# Reactors for sulfuric acid decomposition in hydrogen production by thermo-catalytic cycles


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In the thermochemical cycles: S – I, S – Br hybrid, and S – Hybrid for industrial hydrogen production the decomposition of sulfuric acid into sulfur dioxide and oxygen represents the step with the biggest energetic consumption, according that reaction takes place only at temperature of 850 – 1200°C in the presence of a catalyst.

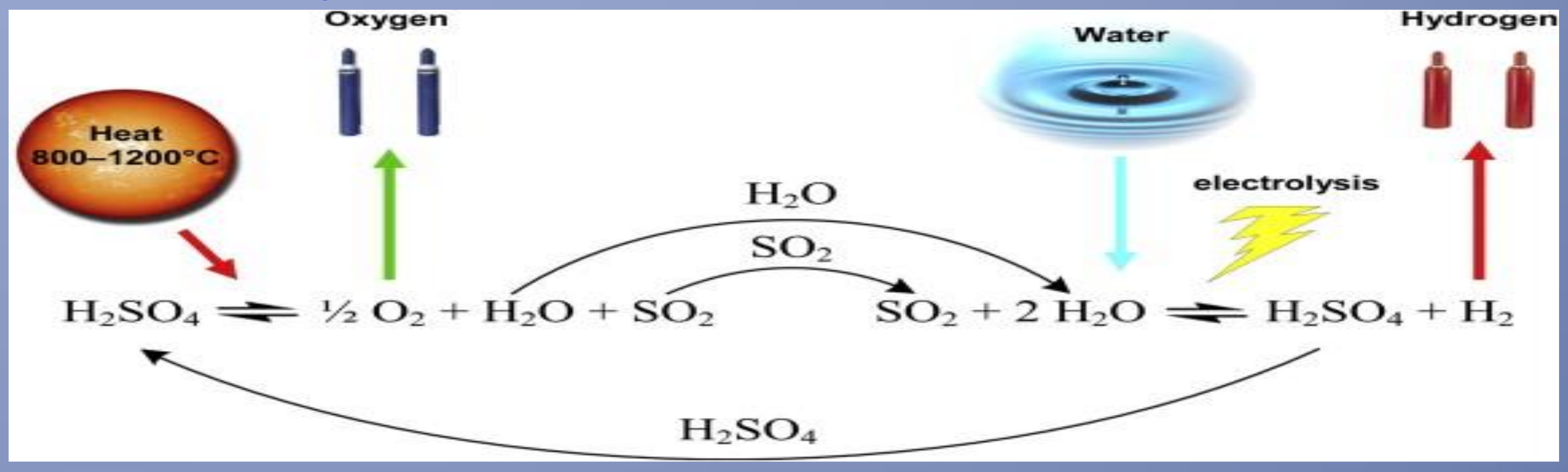



Fig. 1. Hybrid sulfur cycle (Hy-S).

Thermic decomposition of sulfuric acid:

$$H_2SO_{4(l)} \rightarrow SO_{3(g)} + H_2O_{(g)}; \quad \Delta H = 97.54 \text{ kJ/mole}; \quad (400°C) \qquad (1)$$

Thermo-catalytic conversion of sulfur trioxide:

$$SO_{3(g)} \rightarrow SO_{2(g)} + 1/2O_{2(g)}; \quad \Delta H = 98.92 \text{ kJ/mole}; \quad (850 – 900°C) \qquad (2)$$

A silicon carbide reactor, heated by solar radiation, having a honeycomb structure on which $Fe_2O_3$ layer was deposited as catalyst was developed at Institute of Solar Research, Köln, Germany.

*[1] Dennis Thomey, Lamark de Oliveira, Jan-Peter Sack, Martin Roeb, Christian Sattler, Intern. J. Hydrogen Energy, 37, (2012) 16615 – 16622.*

A multi-chambers design was developed to separate the steps and thermodynamically optimize the process. Both components are made of high – alloyed steel AISI 316Ti and closed by quartz window at the front side to avoid discharge of acidic gases and the same time allow solar radiation to enter the system.

