

Numerical simulation of H₂SO₄ thermal decomposer for a VHTR helium loop-based SI hydrogen production test facility

Youngjoon Shin*, Taehoon Lee, Juho Lee, Kiyoun Lee, Changkeun Jo, Minhwan Kim

Korea Atomic Energy Research Institute 150 Dukjin-dong, Yuseong-gu, Daejeon, Republic of Korea 305-600

* Corresponding author: njshin@kaeri.re.kr

1. Introduction

A VHTR-based method of generating hydrogen from the Sulfur-Iodine (SI) cycle is one of the promising approaches to produce massively hydrogen shown in Fig. 1 [1-4].

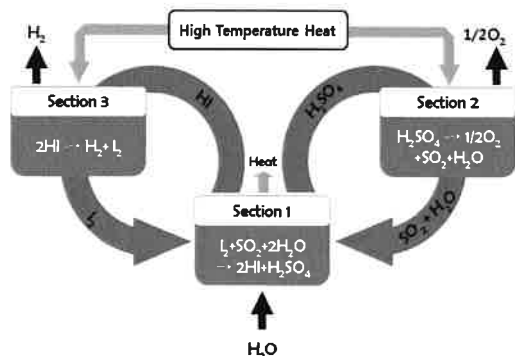


Fig. 1. SI hydrogen production cycle.

Based on the previous study on the experimental performance test of the bayonet type H₂SO₄ thermal decomposer for a 50 NL-H₂/h SI test facility [5], which was directly heated using electrical heating chambers, a H₂SO₄ decomposer for the 1 Nm³-H₂/h SI test facility coupled to an out-of-pile helium loop (SP-SATD-1000L) has been designed, and it was theoretically confirmed that the design specifications satisfy the hydrogen production capacity based on a Computational Fluid Dynamics (CFD) analysis. The effect of the overall heat transfer coefficient on the helium outlet temperature and decomposition percentage of the decomposer was identified. The H₂SO₄ decomposer proposed is capable of outlet helium temperatures of 734 °C for an overall heat transfer coefficient of 5 W/m²-K, which satisfies the operating temperature condition of the out-of-pile helium loop. The average thermal decomposition percentage of the proposed decomposer is 60.4 % for sulfuric acid. The decomposition percentage obtained from the numerical result is acceptable with a hydrogen production rate of 1 Nm³-H₂/h.

2. Description of SP-SATD-1000L

Based on the bayonet type decomposer of the SNL, a multi-bayonet tube reactor for H₂SO₄ decomposition, SP-SATD-1000L, for the 1 Nm³-H₂/h scale SI test facility has been designed and a schematic representation of the decomposer is shown in Fig. 2.

The SP-SATD-1000L is prepared using 19 silicon carbide (SiC) tubes with a hemispheric end. A hexagonal tube bundle of 19 SiC tubes is arrayed with a regular triangle pitch of 39.7 mm. The single SiC tube (31.5 mm-OD, 25.4 mm-ID, 1,300 mm-H) equipped with a SiC pipe (19.1 mm-OD, 16.1 mm-ID, 1,205 mm-H in recuperator zone, 12.7 mm-OD, 9.7 mm-ID, 150

mm-H in catalyst zone) inside the SiC tube has the following multiple-functions: evaporation of a H₂SO₄ aqueous solution, primary thermal decomposition of H₂SO₄, and secondary catalytic thermal decomposition of SO₃ consecutively generated from the primary thermal decomposition of H₂SO₄. The H₂SO₄ aqueous solution is introduced into the distribution header located in the bottom part of the decomposer.

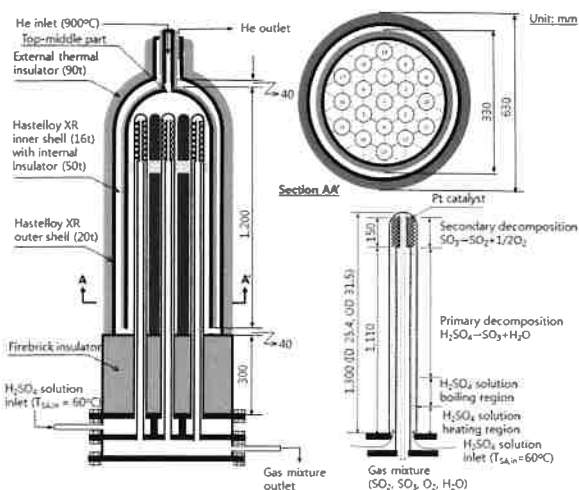


Fig. 2. Schematic of the H₂SO₄ decomposer (SP-SATD-1000L) for the 1 Nm³-H₂/h scale SI test facility.

