Safe, CFC-free, refrigeration system using hydrogen absorbing alloys

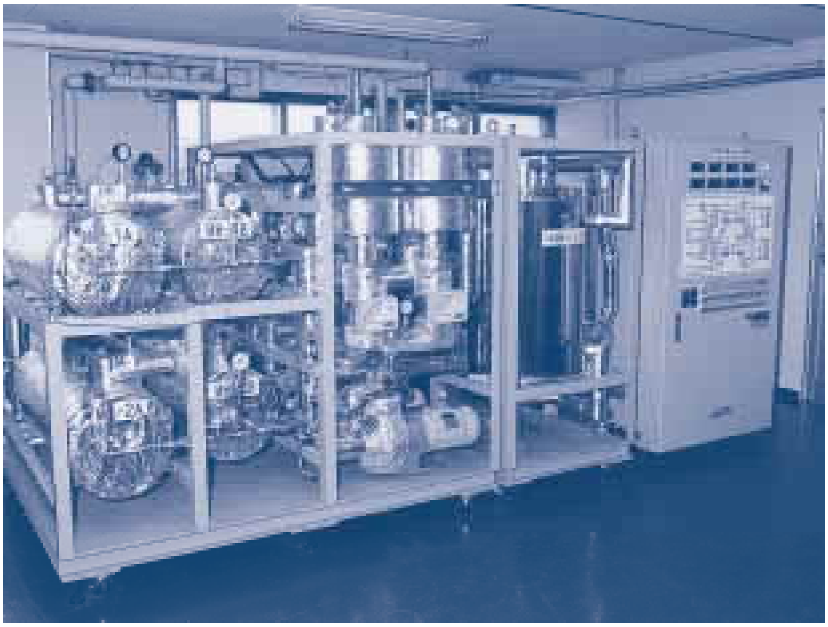
submitted by the Japanese National Team

Aiming at developing CFC-free refrigeration systems, a group of three Japanese companies have succeeded in making operational a metal hydride refrigeration system which uses hydrogen absorption alloys and which can keep the temperature in a cold storage below -30℃. This innovative, CFC-free, MH refrigeration system for low-temperature cold storage is safe, easy to operate and maintain and applicable to wide varieties of use ranging from cold storehouses to automatic vending machines.

It is an internationally urgent issue to develop refrigeration systems operating without the use of substances such as CFCs, HCFCs and HFCs, which have ozone depletion and/or greenhouse effect disadvantages reffered to here as “CFC-free refrigeration systems”. For the first time, a group of Japanese companies have succeeded in making operational an innovative, CFC-free, metal hydride refrigeration system (MH refrigeration system) using hydrogen absorbing alloys (MH alloys) for cold storage at low temperatures.

This state-of-the-art, MH refrigeration system can keep the temperature in a cold storage area below -30°C. Until now this has been difficult to achieve. Furthermore, the MH system can be made as compact in size as a conventional vapour compression refrigeration system. The system can be incorporated easily, therefore, into automatic vending machines and display cabinets for frozen foods. In addition, the system is safe since hydrogen is absorbed and stored in MH alloys. Ammonia absorption refrigerating machines have also been proposed as an alternative CFC-free system for cold storage. However, it is not possible to make ammonia systems as small in size as MH systems, and the strong toxicity and highly irritating odour of ammonia are serious obstacles to their widespread use.

MH refrigeration system for large, low-temperature, cold storehouse.



Japan Steel Works, Ltd., in cooperation with Nichirei Corp. (the largest company in the cold storage and refrigerated distribution business in Japan) and Toyo Koki Co., Ltd. (an engineering firm for refrigeration systems) started a joint research and development project in May 1995. Their objective was to put MH refrigeration systems for F-class (below -20°C) cold storehouses into actual use, by using an MH alloy which can work in practice at temperatures below -40°C. In 1995, the joint R&D group demonstrated an MH regrigeration system under test conditions by cooling a 100m^3 cold storehouse. They succeeded in continuously operating the system with a storeroom temperature below -30°C. At the end of the year, the group also completed a trial model of an automatic vending machine equipped with an MH refrigeration system which can be used for commercial operation once the system size has been reduced.

