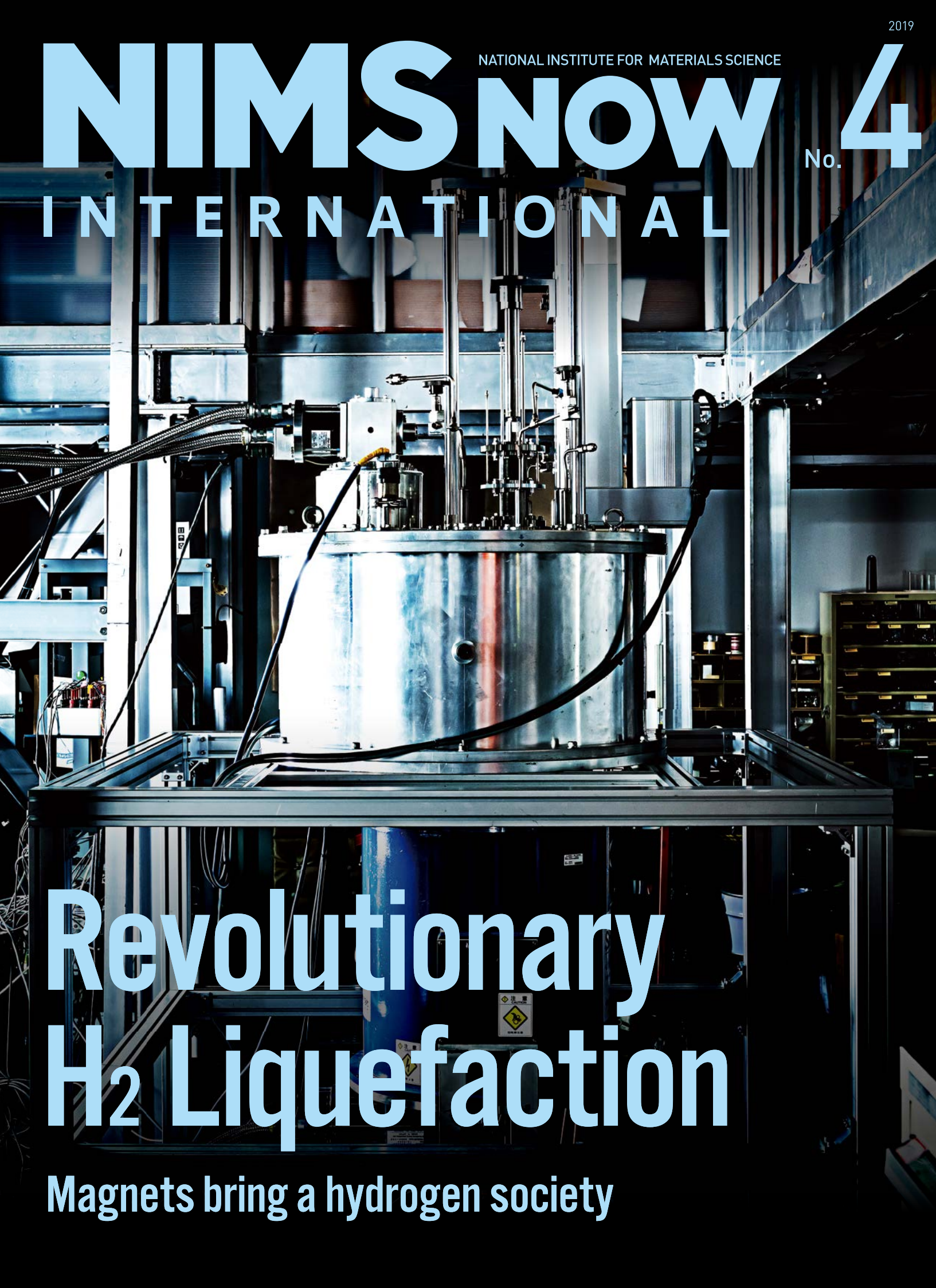


# NIMS NOW No. 4

NATIONAL INSTITUTE FOR MATERIALS SCIENCE

## INTERNATIONAL



# Revolutionary H<sub>2</sub> Liquefaction

Magnets bring a hydrogen society





# Revolutionary H<sub>2</sub> Liquefaction

## Magnets bring a hydrogen society

Hydrogen is favored as a next-generation energy source.

Switching to non-polluting hydrogen is an urgent need amid the global movement to substantially reduce greenhouse gas emissions.

Efforts to achieve widespread use of hydrogen have been encountering major hurdles, such as high production costs, particularly in relation to the liquefaction process.

Although Hydrogen liquefaction — which occurs at  $-253^{\circ}\text{C}$  — is the best solution for storage and transport, cooling with existing technology requires large amounts of energy.

NIMS has a promising solution to this issue.

It has been developing a novel hydrogen liquefaction system that uses magnets to efficiently cool hydrogen gas.

This NIMS NOW issue spotlights a recently launched and highly anticipated research project seeking to develop a practical magnetic refrigeration system.



# Magnets: A key player in the hydrogen society

The “hydrogen society” is a concept for a future in which hydrogen is widely utilized as the ultimate source of clean energy.

The Japanese government was ahead of the world to declare the intention of transforming to a hydrogen society.

Two leaders in the field discussed what will be required to achieve this goal.



**Nobuyuki Nishimiya**

Project Professor, College of Science and Technology, Nihon University  
President of the Hydrogen Energy Systems Society of Japan (HESS)  
Invited Researcher at the National Institute for Materials Science (NIMS)  
Program Manager for the JST project,  
“Innovative hydrogen liquefaction technologies desired in future society”

**Tadashi Shimizu**

Director of the Cryogenic Center  
for Liquid Hydrogen and Materials Science (CLean),  
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Associate Program Manager for the JST project,  
“Innovative hydrogen liquefaction technologies desired in future society”

## Why hydrogen energy?

**Shimizu:** The world is facing serious global warming issues that urgently necessitate reducing emissions of greenhouse gases, such as carbon dioxide. Hydrogen energy has been gaining a great deal of attention for its potential to ease this problem. Hydrogen can be produced from various resources, such as water, natural gas and waste plastics, and it does not release carbon dioxide when used as a fuel. Japan adopted a basic hydrogen strategy in 2017 and it has since been leading the world in the development of a hydrogen society. Professor Nishimiya, I believe that your interest in hydrogen energy goes back many years. You currently serve as president of the Hydrogen Energy Systems Society of Japan (HESS). When was HESS established?

**Nishimiya:** The Hydrogen Energy Research Society, a predecessor to HESS, was founded in July 1973, just before the onset of the first energy crisis in the fall of that year. The founding members anticipated that continued dependence on fossil fuel resources would eventually make ensuring a stable energy supply challenging and invite global environmental issues. They envisioned that hydrogen would be the solution to these issues. I am still amazed by their foresight.

