

Modeling and Simulation of the Sulfur-Iodine Process Coupled to a Very High-Temperature Gas-Cooled Nuclear Reactor

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1. Introduction

Global concern for increased energy demand, energy security, and global warming are leading to heightened interest in using nuclear energy and hydrogen. Hydrogen produced from water using nuclear energy will avoid both the use of fossil fuels and CO₂ emission presumed to be the dominant reason for global warming. A thermo-chemical sulfur-iodine (SI) process coupled to a Very High Temperature Gas-Cooled Reactor (VHTR) is one of the most prospective hydrogen production methods that split water using nuclear energy because the SI process is suitable for large-scale hydrogen production without CO₂ emission.

The SI process was initially introduced by General Atomic (GA) Company [1] and has been widely studied in many countries. Recently, laboratory-scale experimental results of the SI process, which was carried out by Sandia National Laboratory, GA and the French Commissariat à l'Energie Atomique (CEA) were reported [2]. The Japan Atomic Energy Agency (JAEA) has also achieved the continuous operation of the 31 NL H₂/hr scale SI facilities for 175 hours in 2004 [3]. JAEA constructed the High Temperature Engineering Test Reactor (HTTR) which belongs to a high temperature gas-cooled reactor (HTGR), and achieved a reactor-outlet coolant temperature of 950 °C at the reactor [4]. On the other hand, JAEA performed a dynamic calculation of two cases for the thermal load increase events in the HTTR-SI process using their newly developed Advanced Process Heat Exchanger (APHX) module in 2007 [5]. The APHX module consists of 3 modules: a H₂SO₄ decomposition module, SO₃ decomposition module, and HI decomposition module. Their dynamic calculations were performed in the two cases of heating loss at the H₂SO₄ concentration unit and cooling loss at the HI distillation column condenser. At the Institute of Nuclear and New Energy Technology (INET) of Tsinghua University, a lab-scaled integrated facility of the SI cycle was constructed in 2007, and a closed cycle experiment was successfully performed for 7 hours with hydrogen production rate of 10 NL/hr in 2009 [6]. The Korea Atomic Energy Research Institute (KAERI) has introduced an electro-dialysis cell (EDC) and membrane reactor (MR)-embedded SI process with the Korea Institute of Energy Research (KIER) [7].

In the case of the design, construction, and operation of a SI process, one of the key issues is how to operate the SI process such as a start-up operation procedure.

The purpose of this study is to introduce the dynamic simulation code to establish the start-up procedure of

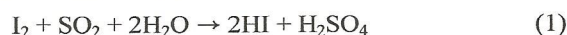
the SI process. To achieve this purpose, several component modules are physically combined into an integrated simulation code applying the time lag concept based on the plug flow model at the pipe line connecting reactors. The dynamic simulation code enables users to manage in/output data based on the graphic user interface (GUI) operating system.

2. VHTR-based SI process

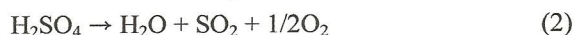
2.1 SI process

The hydrogen production by the SI process coupled to the VHTR through an intermediate heat exchanger (IHX) is achieved by the following three chemical reactions while iodine and sulfur dioxide are recycled throughout the process.

- Bunsen reaction



- Sulfuric acid decomposition



- Hydriodic acid decomposition



The SI process can be divided into three sections based on the chemical reactions representing the characteristics of each section: a Bunsen reaction section (Section 1), a sulfuric acid concentration and decomposition section (Section 2), and a hydriodic acid concentration and decomposition section (Section 3). In Section 1, the exothermic Bunsen reaction (1) splits the water to produce two kinds of acid (H₂SO₄ and HI) from SO₂ and I₂. Reaction products of the Bunsen reaction are separated under excess iodine and water due to a density difference and sent to the decomposition sections for a conversion to O₂ and H₂. The heat required in the SI process can be supplied through an intermediate heat exchanger (IHX) by the VHTR. The primary and secondary helium loops are used as high-temperature energy carrier gas ducts from the VHTR to the SI process through the IHX.