System principles

When MH alloys come into contact with hydrogen, the alloys absorb hydrogen by an exothermic reaction and store it as metal hydrides. In reverse, the alloys easily dissociate and discharge hydrogen by an endothermic reaction. Employing this endothermic reaction when MH alloys discharge hydrogen, MH refrigeration systems implement a refrigeration cycle by a combination of two types of alloy. One type works at a higher temperature and the other each at a lower temperature, under their own equilibrium hydrogen pressure. The working principles of MH refrigeration systems are illustrated in **Figures 1 and 2**.

MH alloys absorb or discharge hydrogen at certain constant equilibrium hydrogen pressure levels, determined by temperature. MH refrigeration systems use an MH alloy (MH-A) driving hydrogen to carry out the regeneration process on the high temperature side of the system and another MH alloy (MH-B), refrigerating brine on the low-temperature side. Each of these alloys has the relation between temperatures and equilibrium hydrogen pressures as shown in **Figure 1**.

- ***Regeneration process***
  (1) To raise the hydrogen pressure of the MH-A by raising its temperature, the alloy is heated (Q2-1). Hydrogen is discharged from the MH-A and moves to the MH-B with lower hydrogen pressure; (2) the MH-B absorbs hydrogen, thus generating heat. However, the circulation of cooling brine (Q1-1) suppresses the rise in the MH-B temperature, thereby preventing the pressure of the MH-B increasing. The MH-B continues to absorb and store hydrogen in this way.

- ***Refrigeration process***
  (3) When all the hydrogen of the MH-A is transferred to the MH-B, the former alloy is cooled by cooling water (Q2-2), thereby lowering its hydrogen pressure.
  (4) Hydrogen is discharged from the MH-B. This has a lower hydrogen pressure than that of the MH-A, and moves to the latter alloy. Reducing its temperature by the hydrogen discharge, the MH-B refrigerates brine (Q1-2).

To continuously cool brine for refrigeration, an MH refrigeration system has two sets of high temperature and low-temperature MH alloy pairs. While one set of the alloys operates in the regeneration process, the other set works in the refrigeration process.

Each of these MH alloys is packed in a heat exchanger cylinder. This enables the exchange of thermal energy with a heating medium (steam, hot water, etc.), cooling water or brine. Shell and tube type heat exchangers are used.

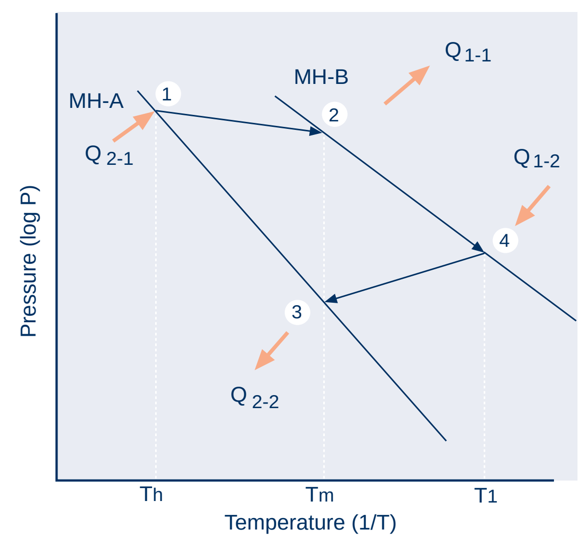
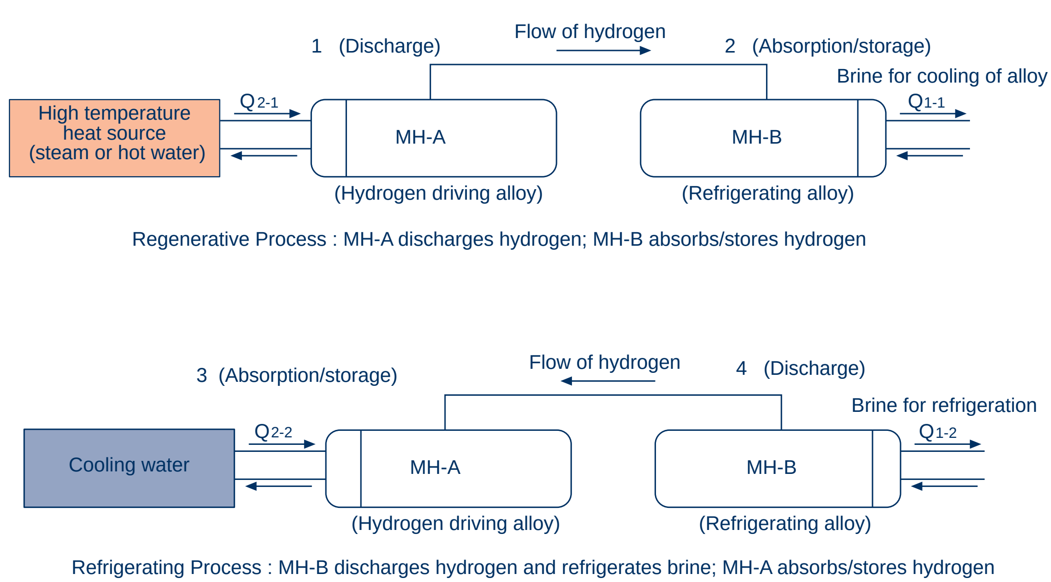