Fig. 2. Solar reactor with foam absorber in evaporator (left) and honeycomb in decomposer.

Table 1. Overview of experiments

| Catalyst | Blank | Fe2O3 | | CuFe2O4 | |
|---|---|---|---|---|---|
| Evaporator | Solar | Solar | | Solar | Electrical |
| Number of experiments | 17 | 17 | 11 | 7 | 20 |
| Sulfuric acid conc. (wt.%) | 50 | 50 | 96 | 96 | 96 |
| Sulfuric acid flow rate (mL/min) | 1…7 | 1…7 | 2…6 | 2…4 | 2…6 |
| Mean honeycomb temp. (C degrees) | 850 | 850 | 650…950 | 650…950 | 750…900 |
| Residence time (s) | 0.3 | 0.3…1 | 0.2…0.5 | 0.5 | 0.5…0.7 |
| Weight hourly space velocity (1/h) | n/a | 0.6…4.0 | 1.4…4.4 | 1.4…2.9 | 1.4…4.4 |

The weight hourly space velocity (WHSV) considers the effective mass of H2SO4 injected into the system and related this to the mass of catalyst applied to absorber:

$$WHSV = mH2SO4 / mcat \qquad (5)$$

Both reactors are made of high-alloyed steel AISI 316 Ti and closed by a quartz glass window at the front side to avoid discharge of acidic gases and the same time allow solar radiation to enter the system. Siliconized silicon carbide (SiSiC) structures are used to absorb the radiation and transfer the produced heat to the reaction gases. Vaporization of sulfuric acid is carried out inside a SiSiC foam structure irradiated at the front side. In the decomposer a SiSiC honeycomb structure is used to dissociate the sulfur trioxide forming sulfur dioxide and oxygen. A catalyst coating is applied to this absorber to increase the reaction rate and reach high reaction rates at temperature below 1000 C degrees.

The conversion of sulfur trioxide is defined as the amount of sulfur dioxide at the outlet of the decomposer related to the amount of sulfur trioxide in the reaction gas before entering the honeycomb:

$$XSO3 = nSO2, out / nSO3, in \qquad (3)$$

$$nSO3, in = Vacid \times \rho acid \times Wacid / MH2SE \qquad (4)$$

where:

M = molar mass, Kg/mole; N = molar flux, mole/s; V = volume, m3; **V** = Volume flow rate, m3/s; X = conversion; P = density, Kg/m3; W = mass concentration, kg/kg

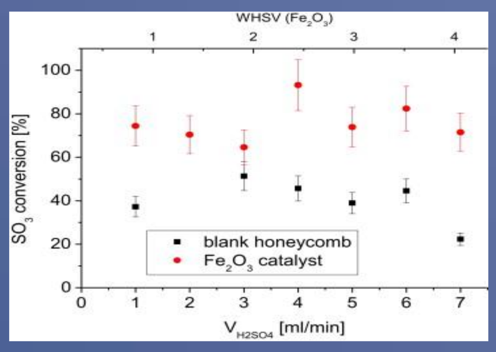


Fig. 3. Conversion of $SO_3$ at 850 °C and different flow rates of sulfuric acid with 50 wt. % for a blank honeycomb and a $Fe_2O_3$ catalyst [1].

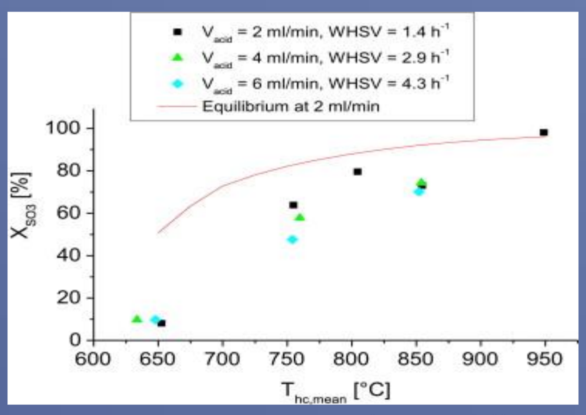


Fig. 4. Conversion of $SO_3$ at different temperatures and flow rates of sulfuric acid with about 94 wt. % for a $Fe_2O_3$.

