In order to acquire the data to estimate the performance of isolation valve provided for HTTR, the test of the helium gas leakage in simulated actual condition using a half-scaled hot gas isolation valve is ongoing.

2) Corrosion test of reformer tube material

In the HTTR hydrogen production system, hydrogen is produced by means of steam reforming of methane in SR using hot secondary helium gas supplied from IHX. Steam reformer is therefore one of the most important equipment in this system.

In SR, helium gas whose maximum temperature is at 880 °C flows outside of tube and process gas that is a maximum of H₂, H₂O, CO, CO₂ and CH₄ flows inside. The reforming tube has to withstand against these conditions.

Hastelloy XR, nickel based high temperature resistant alloy, will be used for the reforming tube of steam reformer because it has already been proved to use under high temperature helium gas. Design database is provided for use in helium gas condition but in process gas condition. So it is required to ensure the integrity of Hastelloy XR against process gas.

Tensile strength, fatigue life, creep life and so on in the process gas as well as in the helium gas are necessary to design the reforming tube. Corrosion tests in the simulated process gas condition and mechanical property tests by using post corrosion specimens have been carried out.

In this corrosion test, oxidation, reduction and carburetion are considered to decide test conditions. Since pressure of the corrosion test cannot be simulated to the real condition, partial pressure of O₂ and carbon activity are simulated in the corrosion tests. From these corrosion tests and mechanical property test it will be confirmed that there are not significant variation of microstructure of aging Hastelloy XR and existing mechanical property data.

2. R&D on IS Process for Thermochemical Hydrogen Production

Hydrogen has ideal characteristics as an energy carrier. Hydrogen can be used as a clean fuel in a variety of energy end-use sectors including the conversion to electricity. It can be stored, and also can be transported long distance with lower loss compared to electricity. After combustion, it produces only water. Therefore, the concept of hydrogen energy system has attracted much interest worldwide, which recently has been strengthened by the growing concern on the environmental issues such as global warming due to the CO₂ emission and by the rapid progress of utilizing technologies, especially of fuel cells, as well.

In order to realize the hydrogen energy system, development of efficient hydrogen production system is an important and urgent issue. Nuclear energy that emits no carbon dioxide and can stably supply massive energy is the promising primary energy for the hydrogen production. HTGR that features high level of safety and can supply heat of about 1000 °C is suitable for this purpose among others. Thermochemical water-splitting process is a method to make an effective use of the high temperature heat for hydrogen production.

![Fig. 2.1.2 Scheme of IS process](image-url)
IS process is composed of the three chemical reactions as shown in Fig. 2.2.1. The raw material, water, reacts with sulfur dioxide and iodine to produce hydrogen iodide and sulfuric acid (the so-called Bunsen reaction), which are then thermally decomposed to produce hydrogen and oxygen, respectively. Thermal decomposition of sulfuric acid has favorable characteristics as the high temperature endothermic reaction for the thermochemical process. It proceeds in two stages with no side reactions. First, H₂SO₄ decomposes into SO₃ and H₂O spontaneously in the temperature range of 350-500°C. By further heating up to over 800°C, SO₃ decomposes into SO₂ and O₂ in the presence of solid catalyst. Both reactions are strongly endothermic and temperature range of the reactions is well matched with that of HTGR.

The IS process has been studied since 1970's and General Atomics (GA) performed an intensive work. In Europe and in Japan, several variations have also been studied which differed in the mode of reaction and/or methods to separate reaction products. Initial efforts were concentrated on how to separate the HI and H₂SO₄ produced in the Bunsen reaction. Researchers at GA found that, when excess iodine is present in the mixture of HI-H₂SO₄-H₂O-I₂, the solution spontaneously separates into HI-rich aqueous solution (so-called HIX solution whose main components are HI, I₂, H₂O) and H₂SO₄-rich aqueous solution. Figure 2.2.2 shows the chemical changes occurring in the IS process that feature the liquid-liquid (LL) phase separation. Enthalpy changes shown

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**Fig. 2.2.2** Chemical Changes in the IS process featuring the liquid-liquid phase separation in the presence of excess iodine. Composition of the phase-separated solution is referred to the General Atomic data. No concrete unit operations are assumed here for other separation steps, i.e. separation of gaseous SO₂ and HI from the corresponding aqueous solutions. Calorific figures denote the enthalpy changes associated with the corresponding chemical changes at standard state.
in the figure indicate the potential of efficient hydrogen production, provided that effective scheme is adopted for the separation of SO$_3$ from sulfuric acid and that of HI from HIx solution. On these separation problems, several ideas have been proposed. As for the sulfuric acid processing, utilization of conventional techniques such as steam recompression or multi-effect evaporation has been proposed. As for the HIx processing, extractive distillation using phosphoric acid or reactive distillation under pressurized condition has been proposed. Flowsheeting studies based on these ideas suggested that the thermal efficiency of hydrogen production in the range of 45-50% could be attained utilizing intensive and efficient heat recovery networks.