Figure 1: Working principle of MH refrigeration system.

Figure 2: Illustration of MH refrigeration system principle.



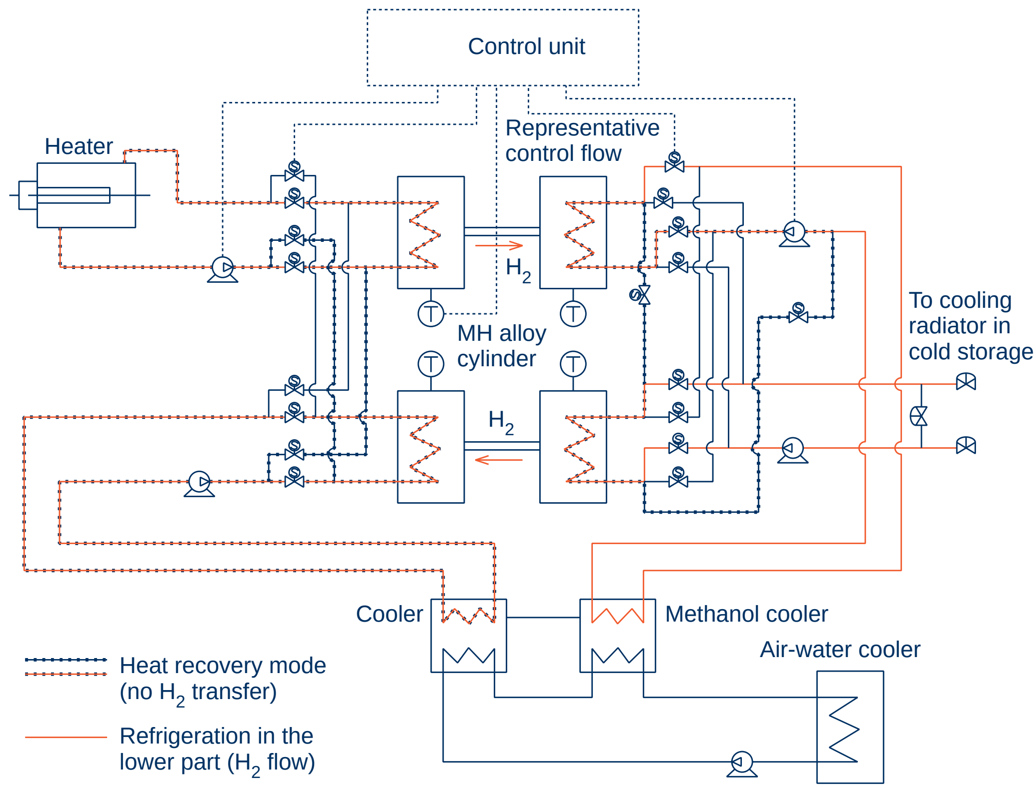


Figure 3: Flow chart of the MH refrigeration system for low-temperature cold storage.

A TiZrCrFe-series MH alloy used in the MH refrigeration system developed by this R&D project can absorb hydrogen within 1-2 minutes at a temperature of -20°C. The alloy underwent 50,000 hydriding/dehydriding test cycles. The alloy was able to absorb 85% of the hydrogen it had absorbed after one cycle. This test corresponded with five years actual use of the alloy, thus showing durability sufficient for practical use.