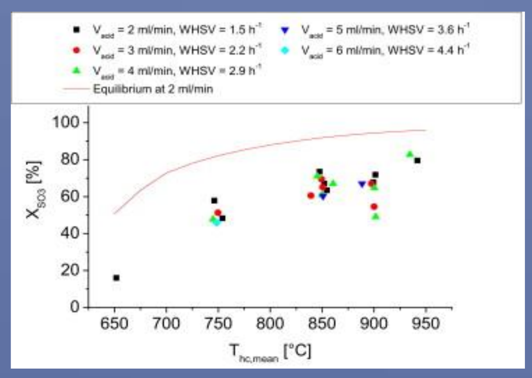
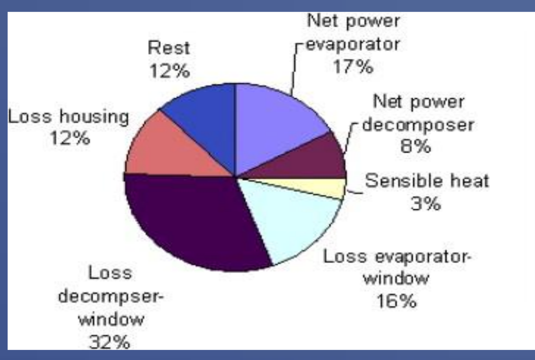


Fig. 5. Conversion of $SO_3$ at different temperatures and flow rates of sulfuric acid with about 94 wt.% for a $CuFe_2O_4$ catalyst.




| | |
|---|---|
| $P_{S,evap}$ | 870 W |
| $P_{S,decomp}$ | 1141 W |
| Catalyst | $Fe_2O_3$ |
| $V_{H2SO4}$ | 6 ml/min |
| $T_{hc,mean}$ | 852 °C |
| Conversion | 82 % |
| $\eta_{net,evap}$ | 39 % |
| $\eta_{net,decomp}$ | 15 % |

Fig. 9. Energy balance of the solar reactor.

**Conclusion 1**

The different proportion of power consumed by the reactor is given in Fig. 9.
In an energy balance of the system, a thermal efficiency of up to 28% was found, while radiation of the solar absorbers was identified as the main heat loss.
The results indicate that higher efficiencies can be reached at higher flow rates of sulfuric acid.
The multi - chambers concept of the reactor is scalable and mainly uses commercial materials like steel and silicon carbide, while only few components are made of quartz.

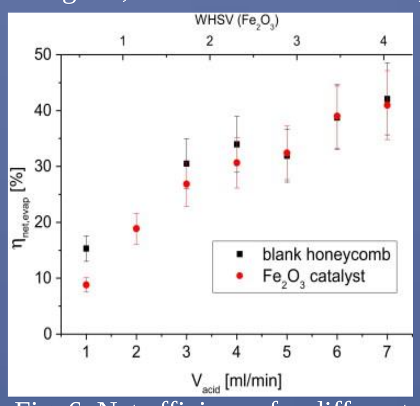


Fig. 6. Net efficiency for different volume flow rates of the evaporator.

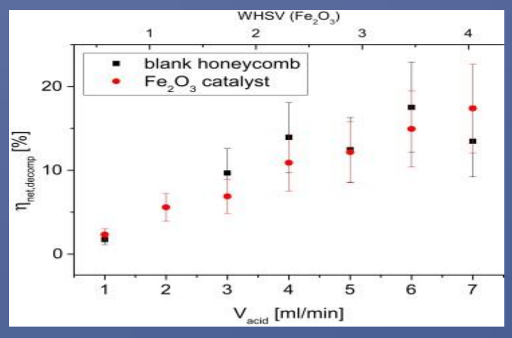


Fig. 7. Net efficiency for different volume flow rates of the decomposer

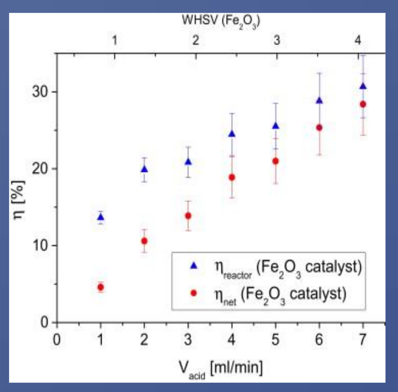


Fig. 8. Overall efficiencies of the solar reactor ($Fe_2O_3$ catalyst).

