STUDY ON THERMOCHEMICAL IODINE-SULFUR PROCESS AT JAEA

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Abstract

Thermochemical water-splitting process of Iodine-Sulfur family (IS process) has been studied in various research institutions. Previous studies cover the chemistry of each reaction section, heat/mass balance analysis of the process flowsheet, screening of corrosion-resistant materials of construction, development of advanced chemical reactor made of ceramics, and small-scale demonstration of the closed-cycle hydrogen production. Based on these studies, a pilot test of IS process is planned at Japan Atomic Energy Agency (JAEA), which consists of (1) hydrogen production test using test apparatus made of industrial materials and electrically-heated helium gas as the process driver, (2) development of analytical code system, (3) R&D on efficient unit operations and on advanced materials, (4) design study on a next-stage test plant to be connected to the HTTR.

Introduction

"Thermochemical method" for hydrogen production offers a technology with which nuclear energy is transformed into hydrogen, the energy carrier. This paper briefly describes the present status of study on Iodine-Sulfur cycle, a promising thermochemical cycle, at JAEA.

Hydrogen production by direct thermal decomposition of water requires high temperature heat of a few thousand Kelvin. However, by combining high-temperature endothermic chemical reactions and low-temperature exothermic chemical reactions, in which the net chemical change resulting from the sequence of component chemical reactions is the water decomposition, it is possible, in principle, to decompose water only with the heat of lower temperature. The cycle of chemical reactions produces the free energy required for water splitting. It is called thermochemical method and has a possibility of large-scale carbon-free hydrogen production.

Thermochemical water splitting cycle was first studied by Funk [1], and an actual example was proposed by researchers of CEC, JRC Ispra establishment, in early 70s [2]. Since then, a number of thermochemical cycles have been proposed assuming high temperature gas-cooled reactor (HTGR) as the heat source, which can supply heat with its maximum temperature of close to 1 000°C. After mid-80s, activities in Europe and in North America slowed down in accordance with the slowing down of their HTGR projects. Recently, however, with the emerging interest in the "hydrogen energy system" in accordance with the progress of fuel cell technology, the thermochemical method attracts growing interest again.

Previous studies on Iodine-Sulfur cycle focusing on the activities of JAERI

Hundreds of cycles have been studied from the viewpoints of the feasibility of component chemical reactions in terms of conversion ratio and/or products separation, theoretical thermal efficiency of hydrogen production etc [3]. Among them, those that utilise thermal decomposition of sulfuric acid, which are categorised as "sulfur cycles", have been considered one of the most promising cycles.

Thermal decomposition of sulfuric acid, reaction (1), proceeds in the following two steps.

$H_2SO_4(aq) = H_2O(g) + SO_3(g)$ 300-500°C

$SO_3(g) = SO_2(g) + 0.5\ O_2(g)$ 800-900°C

$$H_2SO_4 = H_2O + SO_2 + 0.5\ O_2 \qquad (1)$$

Both steps are highly endothermic and proceed smoothly without side reactions and with high conversion ratio at the temperature range indicated. The endothermic characteristics match well with the temperature distribution of the heat source, HTGR. The heat of HTGR is transferred to the chemical process through the sensible heat of helium gas, the temperature of which varies, e.g. 900-400°C. Therefore, the reaction is quite suited as the high temperature endothermic reaction for thermochemical water splitting cycle [4].

Iodine-Sulfur cycle (or Sulfur-Iodine cycle, or ISPRA Mark 16 cycle) combines following chemical reactions with the sulfuric acid decomposition reaction.

$$SO_2 + I_2 + 2H_2O = 2HI + H_2SO_4 \qquad (2)$$

$$2HI = H_2 + I_2 \qquad (3)$$

Here, reaction (2), known as "Bunsen reaction", is the low-temperature exothermic reaction, where raw material, water, reacts with iodine and gaseous sulfur dioxide producing an aqueous solution of hydriodic acid and sulfuric acid. The acids are then separated and thermally decomposed to produce hydrogen and oxygen.

The cycle has been studied in US, Europe and Japan since 1970s, and some important breakthroughs were attained by General Atomics (GA). So far, the research has been carried out in the following fields:

(a) study on the chemistry of each reaction section;

(b) demonstration of the closed-cycle hydrogen production;

(c) heat/mass balance analysis of the process flowsheet;

(d) screening of corrosion-resistant materials and development of advanced chemical reactors.

There are two main issues concerning the chemistry of the reaction and the separation. One is how to separate the hydriodic acid and sulfuric acid produced by the Bunsen reaction. The other is how to carry out the hydrogen iodide decomposition section, where the presence of azeotrope in the vapor-liquid equilibrium of hydriodic acid makes the energy-efficient separation of HI from its aqueous solution difficult and also unfavorable reaction equilibrium limits the attainable conversion ratio of HI to a low level, ca. 20%.