JAERI has been conducting studies on IS process in three research fields, i.e., experimental verification of continuous hydrogen production by IS process featuring LL separation, investigation on process improvement and on materials of construction.

(1) Closed-Cycle Operation of IS Process

The continuous hydrogen production by IS process has been examined using small loop apparatuses in order to develop the operation technique of connecting the three chemical reactions and accompanying product separations while using reactants cyclically.

Initial attempt of the closed-cycle operation was carried out using a glass-made apparatus that was designed to include fundamental reactions and separations of IS process and to produce hydrogen of 1 NL/hr. Figure 7.2.3 shows the simplified flowsheet.

At first, efforts were devoted to determine an appropriate composition of the phase-

![Flowsheet of the laboratory-scale experimental apparatus. Here, the separation of SO$_3$ from sulfuric acid is carried out by evaporation (concentrator and vaporizer), and that of HI from HIx solution (HI-I$_2$-H$_2$O mixture) is by distillation. Two types of apparatus have been set up, both of which were made of glass. Hydrogen production capacity of the first one was 1 NL/hr and that of the second is 50 NL/hr.](image-url)
separated solutions, which enabled to minimize the operational instability due to the occurrence of sulfur forming side reactions etc. Bunsen reaction and the LL separation behaviour were studied in detail. Purification method of the phase-separated acid solution was developed which utilized the reverse reaction of Bunsen reaction. Then, continuous hydrogen production was carried out for 48 hrs. In the experiments, every operation was carried out at ambient pressure and the iodine concentration in the product solution of Bunsen reaction was set to the saturating one at 0°C in order to reduce the technical difficulties caused by the solid iodine precipitation. The experiments demonstrated the feasibility of closed-cycle hydrogen production.

In this studies, it was clarified that the key point of closed-cycle operation was the solution handling process. The chemistry of sulfuric acid decomposition section and that of hydrogen iodide decomposition section are rather straightforward in terms of reaction and separation. On the contrary, in the Bunsen reaction section, possible occurrence of side reactions forming sulfur and/or hydrogen sulfide should be suppressed. Also, line plugging caused by possible solid iodine precipitation and outflow of unabsorbed sulfur dioxide gas along with the product oxygen should be suppressed to maintain the stable operation. Suitable design of Bunsen Reactor and Acids Separator, appropriate selection of the solution composition, and precise control of mass flow were important for this purpose.

Based on the experiences and the acquired chemical data, a scaled-up glass apparatus was set up (Fig. 2.4). Its basic flowsheet was the same as the former one except that recycling of unreacted HI and H₂SO₄ became possible within the HI decomposition step and the H₂SO₄ decomposition step, respectively. However, the experimental apparatus was equipped with newly devised pumps and sensors for monitoring process parameters such as flow rates and liquid levels. Also, it became possible to handle the process solution of enriched iodine concentration at elevated temperature, with
which better separation was anticipated of HI and H₂SO₄. Operation test in each reaction step was performed and the closed-cycle operation test was started in FY 2003. Up to now, continuous and stoichiometric production of hydrogen and oxygen has been successfully demonstrated for 20hrs with the hydrogen production rate of about 32NL/hr (Fig. □ .2.5). This work is being carried out under the contract of research between JAERI and the MEXT.

(2) Innovative Methods for Process Improvement

Process improvement has been pursued on the HI decomposition step, where HI is separated from the Hlx solution supplied from the Bunsen reaction step and decomposed to produce hydrogen and iodine. Simple way to realize the chemical change is the distillation of Hlx solution and the gas phase thermal decomposition of HI. However, because of the presence of azeotropic composition in HI-H₂O system (the molar ratio of H₂O/HI being ca 5), the distillation requires large thermal burden. Also, low equilibrium conversion of HI decomposition (ca 20% at 400 °C) induces excess circulation of HI within the process, which results in the increase of thermal burden.

In order to overcome these difficulties, GA proposed an extractive distillation method using phosphoric acid as the extractive agent and a liquid phase HI decomposition using Pd catalyst. Researchers at RWTH Aachen studied reactive distillation under high pressure. However, there still remain spaces of improvement to reduce the complex process scheme and/or to remedy the very corrosive process environment.

We are pursuing an application of membrane processes. Figure □ .2.6 shows a schematic VLE of Hlx solution at constant I₂ fraction. Since the Hlx solution obtained in the Bunsen reaction step has a composition close to the quasi-azeotropic one, it is impossible to separate HI and H₂O by thermodynamically controlled separation process such as conventional distillation. However, by increasing the molality of HI using kinetically controlled process to over-quasi-azeotropic one, pure HI can be separated from the concentrated Hlx solution by simple distillation owing to the increased volatility of HI in the solution of higher HI molality than the quasi-azeotropic one.

