid hydrogen production process
- System design study of hydrogen production plant with sodium cooled FBR
- Experiment to substantiate the hybrid hydrogen production process
- Conclusion

JNC 2

Background

- In "Feasibility study on Commercialized Fast Breeder Reactor (FBR) Cycle Systems" of JNC, a concept of a multi-purpose (Electricity supply, Hydrogen Production, etc.) small sized reactor has been studied.
- Requirements for hydrogen production system of FBR
  - Maximum temperature : 500-550℃
  - Thermal efficiency : higher than water electrolysis
  - Hydrogen production from water : No use of fossil fuel, no CO_2 emission.

⇩

A new thermochemical and electrolytic hybrid hydrogen production process was proposed by JNC.

JNC 3

Principle

New hybrid process proposed by JNC

$2H_2O + SO_2$	->	$H_2SO_4 + H_2$	<100°C (electrolysis:0.17v)	[1]
H_2SO_4	->	$H_2O + SO_3$	400°C (thermal decomposition)	[2]
SO_3	->	$SO_2 + 1/2O_2$	500-550°C (electrolysis:0.13v)	[3]

Westinghouse process

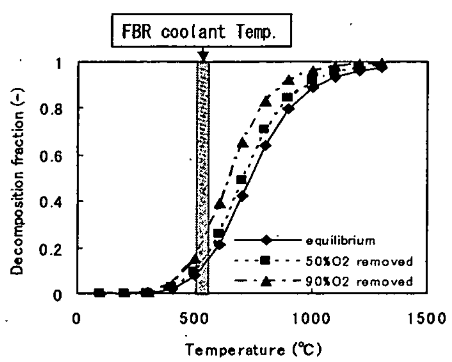
SO_3	->	$SO_2 + 1/2O_2$	>800°C (thermal decomposition)	[3]'

- The hybrid process consists of H_2SO_4 synthesis and decomposition reactions. (Based on "Westinghouse process")
- Maximum operation temperature is about 500-550°C.
- Hydrogen and oxygen are produced from water.

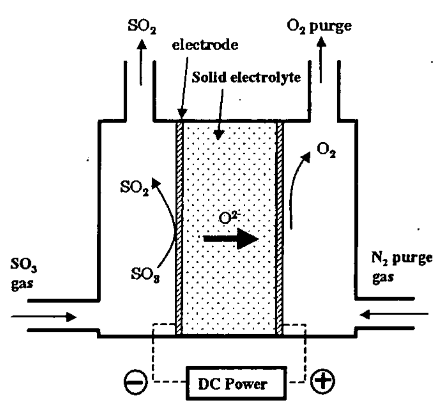
JNC 4

Electrolytic SO_3 splitting with oxygen conductive solid electrolyte

- **Oxygen ion conductive solid electrolyte is used for SO_3 splitting.**



Calculated thermal decomposition fraction of SO_3 under equilibrium condition

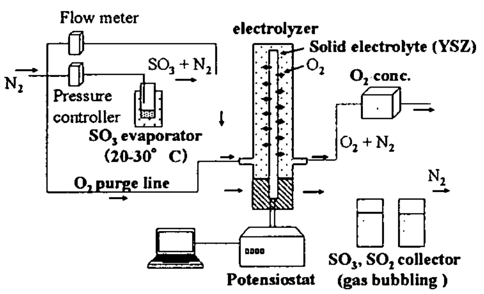


Principle of electrolytic SO_3 splitting with solid electrolyte

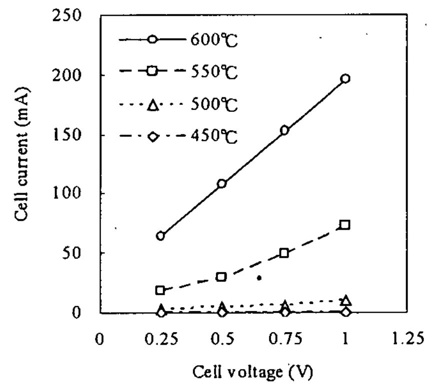
JNC 5

Electrolytic SO_3 splitting experiment

Electrolytic SO_3 splitting was confirmed experimentally.



Test apparatus of SO_3 splitting experiment



Relationship between cell voltage and cell current

JNC

6

Theoretical thermal efficiency

Theoretical thermal efficiency (η) is estimated to be about 55%.

Theoretical thermal efficiency of the hybrid process
(H_2SO_4 concentration:100%)

Hydrogen production method	Reactions	Operating Temperature (°C)	Required energies (kJ/mol) Electrical energy (ΔG)	Thermal energy ($T\Delta S$)	Theoretical splitting voltage (V)	Thermal efficiency (η) (%)
Electrolysis of water	$2H_2O + SO_2 \rightarrow H_2SO_4 + H_2$	25	237.1	48.7	1.23	44.6
New hybrid process	$2H_2O + SO_2 \rightarrow H_2SO_4 + H_2$	50	87.3	-37.2	0.17	54.8
	$H_2SO_4 \rightarrow H_2O + SO_3$	372	0.0	149.8	0.0	
	$SO_3 \rightarrow SO_2 + 1/2O_2$	500	26.1	72.4	0.14	
	Total		113.4	189.0	0.31	

$$\eta = \frac{H_{HHV}}{\frac{\Delta G}{G.E.} + T\Delta S}$$

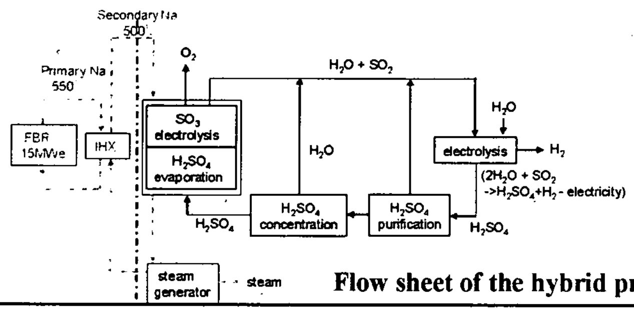
H_{HHV} : Higher heat value of hydrogen (285.8 kJ/mol)
G.E. : Electric generation efficiency (0.4 in this calculation)

JNC

7

Characteristics of the hybrid process

- Maximum operating temperature is 500-550°C.
- Hydrogen and oxygen is produced from water.
- Thermal efficiency of the process is expected to be higher than electrolysis of water.
- Comparison with other thermochemical processes
  - Simple process : number of reactors are less than other processes.
  - Low material corrosion : lower operating temperature, no use of halogens
  - Higher safety : Hydrogen is produced at the temperature lower than 100°C.



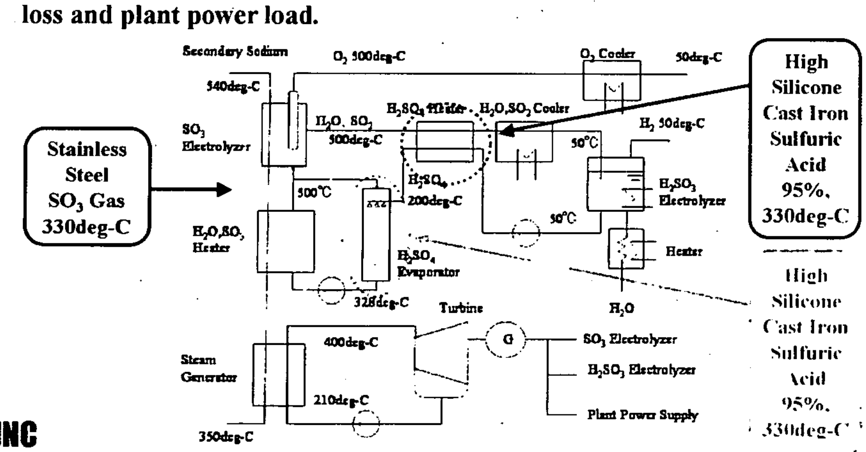
JNC

Flow sheet of the hybrid process

8

System design study of hydrogen production plant with Sodium Cooled FBR

-Conceptual design of a hydrogen production plant (47000Nm³/h with thermal output 395MW) using thermochemical and electrolysis hybrid process has been done.
-Components of hydrogen production system can be made of irons.
-Hydrogen production efficiency is evaluated 42% considering heat exchange loss and plant power load.



JNC

9

Major specification of the hydrogen production plant

Item	Specifications
Thermal Output	395MWt
Primary Sodium Temperature	550／395℃
Secondary Sodium Temperature	540／350℃
Hydrogen Production	47000Nm³/h
Electric Output	82MWe
Sulfur Concentration	95w%
Efficiency of SO_3 Electrolysis (O_2 generation)	85%
Efficiency of SO_2 Solution Electrolysis (H_2 generation)	90%
Efficiency of Hydrogen Production	42%

Required R&D

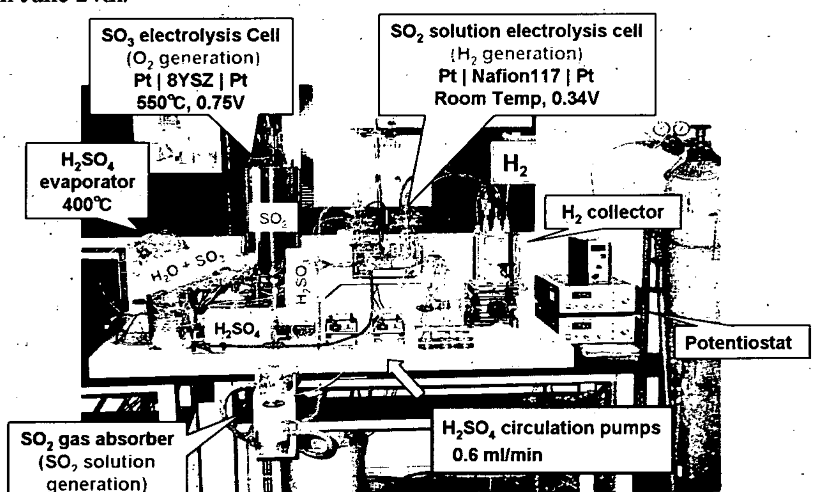
(1) Possible efficiency of electrolysis cells must be confirmed.
 -SO_3 electrolysis (O_2 generation)
 -SO_2 solution electrolysis (H_2 generation)

(2) Durability of iron structural materials in H_2SO_4 atmosphere must be confirmed.

JNC 10

Experiment to substantiate the hybrid hydrogen production process

The hydrogen production experiment with the hybrid process was performed on June 24th.

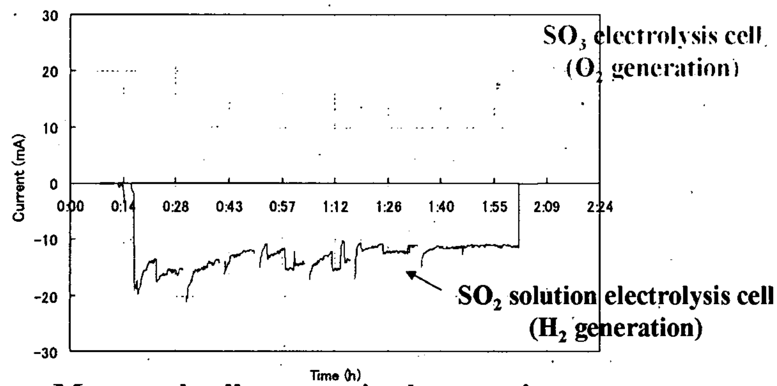


Test apparatus and test conditions

JNC 11

Results of hydrogen and oxygen production experiment (under analysis)

- **Hydrogen and oxygen generation continued for about two hours.**
  - **H_2 generation rate : about 5 ml/h (calculated from measured cell current)**
- **No severe material corrosion was observed.**
- **Experimental data are under analysis.**



Measured cell current in the experiment

JNC 12

Conclusions

- **A new concept of thermochemical and electrolytic hybrid hydrogen production process was proposed.**
  - H_2 and O_2 are produced from water.
  - Maximum operating temperature is about 500°C.
  - Thermal efficiency the process is higher than the efficiency of electrolysis of water when applied to Fast Breeder.
- **A concept of hydrogen production plant with sodium cooled FBR was studied.**
  - **Components of hydrogen production system can be made of irons.** Durability of iron structural materials in H_2SO_4 atmosphere must be confirmed.
  - **Hydrogen production efficiency is evaluated 42% considering heat exchange loss and plant power load:** Possible efficiency of electrolysis cells must be confirmed.
- **The hydrogen production experiment with the hybrid process was with the hybrid process was performed.**
  - H_2 and O_2 generation continued for two hours.
- **1NL/h-H2 production experiment are going to be performed in 2005.**

JNC 13

5.5.4 Electrical Conductivity and Corrosion Resistance of Titanium Pyrochlores Used for Sulfur-based Hybrid Cycle

Hirotaka KAWAMURA, Masashi MORI, Daisuke KUSANO and Masaki UOTANI

Central Research Institute of Electric Power Industry
2-6-1 Nagasaka, Yokosuka, Kanagawa-ken 240-0196
JAPAN
E-mail: kawamuh@criepi.denken.or.jp

Sulfur-based hybrid cycle for hydrogen production (SHC) is a highly efficient hydrogen producing process through the electrolysis of $H_2O + H_2SO_3 \rightarrow H_2 + H_2SO_4$ at approximately 353K and through the thermal decomposition of $H_2SO_4 \rightarrow H_2O + SO_2 + 1/2O_2$ at approximately 1,123K. Ti-based complex oxides are expected as anode materials in the SHC electrolysis cell, instead of Pt group materials, because of their high corrosion resistance under the electrolysis condition, i.e., 50 weight% H_2SO_4 solution. In our previous work, it had been clarified that Ti^{3+} ions with d^1 system could exit stably in the nonstoichiometric pyrochlores at room temperature after reducing at 1,273K in a hydrogen atmosphere, and the concentration of Ti^{3+} ions in the pyrochlores is related to their electrical conductivity. In addition, as possible B-site substituents, transition-metal ions (M=Cr, Mn, Fe, Co, Ni) are appropriate with respect to an appearance of electrical conductivity.

In this study, the crystallographic and electrical properties, and the corrosion resistance in 50 weight% H_2SO_4 solution for the A-site deficient $RE_{2-x}Ti_2O_{7-\delta}$ pyrochlores (RE = Yb, Y, Gd, Sm, Pr, La) and B-site doped $Gd_{2-x}Ti_{2-y}M_yO_{7-\delta}$ pyrochlores have been studied as the anodes. The results obtained are as follows:

(1) The single pyrochlore phase region in the $RE_{2-x}Ti_2O_{7-\delta}$ system, increased with increasing ionic radius at the A-site up to that of Sm^{3+} and then decreased and the widest single phase range of $0 \leq x < 0.5$ was observed in the $Sm_{2-x}Ti_2O_{7-\delta}$ pyrochlores.

(2) $Gd_{2-x}Ti_2O_{7-\delta}$ pyrochlores with cubic symmetry show a single phase in the region of $0 \leq x \leq 0.28$, and the $Gd_{2-x}Ti_{2-y}M_yO_{7-\delta}$ pyrochlores have a tendency to form a single phase with increasing A-site deficiency.

(3) The sintered $RE_{2-x}Ti_2O_{7-\delta}$ and $Gd_{2-x}Ti_{2-y}M_yO_{7-\delta}$ pyrochlores showed in the electrical conductivity range from 10^{-5} to 10^{-2} S/cm at 353K.

(4) $Sm_{2-x}Ti_2O_{7-\delta}$, $Y_{2-x}Ti_2O_{7-\delta}$ and $Gd_{2-x}Ti_{2-y}M_yO_{7-\delta}$ pyrochlores showed high corrosion resistance, and their solubilities were measured to be < 1 %/1000 h.

Keywords: *hydrogen production, sulfur-based hybrid cycle, thermochemical production, anode materials, pyrochlore oxides, electrical conductivity, corrosion resistance*

Workshop on Hydrogen Production Technologies (2004)

Electrical Conductivity and Corrosion Resistance of Titanium Pyrochlores used for Sulfur-based Hybrid Cycle

July 6, 2004
at Oarai Research Establishment JAERI

Central Research Institute of Electric Power Industry (CRIEPI)
Hirotaka KAWAMURA, Masashi MORI, and Masaki UOTANI

CRIEPI

Workshop on Hydrogen Production Technologies (2004)

Contents

- Background
  - Sulfur-based Hybrid Cycle for Hydrogen Production
- Objectives
- Experiments
- Results and Discussions
  - Crystallographic study
  - Electrical conductivity study
  - Corrosion resistance study
- Summary

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Background

◆ According to a desiring of hydrogen energy cycle in the near future, such as coming into wide use of fuel cell and fuel cell vehicle (FCV), the establishments of zero emission and large-scale hydrogen production process have been desired.

◆ Some electrolysis process using Pt electrode have been proposed. On the other hand, Pt is a noble and rare metal.

◆ In order to establish some high electrolysis efficiency and low-cost electrolysis system, Pt-free electrode should be developed.