The helium flows down along the axial direction of the inner shell and provides thermal energy in 19 bayonet tubes, and then flows up along the outer annulus between the inner and outer shells with insulation to prevent heat loss.

The H₂SO₄ solution and gas are heated by high-temperature helium outside the SiC tube and the downstream gas mixture in the SiC pipe. The introduced SA solution flows up along the annulus between the outer SiC tube and inner pipe, assuming a uniform flow at each SiC tube. At the bottom of this annular region, heat is recuperated from the process gas flow downward along the inner SiC pipe, and the heat transferred from the recuperation vaporizes the incoming H₂SO₄ solution. Afterward, the vaporized H₂SO₄ is superheated in the outer annulus and decomposed to SO₃ and H₂O prior to reaching the catalyst region. The catalytic ring is packed into the top of the annulus between the SiC tube and pipe, which acts like a porous zone through which the mixture of SO₃ and H₂O vapor passes. The SO₃ is decomposed into SO₂ and O₂ at the catalyst region. It is expected that the maximum temperature of the process gas stream will be revealed just before entering downward into the inner SiC pipe. The decomposed gas mixture continuously flows down.

The bayonet tubes are contained in an inner Hastelloy XR shell (198.4 mm-ID, 230.4 mm-OD, 1,150 mm-H) with internal insulation to facilitate a heat transfer from the helium to the bayonet tubes. The helium flow path was designed such that the high-temperature helium of 900 °C enters the central top of the inner shell and provides thermal energy to the bayonet SiC tubes for the vaporization and decomposition of the sulfuric acid. And then the helium flows up along the outer annulus between the inner and outer shells with insulation to reduce heat loss from helium to the external air environment. The helium flow inside the inner and outer shells involves conjugate heat transfer and heat loss in the external surrounding air. This shell-and-tube type decomposer for the SI test facility has a firebrick insulator of 300 mm in height to minimize the thermal cycling stress at the bottom connecting joints between the inlet part of the sulfuric acid aqueous solution and the bottom of the outer Hastelloy XR shell (410.4 mm-ID, 450.4 mm-OD, 1,300 mm-H).

3. Simulation results

Fig. 3 shows the velocity contour of the longitudinal plane inside the SP-SATD-1000L at the overall heat transfer coefficient of the outer shell of 5 W/m²-K. The helium velocity displays a maximum velocity of 18.8 m/s just after discharging from the top nozzle, and is reduced to 3.8 m/s after passing through the inner shell. The helium velocity profile inside the inner shell is decreased from 11.3 m/s to 1.9 m/s along the radial direction at the top of the bayonet tubes and decreases from 11.3 m/s to 1.5 m/s in a down direction around the center bayonet tube, as shown in Fig. 3. A circulation region due to the vortex formation is also observed at the top disengagement section of the inner shell.

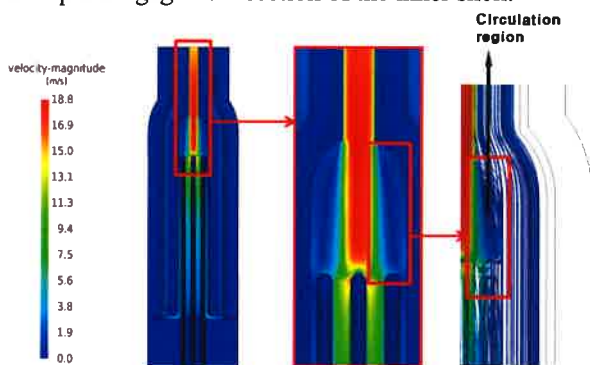


Fig. 3. Velocity contour of a longitudinal plane inside the SP-SATD-1000L at 5 W/m²-K.

However, the uniform inlet flow rate of the sulfuric acid aqueous solution into the 19 tubes is assumed to simplify the numerical calculation. The velocity of the sulfuric acid aqueous solution and vapor inside the single tube is almost negligible when compared with the helium velocity, appearing to be around 0.004 m/s in the H₂SO₄ aqueous zone, 0.06 m/s in the H₂SO₄ mixed-gas zone, and 0.18 m/s in the catalyst zone, as shown in Fig. 4.

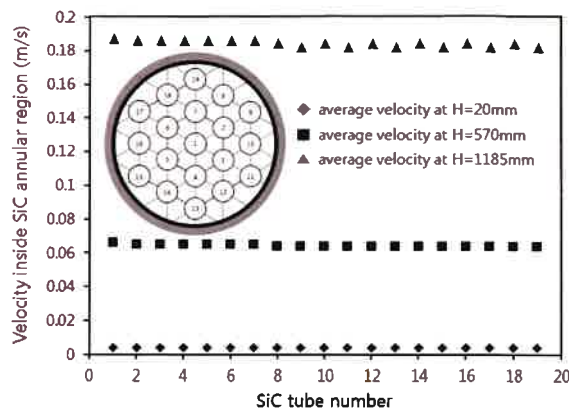


Fig. 4. Velocity distribution inside annular region of each SiC tube at 5 W/m²-K.