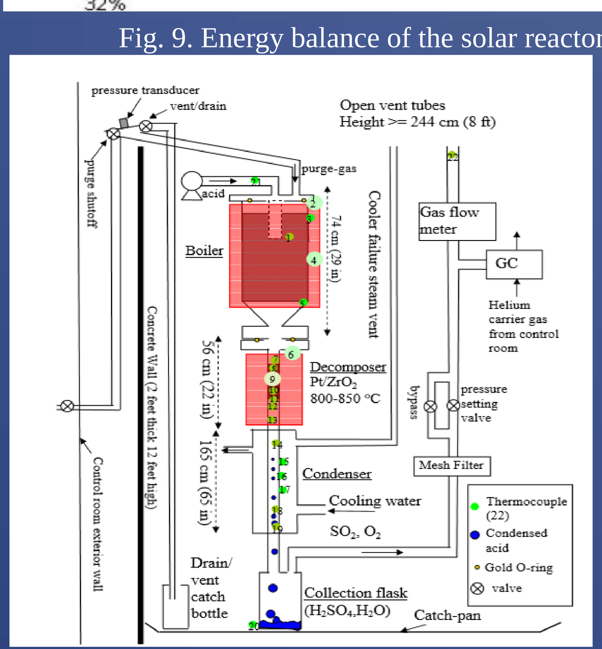


Fig. 10. Schematic of straight-through sulfuric acid boiler, catalytic decomposer and rapid-quench condenser. Red shared regions of the boiler and decomposer represent split-tube heaters [2].

High pressure sulfuric acid decomposition experiments, for the S – I thermochemical cycle for hydrogen production, were done in the apparatus for boiling, decomposing, condensing and collecting liquid effluents is arranged for straight-through downward processing of acid as shown schematically in Fig. 10.

*[2] Fred Gelbard, James C. Andazola, Gerald E. Narango, Carlos E. Velasquez and Andrew R. Reay, SANDIA Report, SAND 2005 – 5598.*

The boiling point of sulfuric acid is 337 C degrees and the boiler is designed to heat the fluid to 500 C degrees, thus all the acid solution is vaporized upon exiting the bottom part of the boiler and entering the decomposer.

The decomposer consists of a Hastelloy C - 276 pipe, 56 cm long and 3.34 cm outside diameter. A split-tube heater of 1650 W as power surrounds the decomposer. Approximately 134g, of 1% Pt on zirconia catalyst, is packed into the decomposer to form a packed bed of 19 cm long. The catalyst is in the form of 4.8 mm diameter and length cylindrical pellets.

Sulfuric acid conversion fraction is given by:

$H = 1/\beta \cdot f_{gas} / f_{acid}$ ; (9) ; where: η = acid conversion fraction; $f_{gas}$ = molar flow rate of uncondensed effluent gas (mole / min); $f_{acid}$ = molar injection rate of acid (mole / min)

gas = PV / RT ; (10); where: V = measured volumetric uncondensed gas flow rate (L / min); P = pressure at which uncondensed gas flow rate is measured; R = ideal gas constant; T = gas temperature where the uncondensed gas flow rate is measured (310 K )