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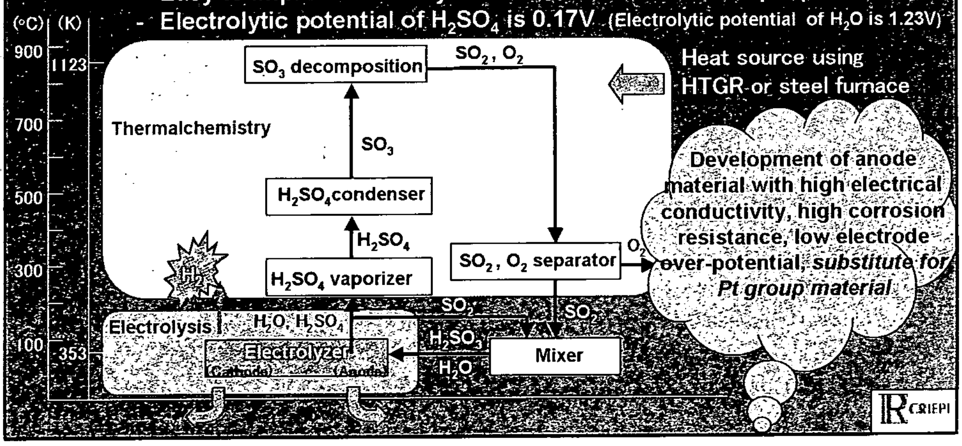
Sulfur-based Hybrid Cycle for Hydrogen Production

- One of nuclear-hydrogen production process (combined with thermochemistry and electrolysis)
- Emission free process
  - No CO_2 gas emission
  - Only water consumption (reuse of H_2SO_4)
- Availability
  - Easy to improve electrolysis efficient because of simple process.
  - Electrolytic potential of H_2SO_4 is 0.17V (Electrolytic potential of H_2O is 1.23V)



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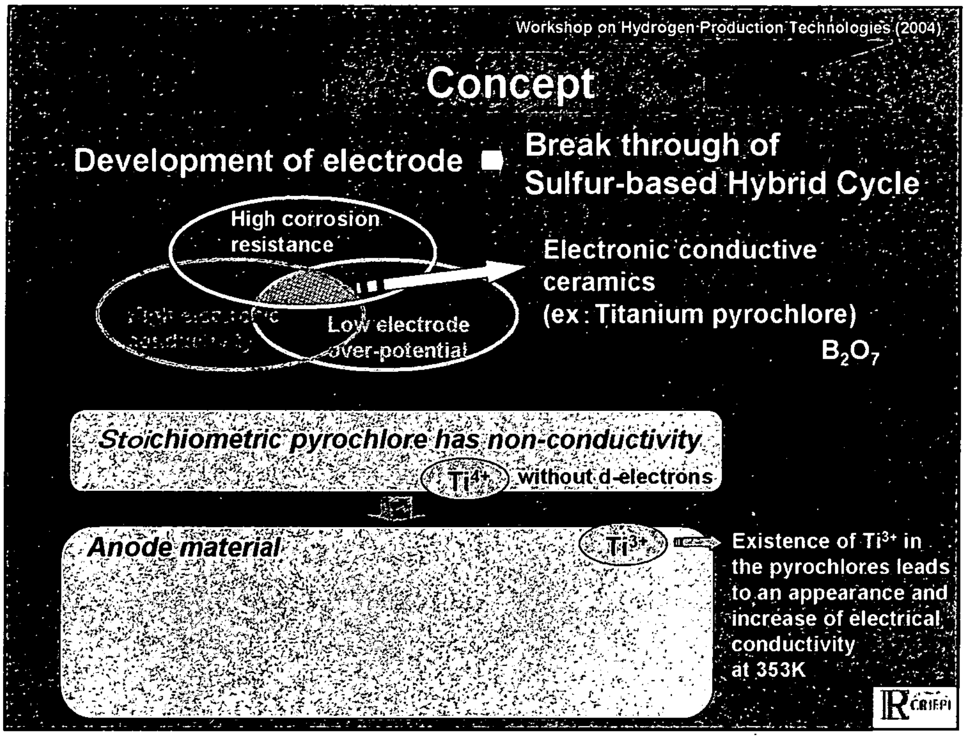
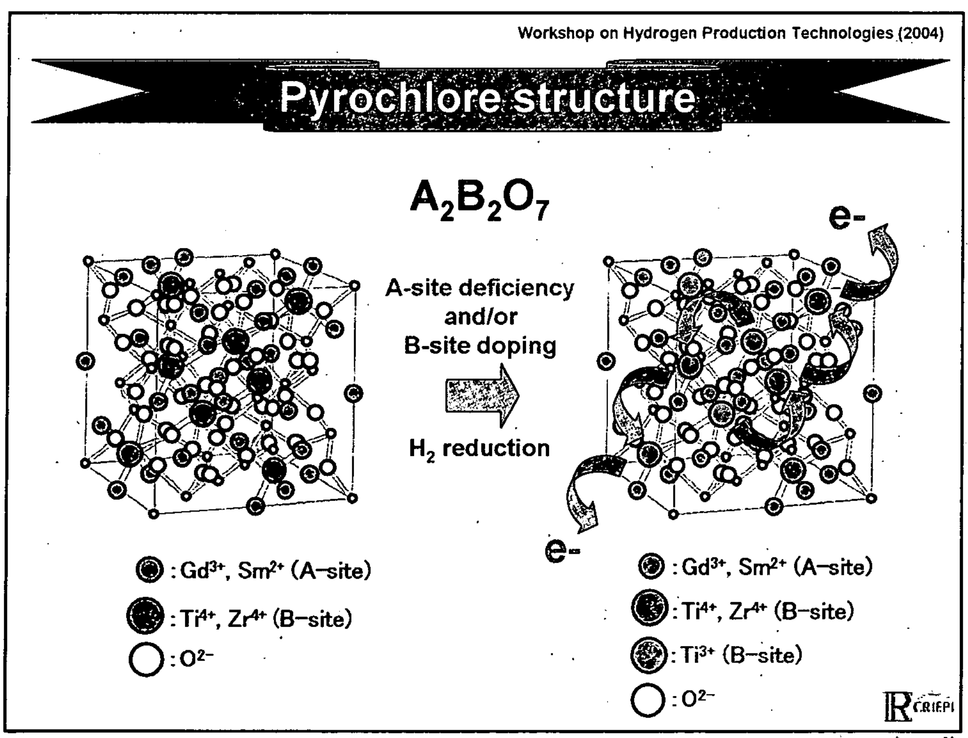
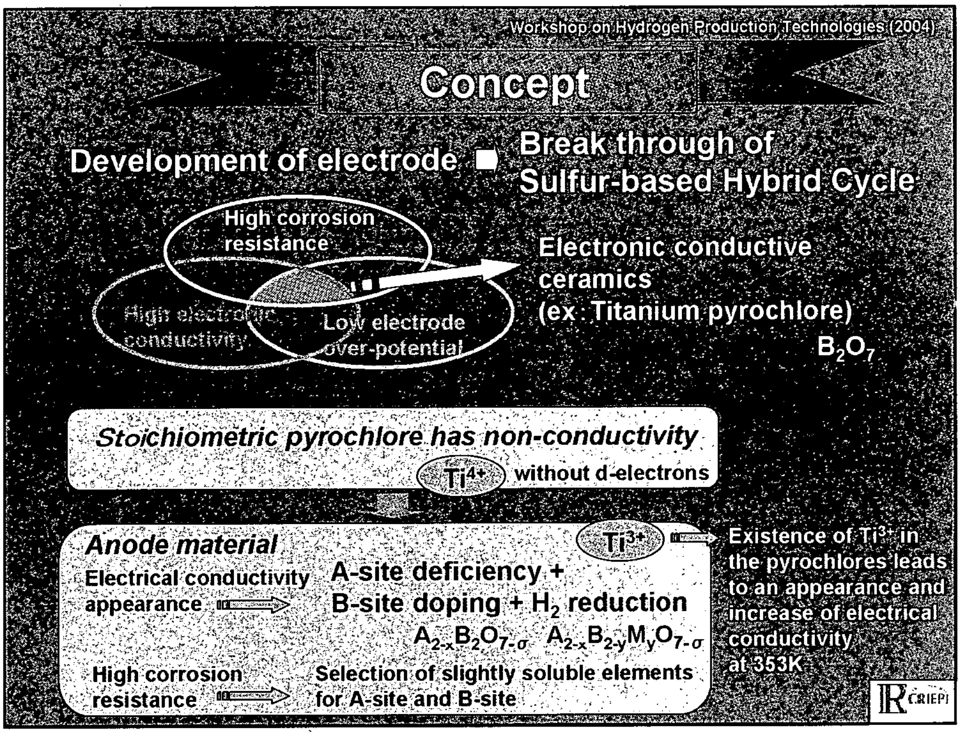

Workshop on Hydrogen Production Technologies (2004)
Concept
Development of electrode
Break through of Sulfur-based Hybrid Cycle
High corrosion resistance
Low electrode over-potential
Electronic conductive ceramics
(ex: Titanium pyrochlore)
B_2O_7
Stoichiometric pyrochlore has non-conductivity
Ti^{4+} without d-electrons
Anode material
Ti^{3+}
Existence of Ti^{3+} in the pyrochlores leads to an appearance and increase of electrical conductivity at 353K
CRIEPI


Workshop on Hydrogen Production Technologies (2004)
Pyrochlore structure
$A_2B_2O_7$
A-site deficiency and/or B-site doping
H_2 reduction
e-
e-
: Gd^{3+}, Sm^{2+} (A-site)
: Ti^{4+}, Zr^{4+} (B-site)
: O^{2-}
: Gd^{3+}, Sm^{2+} (A-site)
: Ti^{4+}, Zr^{4+} (B-site)
: Ti^{3+} (B-site)
: O^{2-}
CRIEPI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Concept
Development of electrode
Break through of Sulfur-based Hybrid Cycle
High corrosion resistance
High electronic conductivity
Low electrode over-potential
Electronic conductive ceramics (ex: Titanium pyrochlore)
B_2O_7
Stoichiometric pyrochlore has non-conductivity
Ti^{4+} without d-electrons
Anode material
Ti^{3+}
Existence of Ti^{3+} in the pyrochlores leads to an appearance and increase of electrical conductivity at 353K
Electrical conductivity appearance
A-site deficiency + B-site doping + H_2 reduction
$A_{2-x}B_2O_{7-\sigma}$ $A_{2-x}B_{2-y}M_yO_{7-\sigma}$
High corrosion resistance
Selection of slightly soluble elements for A-site and B-site
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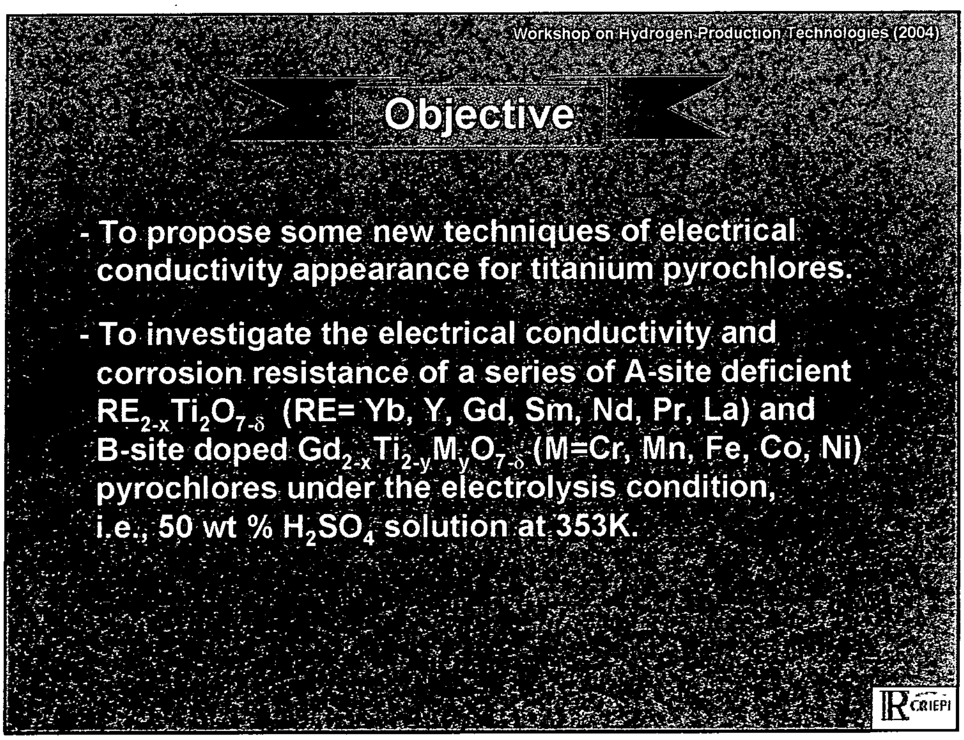
Workshop on Hydrogen Production Technologies (2004)
Objective
- To propose some new techniques of electrical conductivity appearance for titanium pyrochlores.
- To investigate the electrical conductivity and corrosion resistance of a series of A-site deficient $RE_{2-x}Ti_2O_{7-\delta}$ (RE= Yb, Y, Gd, Sm, Nd, Pr, La) and B-site doped $Gd_{2-x}Ti_{2-y}M_yO_{7-\delta}$ (M=Cr, Mn, Fe, Co, Ni) pyrochlores under the electrolysis condition, i.e., 50 wt % H_2SO_4 solution at 353K.
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Experiment

Material

$RE_{2-x}Ti_2O_{7-\sigma}$ (RE= Yb, Y, Gd, Sm, Nd, Pr La)
$Gd_{1.72}Ti_{1.9}M_{0.1}O_{7-\sigma}$ (M=Cr, Mn, Fe, Co, Ni)

Preparation

* Synthesizing by a solid-state reaction
  (pre-heating at 1473K, for 6h, sintering at 1773K, for 12h)
* A-site deficiency + B-site substituent
* Hydrogen reduction (at 1273K for 1h)

Evaluation iteam

* Crystallographic study : XRD study (18kW)
* Conductivity measurement : 353K, D.C. current four-terminal method
* Corrosion test : 353K, 50wt%H_2SO_4 solution

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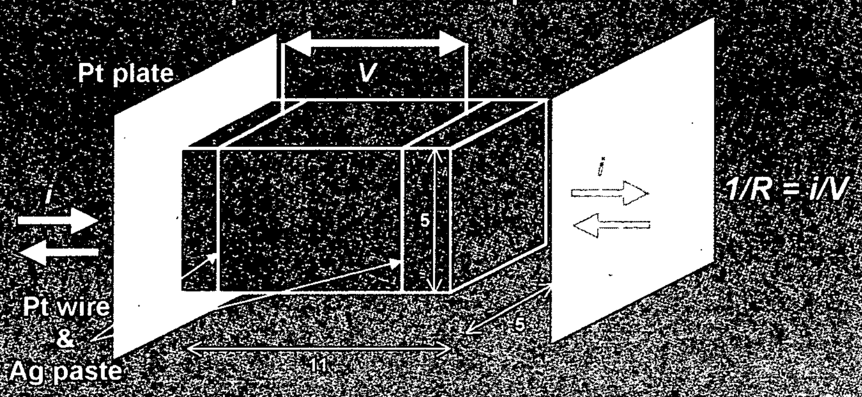
Electrical conductivity measurement

D.C. current four-terminal method

Shape and dimension of specimen



Unit : mm

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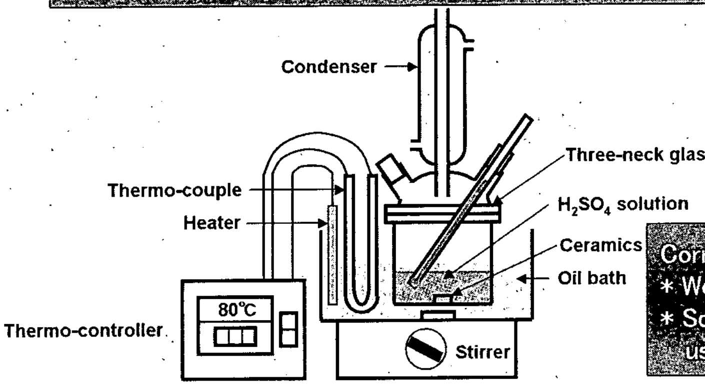
Corrosion resistance measurement

Ceramics material :

$RE_{1.72}Ti_{1.9}M_{0.1}O_{7-\sigma}$ (M=Cr, Mn, Fe, Co, Ni)

ref $RE_{2-x}Ti_2O_{7-\sigma}$ (RE= Yb, Y, Gd, Sm, Nd, Pr La)

Test condition : 353K, 50wt% H_2SO_4 sol. for 65 to 1000hrs



Corrosion resistance :
* Weight change
* Solution analysis using ICP-MS

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Workshop on Hydrogen Production Technologies (2004)