In Fig. 5, the contours of static temperatures inside the SP-SATD-1000L are reported for two simulation results with respect to the overall heat transfer coefficients of the outer shell covered with a thermal insulator of 5 W/m²-K and 10 W/m²-K. The outlet temperatures of helium are 734 °C for an overall heat transfer coefficient of 5 W/m²-K and 565 °C with an overall heat transfer coefficient of 10 W/m²-K. The former case satisfies the inlet temperature condition for the SP-HITD-1000L, but the latter case is lower than 734 °C, which is the inlet temperature condition for the SP-HITD-1000L. Based on this result, the overall heat transfer coefficient should be maintained at least below 5 W/m²-K because outlet temperature of the SP-HITD-1000L is too low to supply heat to the H₂SO₄ distillation column and the HI_x distillation column, if the outlet temperature of the SP-SATD-1000L is below 734 °C. At the bottom of the annular region of the H₂SO₄ aqueous solution inlet, heat is recuperated from the decomposed gas mixture flow downward along the inner pipe. The combined heat from this recuperation and the firebrick heat conduction vaporizes the incoming H₂SO₄ aqueous solution. The boiling region of the 95 % H₂SO₄ solution is located within 7 to 27 mm from the bottom at 5 W/m²-K, and 10 to 30 mm at 10 W/m²-K, which is far from the catalyst-packed region. The predictions for this aqueous level and the boiling region of the H₂SO₄ solution are very important to prevent damage by the H₂SO₄ solution to the catalyst for SO₃ decomposition. The helium around tube number "1" in Fig. 2 is cooled from 900 °C to 746 °C at 5 W/m²-K and 724 °C at 10 W/m²-K, and flows down to the bottom of the shell. The H₂SO₄ vapor evaporated in tube number "1" is super-heated to 789 °C at 5 W/m²-K and 785 °C at 10 W/m²-K, and flows up to the top of the tube. The minimum temperature differences of 66 °C at 5 W/m²-K and 57 °C at 10 W/m²-K between helium and H₂SO₄ stream are revealed at the top of the tube numbers 9, 11, 13, 15, 17, and 19.

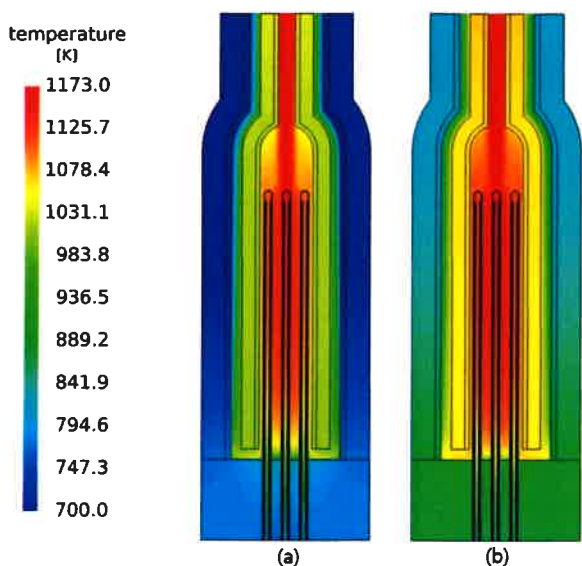


Fig. 5. Temperature contour of a longitudinal plane inside the SP-SATD-1000L; (a) 10 W/m²-K and (b) 5 W/m²-K.

It is expected that the vaporized H₂SO₄ decomposes completely to SO₃ and H₂O prior to reaching the catalyst-packed region, and the decomposition of SO₃ takes place in the catalyst-packed region maintaining the maximum temperature in the process stream flow path inside the tube shown in Fig. 6. The maximum temperatures of 789 °C and 785 °C in both cases are observed for tube number “1” in Fig. 2, and the minimum temperatures of 754 °C and 734 °C at the outside tubes.

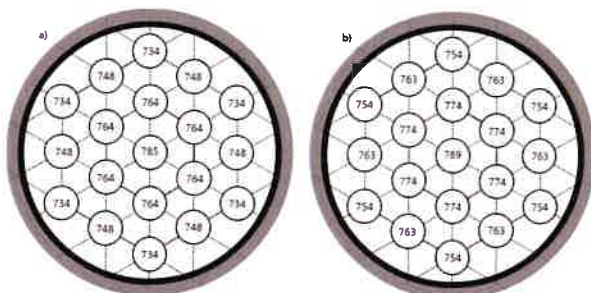


Fig. 6. Maximum temperature (°C) in each tube of the SP-SATD-1000L: (a) 10 W/m²-K and (b) 5 W/m²-K.