$$\eta = 1 / \beta \cdot (PV / R \cdot T \cdot facid) \qquad (11)$$

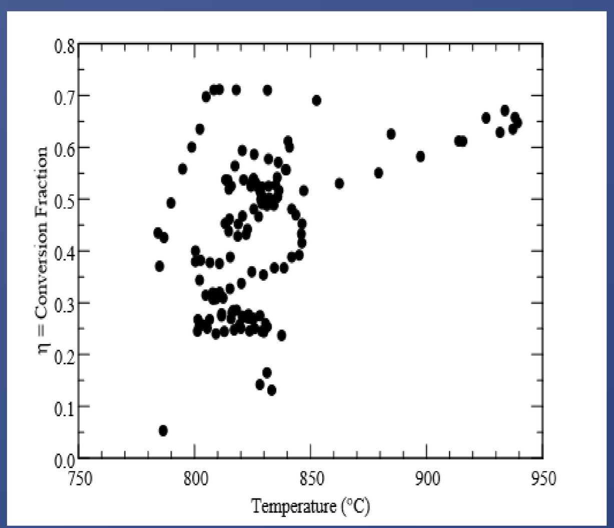


Fig. 11. Acid conversion fraction for pressurized acid test Nr. 1

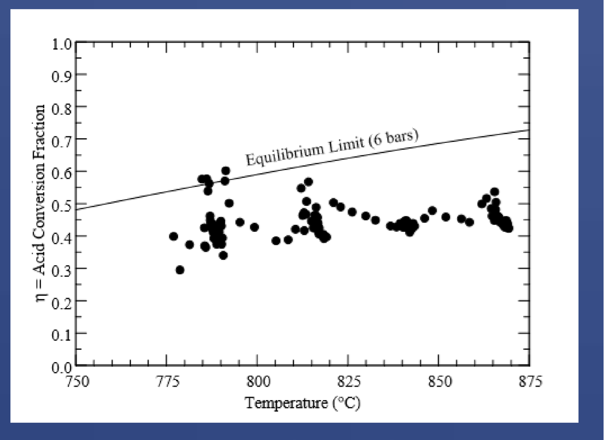


Fig. 12. Acid conversion fraction for pressurized acid test Nr.2

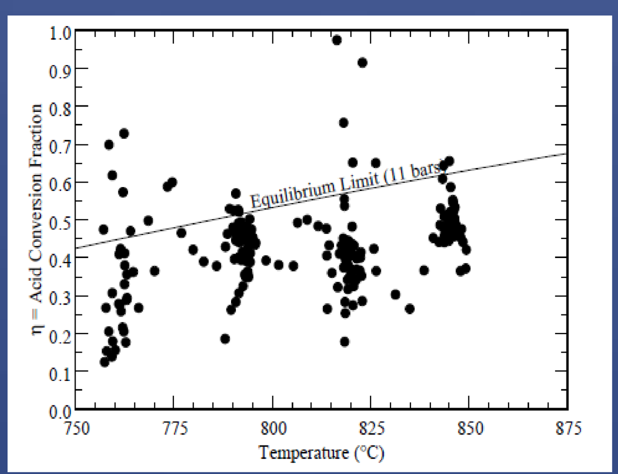


Fig. 13. Acid conversion fraction for pressurized acid test Nr.3

**Conclusion 2**

The data show the trend of increasing acid conversion fraction with increasing temperature. However the measurements did not have the resolution needed to show the decrease in conversion fraction with increasing pressure. For acid vapor temperatures varying from 750 to 875C degrees, the measured conversion fraction ranged from 0.4 to 0.45, respectively at 6 bars and from 0.3 to 0.5, respectively at 11 bars.

At the heart of the acid decomposition section is the silicon carbide integrated boiler / super heater / catalytic decomposer (Fig. 14). The apparatus is similar to a bayonet type heat exchanger introducing a significant modification in the process and eliminate the concerns with corrosion and high temperature.

The apparatus consists of two silicon carbide heat exchanger tubes: a small diameter tube, open at the top, is placed inside a larger tube with closed top.