2.2 Model of VHTR-SI process

A model of the dynamic simulation code for the SI process is shown in Fig. 1. The model consists of the VHTR, the IHX, and the SI process for hydrogen production system. In the SI process, chemical reactors that receive thermal energy directly from the secondary helium of the IHX are as follows: a sulfuric acid vaporizer, a sulfuric acid decomposer, a sulfur trioxide decomposer, and a hydriodic acid decomposer including pre-heating part. On the other hand, two reboilers for the H₂SO₄ and HI distillation are heated by

the sensible or latent heat of the SI process stream [7]. In Fig. 2, stock solution tank 1, stock solution tank 2, and the HI_x vaporizer are additional equipment to establish the start-up procedure.

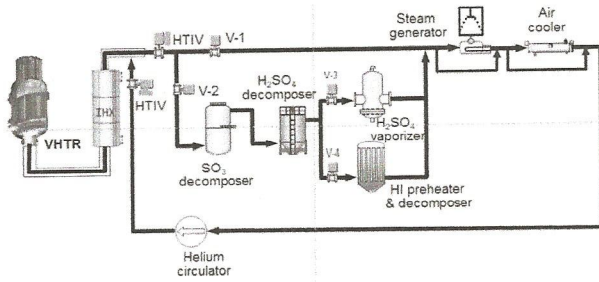


Fig. 1. Model of the VHTR-based SI process.

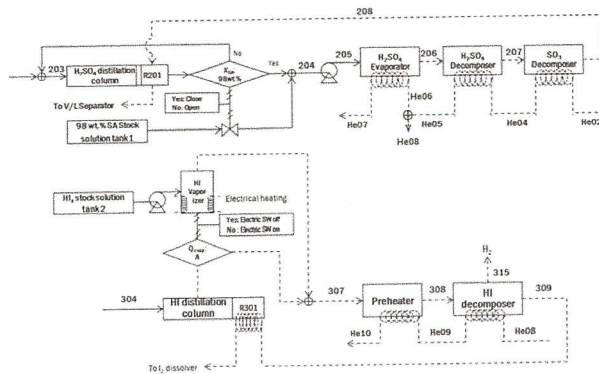


Fig. 2. Process flow diagram for start-up.

Stock solution tank 1 contains a sulfuric acid solution of 98 weight % at 233.8 °C and supplies it into the sulfuric acid vaporizer until a concentration of the bottom product discharged from the sulfuric acid solution distillation reaches at a steady state. Stock solution tank 2 also contains a HI_x mixture solution of weight fraction of [H₂O]:[HI]:[I₂] = 0.133:0.207:0.660 and supplies it into the HI_x vaporizer. The HI_x vaporizer produces a HI mixture vapor using electrical heating and supplies it into the HI pre-heater until the heat of the HI-rich vapor discharged from the top of the HI_x distillation column meets the energy requirement needed to operate the reboiler of the HI_x distillation column (R301).

In Section 2, a sulfuric acid solution of 81 weight % is fed to the H₂SO₄ distillation column through stream 203, where the sulfuric acid solution concentrated up to 98 weight % is obtained at the bottom (stream 204) and the diluted solution is obtained from the top of the column. The concentrated sulfuric acid solution is then fed to the sulfuric acid vaporizer through stream 205, where it is evaporated and a process gas of H₂O/H₂SO₄ is then generated. For the additional decomposition of the H₂SO₄ vapor, the process gas is sent to the sulfuric acid decomposer through stream 206 and the sulfur trioxide decomposer through stream 207, where SO₃ gas made in the sulfuric acid decomposer is catalytically decomposed into SO₂ and O₂ under high-temperature conditions of about 850 °C. The process

gas mixture of SO₃/SO₂/H₂O/O₂ discharged from stream 208 passes over the reboiler (R201) of the H₂SO₄ distillation column to supply heat energy.

In Section 3, a HI_x solution discharged from the cathode chamber of the electro-dialysis cell (EDC) is fed to the HI_x distillation column through stream 304, where HI-rich vapor is obtained from the top (stream 307) and a HI_x solution of a pseudo-azeotropic composition is obtained at the bottom of the column. The HI-rich vapor is fed to the preheater and HI decomposer through streams 307 and 308, where only H₂ is separated from the decomposed gas mixture of H₂/I₂/HI/H₂O. The H₂-removed HI vapor (stream 309) discharged from the HI decomposer passes over the reboiler (R301) of the HI_x distillation to supply heat energy.