Contents

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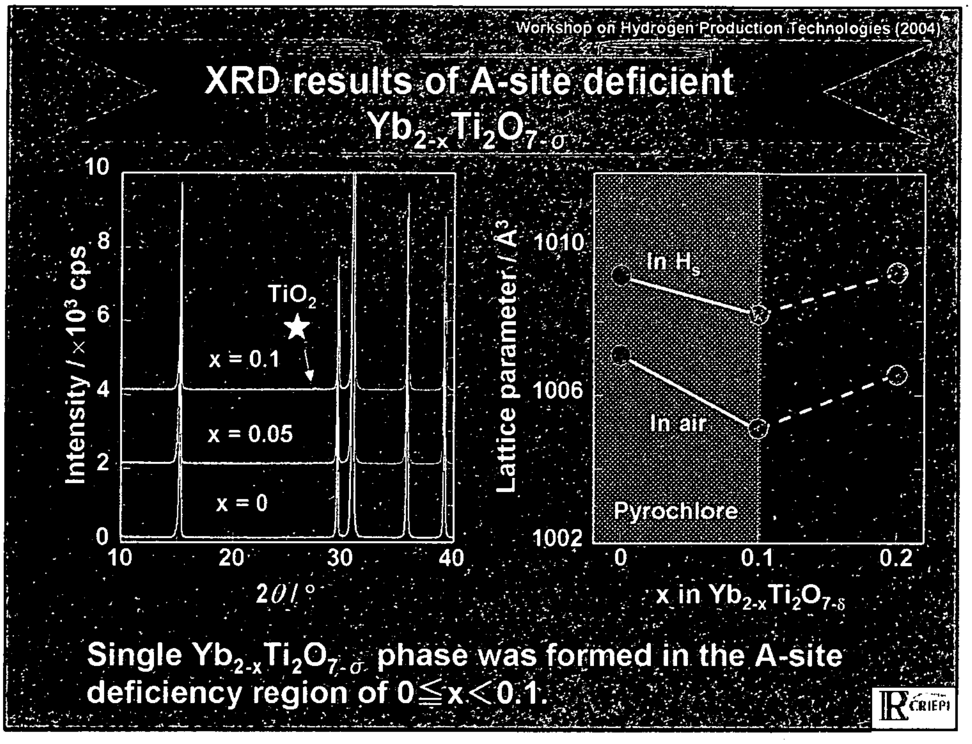
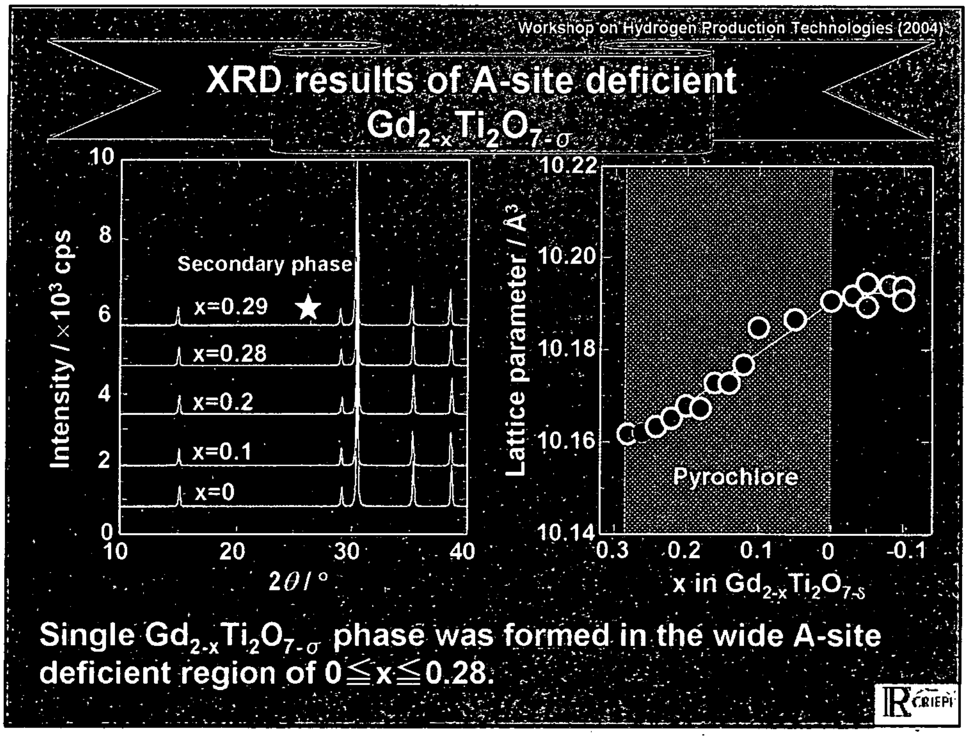
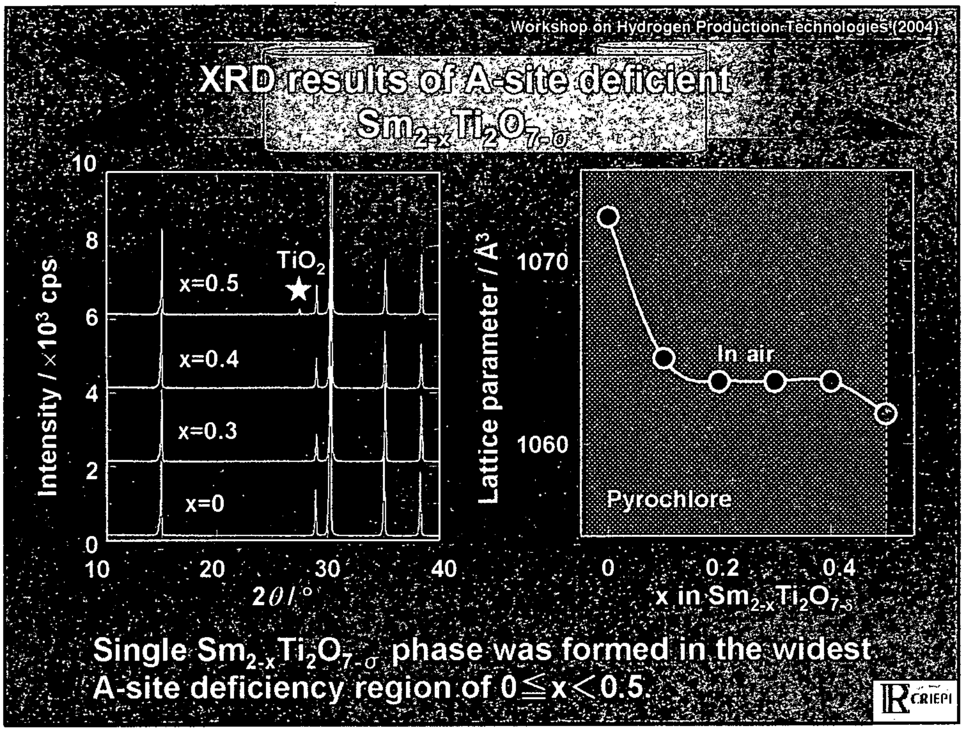
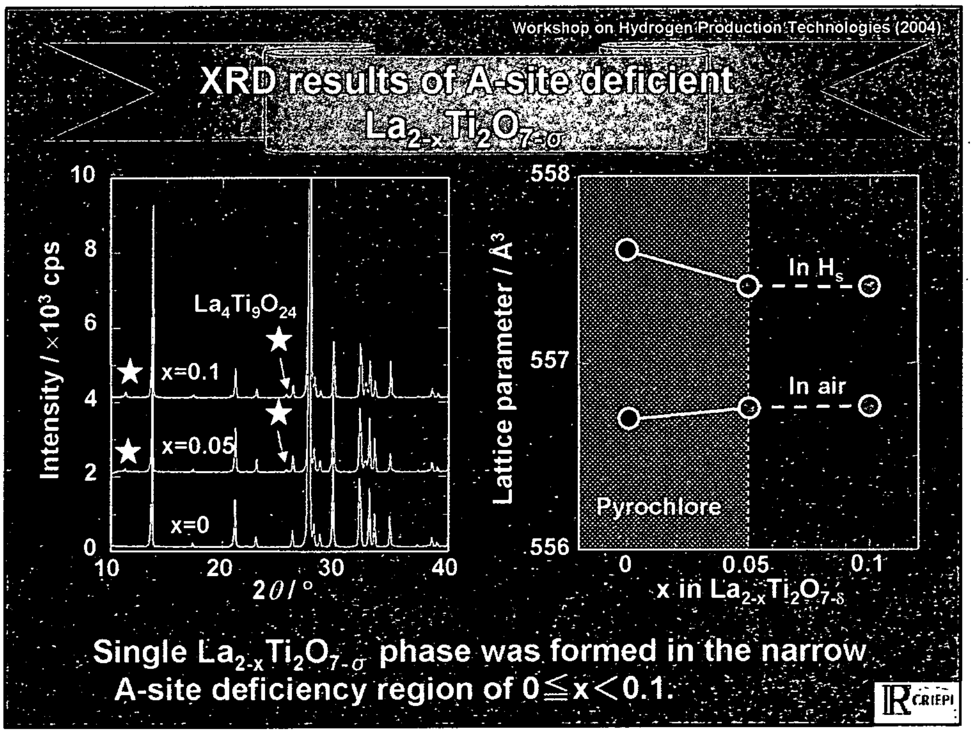
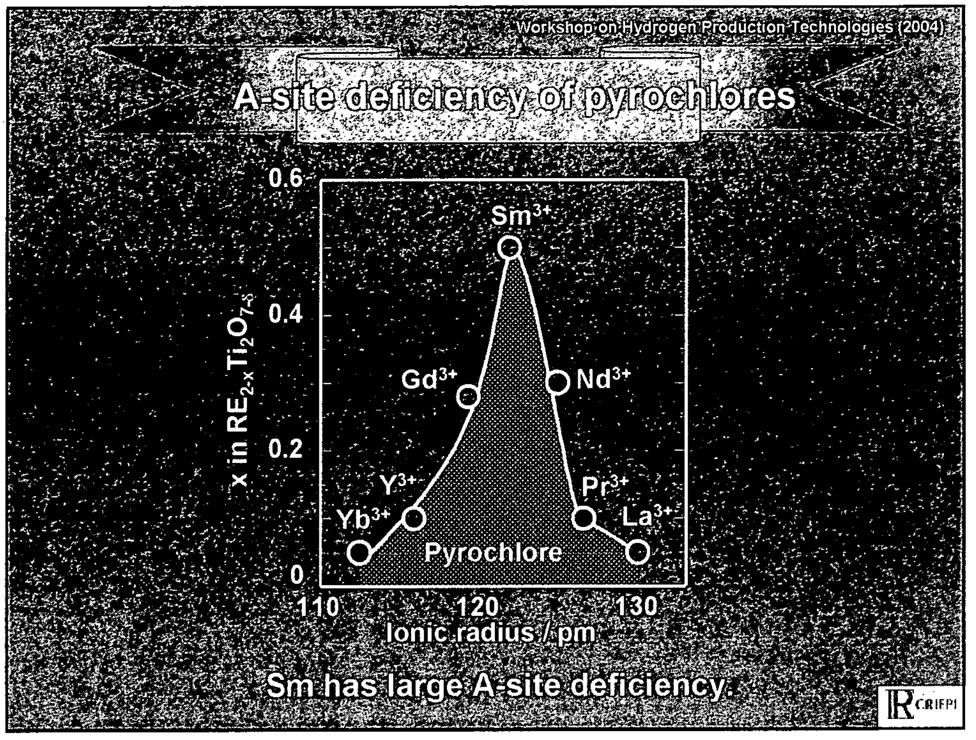
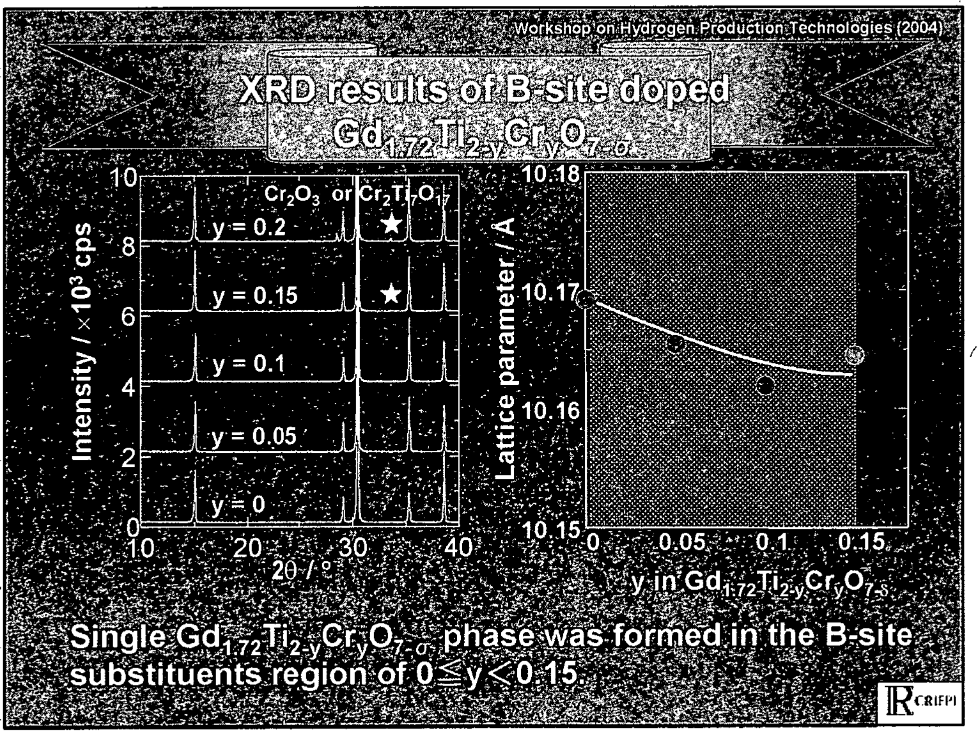

Workshop on Hydrogen Production Technologies (2004)
XRD results of A-site deficient
$Yb_{2-x}Ti_2O_{7-\sigma}$
Intensity / ×10³ cps
TiO₂
x = 0.1
x = 0.05
x = 0
2θ / °
Lattice parameter / Å³
In H₂
In air
Pyrochlore
x in $Yb_{2-x}Ti_2O_{7-\delta}$
Single $Yb_{2-x}Ti_2O_{7-\sigma}$ phase was formed in the A-site deficiency region of $0 \leqq x < 0.1$.
CRIEPI

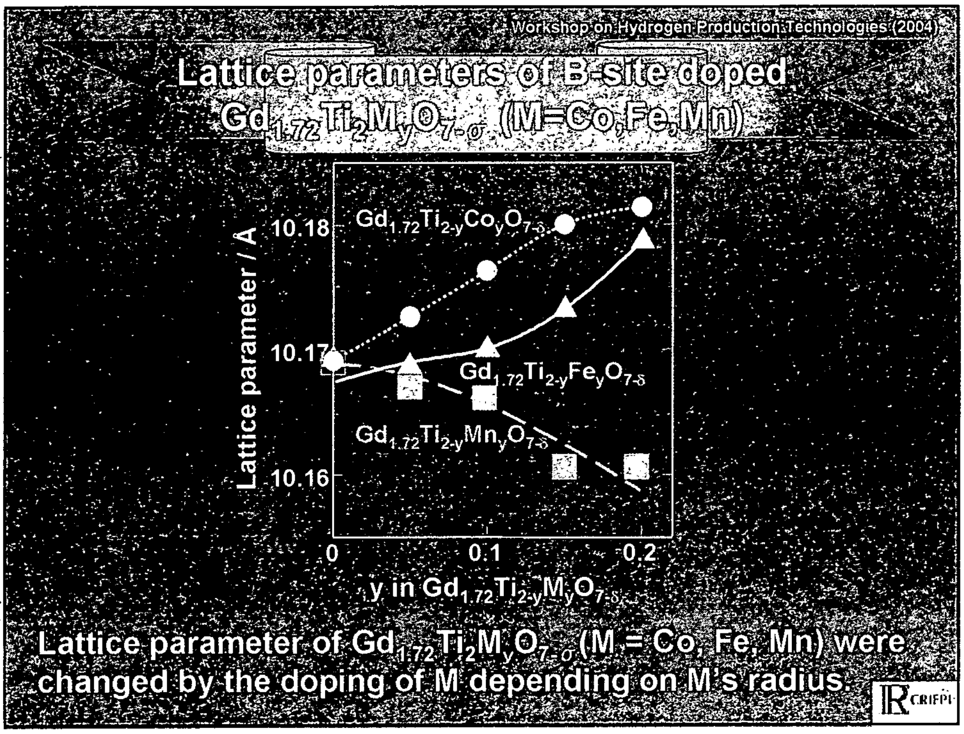

Workshop on Hydrogen Production Technologies (2004)
XRD results of A-site deficient
$Gd_{2-x}Ti_2O_{7-\sigma}$
Intensity / ×10³ cps
Secondary phase
x=0.29
x=0.28
x=0.2
x=0.1
x=0
2θ / °
Lattice parameter / Å³
Pyrochlore
x in $Gd_{2-x}Ti_2O_{7-\delta}$
Single $Gd_{2-x}Ti_2O_{7-\sigma}$ phase was formed in the wide A-site deficient region of $0 \leqq x \leqq 0.28$.
CRIEPI

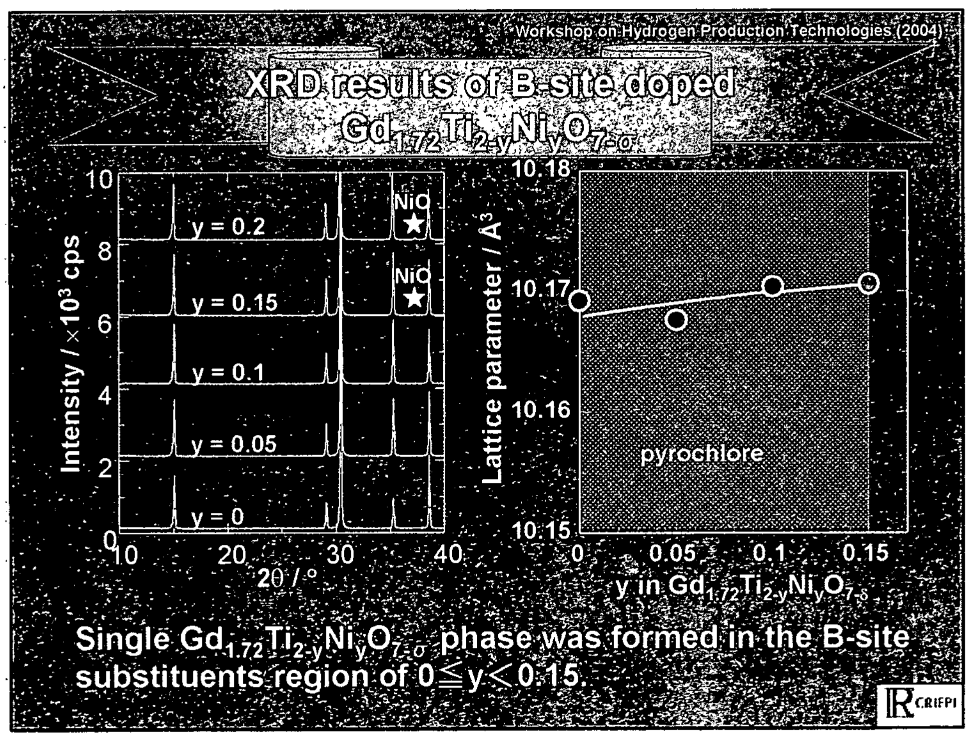

Workshop on Hydrogen Production Technologies (2004)
XRD results of A-site deficient
Sm2-xTi2O7-σ
Intensity / ×10³ cps
TiO2
x=0.5
x=0.4
x=0.3
x=0
2θ / °
Lattice parameter / Å³
In air
Pyrochlore
x in Sm2-xTi2O7-δ
Single Sm2-xTi2O7-σ phase was formed in the widest A-site deficiency region of 0≦x<0.5.
CRIEPI