**Shimizu:** Renewable energy is another viable alternative to fossil fuel resources. Why did you choose hydrogen energy?

**Nishimiya:** The amount of electricity generated from renewable energy sources fluctuates depending on weather conditions. In current systems, when the yield exceeds the capacities of power lines and storage batteries, the surplus electricity goes to waste. However, this surplus electricity could be used to

electrolyze water and produce hydrogen, a form of energy compatible with storage, thereby minimizing renewable energy loss. Assuming that domestic energy demand will grow, Japan might have to consider exploiting overseas renewable energy sources. However, generating electricity from renewable energy sources overseas and transmitting it to Japan via power lines is unrealistic. What, then, would be an appropriate transportation method? I have no doubt that hydrogen is the right option.

## Efficient hydrogen transport and storage

**Shimizu:** To make the vision of a hydrogen society a reality, hydrogen supply chains need to be developed: systems that streamline the production, transport, storage and utilization of hydrogen (Figure 1). Of these steps, the development of transport and storage technologies is particularly important. Because transporting hydrogen molecules great distances through pipelines is impossible, the phases of hydrogen suitable for transport and storage need to be determined. The well-known hydrogen carriers are liquid hydrogen, which is produced by cooling hydrogen, and ammonia and organic hydrides, which are liquid compounds resulting from chemical reactions with hydrogen. Which of these do you think is the most desirable form?

**Nishimiya:** I believe that liquid hydrogen is the best option. It can be transported and stored efficiently; liquid hydrogen has 1/800 the volume of gaseous hydrogen. Another advantage of liquefied hydrogen is its purity, which obviates the need for a separate purification process before actual use.

That said, all hydrogen carriers have

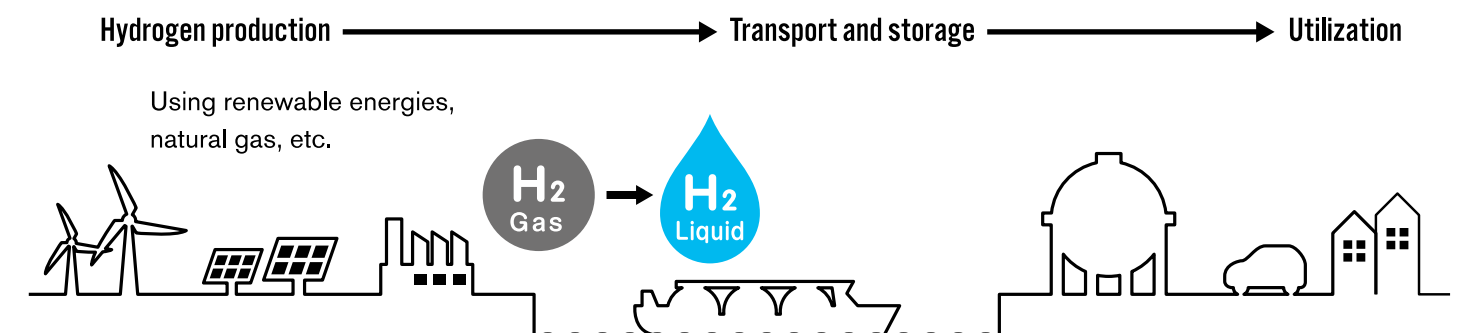
advantages and disadvantages. Hydrogen liquefaction is expensive. Hydrogen needs to be cooled to 20 K (-253°C) to liquefy, and a portion of the liquid hydrogen is lost to vaporization (i.e., boil-off) due to ambient heat input during the transport and storage processes. These two issues are the main causes of the high supply cost. I believe that solving these issues would be the most effective way of expediting the development of a hydrogen society. This is why I have long been interested in the “magnetic refrigeration technology” being developed by Takenori Numazawa at NIMS, a key technology potentially capable of cooling hydrogen to cryogenic temperatures (see p.8).

**Shimizu:** This technology is indeed a crucial driver of the JST project, “Innovative hydrogen liquefaction technologies desired in future society,” which launched in November 2018. We greatly appreciate that you understand our strong desire to contribute to the development of a hydrogen society, and have enabled us to take advantage of NIMS’ strengths by accepting the position of program manager for this project. NIMS, several universities and companies are participating in this nationwide effort: a 10-year plan to develop hydrogen liquefaction technology based on magnetic refrigeration.

## Magnetic refrigeration technology: an innovative approach to hydrogen liquefaction

**Nishimiya:** A vapor compression refrigeration technology is currently used to liquefy hydrogen. In this technology, a refrigerant gas is compressed, increasing its temperature, and this heat is then released. When allowed to

Figure 1. Hydrogen supply chain





expand, the temperature of the gas decreases, allowing it to absorb heat. When applied to hydrogen liquefaction, the refrigerant gas absorbs heat from gaseous hydrogen as it expands and expels absorbed heat as it is compressed. A cycle of these processes cools gaseous hydrogen until it liquefies. By contrast, the magnetic refrigeration technology operates on the basis of different principles: the application of a magnetic field to a magnetic material polarizes all of its electron spins in the same direction, causing it to release heat, while the removal of the magnetic field allows the electron spins to randomize, causing the material to absorb heat. This technology is capable of cooling gaseous hydrogen (seep.8).

Magnetic refrigeration technology does not require the use of a highly energy consumptive compressor as vapor compression refrigeration does. Because magnetic refrigeration technology is

potentially much more energy efficient, it is expected to enable significantly higher liquefaction efficiency. Compared to the approximately 25% liquefaction efficiency of which vapor compression refrigeration technology is capable, magnetic refrigeration technology may achieve 50% or higher liquefaction efficiency. Moreover, while vapor compression refrigeration technology requires the use of greenhouse gases during the precooling process, magnetic refrigeration technology does not use any environmentally harmful refrigerants. This is the main reason why I have such high expectations for NIMS' magnetic refrigeration technology.

**Shimizu:** In addition to the issues you raised, the patent rights to vapor compression refrigeration technologies are exclusively owned by European companies. Continued use of this technology will not prevent hydrogen supply costs in Japan from ever coming up because they are likely to demand

higher patent royalties. The development of magnetic refrigeration technology by Japan will change this situation.

**Nishimiya:** The current liquid hydrogen supply cost is 100 yen for 1Nm<sup>3</sup> (a unit that expresses a volume of gas in cubic meters at 0°C and 1 atm) of hydrogen. Our goal is to reduce the supply cost to 30 yen per Nm<sup>3</sup> by 2030 and to 20 yen per Nm<sup>3</sup> by 2050 by putting magnetic refrigeration technology into practical use. If these goals are met, liquid hydrogen may become a viable alternative to liquefied natural gas (LNG), which currently costs about 16 yen per Nm<sup>3</sup> on a calorie basis. In addition, magnetic refrigeration systems can be designed to be more compact than gas liquefaction systems because no compressor is needed. If this technology is integrated into fuel cell vehicles and hydrogen stations, it will be able to fully recover the liquid hydrogen lost to vaporization during the boil-off process.