The helium at a temperature of 910 °C discharged from the IHX is fed to the shell side of the sulfur trioxide decomposer through stream He02, and the helium vented from the sulfur trioxide decomposer flows into the shell side of the sulfuric acid decomposer through stream He04. The helium discharged from the sulfuric acid decomposer through stream He05 is split into the two streams. One is stream He06 that flows into the tube side of the sulfuric acid evaporator in Section 2, and the other is stream He08 that flows toward the hydriodic acid decomposer in Section 3. The helium vented from the sulfuric acid vaporizer is recycled to the IHX through stream He07, and He10 to receive thermal energy from the primary helium loop of the IHX.

3. Basic equations of the SI components

3.1 H₂SO₄ vaporizer

A short tube vertical evaporator was selected as the vaporizer of the 98 wt% H₂SO₄ solution, which is near an azeotropic composition in Section 2 of the SI process. We can establish the following mathematical models by assuming that the aqueous phase in the vaporizer vessel is homogeneous at a uniform temperature.

$$\text{If } T_{aq,in} \leq T < T_b,$$

$$\rho c_p V \frac{dT}{dt} = UA \left(\frac{T_{He,in} + T_{He,out}}{2} - T \right) \quad (4)$$

$$T_{He,out}(t) = \left\{ \left(\frac{F_{He} c_{p,He}}{UA} - \frac{1}{2} \right) T_{He,in} + T(t) \right\} / \left(\frac{F_{He} c_{p,He}}{UA} + \frac{1}{2} \right) \quad (5)$$

$$\text{If } T = T_b,$$

$$Q = UA \Delta T_{lmd} \quad (6)$$

$$\Delta T_{lmd} = \frac{T_{He,in} - T_{He,out}}{\ln \left(\frac{T_{He,in} - T_b}{T_{He,out} - T_b} \right)} \quad (7)$$

$$\omega = Q / \lambda \quad (8)$$

Where, ρ (mol/m³) and c_p (kJ/(mol K)) are the molar density and heat capacity of the 98 wt% H₂SO₄ solution, V (m³) is the effective volume of the vaporizer charged by the sulfuric acid solution, $T_{aq,in}$ (K) is the temperature of the inlet sulfuric acid solution, T (K) is the average temperature of the sulfuric acid solution in

the vaporizer, T_b (K) is the boiling point of the 98 wt % sulfuric acid solution at a given operation pressure, $T_{He,in}$ (K) and $T_{He,out}$ (K) are the helium inlet and outlet temperatures at the vaporizer, $c_{p,He}$ (kJ/(mol K)) and F_{He} (mol/s) are the heat capacity and molar flow rate of the helium, U (kJ/(m² s K)) is the over-all heat transfer coefficient, A (m²) is the total heat transfer area of the vaporizer, and λ (kJ/mol) and ω (mol/s) are the latent heat and vaporization rate of the 98 wt% H₂SO₄ solution.

3.2 H₂SO₄, SO₃, and HI decomposers

The process gas in the tube side of a shell-and-tube type decomposer is heated by the high temperature helium in the shell side of the decomposer. The process gas and helium stream maintain a count-current flow in the tube and shell sides, respectively. The decomposition of each component takes place inside the tube, and this chemical reaction requires a proper volume to maintain a sufficient residence time.

Based on this type of decomposer, we can establish the following mass and energy balances in a differential volume of the tube side from a longitudinal length L to $L+dL$ at a differential time.

$$-\frac{\partial F_i}{\partial V_{RX}} - (-r_i) = \frac{\partial C_i}{\partial t} \quad (9)$$

$$Ua(T_{He} - T_i) - \sum_i F_i c_{p,i} \frac{\partial T_i}{\partial V_{RX}} + (-r_i)(-\Delta H_{RX}) = \sum_i C_i c_{p,i} \frac{\partial T_i}{\partial t} \quad (10)$$

where F_i (mol/s) is the molar flow rate of the i_{th} component, V_{RX} (m³) is the reactor volume, $-r_i$ (mol/(m³ s)) is the decomposition rate of the i_{th} component, C_i (mol/m³) is the molar concentration of the i_{th} component in the reactor, t (s) is the operation time, U (kJ/(m² s K)) is the overall heat transfer coefficient, a (m²/m³) is the heat transfer area across the wall of the tube per tube volume, T_{He} (K) and T_i (K) are the fluid temperatures of the helium and i_{th} component, respectively, $c_{p,i}$ (kJ/(mol K)) is the heat capacity of the i_{th} component, ΔH_{RX} (kJ/mol) is the heat of the i_{th} component decomposition.