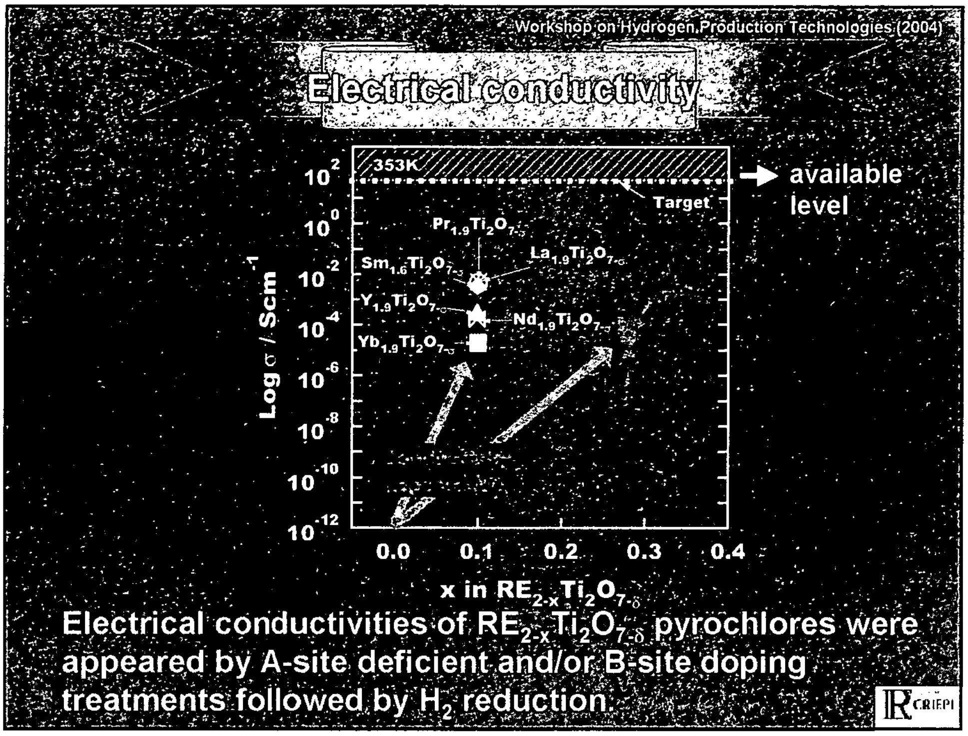

Workshop on Hydrogen Production Technologies (2004)
XRD results of A-site deficient
La2-xTi2O7-σ
Intensity / ×10³ cps
La4Ti9O24
x=0.1
x=0.05
x=0
2θ / °
Lattice parameter / Å³
In H2
In air
Pyrochlore
x in La2-xTi2O7-δ
Single La2-xTi2O7-σ phase was formed in the narrow A-site deficiency region of 0≦x<0.1.
CRIEPI

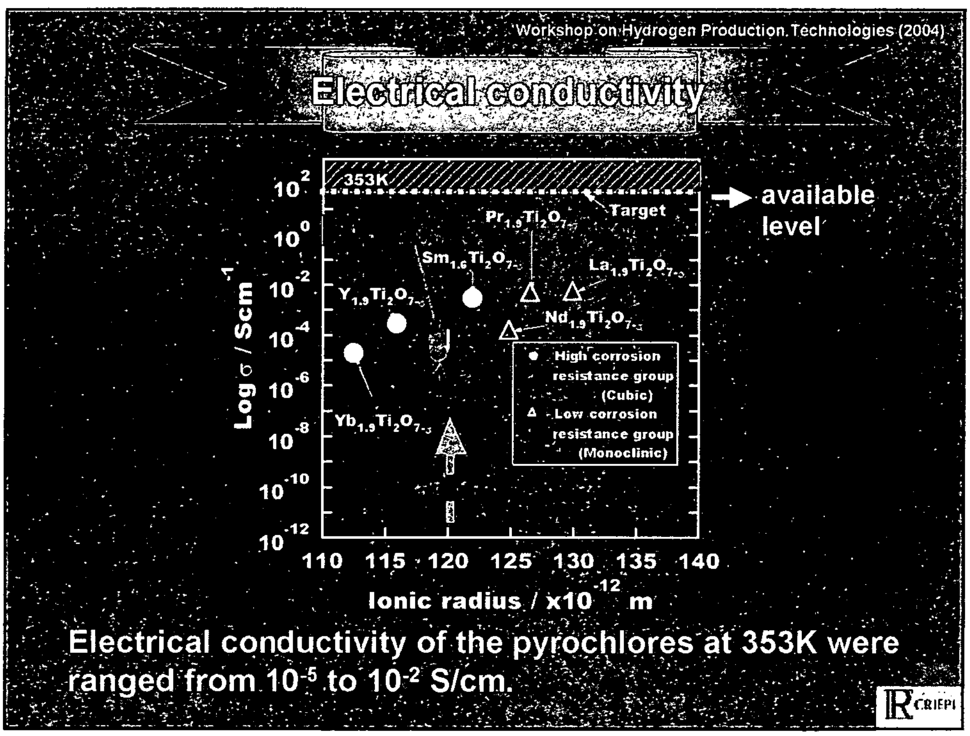

Workshop on Hydrogen Production Technologies (2004)
A-site deficiency of pyrochlores
x in $RE_{2-x}Ti_2O_{7-\delta}$
0.6
0.4
0.2
0
Sm^{3+}
Gd^{3+}
Nd^{3+}
Y^{3+}
Pr^{3+}
Yb^{3+}
La^{3+}
Pyrochlore
110
120
130
Ionic radius / pm
Sm has large A-site deficiency.
CRIEPI


Workshop on Hydrogen Production Technologies (2004)
XRD results of B-site doped $Gd_{1.72}Ti_{2-y}Cr_yO_{7-\sigma}$
Intensity / $\times 10^3$ cps
Cr_2O_3 or $Cr_2Ti_7O_{17}$
y = 0.2
y = 0.15
y = 0.1
y = 0.05
y = 0
10
8
6
4
2
0
10
20
30
40
2θ / °
Lattice parameter / Å
10.18
10.17
10.16
10.15
0
0.05
0.1
0.15
y in $Gd_{1.72}Ti_{2-y}Cr_yO_{7-\delta}$
Single $Gd_{1.72}Ti_{2-y}Cr_yO_{7-\sigma}$ phase was formed in the B-site substituents region of $0 \leqq y < 0.15$.
CRIEPI

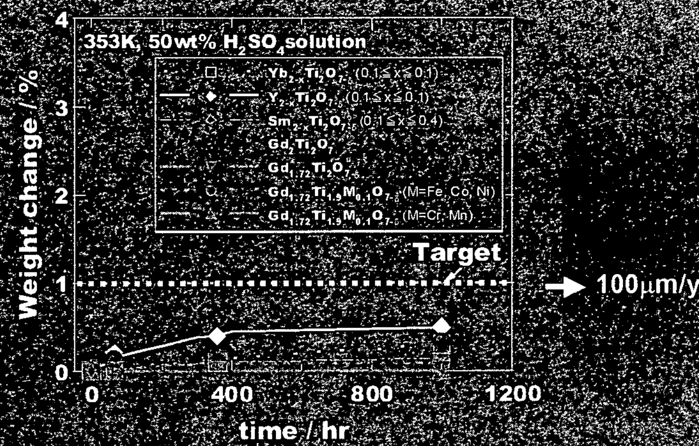

Workshop on Hydrogen Production Technologies (2004)
Lattice parameters of B-site doped
$Gd_{1.72}Ti_2M_yO_{7-\sigma}$ (M=Co,Fe,Mn)
Lattice parameter / Å
10.18
10.17
10.16
0
0.1
0.2
$Gd_{1.72}Ti_{2-y}Co_yO_{7-\delta}$
$Gd_{1.72}Ti_{2-y}Fe_yO_{7-\delta}$
$Gd_{1.72}Ti_{2-y}Mn_yO_{7-\delta}$
y in $Gd_{1.72}Ti_{2-y}M_yO_{7-\delta}$
Lattice parameter of $Gd_{1.72}Ti_2M_yO_{7-\sigma}$ (M = Co, Fe, Mn) were changed by the doping of M depending on M's radius.
CRIEPI


Workshop on Hydrogen Production Technologies (2004)
XRD results of B-site doped
$Gd_{1.72}Ti_{2-y}Ni_yO_{7-\sigma}$
Intensity / $\times 10^3$ cps
10
8
6
4
2
0
y = 0.2
y = 0.15
y = 0.1
y = 0.05
y = 0
NiO
10
20
30
40
2θ / °
Lattice parameter / Å^3
10.18
10.17
10.16
10.15
pyrochlore
0
0.05
0.1
0.15
y in $Gd_{1.72}Ti_{2-y}Ni_yO_{7-\delta}$
Single $Gd_{1.72}Ti_{2-y}Ni_yO_{7-\sigma}$ phase was formed in the B-site substituents region of $0 \leqq y < 0.15$.
CRIEPI


Workshop on Hydrogen Production Technologies (2004)
Electrical conductivity
353K
Target
available level
Log σ / Scm⁻¹
x in RE2-xTi2O7-δ
Pr1.9Ti2O7-δ
Sm1.6Ti2O7-δ
La1.9Ti2O7-δ
Y1.9Ti2O7-δ
Nd1.9Ti2O7-δ
Yb1.9Ti2O7-δ
Electrical conductivities of RE2-xTi2O7-δ pyrochlores were appeared by A-site deficient and/or B-site doping treatments followed by H2 reduction.
CRIEPI


Workshop on Hydrogen Production Technologies (2004)
Electrical conductivity
353K
Target
available level
Log σ / Scm⁻¹
Ionic radius / x10⁻¹² m
Pr1.9Ti2O7-δ
Sm1.6Ti2O7-δ
La1.9Ti2O7-δ
Y1.9Ti2O7-δ
Nd1.9Ti2O7-δ
Yb1.9Ti2O7-δ
High corrosion resistance group (Cubic)
Low corrosion resistance group (Monoclinic)
Electrical conductivity of the pyrochlores at 353K were ranged from 10⁻⁵ to 10⁻² S/cm.
CRIEPI

Corrosion resistance



Corrosion resistances of $RE_{2-x}Ti_2O_{7-\delta}$ (RE=Yb, Y, Gd, Sm) and $Gd_{2-x}Ti_{1.9}M_{0.1}O_{7-\delta}$ (M=Fe, Co, Ni, Cr, Mn) were high, and the corrosion loss were below 100μm/y.

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Summary

(1) Crystallographic study showed that A-site deficient $RE_{2-x}Ti_2O_{7-\delta}$ (RE=Yb, Y, Gd, Sm, Pr, Nb) and B-site doped $Gd_{2-x}Ti_{2-y}M_yO_{7-\delta}$ (M=Cr, Mn, Fe, Co, Ni) pyrochlores were stable at room temperature.

(2) Electrochemical conductivity measurement showed that the conductivities of $RE_{2-x}Ti_2O_{7-\sigma}$ (RE=Yb, Y, Gd, Sm, Pr, Nb) and $Gd_{2-x}Ti_{2-y}M_yO_{7-\delta}$ pyrochlores were 10^{-5} to 10^{-2} S/cm.

(3) Corrosion test results showed that $Yb_{2-x}Ti_2O_{7-\sigma}$, $Y_{2-x}Ti_2O_{7-\sigma}$, $Gd_{2-x}Ti_2O_{7-\sigma}$, $Sm_{2-x}Ti_2O_{7-\sigma}$ and $Gd_{1.72}Ti_{1.9}M_{0.1}O_{7-\delta}$ pyrochlores had high corrosion resistance in the H_2SO_4 solution.

Based on the above results, the possibility of titanium pyrochlores to the anode were shown by A-site deficiency and/or B-site doping.

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Future Work

- Improvement of electrical conductivity of the pyrochlores and/or perovskits to the available level.
  (Try to some new techniques, such as compound of Pt powder or carbon and pyrochlores)

- Measurement of hydrogen production and electrode over-potential of the pyrochlores and/or perovskits under the electrolysis condition.

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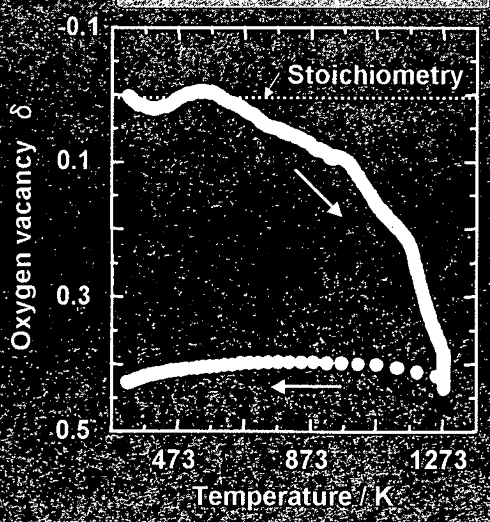
Oxygen Vacancy



Oxygen vacancies of $Sm_{2-x}Ti_2O_{7-\delta}$ pyrochlores were 0.4.

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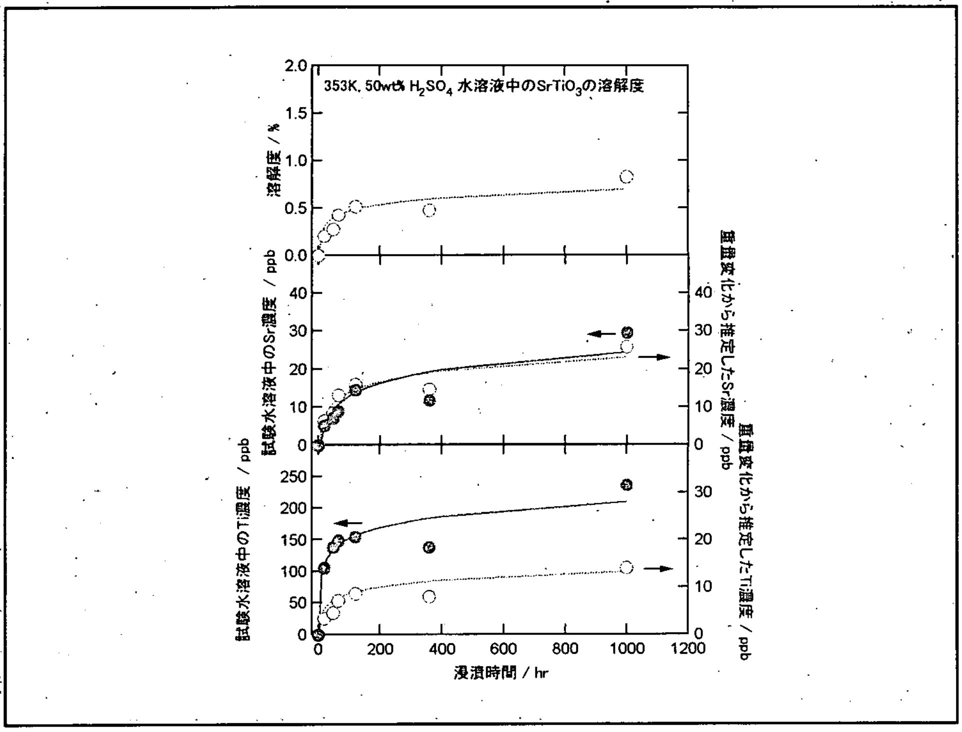
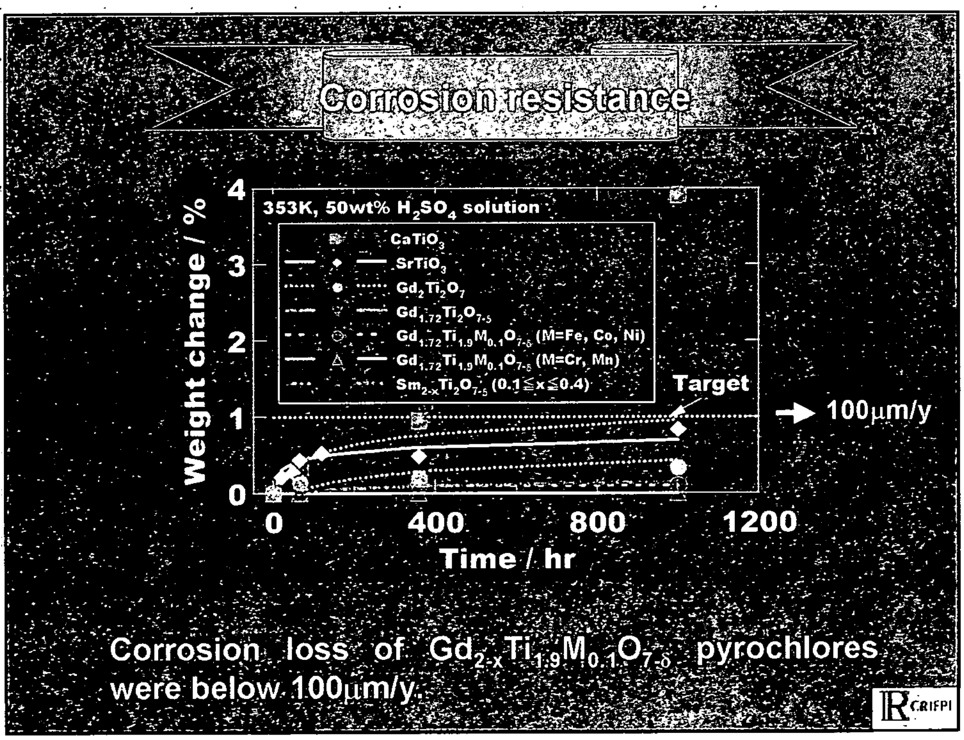