For these reasons, magnetic refrigeration technology is capable of lowering hydrogen mass transport and storage costs and is therefore absolutely necessary to achieving widespread use of hydrogen energy. Putting this technology into practice requires the design of a system capable of efficiently cooling hydrogen to its liquefaction temperature (seep.8), the identification of magnetic materials with desirable properties and techniques to process magnetic materials into small spherical particles (seep.11). I believe that NIMS has expertise in these areas.

### Achieving a cheap supply and safe utilization: NIMS' contribution

**Shimizu:** NIMS established the Cryogenic Center for Liquid Hydrogen and Materials Science (CLEAN) in April 2019. Achieving the vision of a hydrogen society will require a cheap hydrogen supply that can be safely utilized. CLEAN will work to satisfy these two requirements: cheap and safe. Magnetic refrigeration technology is the solution to reducing the hydrogen supply cost. While, the mechanisms of hydrogen embrittlement and low-temperature embrittlement are both

known to make metals fragile. The ability of liquid hydrogen transport and storage tanks to withstand liquid hydrogen has not yet been verified. We therefore plan to evaluate the durability of tank materials exposed to liquid hydrogen. Based on the data collected, we will then develop optimum materials that can be used to ensure safe utilization of hydrogen energy.

**Nishimiya:** Only NIMS has the capability to adequately evaluate the reliability of materials. I am also impressed by the research environment NIMS offers, which allows long-term, in-depth R&D, such as the development of magnetic refrigeration technology by Dr. Numazawa, which has been pursued over the course of many years.

**Shimizu:** Dr. Numazawa was initially developing cryogenic technologies used to induce superconductivity phenomena in which electrical resistance becomes zero. However, the discovery of high-temperature superconductors in 1986 made many scientists in this field presume that demand for cryogenic technologies would rapidly dwindle. Despite this commonly held view, Dr. Numazawa continued his research in the belief that cryogenic technologies would be demanded in scientific fields other than superconductivity research. His instinct turned out to be correct: magnetic refrigeration is now drawing a great deal of interest as a key technology in the development of a hydrogen society. What a dramatic story!

30 years after the discovery of high-temperature superconductors, their use by the general public is still very limited.

**“We will work to satisfy the two requirements of a hydrogen society: ensuring a cheap supply of hydrogen that can be safely utilized.”**

— Tadashi Shimizu

Magnetic refrigeration technology offers these superconductors a great opportunity to play a vital role. They can be used as magnets capable of applying magnetic fields to other magnetic materials. CLEAN's long-term plans call for the integration of high-temperature superconductors into magnetic refrigeration technology, finally joining two technologies that were thought to be incompatible 30 years ago.

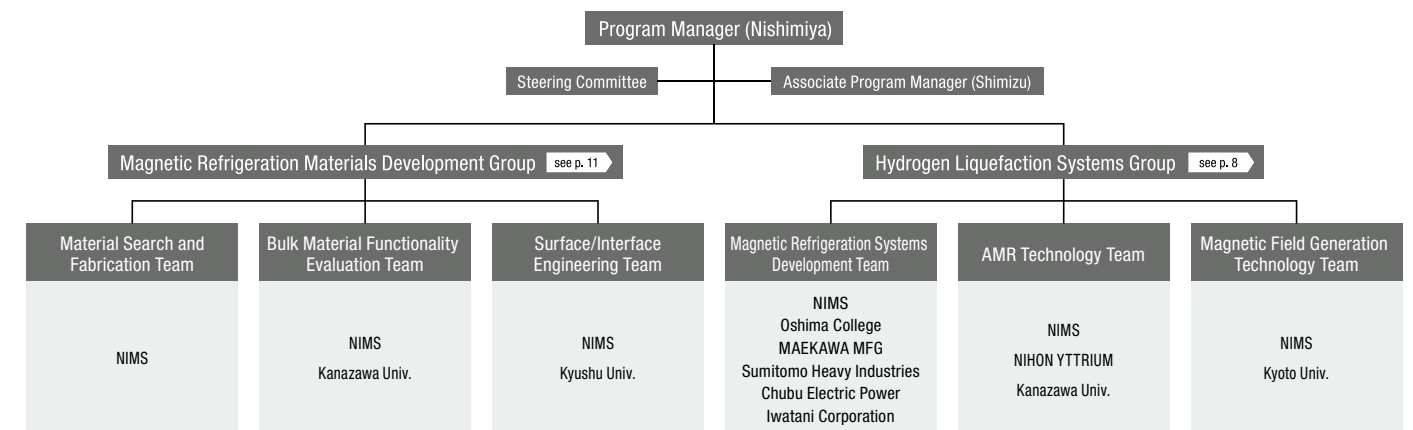
**Nishimiya:** NIMS has a variety of resources that could potentially give rise to novel technologies. We should take full advantage of these resources and work together to complete the magnetic refrigeration technology, thereby greatly expediting the realization of a hydrogen society.  
(by Shino Suzuki, PhotonCreate)



**“Magnetic refrigeration technology is absolutely necessary in achieving widespread use of hydrogen energy.”**

— Nobuyuki Nishimiya

Figure 2. Systematic representation of the research groups participating in the JST Mirai Program's "Innovative hydrogen liquefaction technologies desired in future society" project





# NIMS' magnetic refrigeration cycle system: a promising technology in boosting liquefaction efficiency

As the lightest gas, hydrogen gas occupies a substantial volume under normal pressure. Finding a way to efficiently store and transport large amounts of hydrogen is therefore one of the challenges in developing a “hydrogen society.” The liquefaction process had received a great deal of research attention because it can condense hydrogen to 1/800 of its gaseous volume. Although hydrogen liquefaction technologies are already in practical use, their efficiency has been inadequate. NIMS has a technology that is potentially capable of dramatically increasing liquefaction efficiency. We asked Takenori Numazawa about this technology and the liquefaction strategy.

## Limits of conventional technology

Liquid hydrogen is a promising energy carrier for the transport and storage of hydrogen. Liquefaction condenses hydrogen to 1/800 of its gaseous volume, thereby increasing hydrogen transportation and storage efficiencies. In addition, liquid hydrogen has many advantages over hydrogen compounds. For example, liquid hydrogen is readily available for use as a fuel without the need to extract hydrogen from a compound and it is perfectly compatible with fuel cell vehicles and other equipment requiring highly purified hydrogen.

However, hydrogen liquefaction is very

costly. To liquefy hydrogen gas, it has to be cooled from room temperature to an ultralow temperature of 20 K (-253°C). This has already been achieved using the so-called vapor compression refrigeration technology, and refrigeration systems based on this technology have been put into practical use. However, the compressor this method uses to cyclically compress and expand a refrigerant gas—thereby cooling hydrogen—consumes large amounts of energy. Efforts to increase the energy efficiency of this process have nearly reached their limit.