Table 2. Pressurized acid test conditions

| | Test Nr. 1 | Test Nr. 2 | Test Nr. 3 |
|---|---|---|---|
| Operating pressure | 1.9 bars absolute | 6.0 bars absolute | 10.9 bars absolute |
| Acid injection rate | 4 mL/min (0.070 mole/min) | 4.2 mL/min (0.074 mole/min) | 2.9 mL/min (0.050 mole/min) |
| Injected acid concentration | 96.5 wt.% 83.5 mole % | 96.5 wt.% 83.5 mole % | 95.5 wt.% 79.6 mole % |
| β | 1.5 | 1.5 | 1.07 |

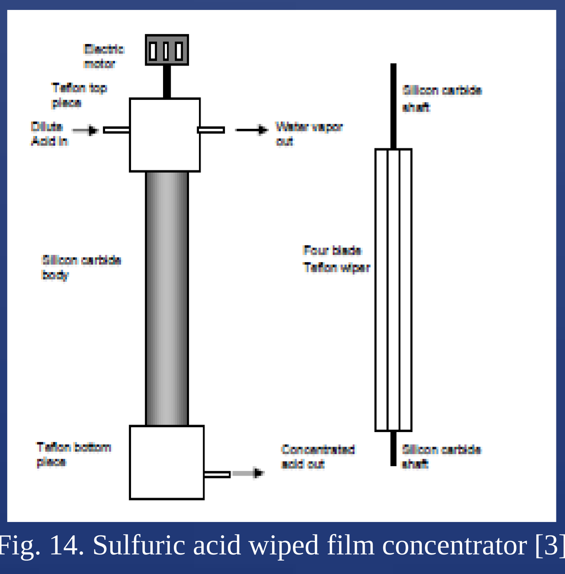


Fig. 14. Sulfuric acid wiped film concentrator [3]

*[3] Robert Moore, Fred Gelbard, Edward Parma, Milton Vernon, Roger Lenard and Paul Pickard, "A laboratory – scale sulfuric acid decomposition apparatus for use in hydrogen production cycles", SANDIA National Lab. Albuquerque N. M. USA, Report SAND2007-2237 C.*

The body of concentrator is constructed of Hexaloy (a silicon carbide alloy)
The apparatus is approximately 8.9 cm in diameter and 41 cm tall.

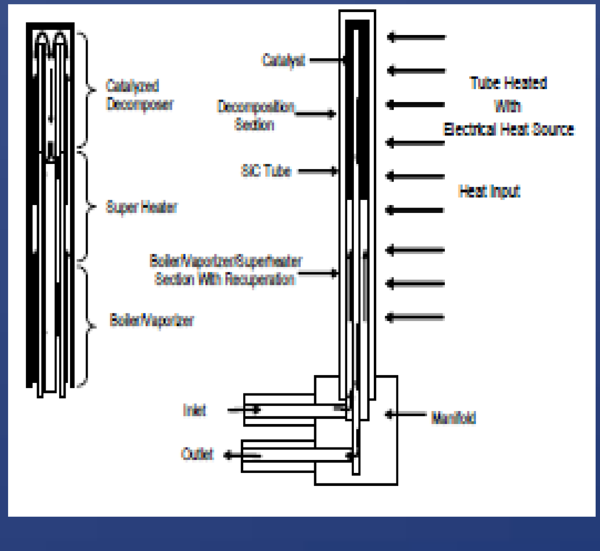


Fig. 15. Silicon carbide acid decomposer [3]

**Conclusion 3**

Based on the experiments performed at SANDIA a 137 cm length unit is capable of producing sufficient $SO_2$ for hydrogen production rates of 200 L/h, by using S – I thermochemical cycle.
The novel design for the acid decomposer has eliminated past problems with corrosion and failure of high temperature connections.