3.3 Distillation columns for H₂SO₄ and HI_x aqueous solutions

The dynamic simulation code has two modules corresponding to two distillation columns in the SI process. One is the module to simulate the dynamic behavior of the H₂SO₄/H₂O binary system distillation column to obtain the 98 weight % H₂SO₄ solution, and the other is the module for the HI/I₂/H₂O ternary system distillation column. The total mass and component balances and heat balance commonly applied in the mathematical model of the two distillation columns are as follows.

Total Mass balance:

$$\frac{dM_n}{dt} = V_{n+1} + L_{n-1} - V_n - L_n + F_{nf} \quad (11)$$

Component balance:

$$\frac{dM_n^{x_{n,i}}}{dt} = V_{n+1}(y_{n+1,i} - x_{n,i}) + L_{n-1}(x_{n-1,i} - x_{n,i}) - V_n(y_{n,i} - x_{n,i}) + F_{nf}(x_{nf,i} - x_{n,i}) \quad (12)$$

Heat balance:

$$\frac{dM_n h_n^L}{dt} = V_{n+1}(h_{n+1}^V - h_n^L) + L_{n-1}(h_{n-1}^L - h_n^L) - V_n(h_n^V - h_n^L) + F_{nf}(h_{nf}^L - h_n^L) \quad (13)$$

where M_n (mol) is a holdup, L_n (mol/s) is the flow rate of liquid leaving stage n , V_n (mol/s) is the flow rate of vapor leaving stage n , and F_{nf} (mol/s) is the flow rate of liquid feeding stage n . $x_{n,i}$ is the mole fraction of component i in the liquid phase leaving stage n , $y_{n,i}$ is the mole fraction of component i in the vapor phase leaving stage n , and $x_{nf,i}$ is the mole fraction of component i in the liquid feeding stage n . Also, h_n^L (kJ/mol) is the enthalpy of liquid leaving stage n , h_n^V (kJ/mol) is the enthalpy of vapor leaving stage n , and h_{nf}^L (kJ/mol) is the enthalpy of liquid feeding stage n .

4. Simulation Results

In order to simulate the start-up dynamic behaviors of a VHTR-based SI process coupling system, the prepared individual component modules should be integrated sequentially according to the model of the VHTR-SI process coupling system shown in Fig. 1. The inlet helium temperature is 910°C and the inlet temperature of the H₂SO₄ is 233.8°C. The operation pressure of Sections 2 and 3 is 7 bar and 40bar, respectively. Helium of 910°C is introduced into the SO₃ decomposer and the same molar flow rate of 16,698mol/s is maintained at the H₂SO₄ decomposer. However, the outlet helium from the H₂SO₄ decomposer is introduced into two separated pipes, one is connected to the H₂SO₄ vaporizer and the other to the HI decomposer. In this case, the normal flow rate conditions of the helium are 12,483mol/s for the H₂SO₄ vaporizer and 4,215mol/s for the HI decomposer.

When the individual modules are interlinked with each other through pipelines for the SI process stream and helium flow, the time lag between two connected modules through pipeline has to be considered for the start-up dynamic simulation results on a correct time domain. In this study, the time lags were therefore calculated by dividing the internal pipeline volumes based on the volumetric flow rates of the SI process stream and helium flow.

As a precondition before the dynamic simulation of the SI process, it has been assumed that helium of 910 °C discharged from the IHX is recycling through the secondary helium loop without any heat loss and thermally equilibrated with the stagnant helium filled out at the tube sides of the H₂SO₄ and SO₃ decomposers and the HI pre-heater including the HI decomposer. On the other hand, the sulfuric acid solution of 98wt% H₂SO₄ and 2wt% H₂O filled up to the predetermined level in the short tube vertical vaporizer are maintained at 233.8°C initially owing to the closing of the three-way valve to pass the helium.

The start-up dynamic simulation of the VHTR-SI coupling system is commenced by turning on a switch of the pump connected to stock solution tank 1, and the operation of the HI_x vaporizer begins at the same time. Fig. 3 shows the start-up behaviors of the temperatures

of helium at the helium pipelines and concentrations of the SI process streams. As shown in Fig. 3, the start-up behaviors of the helium temperatures at the helium pipelines were finally confirmed that the coupling system reached a steady state. The start-up behaviors of the chemical reactors took 20 and 180 seconds to reach the steady state conditions of Section 2 and 3, respectively.