As can be seen from Fig. 7, the equilibrium conversion percentage of H₂SO₄ to SO₂ in each tube was 57.8 to 65.6 % for an overall heat transfer coefficient of 5 W/m²-K, and 53.0 to 64.8 % at the overall heat transfer coefficient of 10 W/m²-K.

Taking the equilibrium conversion percentage ($P_{i,j}^e$) and flow rate ($m_{i,j}$) of sulfuric acid gas in the j th tube into account using Eq. (1), the average equilibrium conversion percentage ($P_{i,mean}^e$) of H₂SO₄ in the SP-SATD-1000L can be calculated.

$$P_{i,mean}^e = \frac{\sum_j P_{i,j}^e m_{i,j}}{\sum_j m_{i,j}} \quad (1)$$

By assuming the uniform inlet flow rate of the H₂SO₄ aqueous solution into the 19 tubes, the average H₂SO₄ thermal decomposition percentages for SO₂ of 60.4 % and 56.9 % are anticipated at overall heat transfer coefficients of 5 W/m²-K and 10 W/m²-K, respectively. The value of 60.4 % satisfies the design basis of 1 Nm³-H₂/h hydrogen productivity; however, the value of 56.9 % is the insufficient decomposition percentage equivalent to 0.9 Nm³-H₂/h.

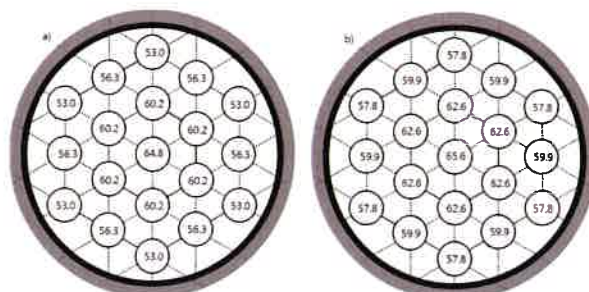


Fig. 7. Equilibrium conversion (%) of sulfuric acid decomposition in each tube of the SP-SATD-1000L: (a) 10 W/m²-K and (b) 5 W/m²-K.

4. Conclusions

A creative semi-pilot scale H₂SO₄ thermal decomposer (SP-SATD-1000L) for a 1 Nm³-H₂/h SI test facility incorporating heat transfer devices through coupling with the out-of-pile helium loop were newly designed. A numerical analysis was carried out using Computational Fluid Dynamics (CFD) software to simulate and analyze the helium flow pattern, temperature distribution, and thermal decomposition percentages of H₂SO₄. The work highlighted the effect of the overall heat transfer coefficient on the helium outlet temperatures, maximum temperature in the reactor tubes, and the decomposition percentages. Outlet helium temperatures of the H₂SO₄ decomposer was 734 °C for an overall heat transfer coefficient of 5 W/m²-K, which satisfy the operating temperature conditions of the out-of-pile helium loop. The average thermal decomposition percentages of the proposed decomposers was shown to be 60 % for H₂SO₄ in the case of an overall heat transfer coefficient of 5 W/m²-K.

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (No. 2017M2A8A1014757).

REFERENCES

- [1] G. E. Besenbruch, L. C. Brown, D. R. O’Keefe, and C. L. Allen, “Thermochemical Water-splitting Cycle, Bench-scale Investigations, and Process Engineering”, DOE/ET/26225-1, General Atomic Company; 1982.
- [2] S. Kasahara, S. Kubo, K. Onuki, and M. Nomura, “Thermal Efficiency Evaluation of HI Synthesis/Concentration Procedures in the Thermochemical Water Splitting IS Process”, International Journal of Hydrogen Energy, Vol. 29, p. 579, 2004.
- [3] S. Goldstein, J. M. Borgard, and X. Vitart, “Upper Bound and Best Estimate of the Efficiency of the Iodine Sulfur

Cycle”, *International Journal of Hydrogen Energy*, Vol. 30, p. 619, 2005.

[4] Y. Shin, K. Lee, Y. Kim, J. Chang, W. Cho, and K. Bae, “A Sulfur-Iodine Flowsheet Using Precipitation, Electrodialysis, and Membrane Separation to Produce Hydrogen”, *International Journal of Hydrogen Energy*, Vol. 37, p. 16604, 2012.

[5] J. Park, J. Cho, H. Jung, K. Jung, S. Kumar, and I. Moon, “Simulation and experimental study on the sulfuric acid decomposition process of SI cycle for hydrogen production”. *International Journal of Hydrogen Energy*, Vol. 38, p. 5507, 2013.