353K, 50wt% H$_2$SO$_4$ 水溶液中のSrTiO$_3$の溶解度
溶解度 / %
試験水溶液中のSr濃度 / ppb
重量変化から推定したSr濃度 / ppb
試験水溶液中のTi濃度 / ppb
重量変化から推定したTi濃度 / ppb
浸漬時間 / hr
2.0
1.5
1.0
0.5
0.0
40
30
20
10
0
250
200
150
100
50
0
200
400
600
800
1000
1200


Corrosion resistance
353K, 50wt% H$_2$SO$_4$ solution
CaTiO$_3$
SrTiO$_3$
Gd$_2$Ti$_2$O$_7$
Gd$_{1.72}$Ti$_2$O$_{7-\delta}$
Gd$_{1.72}$Ti$_{1.9}$M$_{0.1}$O$_{7-\delta}$ (M=Fe, Co, Ni)
Gd$_{1.72}$Ti$_{1.9}$M$_{0.1}$O$_{7-\delta}$ (M=Cr, Mn)
Sm$_{2-x}$Ti$_2$O$_{7-\delta}$ (0.1≦x≦0.4)
Target
100μm/y
Weight change / %
Time / hr
0
1
2
3
4
400
800
1200
Corrosion loss of Gd$_{2-x}$Ti$_{1.9}$M$_{0.1}$O$_{7-\delta}$ pyrochlores were below 100μm/y.
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Element with d-orbital electron

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Ac	Th	Pa	U						

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Pyrochlore Possibility of B-site element

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Ac	Th	Pa	U						

Pyrochlore
Ti^{4+}

(1) Sc, Y, La, and Ac are not B-site element, because of they are rare earth metal
(2) Th, Pa, and U are radio-nuclide. Tc is artificial radio-nuclide.
(3) Cd and Hg are pollution element.
(4) Cu is not B-site element, because Cu has K_2NiF_4 structure.
(5) Zn and Ag are not B-site element, because Zn and Ag are di-valence and mono valence.
(6) Hard to reduction → Non-conductive pyrochlore
(7) Au oxide is not stable (Only metalic Au is stable)
(8) Ru (0.001ppm), Rh (0.0002ppm), Pd (0.0006ppm), Os (0.0004ppm), Ir (0.000003ppm) Pt (0.003ppm) are very expensive and rare earth elements.
Ru and Ir has high corrosion resistance iunder acidic condition.
(9) Re (0.004ppm) is rare earth elements.

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Workshop on Hydrogen Production Technologies (2004)

Electrical Conductivity and Corrosion Resistance of Titanium Pyrochlores used for Sulfur-based Hybrid Cycle

July 6, 2004

at Oarai Research Establishment JAERI

Central Research Institute of Electric Power Industry (CRIEPI)

Hirotaka KAWAMURA, Masashi MORI, and Masaki UOTANI

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Workshop on Hydrogen Production Technologies (2004)

Contents

- Background
  - Sulfur-based Hybrid Cycle for Hydrogen Production
- Objectives
- Experiments
- Results and Discussions
  - Crystallographic study
  - Electrical conductivity study
  - Corrosion resistance study
- Summary

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Background

◆ According to a desiring of hydrogen energy cycle in the near future, such as coming into wide use of fuel cell and fuel cell vehicle (FCV), the establishments of zero emission and large-scale hydrogen production process have been desired.

◆ Some electrolysis process using Pt electrode have been proposed. On the other hand, Pt is a noble and rare metal.

◆ In order to establish some high electrolysis efficiency and low-cost electrolysis system, Pt-free electrode should be developed.

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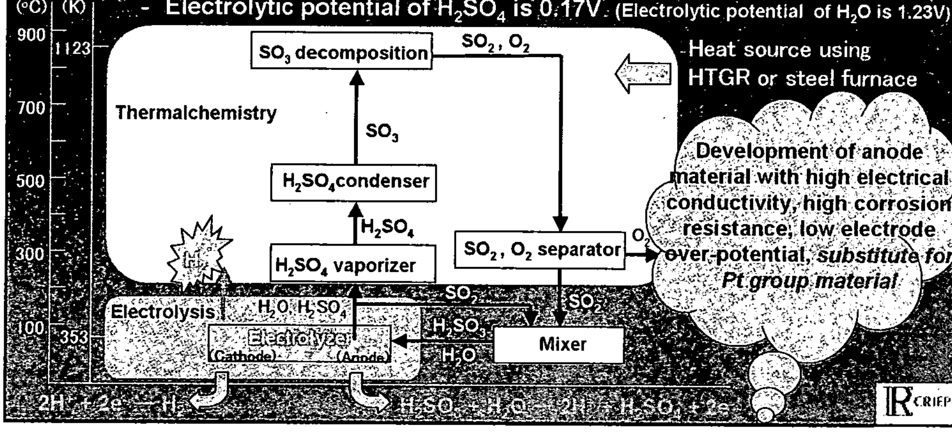
Sulfur-based Hybrid Cycle for Hydrogen Production

- One of nuclear-hydrogen production process (combined with thermochemistry and electrolysis)
- Emission free process
  - No CO_2 gas emission
  - Only water consumption (reuse of H_2SO_4)
- Availability
  - Easy to improve electrolysis efficient because of simple process.
  - Electrolytic potential of H_2SO_4 is 0.17V. (Electrolytic potential of H_2O is 1.23V)



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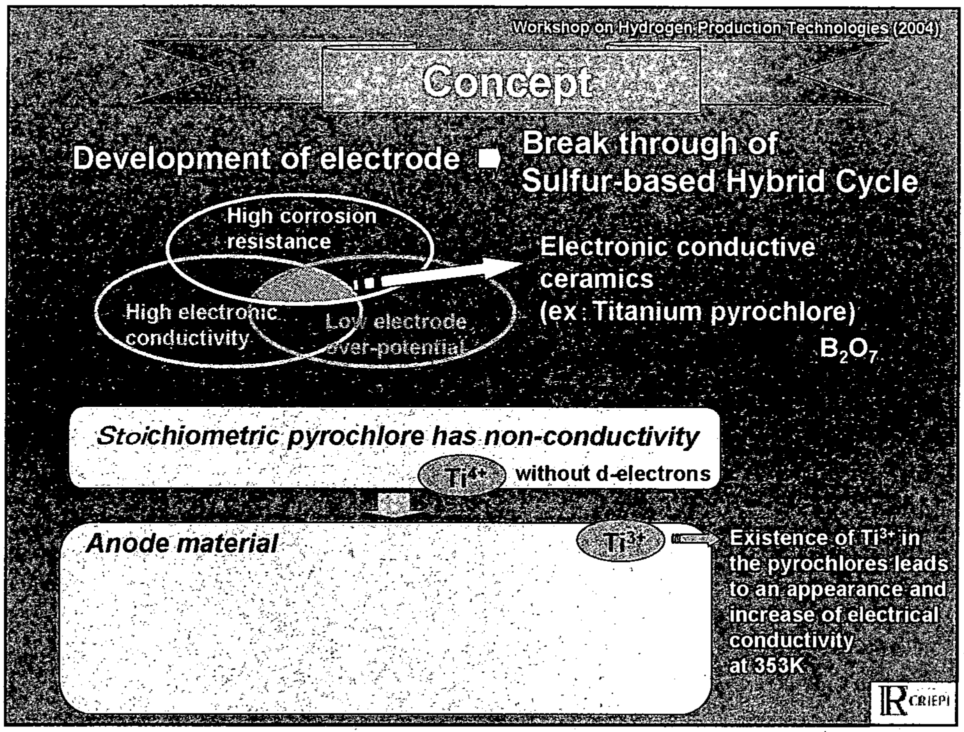
Workshop on Hydrogen Production Technologies (2004)
Concept
Development of electrode
Break through of Sulfur-based Hybrid Cycle
High corrosion resistance
High electronic conductivity
Low electrode over-potential
Electronic conductive ceramics (ex: Titanium pyrochlore)
B2O7
Stoichiometric pyrochlore has non-conductivity
Ti4+ without d-electrons
Anode material
Ti3+
Existence of Ti3+ in the pyrochlores leads to an appearance and increase of electrical conductivity at 353K
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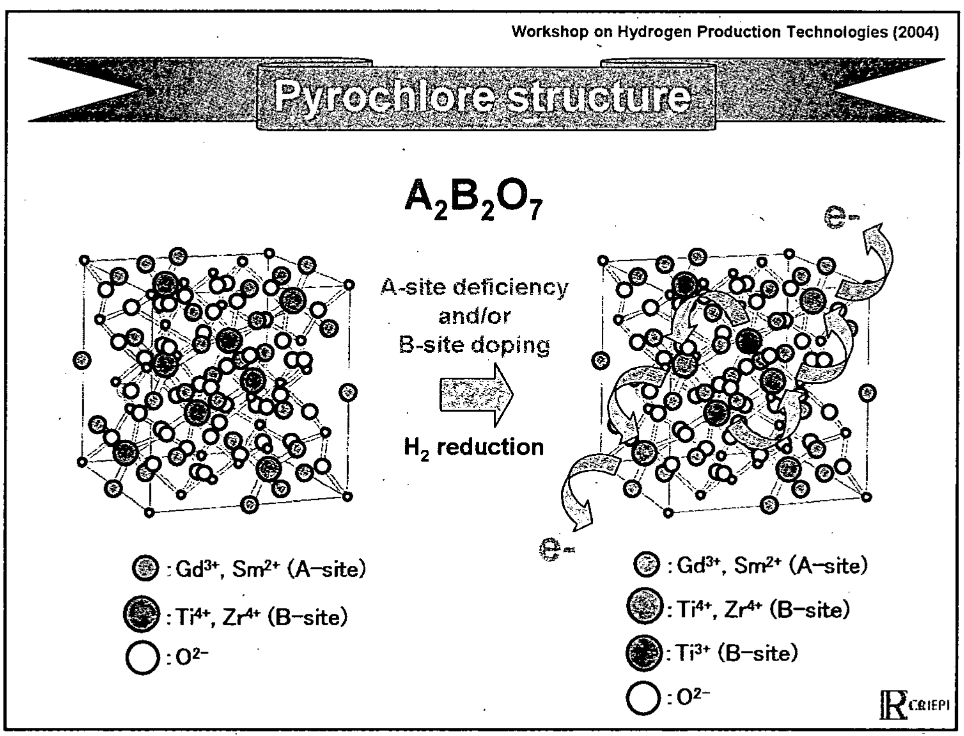
Workshop on Hydrogen Production Technologies (2004)
Pyrochlore structure
A2B2O7
A-site deficiency and/or B-site doping
H2 reduction
e-
e-
: Gd3+, Sm2+ (A-site)
: Ti4+, Zr4+ (B-site)
: O2-
: Gd3+, Sm2+ (A-site)
: Ti4+, Zr4+ (B-site)
: Ti3+ (B-site)
: O2-
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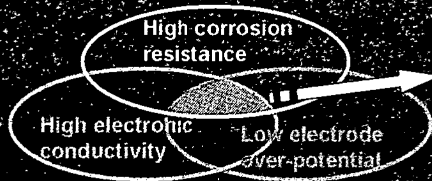
Concept

Development of electrode ■ Break through of Sulfur-based Hybrid Cycle



Electronic conductive ceramics
(ex: Titanium pyrochlore)
B_2O_7

Stoichiometric pyrochlore has non-conductivity

Ti^{4+} without d-electrons

Anode material

Ti^{3+}

Electrical conductivity appearance ⇨ A-site deficiency + B-site doping + H_2 reduction

$A_{2-x}B_2O_{7-\sigma}$ $A_{2-x}B_{2-y}M_yO_{7-\sigma}$

High corrosion resistance ⇨ Selection of slightly soluble elements for A-site and B-site

Existence of Ti^{3+} in the pyrochlores leads to an appearance and increase of electrical conductivity at 353K

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Objective

- To propose some new techniques of electrical conductivity appearance for titanium pyrochlores.
- To investigate the electrical conductivity and corrosion resistance of a series of A-site deficient $RE_{2-x}Ti_2O_{7-\delta}$ (RE= Yb, Y, Gd, Sm, Nd, Pr, La) and B-site doped $Gd_{2-x}Ti_{2-y}M_yO_{7-\delta}$ (M=Cr, Mn, Fe, Co, Ni) pyrochlores under the electrolysis condition, i.e., 50 wt % H_2SO_4 solution at 353K.

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Experiment

Material

$RE_{2-x}Ti_2O_{7-\sigma}$ (RE= Yb, Y, Gd, Sm, Nd, Pr La)
$Gd_{1.72}Ti_{1.9}M_{0.1}O_{7-\sigma}$ (M=Cr, Mn, Fe, Co, Ni)

Preparation

* Synthesizing by a solid-state reaction
  (pre-heating at 1473K, for 6h, sintering at 1773K, for 12h)
* A-site deficiency + B-site substituent
* Hydrogen reduction (at 1273K for 1h)

Evaluation iteam

* Crystallographic study : XRD study (18kW)
* Conductivity measurement : 353K, D.C. current four-terminal method
* Corrosion test : 353K, 50wt%H_2SO_4 solution

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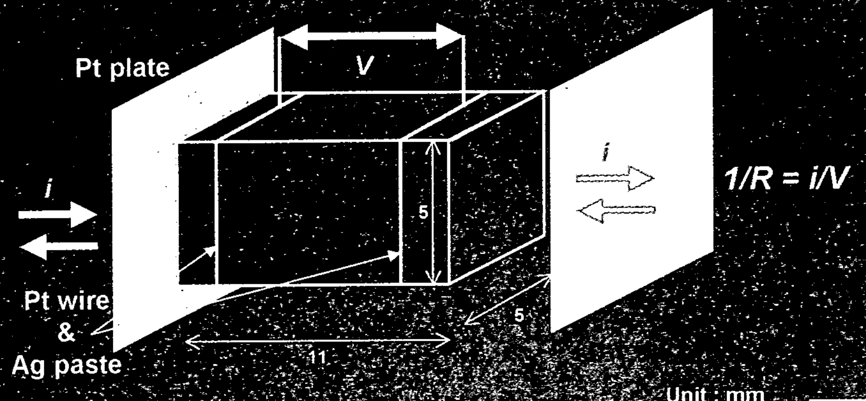
Electrical conductivity measurement

D.C. current four-terminal method

Shape and dimension of specimen



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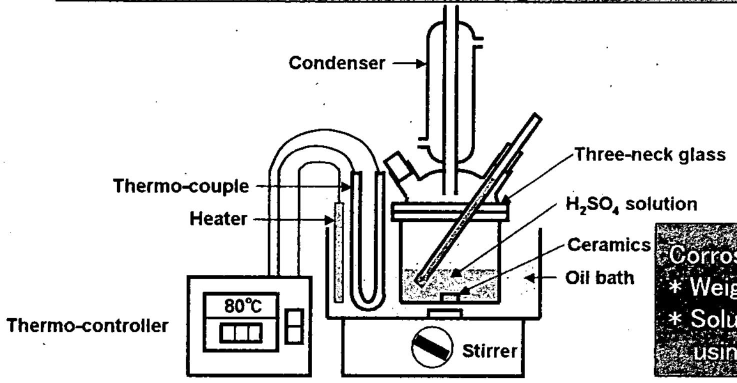
Corrosion resistance measurement

Ceramics material :
$RE_{1.72}Ti_{1.9}M_{0.1}O_{7-\sigma}$ (M=Cr, Mn, Fe, Co, Ni)
ref. $RE_{2-x}Ti_2O_{7-\sigma}$ (RE= Yb, Y, Gd, Sm, Nd, Pr La)
Test condition : 353K, 50wt% H_2SO_4 sol. for 65 to 1000hrs



Corrosion resistance :
* Weight change
* Solution analysis using ICP-MS

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Workshop on Hydrogen Production Technologies (2004)

Contents

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◆ Objectives

◆ Experiments

◆ Results and Discussions
- Crystallographic study
- Electrical conductivity study
- Corrosion resistance study