Magnetic refrigeration technology is potentially capable of significantly increasing liquefaction efficiency. Numazawa, who

has been engaged in cryogenic technology research for 30 years, tells us that this technology could double the liquefaction efficiency of conventional technology. What is magnetic refrigeration technology?

## How to lower the temperature with magnets

Electron spins (a source of magnetism) in a magnetic material are normally irregular in orientation. The application of a magnetic field to the material polarizes all of its electron spins in the same direction. If the magnetic field is then removed adiabatically, the electron spins absorb external heat as they return to their irregular orientations

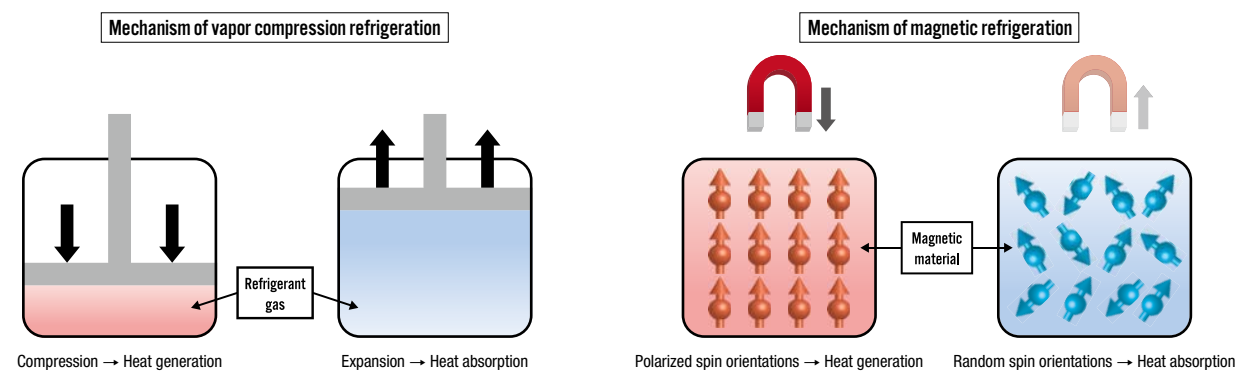


Figure 1. Comparison between vapor compression refrigeration and magnetic refrigeration technologies

Vapor compression refrigeration technology works based on the mechanism that a gas generates heat when compressed and absorbs heat when it expands. The compression and expansion of a gas require large amounts of energy. Magnetic refrigeration technology, on the other hand, operates based on the principle that a magnetic material generates heat when all of its electron spins are polarized in the same direction and absorbs heat when they have random orientations. Spin orientation can be externally manipulated by simply varying the distance between a magnet and a magnetic material, requiring only small amounts of energy.



**Takenori Numazawa**

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(Figure 1). This phenomenon is called a magnetocaloric effect. Magnetic refrigeration technology uses this effect to achieve cooling. In other words, this technology cools a target gas by repeating the cycle of generating and absorbing heat in response to the application and removal of a magnetic field.

“Using this cooling principle, all magnetic materials involved instantaneously change temperature, minimizing energy loss and increasing liquefaction efficiency,” Numazawa said.

## Two key factors in achieving liquefaction

Although the innovative magnetic refrigeration technology appears to be a simple mechanism, applying it to hydrogen liquefaction is far from simple. This is because hydrogen needs to be cooled in a specific temperature range. “Hydrogen liquefaction is two-step processes: hydrogen gas is first cooled from room temperature to 77 K (-196°C) using liquid nitrogen. The cooled hydrogen gas is then further cooled from

77 K to 20 K using the magnetic refrigeration technology,” Numazawa said. “This latter temperature range has proven very difficult to handle.”

The magnetic refrigeration technology has been used mainly to cool target substances which have already been cooled to an extremely low temperature of about 4 K (-269°C) using liquid helium, etc. to 0.1 K (-273°C) or lower. Numazawa has experience in generating temperatures this low from his work on the development of NASA X-ray astronomy equipment to be used in space for the investigation of cosmic mysteries. However, magnetic refrigeration has never succeeded in the temperature range between 77 K and 20 K due to a number of issues, including a lack of magnetic materials/systems with adequate cooling capabilities and energy efficient magnets.

“We are confident that we can overcome these issues,” Numazawa said. “We have succeeded in developing a magnetic refrigeration device capable of cooling the gaseous hydrogen from 34 K (-239°C) to

22 K (-251°C), a temperature range in which magnetic refrigeration technology had previously proven ineffective. This is the first time that a single device has been able to lower the temperature of the hydrogen by as much as 12 degrees Kelvin in the cryogenic temperature range. This cooling range can theoretically be expanded to 30 degrees Kelvin. By combining several devices, each capable of lowering the temperature of the hydrogen by 30 degrees Kelvin in different temperature ranges, we should be able to create a system capable of cooling the hydrogen from 77 K to 20 K.”

An active magnetic regenerator (AMR) cycle—the basic mechanism used in the research by Numazawa’s group—has been applied mainly to the development of near-room-temperature cooling technologies. The AMR cycle operates in a cylindrical container containing magnetic materials and a so-called heat exchange fluid. Manipulating the magnetic field applied to the cylinder causes the magnetic materials in it to generate or absorb heat, which in turn warms or cools

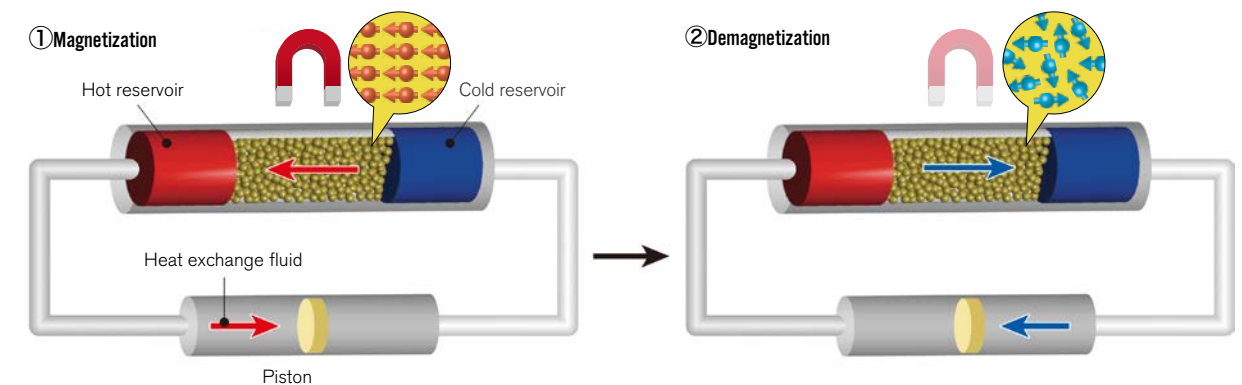


Figure 2. Mechanism of an active magnetic regenerator (AMR) cycle

①The application of a magnetic field to a cylinder filled with magnetic materials causes electron spins in the materials to polarize in the same direction. This induces the magnetic materials to generate heat, warming the heat exchange fluid. The piston then pushes the warmed fluid toward one end of the cylinder (hot reservoir) from which heat is released. ②The adiabatic removal of the magnetic field allows the electron spins in the magnetic materials to resume their random orientations. This causes the magnetic materials to absorb heat, cooling the heat exchange fluid. The piston then pushes the cooled fluid toward the opposite end of the cylinder (cold reservoir). The repetition of this cycle progressively cools the cold reservoir.



the heat exchange fluid. The controlled movement of the warmed/cooled fluid in the cylinder produces localized cooling at one end of the cylinder (Figure 2).