Figure 3 shows, a flowchart of MH refrigeration system for low-temperature cold storage, using methanol as the heat transfer medium for the low-temperature side and hot/cooling water as the heat transfer medium for the high-temperature side. In this chart, MH alloy cylinders (heat exchangers) are shown as forming part of the refrigerating process.

Advantages

The MH refrigeration system is a very safe as well as a clean and environmentally friendly, CFC-free refrigeration system. Hydrogen is sealed in gas-tight cylinders, and, being far lighter than air, rapidly diffuses into the atmosphere in the accidental event of its leakage. Thus, the danger of explosion caused by hydrogen is slight. In addition, the system has other advantages as described below.

- By not using CFCs or ammonia, the system is applicable to wide-ranging uses.
- The system needs a heating source to generate energy for refrigeration, but can save energy consumption for this purpose by the use of waste heat or by operating in combination with a cogeneration system.
- It has no moving elements except for pumps circulating water and brine. In particular, its hydrogen system, driven solely by heat input, does not need the manipulation of valves. Thus, rarely suffering breakdowns, the MH system is easy and simple to operate and maintain.
- Driven by heat, the system consumes 20% less electric power than conventional electrically powered compression refrigeration machines.
- Having no sliding and vibrating components such as compressors, the system operates with low noise levels.
- Because the MH refrigeration system is safe and simple to control, it is possible to design refrigerating units using this technology with wide varieties of cooling capacities ranging from 10 -10,000 kW.

Small-sized, safe refrigeration units can be built by using MH refrigeration technology. This is a particularly attractive feature of the MH refrigeration system which ammonia absorption refrigerating machines cannot match. Hence, applications as automatic vending machines and display cabinets for frozen foods, which can take full advantage of this technology, are expected to be one of the most promising markets.

Demonstration test plant and vending machine

In addition to the development of MH alloys to construct high-performance MH refrigeration systems, heat exchangers for MH refrigeration units were studied and better operation cycles were pursued. As a result, the joint R&D group succeeded in approximately doubling the refrigerating power per kilogram of MH alloy, in comparison with former MH refrigeration systems. The MH refrigeration unit designed for the demonstration test plant, developed by these R&D efforts, operates in a 50 minute cycle. It reduces the temperature of the refrigerating alloy down to -40°C, cools a 100 m^3 cold storehouse to less than -30°C in about 4 hours and can maintain this temperature level. The working pressures of the system are kept under 9.9 kg/cm^2G (971 kPaG) which avoids falling within the High Pressure Gas Control Law. The working temperatures are -30 to +30°C (methanol) on the low temperature side of the system and 30 to 160°C (steam and cooling water) on the high temperature side. Of the four MH alloy cylinders (shell and tube type heat exchangers), two are on the low temperature side and two are on the high temperature side. 87 kg of a TiZrCrFe-series 6 element MH alloy is packed in each of the high temperature side cylinders, and 57 kg of a TiZrCrFe-series 7 element alloy is packed in each of the low-temperature side cylinders. The 100 m^3 cold storehouse meets the requirements for storage at -40°C.

As mentioned above, one of the most attrictive features of MH refrigeration systems is that they can be safely scaled down. To show this to advantage, the joint R&D group developed a compact-sized MH refrigeration unit with an automatic vending machine for frozen food, for market introduction. MH alloys used in this automatic vending machine are expected to be degraded by operation after seven years. An MH alloy cassette system was therefor developed to make the replacement of the degraded alloys easier. The specifications of the MH refrigerating unit for this vending machine, now under investigation, are summarised as follows:

- the pressure of hydrogen is 9.9 kg/ cm^2G (971 kPaG);
- the highest temperature on the high-temperature side is 140°C;
- the lowest temperature on the low-temperature side is -30°C;
- the construction of alloy cylinders is of the shell and tube heat exchanger type;
- the alloys used are: 4.0 kg/cylinder of TiZrCrFe-series 6 element alloy for the hydrogen driving, and 2.8 kg/cylinder of TiZrCrFe-series 7 element alloy for the refrigerating, respectively;
- the heat transfer medium on the low-temperature side is methanol.

For further information, please contact the Japanese National Team (address on back cover).