◆ Summary

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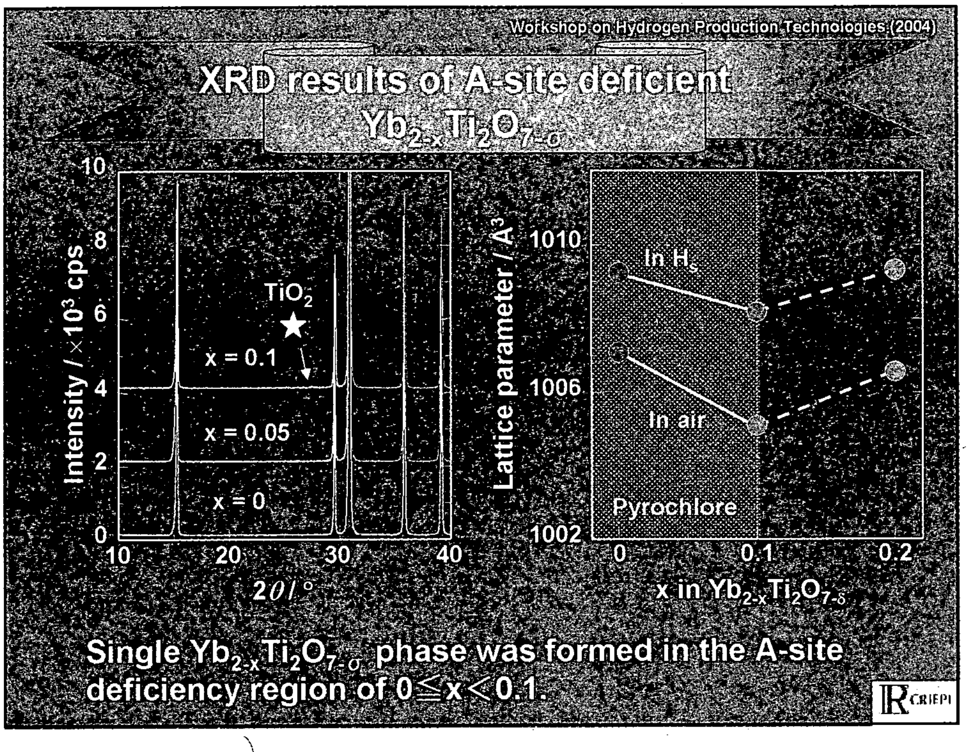
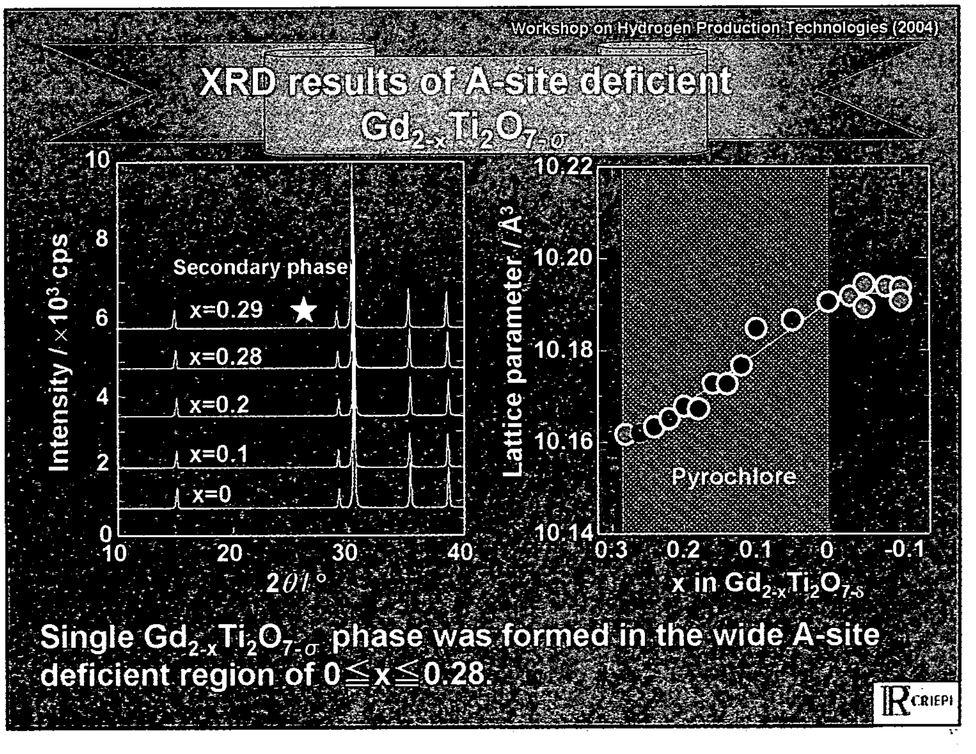
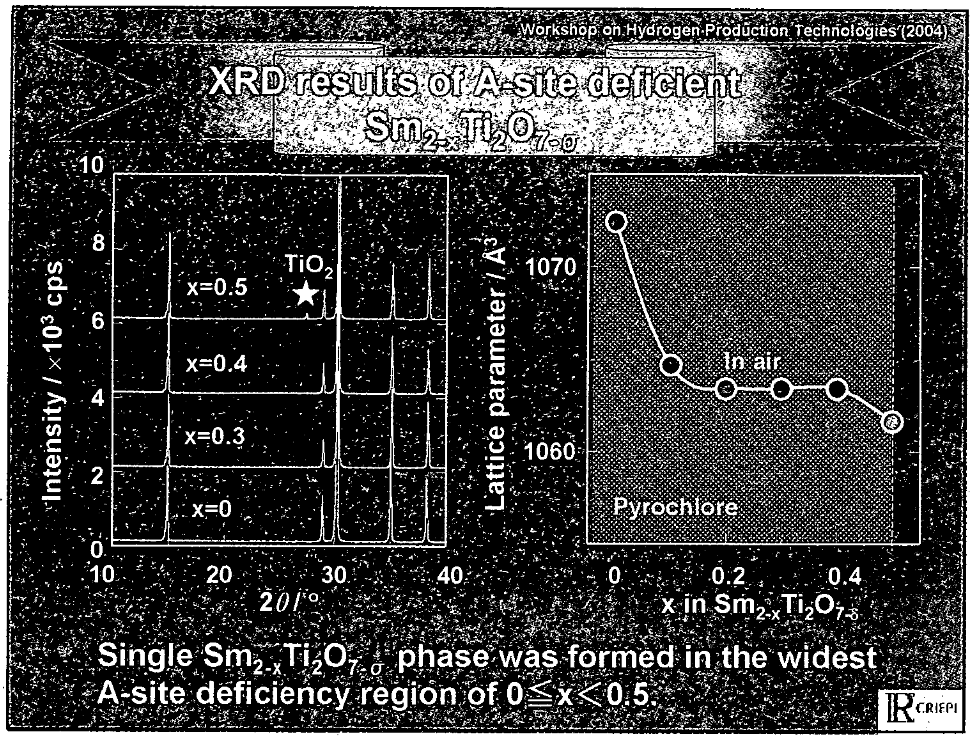
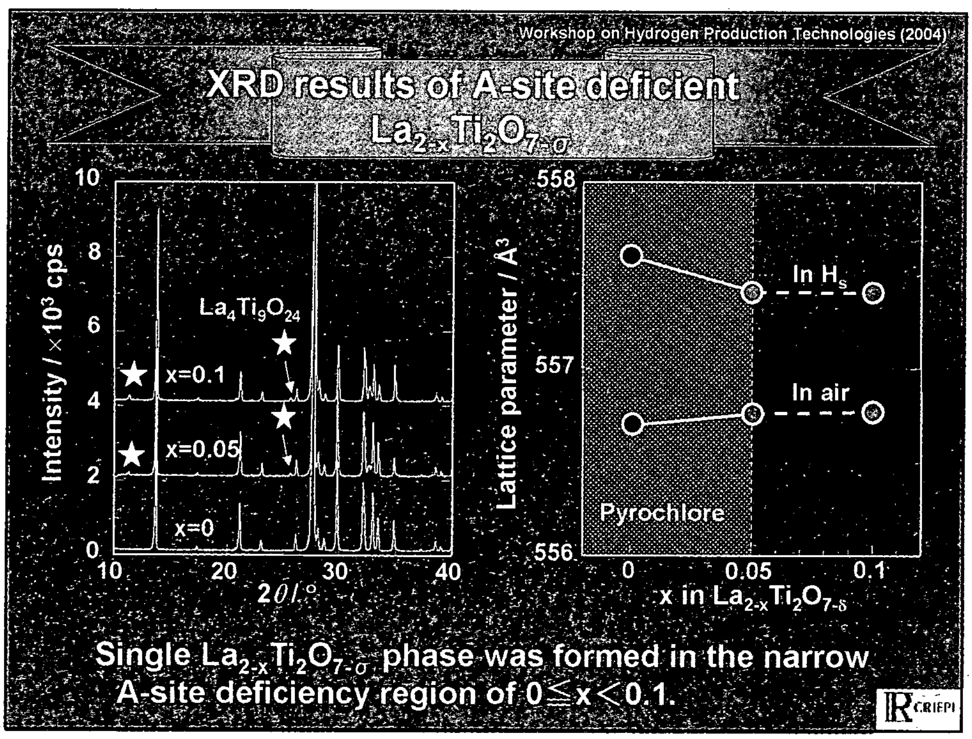
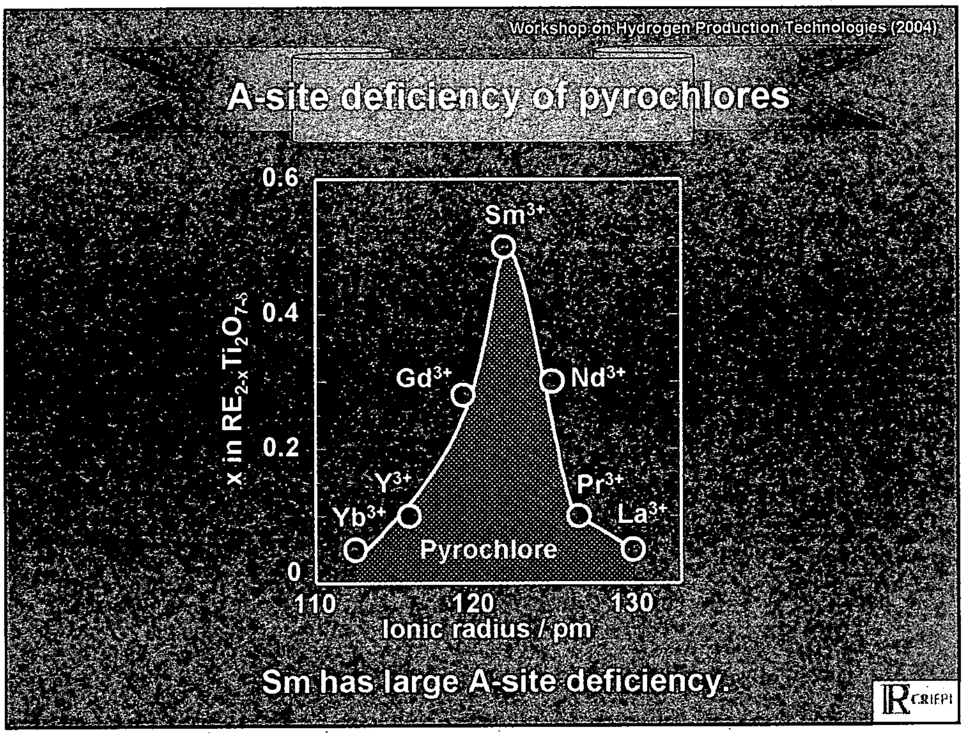
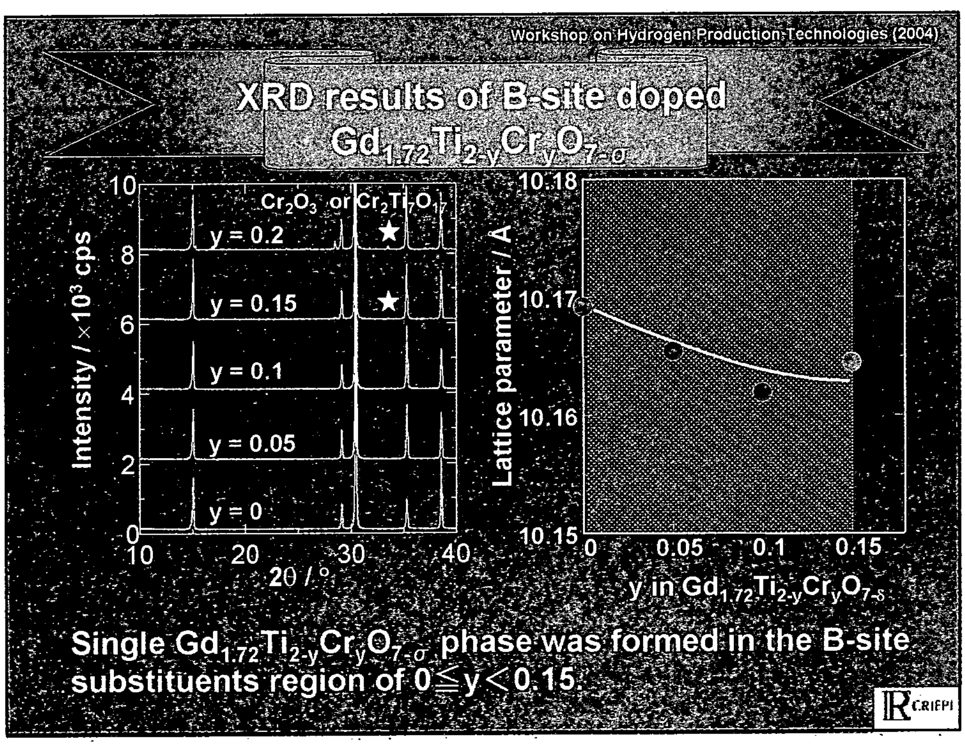

Workshop on Hydrogen Production Technologies (2004)
XRD results of A-site deficient $Yb_{2-x}Ti_2O_{7-\sigma}$
Intensity / ×10³ cps
TiO₂
x = 0.1
x = 0.05
x = 0
2θ / °
Lattice parameter / Å³
In H₂
In air
Pyrochlore
x in $Yb_{2-x}Ti_2O_{7-\delta}$
Single $Yb_{2-x}Ti_2O_{7-\sigma}$ phase was formed in the A-site deficiency region of 0≦x<0.1.
CRIEPI

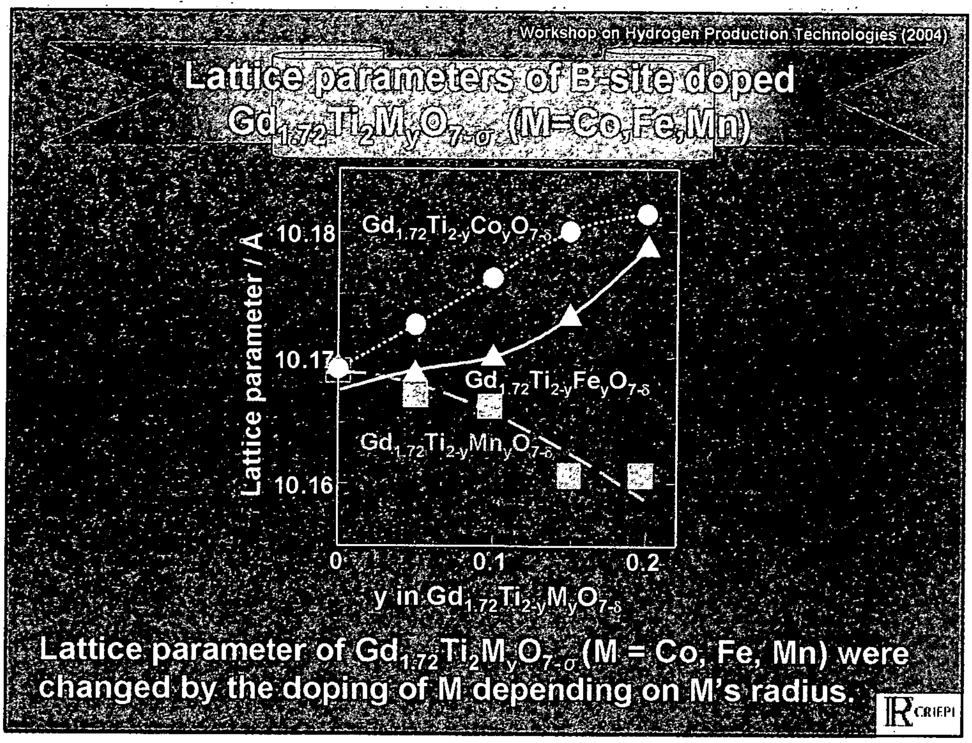

Workshop on Hydrogen Production Technologies (2004)
XRD results of A-site deficient $Gd_{2-x}Ti_2O_{7-\sigma}$
Intensity / ×10³ cps
Secondary phase
x=0.29
x=0.28
x=0.2
x=0.1
x=0
2θ / °
Lattice parameter / Å³
Pyrochlore
x in $Gd_{2-x}Ti_2O_{7-\delta}$
Single $Gd_{2-x}Ti_2O_{7-\sigma}$ phase was formed in the wide A-site deficient region of 0≦x≦0.28.
CRIEPI