“Increasing the performance of the AMR cycle is indeed very challenging as it requires the simultaneous enhancement of materials (i.e., magnetic materials, heat exchange fluids and magnets used to generate magnetic fields) and systems (i.e., optimal arrangement and use). NIMS has experts in a wide array of technical fields, making it the ideal place at which to pursue this goal. In fact, a major R&D project led by NIMS was launched last year.”

Two key objectives—the development of materials and systems—were set for the JST project, “Innovative hydrogen liquefaction technologies desired in future society,” which started in November 2018. Numazawa is leading the system development team.

Numazawa already has a significant system development accomplishment: he designed a novel magnetic refrigeration system.

The conventional AMR cycle uses an external piston to drive the movement of the heat exchange fluid. In this system, the fluid needs to travel from the cylinder to the external piston unit, resulting in energy loss. The system Numazawa designed is equipped with an innovative mechanism to eliminate this energy loss.

“Because there is a pending patent application, I cannot explain in very great detail,” Numazawa warned in advance. “I have designed a new system composed of a series of AMR cycle units, thereby minimizing energy loss (Figure 3). This system can cool hydrogen by repeating the magnetization and demagnetization cycle without needing an external piston to drive the movement of the heat exchange fluid. We created a prototype system and verified that it is able to dramatically reduce energy loss compared to a conventional AMR cycle system.”

During this 10-year project, the system

development team plans to examine whether this system is capable of operating in an energy efficient manner even under cryogenic conditions. The team also intends to develop a large-scale hydrogen liquefaction system with a liquefaction efficiency at least 50% higher than conventional systems with the ability to liquefy more than 100 kg of hydrogen per day. Moreover, the team plans to develop a lightweight, compact re-condensing system capable of liquefying a portion of the liquid hydrogen vaporized during transportation and storage.

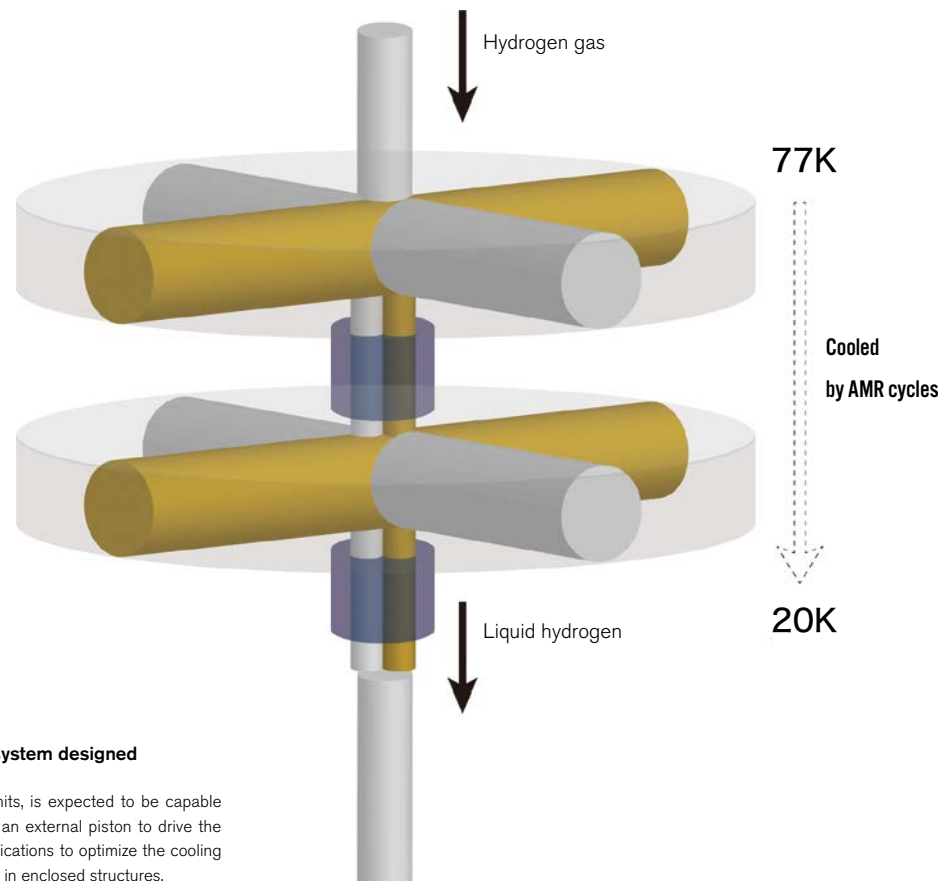
### The time is ripe for development

The 10-year duration of this program implies that the development of these technologies will be a huge challenge. However, there is some encouraging news: a succession of new room-temperature magnetic materials have been developed in recent years and valuable data on magnetocaloric effect phenomena has been accumulating. Furthermore, magnetic refrigeration is drawing a great deal of

public interest as a cooling technology that uses no refrigerant gas—a source of the greenhouse gas emissions associated with conventional refrigerators—and research on the technology is rapidly progressing. This new data and technical advancements are expected to expedite the development of new hydrogen liquefaction technologies by enabling gaseous hydrogen to be efficiently cooled under cryogenic conditions.

In addition, NIMS has developed a number of materials that are needed to generate a magnetocaloric effect under cryogenic conditions, such as superconducting materials that can be used to generate a strong magnetic field. The 10-year program has also allowed NIMS to coordinate and collaborate with the private sector. “The time is ripe for the development of magnetic refrigeration technology,” Numazawa said. The large number of research accomplishments built by Numazawa are expected to play a vital role in the hydrogen society.

(by Akiko Ikeda, Sci-Tech Communications)



**Figure 3. Schematic diagram of the hydrogen liquefaction system designed by Numazawa**

This energy efficient system, composed of a series of AMR cycle units, is expected to be capable of continuously repeating adiabatic demagnetization without needing an external piston to drive the movement of the heat exchange fluid. Numazawa plans to make modifications to optimize the cooling capabilities of this system, in which magnetic materials are manipulated in enclosed structures.