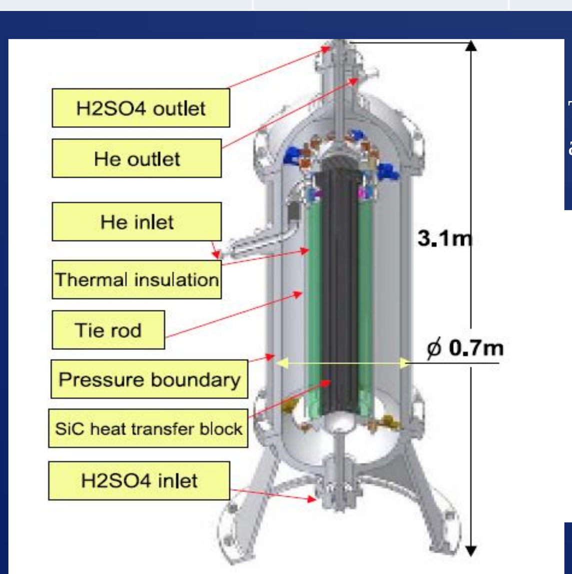



Fig. 16. Concept of H2SO4 decomposer

Table 3 Design conditions of sulfuric acid decomposer

| | Conditions |
|---|---|
| Thermal Rating | 82.7 kW |
| He Inlet / Outlet Temp. | 710 / 535°C |
| Process Inlet / Outlet Temp. | 435 / 460°C |
| He Pressure | 4 MPaG |
| Process Pressure | 2 MPaG |
| He Flow Rate | 0.091 kg/s |
| Process Flow Rate | 0.066 kg/s |

The heat exchanger components were made of atmospheric pressure sintered SiC to provide the flow channels of He and sulfuric acid alternately in the cylindrical block. The block was 0.25 m in outer diameters and 1.5 m in height. The number of the flow channels for sulfuric acid and He were 32 and 38 respectively; diameter of those flow channels was 14.8 mm.

Table 4 Design conditions of SO3 decomposer in pilot test plant

| Item | Conditions for hydrogen production 30 N $m^3$/h |
|---|---|
| Process gas pressure | 2.0 (MPaG) |
| Process gas temperature (inlet/outlet) | 527/850 (°C) |
| He pressure (inlet) | 4.0 (MPaG) |
| He flow rate | 100 (g/s) |
| He temperature (inlet) | 880 (°C) |
| Heat exchange | 100(kW) |

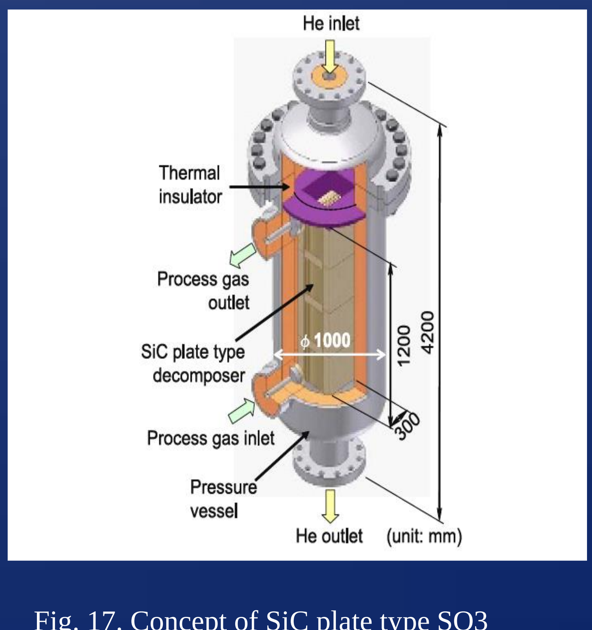


Fig. 17. Concept of SiC plate type SO3 decomposer

**Conclusion 4**

The rated space velocity (SV) in a SO3 catalyst layer is necessary to be kept less than 10000 (1/h) in order to keep high reactivity of SO3 decomposition. The internal volume charged with catalyst is around 17.64 L. The space velocity (SV) becomes 1.71 (mole/s) x 22.4 (NL/mole) x 3600 / 17.64 = 7817 (1/h).
Concept of the H2SO4 and SO3 decomposer for the pilot test plant were proposed featuring corrosion resistant performance under high temperature H2SO4 and SO3 operations, which were mainly composed of SiC ceramics.
The feasibility of the proposed concepts were confirmed by mechanical strength analyses and test fabricated mock-up models. As for the H2SO4 decomposer, the seal performance with gold gaskets showed very good performance.