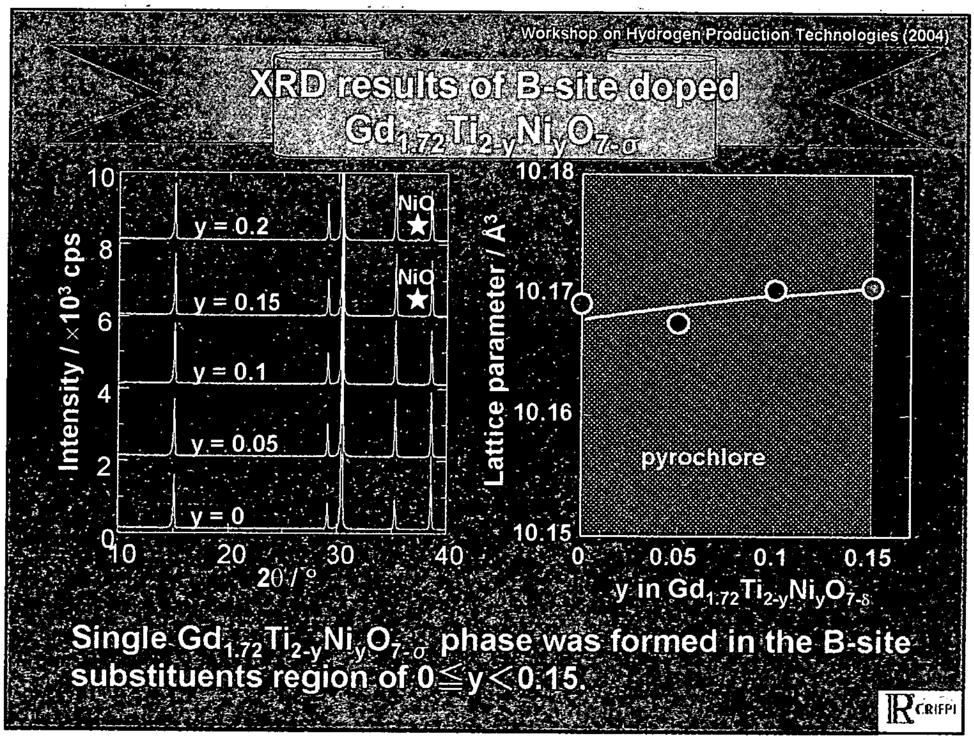

Workshop on Hydrogen Production Technologies (2004)
XRD results of A-site deficient $Sm_{2-x}Ti_2O_{7-\sigma}$
Intensity / ×10³ cps
10
8
6
4
2
0
10
20
30
40
2θ / °
TiO_2
x=0.5
x=0.4
x=0.3
x=0
Lattice parameter / Å³
1070
1060
In air
Pyrochlore
0
0.2
0.4
x in $Sm_{2-x}Ti_2O_{7-\delta}$
Single $Sm_{2-x}Ti_2O_{7-\sigma}$ phase was formed in the widest A-site deficiency region of 0≦x＜0.5.
CRIEPI

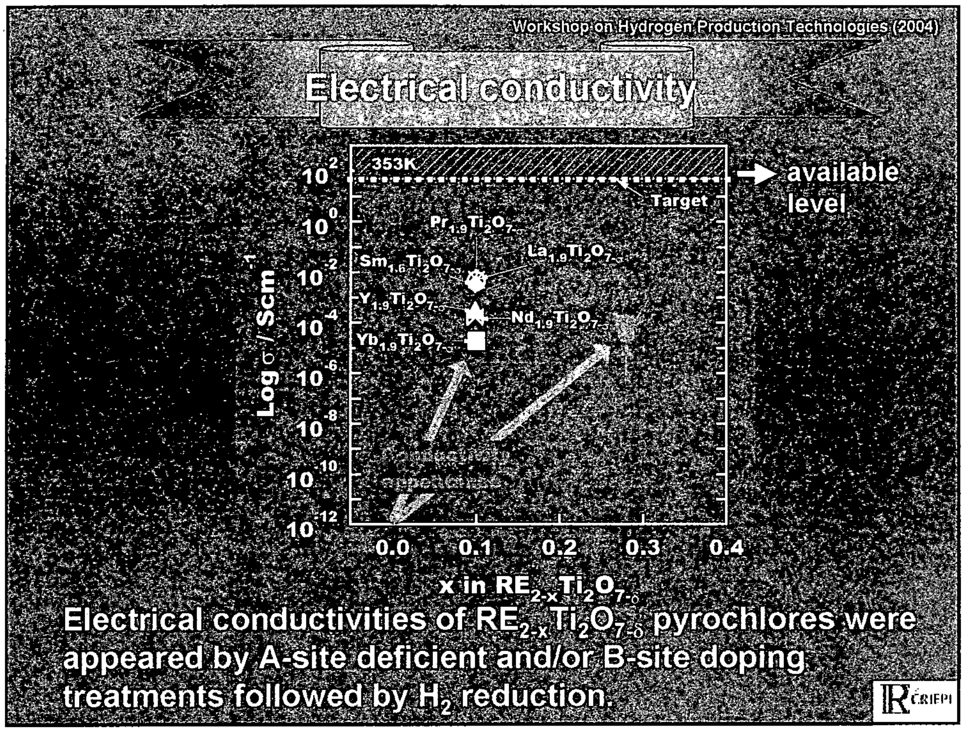

Workshop on Hydrogen Production Technologies (2004)
XRD results of A-site deficient $La_{2-x}Ti_2O_{7-\sigma}$
Intensity / ×10³ cps
10
8
6
4
2
0
10
20
30
40
2θ / °
$La_4Ti_9O_{24}$
x=0.1
x=0.05
x=0
Lattice parameter / Å³
558
557
556
In H_s
In air
Pyrochlore
0
0.05
0.1
x in $La_{2-x}Ti_2O_{7-\delta}$
Single $La_{2-x}Ti_2O_{7-\sigma}$ phase was formed in the narrow A-site deficiency region of 0≦x＜0.1.
CRIEPI

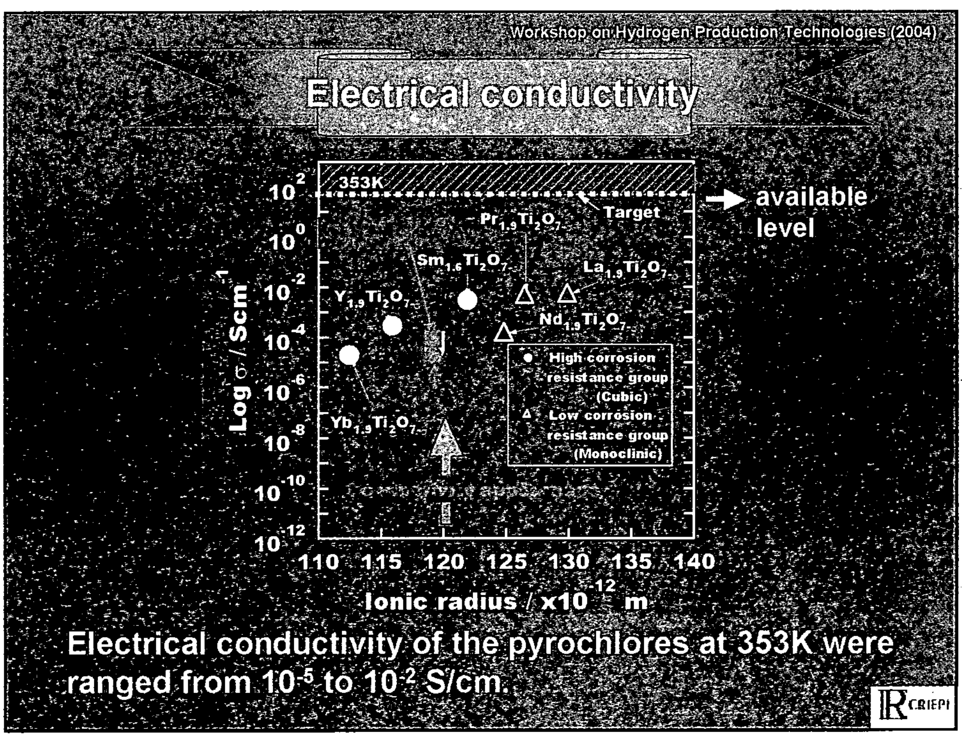

Workshop on Hydrogen Production Technologies (2004)
A-site deficiency of pyrochlores
x in RE2-xTi2O7-δ
Ionic radius / pm
Sm3+
Gd3+
Nd3+
Y3+
Yb3+
Pr3+
La3+
Pyrochlore
0.6
0.4
0.2
0
110
120
130
Sm has large A-site deficiency.
CRIEPI


Workshop on Hydrogen Production Technologies (2004)
XRD results of B-site doped Gd1.72Ti2-yCryO7-σ
Intensity / ×10³ cps
2θ / °
Cr2O3 or Cr2Ti7O17
y = 0.2
y = 0.15
y = 0.1
y = 0.05
y = 0
Lattice parameter / Å
y in Gd1.72Ti2-yCryO7-δ
10.18
10.17
10.16
10.15
0
0.05
0.1
0.15
Single Gd1.72Ti2-yCryO7-σ phase was formed in the B-site substituents region of 0≦y<0.15.
CRIEPI


Workshop on Hydrogen Production Technologies (2004)
Lattice parameters of B-site doped
Gd1.72Ti2MyO7-σ (M=Co,Fe,Mn)
Lattice parameter / Å
10.18
10.17
10.16
Gd1.72Ti2-yCoyO7-δ
Gd1.72Ti2-yFeyO7-δ
Gd1.72Ti2-yMnyO7-δ
0
0.1
0.2
y in Gd1.72Ti2-yMyO7-δ
Lattice parameter of Gd1.72Ti2MyO7-σ (M = Co, Fe, Mn) were changed by the doping of M depending on M's radius.
CRIEPI

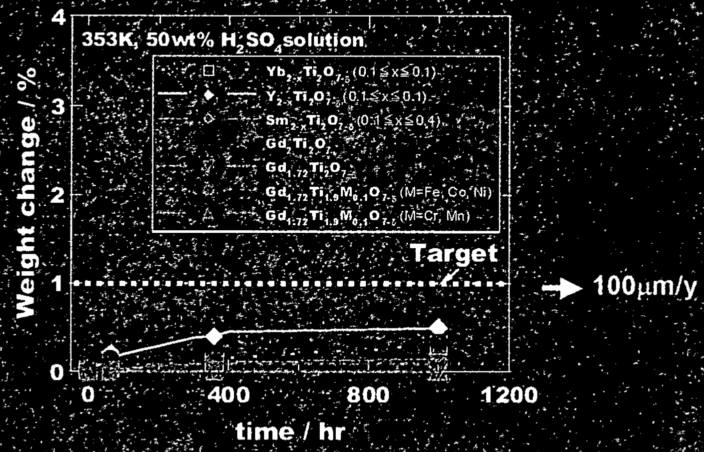

Workshop on Hydrogen Production Technologies (2004)
XRD results of B-site doped
Gd1.72Ti2-yNiyO7-σ
Intensity / ×10³ cps
10
8
6
4
2
0
y = 0.2
y = 0.15
y = 0.1
y = 0.05
y = 0
NiO
10
20
30
40
2θ / °
Lattice parameter / Å³
10.18
10.17
10.16
10.15
pyrochlore
0
0.05
0.1
0.15
y in Gd1.72Ti2-yNiyO7-δ
Single Gd1.72Ti2-yNiyO7-σ phase was formed in the B-site substituents region of 0≦y<0.15.
CRIEPI


Workshop on Hydrogen Production Technologies (2004)
Electrical conductivity
353K
Target
available level
Pr1.9Ti2O7
Sm1.6Ti2O7
La1.9Ti2O7
Y1.9Ti2O7
Nd1.9Ti2O7
Yb1.9Ti2O7
Log σ / Scm-1
10^2
10^0
10^-2
10^-4
10^-6
10^-8
10^-10
10^-12
0.0
0.1
0.2
0.3
0.4
x in RE2-xTi2O7-δ
Electrical conductivities of RE2-xTi2O7-δ pyrochlores were appeared by A-site deficient and/or B-site doping treatments followed by H2 reduction.
CRIEPI


Workshop on Hydrogen Production Technologies (2004)
Electrical conductivity
353K
Target
available level
Pr1.9Ti2O7
Sm1.6Ti2O7
La1.9Ti2O7
Y1.9Ti2O7
Nd1.9Ti2O7
Yb1.9Ti2O7
High corrosion resistance group (Cubic)
Low corrosion resistance group (Monoclinic)
Log σ / Scm-1
10^2
10^0
10^-2
10^-4
10^-6
10^-8
10^-10
10^-12
110
115
120
125
130
135
140
Ionic radius / x10^-12 m
Electrical conductivity of the pyrochlores at 353K were ranged from 10^-5 to 10^-2 S/cm.
CRIEPI

Workshop on Hydrogen Production Technologies (2004)

Corrosion resistance



Corrosion resistances of $RE_{2-x}Ti_2O_{7-\delta}$ (RE=Yb, Y, Gd, Sm) and $Gd_{2-x}Ti_{1.9}M_{0.1}O_{7-\delta}$ (M=Fe, Co, Ni, Cr, Mn) were high, and the corrosion loss were below 100μm/y.

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Workshop on Hydrogen Production Technologies (2004)

Summary

(1) Crystallographic study showed that A-site deficient $RE_{2-x}Ti_2O_{7-\delta}$ (RE=Yb, Y, Gd, Sm, Pr, Nb) and B-site doped $Gd_{2-x}Ti_{2-y}M_yO_{7-\delta}$ (M=Cr, Mn, Fe, Co, Ni) pyrochlores were stable at room temperature.

(2) Electrochemical conductivity measurement showed that the conductivities of $RE_{2-x}Ti_2O_{7-\sigma}$ (RE=Yb, Y, Gd, Sm, Pr, Nb) and $Gd_{2-x}Ti_{2-y}M_yO_{7-\delta}$ pyrochlores were 10^{-5} to 10^{-2} S/cm.

(3) Corrosion test results showed that $Yb_{2-x}Ti_2O_{7-\sigma}$, $Y_{2-x}Ti_2O_{7-\sigma}$, $Gd_{2-x}Ti_2O_{7-\sigma}$, $Sm_{2-x}Ti_2O_{7-\sigma}$ and $Gd_{1.72}Ti_{1.9}M_{0.1}O_{7-\delta}$ pyrochlores had high corrosion resistance in the H_2SO_4 solution.

Based on the above results, the possibility of titanium pyrochlores to the anode were shown by A-site deficiency and/or B-site doping.

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Future Work

- Improvement of electrical conductivity of the pyrochlores and/or perovskits to the available level.
  (Try to some new techniques, such as compound of Pt powder or carbon and pyrochlores)

- Measurement of hydrogen production and electrode over-potential of the pyrochlores and/or perovskits under the electrolysis condition.

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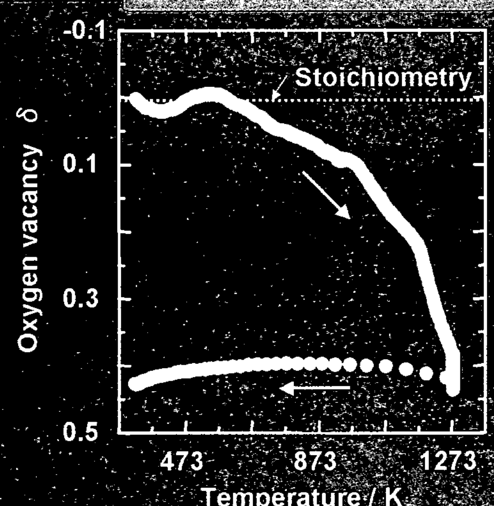
Oxygen Vacancy



Oxygen vacancies of $Sm_{2-x}Ti_2O_{7-\delta}$ pyrochlores were 0.4.