## Challenge 2 | material development

# Magnetic materials and processing techniques: requirements for an efficient liquefaction system

The magnetic materials used in a liquefaction system play a key role in refrigerating hydrogen, and their performance greatly influences the system’s efficiency.

What do ideal magnetic materials require and how can they be created?

Hideaki Kitazawa has been developing high-performance magnetic materials, while Hiroyuki Takeya has been developing magnetic material processing techniques. We asked them about their work.



### Only effective magnetic materials can increase a system’s efficiency

“The first hurdle that has to be overcome in the development of an efficient hydrogen liquefaction system is creating magnetic materials that enable a large magnetocaloric effect to be generated,” said Kitazawa.

Kitazawa is leading the development of magnetic materials under the JST’s “Innovative hydrogen liquefaction technologies desired in future society” program. A magnetocaloric effect is a phenomenon

in which the temperature of a magnetic material changes in response to changes in the magnetic field applied to it. Magnetic refrigeration technology leverages this effect to cool hydrogen gas and is potentially capable of liquefying hydrogen. The cooling efficiency of the hydrogen liquefaction system under development (see p.8) will increase if the system incorporates magnetic materials with the ability to cool hydrogen by many degrees.

The magnetic materials used in this hydrogen liquefaction system are required to be

able to lower the temperature of hydrogen gas from 77 K (-196°C) to 20 K (-253°C). However, no single magnetic material currently known has the ability to cool hydrogen by this many degrees Kelvin. The largest temperature drop achievable is estimated to be no more than 20 degrees Kelvin. Therefore, the combined use of different magnetic materials to cool hydrogen in steps is necessary.

“Different magnetic materials have different temperature ranges in which they perform effectively or ineffectively (Figure 1),” Kitazawa said. “Teaming them up is therefore





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### Hiroyuki Takeya

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the most realistic cooling approach."

An active magnetic regenerator (AMR) cycle is the basic mechanism used in the hydrogen liquefaction system being developed. As the AMR cycle operates, magnetic materials contained in a cylinder generate or absorb heat, warming or cooling a heat exchange fluid. The controlled movement of the warmed/cooled fluid produces localized cooling at one end of the cylinder. "One way of achieving high cooling efficiency would be to arrange several different magnetic materials with different effective temperature ranges in the cylinder, allowing heat to be transferred sequentially between them (Figure 2)," Kitazawa said. Based on this approach, Kitazawa plans to divide the 77 K-to-20 K temperature range into several sub-ranges and develop magnetic materials capable of generating large magnetocaloric effects in these sub-ranges.

"Heavy rare earth elements (e.g., Gd, Dy, Ho and Er) are generally believed capable of inducing large magnetocaloric effects. The first step is to create new magnetic materials using them as the base ingredients and adding various other chemical elements to create desirable properties," Kitazawa said. "I plan to use cutting-edge techniques in this effort and hope to avoid the inefficiencies of material development that have resulted from insufficient data and an overreliance on researchers' past experience."

One possible procedure for developing efficient magnetic materials would be to first collect large datasets related to magnetocaloric effects (e.g., transition temperatures and changes in magnetic entropy) and organize them into a database.

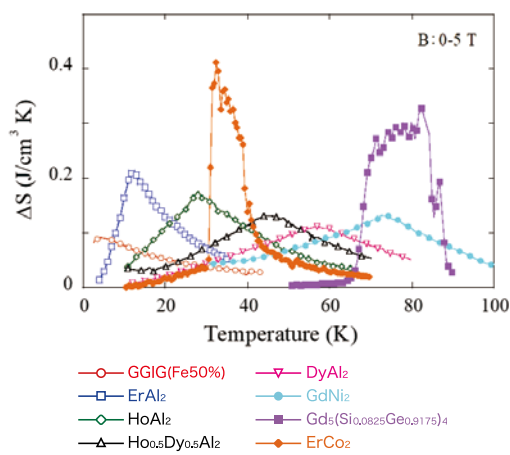
Machine learning could then be applied to these datasets to predict the physical properties of potentially desirable magnetic materials and R&D could be carried out based on this information. Kitazawa is also considering the use of other techniques, such as first principle simulations.

The development of magnetic materials capable of generating large magnetocaloric effects across a temperature range between 40 K (-233°C) and 20 K is expected to produce significant benefits. These materials may be used to re-condense vaporized liquid hydrogen in storage tanks, thereby fully recovering hydrogen lost.

#### Quest for processing techniques capable of optimizing magnetic material properties

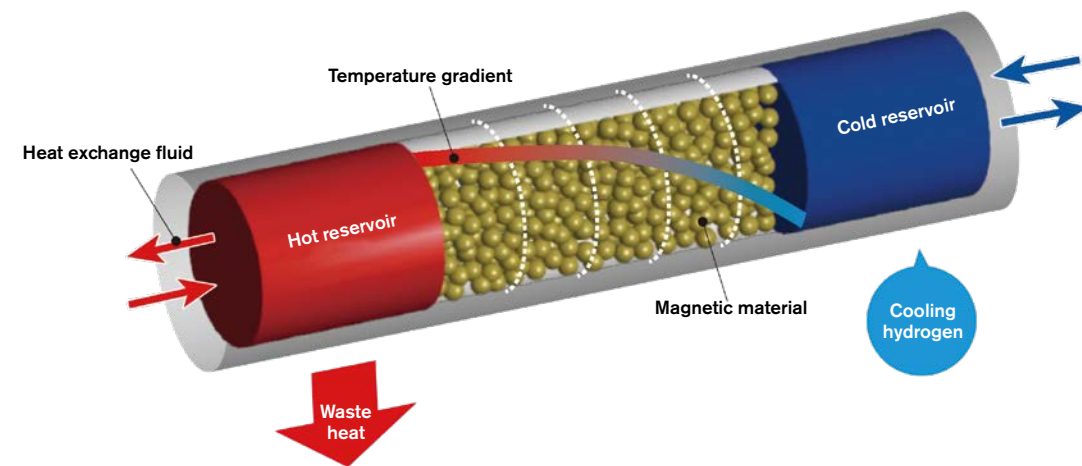
After desirable magnetic materials are created, they are processed into shapes suitable for installation in devices and systems. "The ability to induce a large magnetocaloric effect is not the only requirement for high-performance magnetic

materials," Takeya said. "Other material properties, for example, thermal conductivity, mechanical properties and resistance to hydrogen, and shapes also may influence the performance of magnetic materials in complex and important ways when used in a system." The thermal conductivity of magnetic materials greatly affects the cooling efficiency of a hydrogen liquefaction system. Physical strength and other mechanical properties of magnetic materials are significant factors in determining the durability of devices and their resistance to repeated use. In addition, the direct use of magnetic materials to cool hydrogen would be a viable option. If magnetic materials are used in this way, hydrogen molecules—which are extremely small—may penetrate and weaken them. Therefore, the effect of hydrogen molecule penetration on liquefaction efficiency and measures to prevent this should be studied. Moreover, the properties of magnetic materials are influenced by their shapes. Takeya has been developing processing techniques capable of optimizing the properties of magnetic



**Figure 1. Examples of magnetic materials potentially effective in hydrogen liquefaction through magnetic refrigeration**

The vertical axis indicates changes in the degree of electron spin disorder (magnetic entropy) in response to magnetic field changes from 0 T to 5 T, while the horizontal axis represents temperature. Higher peaks indicate higher cooling capabilities for the corresponding materials. Lines extending more widely along the horizontal axis indicate that the corresponding materials have wider effective temperature ranges. While a magnetic material with both a high peak and wide coverage is considered to be ideal, in reality, the balance between these parameters and the temperature range in which the material's performance peaks varies widely depending on materials.



