ARTICLE IN PRESS

Renewable and Sustainable Energy Reviews xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Progress of nuclear hydrogen production through the iodine–sulfur process in China

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ARTICLE INFO

Keywords:
Nuclear hydrogen production
Progress
Iodine–sulfur process
Simulation
Closed-cycle operation

ABSTRACT

Nuclear hydrogen production is one of the most prospective methods of efficiently producing CO_2-free hydrogen in large scale. In the Institute of Nuclear and New Energy Technology of Tsinghua University in China, research and development on nuclear hydrogen production have been conducted since 2005. This paper presents the progress of nuclear hydrogen production through the iodine–sulfur (IS) process over the past 10 years, including highlights of fundament studies such as the Bunsen reaction and separation characteristics of the $HI/I_2/H_2SO_4/H_2O$ system, the purification of HI_x and sulfuric acid phases, the development of electro–electrodialysis stacks for HI acid preconcentration, and the catalysts used for HI and SO_3 decomposition. Based on the experimental results, the methodology and semi-empirical models for the simulation of key units and the entire IS process were established and verified. Furthermore, two IS facilities aimed at proof-of-concept was created, and an integrated laboratory-scale demonstration of IS process was performed. Closed-cycle experiments were then successfully conducted on these facilities, thereby confirming the feasibility and controllability of the process. Finally, a future plan for nuclear hydrogen was introduced.

1. Introduction

Hydrogen is an important industrial material and a clean, renewable energy carrier with wide-ranging applications in ammonia and methanol synthesis. Hydrogen use in oil refinery and coal-to-oil conversion has also increased in recent years. In addition, H_2 has great application potential in the transportation sector as a fuel and in the production of direct reduction ion as a reductant [1,2]. However, the current hydrogen production approaches, such as steam methane reforming, coal gasification, and alkali electrolysis, cannot meet the huge demand in terms of the atmospheric effect of CO_2 emission and the depletion of fossil fuels in the future. A nuclear hydrogen production utilizes the heat of nuclear reactor; more specifically, a high-temperature gas-cooled reactor (HTGR) is used to split water into H_2 and O_2; this approach is one of the most promising methods with several merits, such as CO_2-free, massive, and efficient hydrogen production [3].

Since the 1970s, high-temperature gas-cooled reactor (HTGR) technology has been undergoing development in China [4]. The 10 MW_{th} test reactor (HTR-10) with spherical fuel elements was constructed in 2000 and reached criticality. In 2003, full power operation was achieved, and a number of safety-related experiments have been conducted on HTR-10. Based on the experiences and research and development (R & D) results of HTR-10, a commercial demonstration plant project, HTR-PM (Pebble Module) was approved and supported by central government of China; this project aimed to build a 200MWe modular HTGR demonstration power plant and to complete related R & D issues. Based on the framework of the 16 top priority projects of the “State Science and Technology Development plan for the period of 2006–2020”, the first concrete pouring of HTR-PM was performed by the end of 2012. Thus, the construction of the HTR-PM was irreversibly started. To date, the project has been smoothly conducted and is predicted to be operational by the end of 2017 [5,6].

HTGR is the most suitable reactor for hydrogen production, R & D on nuclear hydrogen, as a part of the R & D of the HTR-PM project, has been initiated in the Institute of Nuclear and New Energy Technology (INET) in Tsinghua University of China [7]. The iodine–sulfur (IS) thermo-chemical cycle for splitting water and high-temperature steam electrolysis (HTSE) were selected as the main processes for nuclear hydrogen production. Since 2005, INET has conducted fundamental studies on the IS and HTSE processes. A laboratory with the necessary facilities has been established for process studies of nuclear hydrogen. Simultaneously, the HTR-10 constructed in INET will provide a

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http://dx.doi.org/10.1016/j.rser.2017.05.275
Received 6 June 2016; Received in revised form 22 April 2017; Accepted 29 May 2017
1364-0321/

Please cite this article as: Zhang, P., Renewable and Sustainable Energy Reviews (2017), http://dx.doi.org/10.1016/j.rser.2017.05.275

suitable nuclear reactor facility for future R & D of nuclear hydrogen production technology.

The phases of development of nuclear hydrogen in China are as follows. Phase I (2006–2010) involves the fundamental study and process verification of nuclear hydrogen process. Phase II (2011–2015) includes the integrated laboratory-scale test. Phase III (2016–2020) develops the key technologies of pilot scale demonstration. Phase IV (2021–2025) includes the coupling technology with the reactor, nuclear hydrogen production safety, and the pilot- scale test. Phase V goes beyond 2030 and aims at the commercialization of nuclear hydrogen production in China.

The IS process, which was initially proposed by General Atomics Corp. and is considered as the most suitable process for hydrogen production coupled with HTGR, is composed of the following three chemical reactions [4]:

$$\text{Bunsen reaction:}\ \ I_2 + SO_2 + 2H_2O = H_2SO_4 + 2HI \tag{1}$$

$$\text{HI decomposition:}\ \ 2HI = H_2 + I_2 \tag{2}$$

$$\text{Sulfuric acid decomposition:}\ \ H_2SO_4 = SO_2 + 1/2O_2 + H_2O \tag{3}$$

The process has been widely investigated in several institutes worldwide, including the Japan Atomic Energy Agency (JAEA), General Atomics, the Sandia National Laboratory, the French Commissariat à l'Energie Atomique (CEA), the Korean Atomic Energy Research Institute (KAERI), the Korea Institute of Energy Research (KIER) [8–11], and INET.