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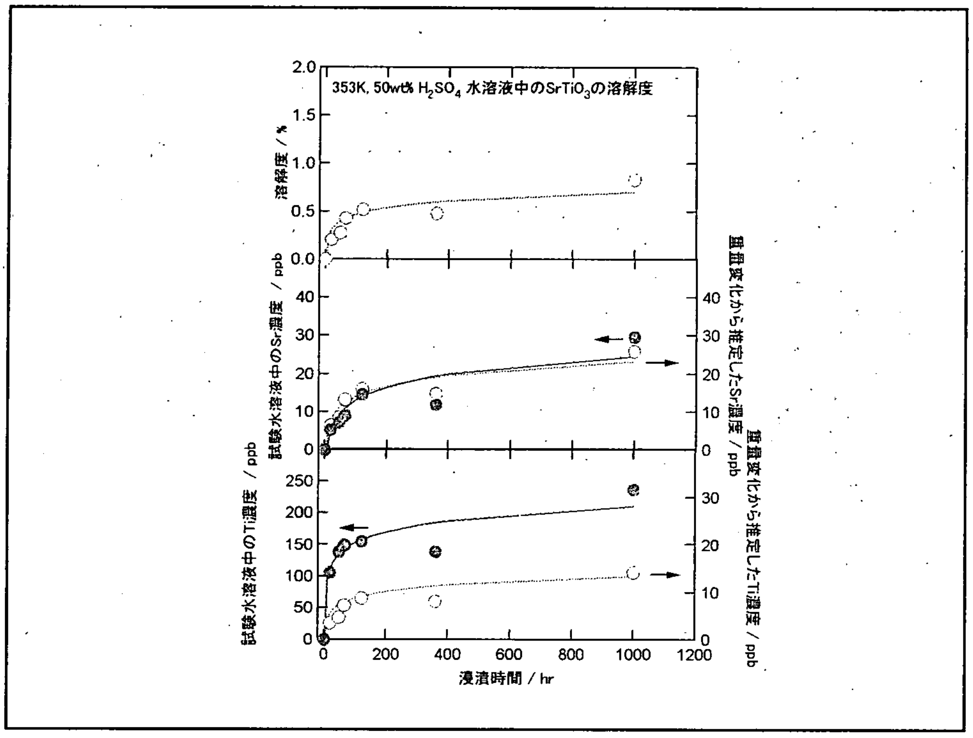
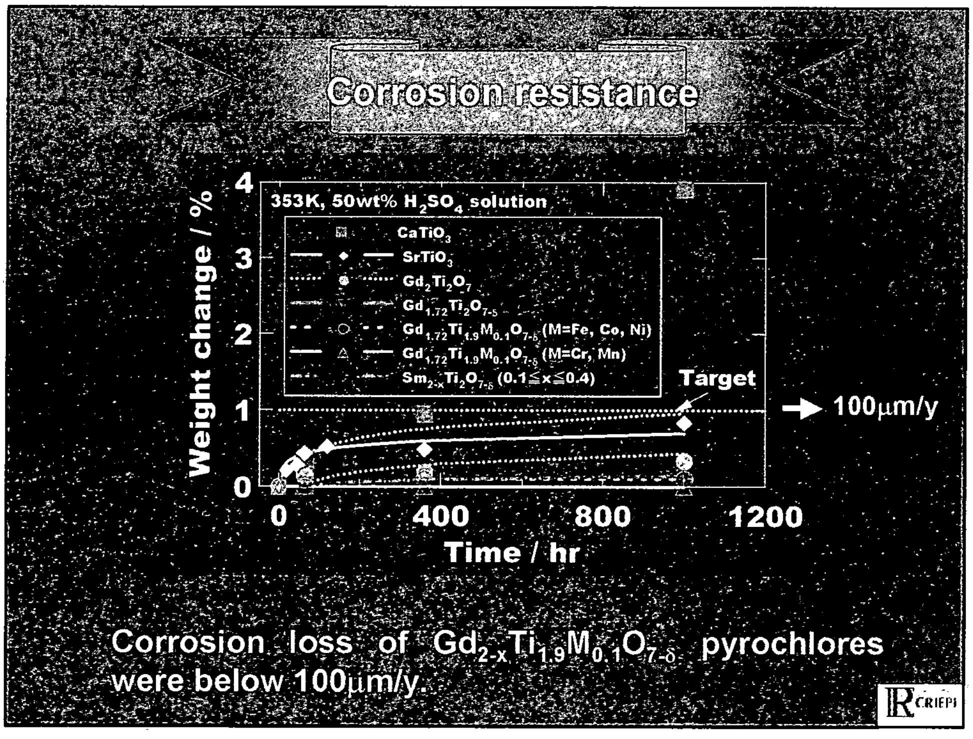
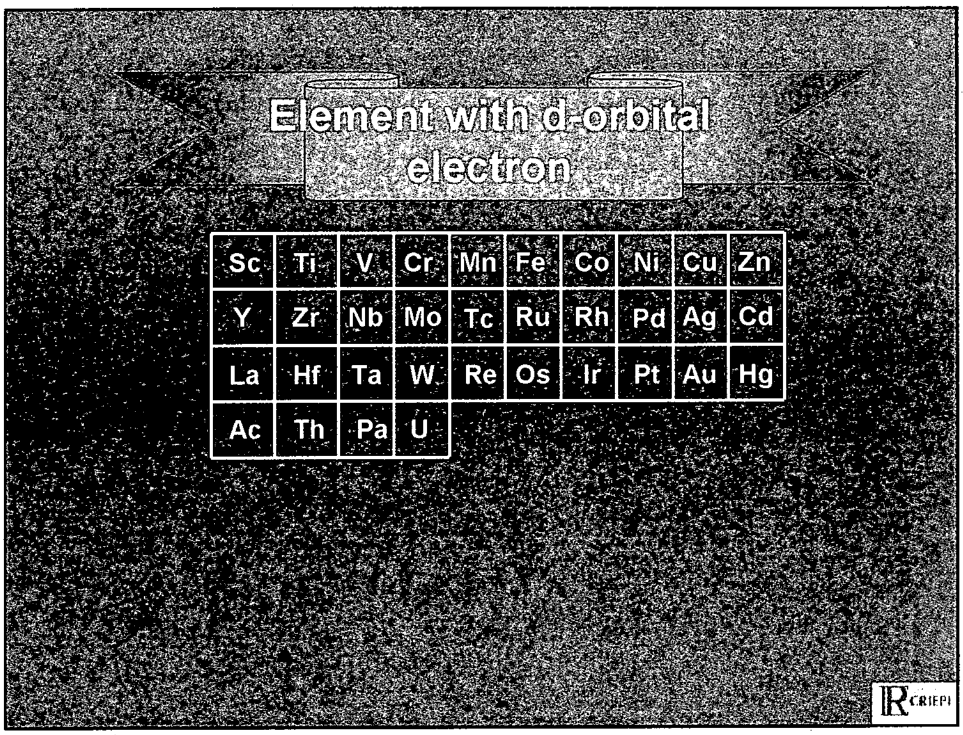
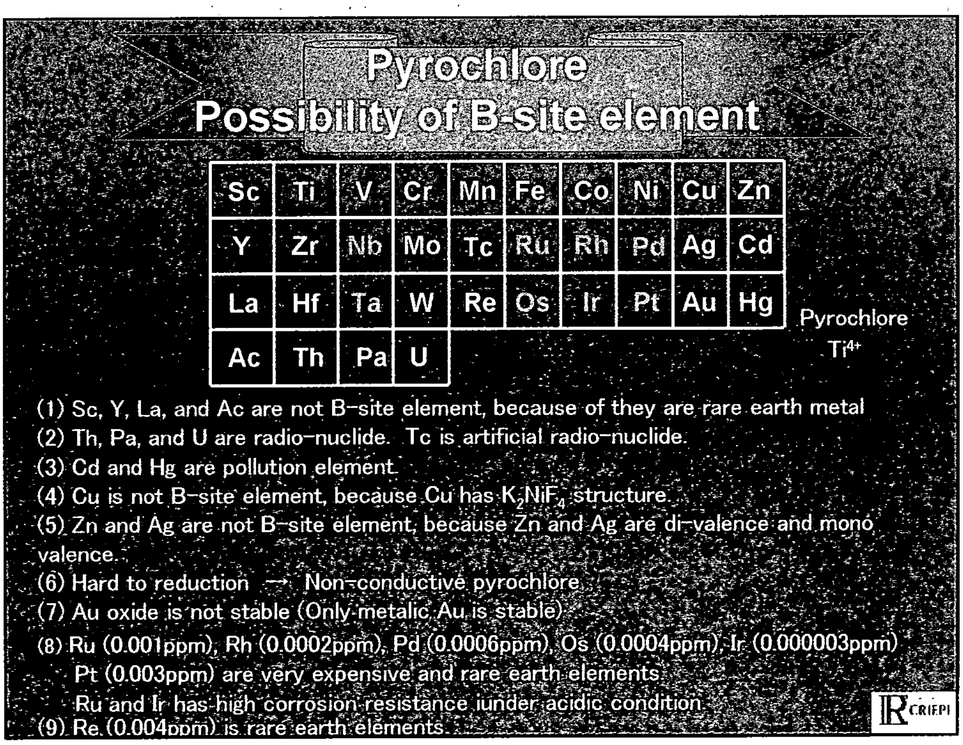

353K, 50wt% H2SO4 水溶液中のSrTiO3の溶解度
溶解度 / %
試験水溶液中のSr濃度 / ppb
重量変化から推定したSr濃度 / ppb
試験水溶液中のTi濃度 / ppb
重量変化から推定したTi濃度 / ppb
浸漬時間 / hr


Corrosion resistance
353K, 50wt% H2SO4 solution
CaTiO3
SrTiO3
Gd2Ti2O7
Gd1.72Ti2O7-δ
Gd1.72Ti1.9M0.1O7-δ (M=Fe, Co, Ni)
Gd1.72Ti1.9M0.1O7-δ (M=Cr, Mn)
Sm2-xTi2O7-δ (0.1≦x≦0.4)
Weight change / %
Time / hr
Target
100μm/y
Corrosion loss of Gd2-xTi1.9M0.1O7-δ pyrochlores were below 100μm/y.
CRIEPI


Element with d-orbital electron
Sc Ti V Cr Mn Fe Co Ni Cu Zn
Y Zr Nb Mo Tc Ru Rh Pd Ag Cd
La Hf Ta W Re Os Ir Pt Au Hg
Ac Th Pa U
CRIEPI


Pyrochlore
Possibility of B-site element
Sc Ti V Cr Mn Fe Co Ni Cu Zn
Y Zr Nb Mo Tc Ru Rh Pd Ag Cd
La Hf Ta W Re Os Ir Pt Au Hg
Ac Th Pa U
Pyrochlore
Ti^{4+}
(1) Sc, Y, La, and Ac are not B-site element, because of they are rare earth metal
(2) Th, Pa, and U are radio-nuclide. Tc is artificial radio-nuclide.
(3) Cd and Hg are pollution element.
(4) Cu is not B-site element, because Cu has K_2NiF_4 structure.
(5) Zn and Ag are not B-site element, because Zn and Ag are di-valence and mono valence.
(6) Hard to reduction → Non-conductive pyrochlore
(7) Au oxide is not stable (Only metalic Au is stable)
(8) Ru (0.001ppm), Rh (0.0002ppm), Pd (0.0006ppm), Os (0.0004ppm), Ir (0.000003ppm)
Pt (0.003ppm) are very expensive and rare earth elements.
Ru and Ir has high corrosion resistance iunder acidic condition.
(9) Re (0.004ppm) is rare earth elements.
CRIEPI

6. Concluding Remarks

Seigoh FUJIKAWA

Director of HTTR Project, JAERI

Ladies and Gentlemen,
It is my honor and pleasure to be invited to close this HTTR Workshop on Hydrogen Production Technologies that is actually a most interesting and useful workshop.

First of all, I would like to thank everybody on behalf of JAERI for attending this Workshop in Oarai. Especially, foreign delegates from the United State, France, Korea, Germany, Canada, and the United Kingdom are once again welcomed to this Workshop.

We are definitely very pleased to have the opportunity to work with all of you. We found that this Workshop very successful and I think everyone has found this Workshop very successful.

At the present day, due to the global energy and environmental problems caused by large consumption of fossil fuels, special attention has been given to the technology development of hydrogen production by the use of HTGR in many countries. As presented in the session one yesterday, JAERI has succeeded in high-temperature operation of the HTTR at 950 degree C and also succeeded in long-time continuous operation of IS process for one week. So this Workshop must be a really timely event.

During the course of these two days of the Workshop, we have had very useful and constructive information exchange and discussion about various aspects of hydrogen production technologies.

In the sessions of the Workshop, we have got knowledge that national and international hydrogen production programs have been progressed for recent several years.

Also we have got knowledge that technical researches for hydrogen production have been widely spread, especially research in thermo-chemical process has been spread in many countries.

In the discussion session, I confirmed that the hydrogen production by nuclear energy could become one of the competitive techniques for hydrogen production in near future.

In all of the sessions throughout our two day program, we could found that further contact and discussion could significantly widen that area of common ground.

I am pleased to say a few words to close this Workshop. It is my understanding that, this Workshop is JAERI's initial attempt to provide an opportunity bringing together experts in advanced hydrogen production technology to encourage the exchange of information on state-of-the-art technology, to identify major R&D issues, to assess its feasibility and to explore the future development. It is also aiming at offering assistance to improve links between experts from various disciplines and from various nations for further cooperation.

JAERI is willing to play an increasing role as a center in developing technology of HTGR and nuclear heat utilization.

To make the way towards the goal, we are planning to organize the second Workshop in Japan in autumn next year 2005, taking an opportunity of JAERI's hosting the coming third OECD/NEA information exchange meeting on Nuclear Hydrogen Energy that will be held about that time. We would like courteously to invite all of you to the next HTTR Workshop, looking forward to seeing you again.

I would like to end by thanking again all participants for having attended this Workshop and also thanking all of the chairmen, speakers and organizing staff for having made this Workshop great success.

It is my pleasure to declare this Workshop closed.
Thanking you everybody,

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Appendix. List of Participants

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国際単位系（SI）と換算表

表1　SI基本単位および補助単位

量	名称	記号
長さ	メートル	m
質量	キログラム	kg
時間	秒	s
電流	アンペア	A
熱力学温度	ケルビン	K
物質量	モル	mol
光度	カンデラ	cd
平面角	ラジアン	rad
立体角	ステラジアン	sr

表2　SIと併用される単位

名称	記号
分，時，日	min, h, d
度，分，秒	°, ′, ″
リットル	l, L
トン	t
電子ボルト	eV
原子質量単位	u

$1\ eV = 1.60218 \times 10^{-19} J$
$1\ u = 1.66054 \times 10^{-27} kg$

表5　SI接頭語

倍数	接頭語	記号
10^{18}	エクサ	E
10^{15}	ペタ	P
10^{12}	テラ	T
10^{9}	ギガ	G
10^{6}	メガ	M
10^{3}	キロ	k
10^{2}	ヘクト	h
10^{1}	デカ	da
10^{-1}	デシ	d
10^{-2}	センチ	c
10^{-3}	ミリ	m
10^{-6}	マイクロ	μ
10^{-9}	ナノ	n
10^{-12}	ピコ	p
10^{-15}	フェムト	f
10^{-18}	アト	a

表3　固有の名称をもつSI組立単位

量	名称	記号	他のSI単位による表現
周波数	ヘルツ	Hz	s^{-1}
力	ニュートン	N	$m \cdot kg/s^2$
圧力，応力	パスカル	Pa	N/m^2
エネルギー,仕事,熱量	ジュール	J	$N \cdot m$
工率，放射束	ワット	W	J/s
電気量，電荷	クーロン	C	$A \cdot s$
電位，電圧，起電力	ボルト	V	W/A
静電容量	ファラド	F	C/V
電気抵抗	オーム	Ω	V/A
コンダクタンス	ジーメンス	S	A/V
磁束	ウェーバ	Wb	$V \cdot s$
磁束密度	テスラ	T	Wb/m^2
インダクタンス	ヘンリー	H	Wb/A
セルシウス温度	セルシウス度	℃	
光束	ルーメン	lm	$cd \cdot sr$
照度	ルクス	lx	lm/m^2
放射能	ベクレル	Bq	s^{-1}
吸収線量	グレイ	Gy	J/kg
線量等量	シーベルト	Sv	J/kg

表4　SIと共に暫定的に維持される単位

名称	記号
オングストローム	Å
バーン	b
バール	bar
ガル	Gal
キュリー	Ci
レントゲン	R
ラド	rad
レム	rem

$1\ Å = 0.1 nm = 10^{-10} m$
$1\ b = 100 fm^2 = 10^{-28} m^2$
$1\ bar = 0.1 MPa = 10^5 Pa$
$1\ Gal = 1 cm/s^2 = 10^{-2} m/s^2$
$1\ Ci = 3.7 \times 10^{10} Bq$
$1\ R = 2.58 \times 10^{-4} C/kg$
$1\ rad = 1 cGy = 10^{-2} Gy$
$1\ rem = 1 cSv = 10^{-2} Sv$

（注）

1. 表1－5は「国際単位系」第5版，国際度量衡局 1985年刊行による。ただし，1 eV および 1 u の値はCODATAの1986年推奨値によった。
2. 表4には海里，ノット，アール，ヘクタールも含まれているが日常の単位なのでここでは省略した。
3. bar は，JISでは流体の圧力を表わす場合に限り表2のカテゴリーに分類されている。
4. EC閣僚理事会指令では bar，barnおよび「血圧の単位」mmHgを表2のカテゴリーに入れている。

換算表

力	$N(=10^5 dyn)$	kgf	lbf
	1	0.101972	0.224809
	9.80665	1	2.20462
	4.44822	0.453592	1

粘度　$1\ Pa \cdot s (N \cdot s/m^2) = 10\ P$（ポアズ）$(g/(cm \cdot s))$

動粘度　$1 m^2/s = 10^4 St$（ストークス）(cm^2/s)

圧力	MPa(=10bar)	kgf/cm^2	atm	mmHg(Torr)	lbf/in^2(psi)
	1	10.1972	9.86923	7.50062×10^3	145.038
	0.0980665	1	0.967841	735.559	14.2233
	0.101325	1.03323	1	760	14.6959
	1.33322×10^{-4}	1.35951×10^{-3}	1.31579×10^{-3}	1	1.93368×10^{-2}
	6.89476×10^{-3}	7.03070×10^{-2}	6.80460×10^{-2}	51.7149	1

エネルギー・仕事・熱量	$J(=10^7 erg)$	kgf·m	kW·h	cal(計量法)	Btu	ft·lbf	eV
	1	0.101972	2.77778×10^{-7}	0.238889	9.47813×10^{-4}	0.737562	6.24150×10^{18}
	9.80665	1	2.72407×10^{-6}	2.34270	9.29487×10^{-3}	7.23301	6.12082×10^{19}
	3.6×10^6	3.67098×10^5	1	8.59999×10^5	3412.13	2.65522×10^6	2.24694×10^{25}
	4.18605	0.426858	1.16279×10^{-6}	1	3.96759×10^{-3}	3.08747	2.61272×10^{19}
	1055.06	107.586	2.93072×10^{-4}	252.042	1	778.172	6.58515×10^{21}
	1.35582	0.138255	3.76616×10^{-7}	0.323890	1.28506×10^{-3}	1	8.46233×10^{18}
	1.60218×10^{-19}	1.63377×10^{-20}	4.45050×10^{-26}	3.82743×10^{-20}	1.51857×10^{-22}	1.18171×10^{-19}	1

1 cal = 4.18605J（計量法）
= 4.184J（熱化学）
= 4.1855J（15℃）
= 4.1868J（国際蒸気表）

仕事率　1 PS(仏馬力)
= 75 kgf·m/s
= 735.499W

放射能	Bq	Ci
	1	2.70270×10^{-11}
	3.7×10^{10}	1

吸収線量	Gy	rad
	1	100
	0.01	1

照射線量	C/kg	R
	1	3876
	2.58×10^{-4}	1

線量当量	Sv	rem
	1	100
	0.01	1

（86年12月26日現在）

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