**Figure 2. Design of the cylinder in which the AMR cycle takes place**

A temperature gradient is generated along the length of the cylinder by the movement of a heat exchange fluid. Efficient cooling may be achieved by placing several different magnetic materials with different temperature-specific cooling capabilities side by side (as indicated by the white dotted lines). Magnetic materials are required to have a number of desirable properties, including high responsiveness to magnetic fields, the ability to cool hydrogen across a wide temperature range and the ability to efficiently transfer heat to a heat exchange fluid.

materials using conventional magnetic materials, while waiting for Kitazawa to complete the development of new magnetic materials.

Takeya has faced challenges during his efforts. Most magnetic materials that are able to generate large magnetocaloric effects are heavy rare earth element compounds. These compounds share a number of disadvantages when used for hydrogen liquefaction: they exhibit poor thermal conductivity, are brittle and difficult to process and readily absorb hydrogen. In order to overcome these disadvantages while preserving their advantageous properties, Takeya is studying processing techniques, including coating processes and formation processes and the resulting shapes.

One of Takeya's objectives is to maximize the surface area of the magnetic materials in the cylinder so that they can cool the heat exchange fluid as efficiently as possible. Among the several candidate shapes, Takeya is attempting to process magnetic materials into spherical particles 0.3 mm to 0.5 mm in diameter. The use of magnetic materials of this shape and size is expected to increase the system's cooling efficiency because they can be densely packed in the AMR cylinder while allowing gaps to be present between them sufficient for the heat exchange fluid to flow. Taking processing precision, mass production cost and other factors (Figure 3) into account, Takeya selected the gas atomization process to create spherical particles. In this process, a molten raw material is allowed to fall through a hole. As soon as the material passes through the hole, it is sprayed with a high-velocity gas jet and rapidly cooled until it solidifies.

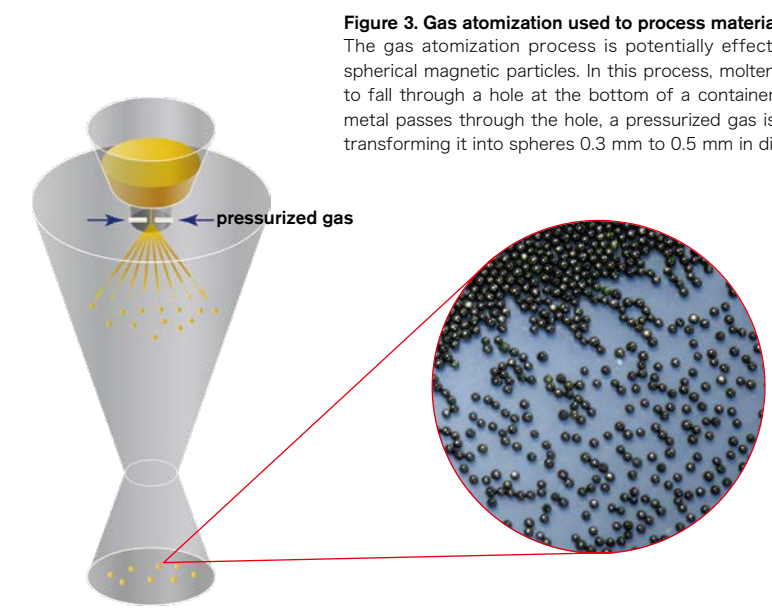
Takeya is studying the optimum gas pressure as this partly determines the size and shape of the particles. Gas pressure optimization is also important because inappropriate pressure may produce particles with defects (e.g., minute internal pores). In this project, various analytical instruments are also developed, including a hydrogen microscope capable of visualizing the impact of hydrogen on magnetic materials.

#### Organizing a team to put the technology into practice

"Materials can serve their intended purposes only after they are properly processed and integrated into a system," Kitazawa said. "We will therefore work comprehensively on all of the processes involved in developing a hydrogen liquefaction system during

this program, from material development to material design, system design and reliability testing. We are determined to put this technology—which is so vital to the realization of a hydrogen society—into practice." Takeya continued, "All of the members participating in this program are experts in their respective fields and their research has been very productive. We have been actively engaged in discussions on sharing each other's cryogenic technology expertise, material development and material processing techniques." The JST program was finally launched by these researchers, who have a rich array of experience related to hydrogen liquefaction. Over the next 10 years, they will take the lead in developing Japan's new energy infrastructure while encouraging young researchers to get involved.

(by Akiko Ikeda, Sci-Tech Communications)



**Figure 3. Gas atomization used to process materials**

The gas atomization process is potentially effective in producing spherical magnetic particles. In this process, molten metal is allowed to fall through a hole at the bottom of a container. As soon as the metal passes through the hole, a pressurized gas is sprayed onto it, transforming it into spheres 0.3 mm to 0.5 mm in diameter.





Prototype of an AMR magnetic refrigerator. In this project, the prototype is used to verify the basic theory such as the performance and energy efficiency evaluation of magnetic materials developed by the group led by Kitazawa and Takeya. Based on this information, the group led by Numazawa and Chief Researcher Koji Kamiya (photo) has been developing a new hydrogen liquefaction system (see Figure 3 on p. 10).

## INTERVIEW

# Contributions by NIMS and private companies to the development of a hydrogen society

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### What has been Kawasaki Heavy Industries' vision for hydrogen energy?

The energy crisis of the early 1970s prompted discussion of alternatives to petroleum that could be supplied stably. Hydrogen was one of the possible alternatives proposed at that time. Although the public eventually forgot this issue completely after oil prices stabilized, Kawasaki Heavy Industries has continued its hydrogen-related program motivated by energy security concerns and based on the vision that Japan should pursue energy self-sufficiency. Since about 2009, we have been making company-wide efforts to develop hydrogen energy-related technologies.

### Kawasaki Heavy Industries has been participating in a large-scale hydrogen-related project since 2016. Can you tell us about the project?