Although the IS thermochemical cycles was primarily developed for hydrogen production with HTGR as the heat source, this cycles can also be powered by solar heat, as the temperature requirements for the cycle can be met by both sources [12,13].

In recent years, the interest of iodine sulfur for solar hydrogen production is increasing, the cycle is considered as the most promising one to achieve industrial production of high temperature thermochemical cycle technology [14,15]. The sulfuric acid decomposition step has been widely investigated and experimentally demonstrated with solar heat [16]. In addition, the cycle is considered as an effective mean for energy storing in the form of non-degradable chemical bonds, because of its simplicity and efficiency [17].

According to the general schedule of INET, the final objective of the R & D of Chinese nuclear hydrogen program is to achieve the coupling of hydrogen-production technology to the test reactor HTR-10 after 2020 such that nuclear hydrogen production would be demonstrated.

From 2005 onward, intensive fundamental studies have been performed at INET, a proof-of-concept facility (IS-10) and an integrated lab scaled facility (IS-100) were constructed one after another. The closed-cycle continuous operation was successfully conducted with these facilities.

This paper summarizes the main progress of R & D on the IS process in China. Firstly, the key fundamental researches of IS cycle, including phase separation characteristics in Bunsen reaction, purification of HI_x and sulfuric acid phases, electro-electrodylysis, catalysts for the decomposition of HI and sulfuric acid decomposition are summarized and reviewed; then an overview of IS cycle simulation, including the custom-built models for Bunsen section, EED and HI_x distillation unit; the whole process simulation methodology, and process optimization, is presented. Thirdly, the closed cycle facilities and continuous operation results is introduced. Finally, the future plan on the R & D of nuclear hydrogen production is put forward.

2. Fundamental studies on IS process

As described, the IS process consists in three chemical reactions, with several important separation and purification units. In addition, electro-electrodialysis (EED) was used to preconcentrate the HI solution over pseudo-azeotropic composition. A typical diagram of the IS process developed in INET is shown in Fig. 1 to demonstrate the main unit operation, the entire process can be divided into three sections according to the corresponding reaction. The main fundamental studies focused on the unit operations, which greatly influences the closed-cycle operation or process efficiency, including the Bunsen reaction and product separation, the purification of HI_x (refers to the mixture of HI, I_2 and H_2O) and H_2SO_4 phases formed by Bunsen reaction, the preconcentration of HI_x, and the catalysts used for HI and SO_3 decomposition, among others.

2.1. Bunsen reaction and phase separation

The Bunsen reaction cannot spontaneously proceed with its positive thermodynamic free energy change (ΔG^0_{400K} = +82 kJ/mol) [18]. Excessive water and iodine are needed for making the reaction thermodynamically favorable. In addition, excessive iodine is also needed to separate the formed H_2SO_4 and HI. Therefore, the actual Bunsen reaction usually proceeds according to following formula [19]:

$$\begin{aligned} xI_2 + SO_2 + (n+2)H_2O \ \Leftrightarrow\ & [H_2SO_4 + (n-m)H_2O] \\ & + [2HI + (x-1)I_2 + mH_2O] \end{aligned} \tag{4}$$

The amounts of water and iodine affect the thermodynamics, phase separation characteristics, and the impurity content in the separated acids. Several studies were focused on the optimization of reaction conditions and phase separation characteristics. Numerous studies on the reaction and phase separation behaviors of $HI–H_2SO_4–I_2–H_2O$ quaternary mixture have been conducted and published. We summarized the primary objectives of the optimization. Both the reaction and the phase separation can spontaneously occur, and cross-contamination is minimized. To meet these requirements, the amount of excess of water and iodine is minimized because the excess of water and iodine will lead to decreasing of the efficiency of the process.

Unlike other institutions, we studied the separation characteristics of the Bunsen products in terms of phase equilibrium. The phase states and compositions of the quaternary mixture $HI/I_2/H_2SO_4/H_2O$ were experimentally investigated at 20–80 °C; the critical conditions of the phase separation, iodine solubility in the mixture, and inter-miscibility of the constituents in the solution were ascertained [20,21]. The favorable concentration range of each component in the Bunsen products mixture was illustrated with a tetrahedral diagram shown in Fig. 2. Within the desired concentration range, the solution spontaneously separates into two liquid phases without iodine precipitation. In addition, a computer program was developed to easily ascertain the phase state of the quaternary mixture with a given composition.

Compare with the common reactions, the reactants and operational parameters under the continuous IS closed-cycle conditions differ from those under initial conditions of Bunsen reaction. However, only a few studies have considered the situation under recycled conditions. We studied the Bunsen reaction under simulated closed-cycle conditions, i.e., the reaction between a $I_2/HI/H_2O$ solution and SO_2 [22]. The effects of reaction conditions, including SO_2 flow rate, HI acid concentration, I_2/HI molar ratio, and temperature, on the characteristics of the Bunsen products were examined. These characteristics include the phase states, volume ratio, and compositions of the HI_x and H_2SO_4 phases. The concentration of HI acid and the I_2/HI molar ratio of the initial solution, rather than other factors, predominantly affect the phase states and compositions of the products. The empirical models for phase states prediction and calculation of the compositions of products were built based on the experimental studies. The calculation results well agreed with the experimental ones. These results validated the reliability of the models and offered crucial reference and guidance for the operation of the closed-cycle IS process.

Thus far, published data implies that the issues of thermodynamics, parameter optimization, and phase separation are well addressed. However, other crucial issues affecting design and scale-up of reactors are seldom considered or studied. One such issue is the reaction kinetics under various conditions, especially the effect of phase