5. Conclusions

The dynamic simulation code to evaluate the start-up behavior of the chemical reactors placed on the secondary helium loop of the SI process has been developed and partially verified using the steady state values obtained from the Aspen Plus™ Code simulation. As the start-up dynamic simulation results of the SI process coupled to the IHX, which is one of components in the VHTR system, it is expected that the integrated secondary helium loop of the SI process can be successfully and safely approach the steady state condition. To experimentally validate and verify the dynamic simulation program, the integrated SI process test facilities of 50 NL_{H₂}/h, which will be operated under a maximum operation pressure of 10 bars, has been installed.

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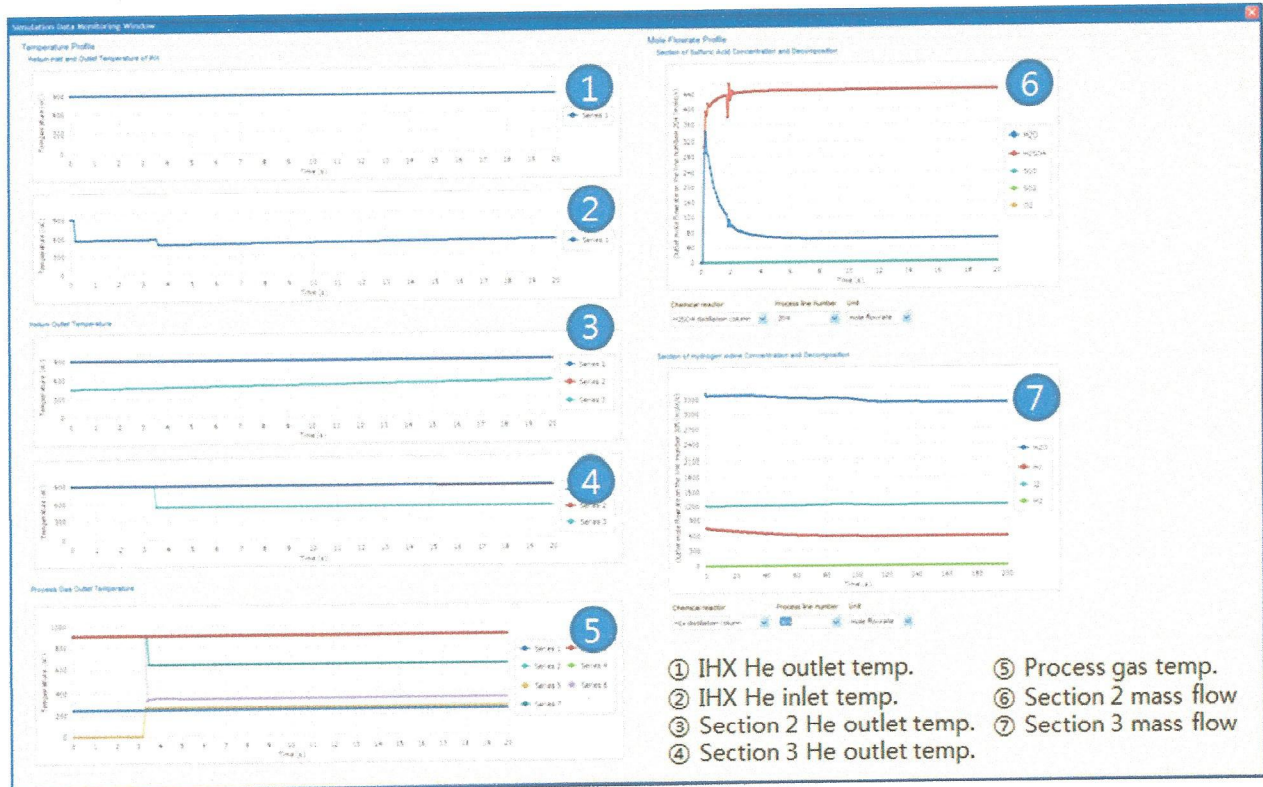


Fig. 3. Start-up behaviors of SI process.