As for the former problem, the researchers of GA found that the mixed acid solution produced by the Bunsen reaction separates spontaneously into two liquid phases in the presence of excess amount of iodine [4]. The heavier phase is mainly composed of HI, I_2, and H_2O, and is called "HIx" solution. The main components of the lighter phase are H_2SO_4 and H_2O. The phenomenon (LL phase separation) offered an easy way of separating the hydriodic acid and the sulfuric acid. As for the hydrogen iodide processing, some ideas have been proposed by GA [4], RWTH Aachen [5] and JAERI. JAERI studied a utilization of membrane technologies for concentrating the HIx solution to facilitate the HI separation and also for enhancing the one-pass conversion of HI decomposition [6,7].

One of the specific and important characteristics of thermochemical water splitting cycles is that the reactants except water are cyclically used in the process. The closed-cycle continuous hydrogen production by Iodine-Sulfur process featuring the LL phase separation has been examined at JAERI. Although the chemistry of sulfuric acid decomposition section and that of hydrogen iodide decomposition section are rather straightforward in terms of reaction and separation, in the Bunsen reaction section, occurrence of side reactions forming sulfur and/or hydrogen sulfide should be suppressed while maintaining the liquid-liquid phase separation. JAERI has devised a basic methodology for the closed-cycle continuous hydrogen production and also for the reaction control in the Bunsen reaction step. Feasibility of the methodology has been demonstrated in small-scale continuous hydrogen production experiments of 1NL-H_2/h and of 30NL-H_2/h, as well [8,9].

Preliminary flowsheeting studies carried out at GA [10,11], RWTH Aachen [5,12], Ecole Polytechnique Montreal [13], CEA [14] and JAERI [15] suggested that the "process thermal efficiency" in the range of 35-50% could be possible assuming intensive heat recovery. Here, the thermal efficiency is defined as the ratio of the Higher Heating Value (HHV) of hydrogen to the net energy input for the process. Precise thermodynamic data concerning the concentrated process solutions is desired for the accurate evaluation of the heat/mass balance.

Since sulfuric acid and halogen are very corrosive, selection of the structural materials is an important issue. Screening tests have been carried out using test pieces of commercially available materials at GA [16], JAERI [17] etc. As for the gas phase environment of H_2SO_4 decomposition step, some refractory alloys that have been used in conventional chemical plants showed good corrosion resistance. Also, in 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, Ta etc showed corrosion resistance. In the environment of HIx distillation, Ta showed excellent corrosion resistance. The severest environment is the boiling condition of concentrated sulfuric acid under high pressure (e.g. 20bar), where ceramic materials containing Si such as SiSiC, SiC, and Si3N4 were the only materials that showed excellent corrosion resistance [18]. In summary, for gas phase service, there exists 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.

One of the key components to be used in the boiling sulfuric acid environments is the sulfuric acid decomposer, in which sulfuric acid solution with concentration of more than 90 wt% is evaporated and, simultaneously, H_2SO_4 is decomposed into gaseous SO_3 and H_2O under high temperature conditions of up to 500°C. Recently, JAERI proposed a concept of the sulfuric acid decomposer, in which multi-hole-blocks made of SiC is used as the heat exchanging units. Feasibility of the concept has been confirmed by preliminary analysis of the mechanical strength and thermal-hydraulic performance, and also by a test-fabrication of prototype ceramic block [19].

JAEA's Pilot Test Plan

At present, JAEA is conducting R&D programmes to develop technologies for the thermochemical hydrogen production using HTGR. The programme covers R&D on HTGR technology, R&D on the system integration technology to connect HTGR and hydrogen production plant, and R&D on Iodine-Sulfur cycle.

As for Iodine-Sulfur cycle, a pilot test is planned as a logical evolution of the above-mentioned studies. In the pilot test, following studies will be carried out [20].

(1) Development of IS process test plant made of engineering materials. Capacity of the plant may be in the range of 10-30m^3-H_2/h, with which smallest components used in industrial chemical plants can be tested such as valves, pumps, etc.

(2) Hydrogen production test using the test apparatus driven by electrically-heated helium gas. Operation of the test plant will demonstrate the technical feasibility of Iodine-Sulfur cycle, and, also, the test data will be used to verify the analytical codes to be developed.

(3) Development of computer code system for analysing the heat/mass balance, for dynamic process simulation, for supporting the component design works, etc.

(4) R&D on advanced low-cost materials that exhibit corrosion resistance in the severe process environments.

(5) R&D on advanced unit operations that enable to improve the heat/mass balance.

(6) Design study on a next-stage test plant to be connected to the HTTR.

After completion of the pilot test of Iodine-Sulfur cycle, it is planned to proceed to the demonstration test of nuclear hydrogen production using HTTR.

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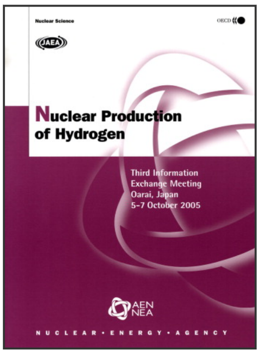

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