We are one of five companies collaborating in the NEDO (New Energy and Industrial Technology Development Organization)-funded "Hydrogen Energy Supply Chain Project." The goal of this project is to generate hydrogen by decomposing Australia's large reserves of brown coal—a type of coal with a high water content—and to transport it 9,000 km to Japan. The hydrogen produced will be liquefied using a gas liquefaction technology to increase its transportability before shipment to Japan. In addition to this advantage, liquid hydrogen is favorable because it is highly compatible with other energy-related equipment and technologies our company has developed, such as tankers used to transport liquefied natural gas and tanks used to store liquid hydrogen rocket fuel.

Hydrogen also has some issues, however. Hydrogen liquefaction is energy intensive and costly, and other energy sources have therefore been outcompeting hydrogen in the market. However, the magnetic

refrigeration technology NIMS is developing works differently from current gas liquefaction technologies. If this technology is successfully reduced to practice, it is expected that it will enable more energy-efficient liquefaction, leading to substantial cost savings. In addition, commercial-scale hydrogen production necessitates the development of a mass production system with a liquefaction capacity of 100 tons per day. Although the development of these technologies is a major challenge, we sincerely hope that NIMS succeeds in this ambitious endeavor.

### What types of materials do you think are necessary for the development of a hydrogen society?

### What do you expect from NIMS for this project?

By the time that the hydrogen society becomes fully operational, we will need much more technical know-how and technologies capable of handling much greater amounts of hydrogen than we can today. I anticipate that some innovative materials will bring a technological breakthrough. For example, if materials can be developed that exhibit high strength at extremely low temperatures, they could be

used to reduce the thickness and weight of the inner walls of the liquid hydrogen tanks installed in tankers, freeing up room to carry more hydrogen. Current liquid hydrogen tanks also have another issue: regular tank inspections warm them to ambient temperatures. When warmed tanks are refilled with liquid hydrogen, some hydrogen is lost through evaporation until the tanks are sufficiently chilled. Thinning the tank's inner walls would reduce the amount of evaporation.

Long-term quantitative data indicating changes in the performance of materials at ultralow temperatures has been generated but more data is necessary. NIMS has a long tradition of carrying out high-quality materials evaluations, such as creep tests and fatigue tests, and the data generated by these tests has proven highly reliable. That is why we would like NIMS to take the lead in evaluating materials at ultralow temperatures. If NIMS were to assume this role, we could be more confident in the materials we use.

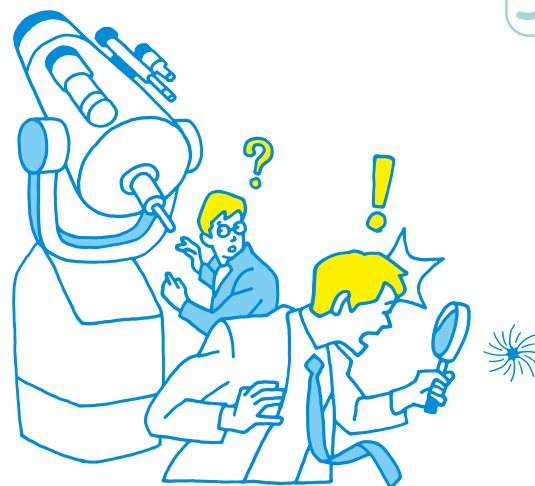
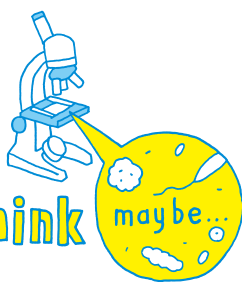
We have developed a wide variety of hydrogen-related technologies. However, we alone cannot advance the development of a hydrogen society. We look forward to working with NIMS to achieve this goal.



Photo by Kawasaki Heavy Industries, Ltd.



Science is even more amazing than you think



## First ever image of a black hole captured

Text by Akio Etori

Illustration by Joe Okada (vision track)

Black holes had long been believed to be absolutely invisible to humans because they swallow everything, even light. That is why people around the world were astonished by the recent news that a black hole was actually observed.

Coordinated press conferences were held shortly after 10:00 pm on April 10, 2019 in six cities simultaneously—including Tokyo, Washington, D.C. and Brussels—and were broadcasted worldwide via the internet. During this event, the first ever image of a black hole was unveiled.

The press conference in Tokyo was hosted by Professor Mareki Honma from the National Astronomical Observatory of Japan. He presented the accomplishments made by the EHT (Event Horizon Telescope) project in which an international group of more than 200 researchers participated, including 13 research organizations. Professor Honma is a leading member.

The actual black hole observations were made on four dates in 2017: April 5, 6, 10 and 11. A gigantic virtual telescope (10,000 km in diameter; comparable to the diameter of the Earth) was created by synchronizing eight radio telescopes at

various global locations. The performance of this telescope was truly revolutionary as its resolution was said to be sufficient to identify a golf ball on the lunar surface.

The target of this imaging project was a huge black hole at the center of the M87 galaxy about 55 million light years from Earth. The image depicted the “black hole shadow,” a dark area surrounding the actual black hole.

The image shows a bright ring encircling a central black shadow. Before the observation, the EHT group made a prediction based on simulation studies that the black hole’s periphery would appear brilliant due to plasma flowing in every direction in the region but its center would look completely dark. Thus, the image taken turned out to be fully consistent with the prediction. It took the group two years to analyze the telescope data and produce the final visual image.

The diameter of the “black hole shadow” was estimated to be 40 billion kilometers, comprising about 40% of the diameter of its surrounding shadow (100 billion km). The diameter of the black hole is about 29,000 times that of the sun. However, the mass comparison is even more impressive: the mass of the black hole is about 6.5

billion times that of the sun.

The first black hole was discovered in the 1970s when a star in the Cygnus constellation was observed to be moving strangely. Its periodic motion appeared to be driven by gravitational force from another invisible star. Astronomers named the invisible star “X-1” and calculated its size and weight. They found that X-1 had to be extremely heavy despite its very small size and concluded that it must be a black hole.

However, because this earlier discovery was made based only on indirect evidence, the recent success in actually capturing an image of a black hole was truly a major achievement for EHT researchers.

In relation to this topic, some scientists believe that micro black holes exist in addition to the widely accepted massive black holes. They argue that these black holes are subatomic in size, were created in the very early history of the universe and are scattered across space even today. Although their existence has been predicted only theoretically, further advances in observation technology may someday enable us to see them.

The universe is still filled with mysteries that stimulate our imaginations.

Akio Etori: Born in 1934. Science journalist. After graduating from College of Arts and Sciences, the University of Tokyo, he produced mainly science programs as a television producer and director at Nihon Educational Television (current TV Asahi) and TV Tokyo, after which he became the editor in chief of the science magazine Nikkei Science. Successively he held posts including director of Nikkei Science Inc., executive director of Mita Press Inc., visiting professor of the Research Center for Advanced Science and Technology, the University of Tokyo, and director of the Japan Science Foundation.



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Percentage of Waste Paper pulp 70%