Electro-electrodialysis (EED) process has

![Graph showing hydrogen and oxygen production](image)

Fig. □ .2.5 Results of hydrogen production test. Continuous and stoichiometric production of H₂ and O₂ could be carried out for 20hrs.

![Vapor-Liquid Equilibrium (VLE) graph](image)

Fig. □ .2.6 Vapor-Liquid Equilibrium (VLE) of Hlx solution at constant fraction of I₂. The ordinate and the abscissa denote molar ratio of HI/(HI+H₂O) in vapor and in liquid, respectively. The arrow indicates the composition of Hlx solution obtained in the Bunsen reaction section.
been examined for this purpose. The principle of EED is shown in Fig. \( \text{ Fig. } \). The HIx solution is fed to the EED cell equipped with a cation-exchange membrane. By applying DC current, redox reaction of \( \text{I}\^-/\text{I} \) occurs at both electrodes. Owing to the selective permeation of proton through the membrane, HI molality of the HIx solution increases in the catholyte and decreases in the anolyte. So far, it has been successfully demonstrated to increase the HI molality by about 50% with relatively low energy consumption (Fig. \( \text{ Fig. } \)).

As for the HI decomposition reaction, utilization of membrane reactor equipped with hydrogen separation membrane is under study to achieve higher one-pass conversion than the equilibrium one. The hydrogen separation membrane is required to exhibit not only high separation performance but also high thermal and chemical stability in the environment of decomposition reaction. Therefore, ceramic membranes have been investigated. Silica membrane based on porous alumina substrate was prepared by chemical vapor deposition method on a trial basis. The test-fabricated membrane showed good separation performance, the ratio of permeation rates of \( \text{H}_2/\text{HI} \) being ca. 600/1 at 450 \(^\circ\)C (Fig. \( \text{ Fig. } \)). Computer simulation of the membrane reactor was carried out using one-dimensional model that took the reaction rate, the permeation rate and mass balance into consideration. The simulation results indicated that an ideal one-pass conversion of HI be over 90%.

A possible scheme of HI decomposition step featuring the membrane processes is shown in Fig. \( \text{ Fig. } \). Preliminary heat/mass balance analysis of the flowsheet featuring the membrane processes suggested that a similar process thermal efficiency as that reported on extractive distillation process might be possible with simpler process scheme (Fig. \( \text{ Fig. } \)).

(3) Materials of Construction

In order to select the candidate materials for constructing large-scale plant, commercially available materials have been examined mainly from the viewpoint of corrosion resistance in the representative process environments.

Figure \( \text{ Fig. } \) summarizes the candidate materials that showed corrosion resistance in the simulated process environments. In preparing the figure, test results reported from
Gas permeation through the silica membrane fabricated by chemical vapor deposition at 600°C

Fig. 2.8 Concept of membrane reactor for HI decomposition. The selective separation of hydrogen from the reaction field enables to enhance the equilibrium-limited reaction. Gas permeation characteristics of the test-fabricated silica membrane indicated the ideal separation factor of $H_2$/HI higher than 600 at 450°C.

Several research groups are considered on the corrosion in the concerned environments. As for the gas phase environment of HI decomposition step, a Ni-Cr-Mo-Ta alloy was found to show good corrosion resistance. As for the Bunsen reaction step, glass-lining materials, Zr, Ta showed corrosion resistance. In the environment of HIX distillation at 20bar, Ta showed

Fig. 2.9 HI processing scheme incorporating the two types of membrane separation processes. HIX solution supplied from the Bunsen reaction step is concentrated by electrodialysis to over-quasi-azeotropic composition, so that pure HI can be separated by distillation. Membrane reactor equipped with hydrogen separation membrane enables to decompose HI with higher one-pass conversion than the equilibrium one (ca. 20% at 400°C).
excellent corrosion resistance. The severest environment is the boiling condition of concentrated sulfuric acid under high pressure (e.g. 20bar), where ceramic materials containing silicone such as SiSiC, SiC, and Si₃N₄, were the only materials that showed excellent corrosion resistance.

In summary, for gas phase service, there seem to exist little concern on the structural materials. As for the equipments used in the Bunsen reaction step, lining materials should be used. Special design consideration is required for the equipments to be used in the boiling and condensing conditions of the acids.

Fig. 2.10 Estimated effects of final HI molality and of overpotential in EED on the thermal efficiency of hydrogen production. Heat/mass balance of the HI step was evaluated assuming intensive heat recovery, Tmin (in heat exchangers) =0, etc. As for the Bunsen step and the sulfuric acid step, heat/mass balances reported from GA and RWTH Aachen were used.

Fig. 2.11 Candidates for the materials of construction of IS process plant. This figure summarizes the former results of corrosion tests carried out in the typical process environment. Information from other research groups is also considered in drawing this figure.