DESIGN OF RECUPERATIVE SULFURIC ACID DECOMPOSITION REACTOR FOR HYDROGEN GENERATION PROCESSES

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Executive Summary

The Hybrid Sulfur Process (HyS), as well as similar sulfur cycles for the production of nuclear hydrogen, requires the decomposition of sulfuric acid into sulfur dioxide, oxygen, and water at temperatures above 800°C and a pressure near 9 MPa. The design of a reactor for this process presents numerous challenges in terms of maintaining small pressure differentials and utilizing currently available materials of construction. This paper focuses on design calculations for a recuperative decomposition reactor for use in the production of hydrogen. The decomposition reaction takes place within individual tubes of a multi-tube reactor that are is fed liquid H_2SO_4 at 50 to150°C.

Previous calculations involved modeling to produce a detailed temperature-enthalpy (T-H) diagram for the H_2SO_4-SO_3-SO_2-O_2-H_2O system of the evaporation and decomposition processes for pinch analysis. Previous detailed modeling and analysis has been performed for the Westinghouse design by Connolly, et al.(2) Current analysis involves detailed modeling and sizing of the recuperative concept. This design phase entailed detailed heat transfer analysis and sizing of the reactor. Calculations were performed with a multi-tube reactor design in which the outer shell of the reactor contained structured packing to facilitate heat transfer on the shell side. This resulted in a design consisting of a total of 750 tubes at 6.7 meters in length contained in two vessels with an inner diameter of 3.7 meters.

1. Introduction

1.1 Background

The sulfur cycles, including the Hybrid Sulfur Process and the Sulfur-Iodine Process, are a group of processes designed to generate hydrogen via electrolysis and thermochemistry. The Hybrid Sulfur Process (HyS), or the Westinghouse Sulfur Process (WSP), uses both thermal and electrical energy from a Pebble Bed Modular Reactor (PBMR) to produce hydrogen. The thermal energy is provided by helium that is used as a coolant in the nuclear reactor and is transferred via an intermediate heat exchange loop to a second helium stream. The thermal energy from the intermediate loop is used to decompose H_2SO_4 into SO_2, O_2, and H_2O. Oxygen is then separated from the stream and the water-SO_x mixture is electrolyzed to generate H_2 gas and H_2SO_4 via the reaction:

$$2\ H_2O + SO_2 \rightarrow H_2 + H_2SO_4 \qquad \textbf{Equation 1}$$

The H_2SO_4 can then be recycled back into decomposition reactor. A diagram of the HyS process is shown in Figure 1.

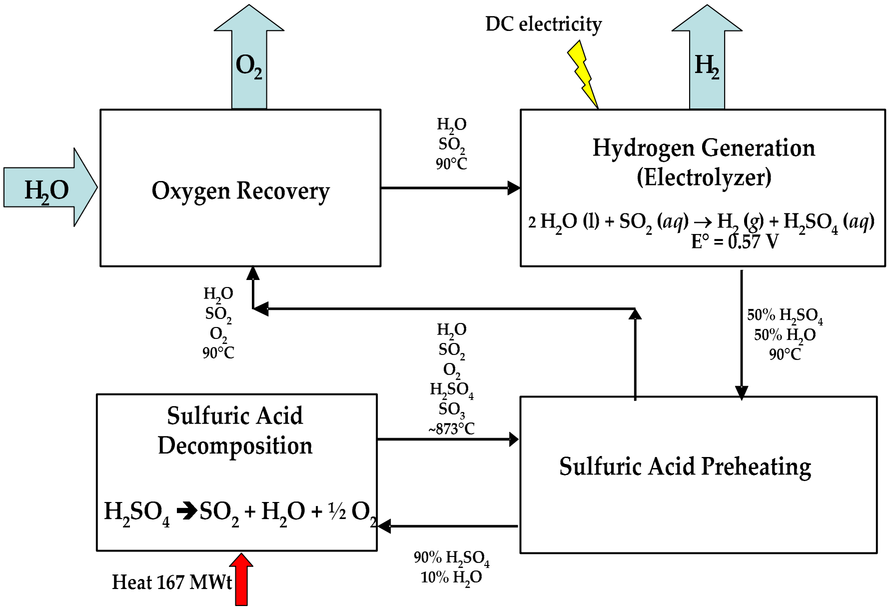

Figure 1 – Diagram of HyS Process

1.2 Design Challenges

All of the sulfur cycle processes require the decomposition of concentrated sulfuric acid into sulfur dioxide, oxygen, and water at temperatures exceeding 800°C. Additionally, the lower condensation temperature of the decomposition products relative to the feed stream requires operating pressures near 9 MPa. The high temperatures and pressures in combination with the extremely corrosive nature of the materials present considerable challenges in designing a reactor system.

It is possible to overcome the challenges presented by both the high temperatures and the corrosive nature of the H_2SO_4 by using a ceramic material such as silicon carbide (SiC) or alumina (Al_2O_3). However, the use of ceramics then presents the problem of creating seals between the low-temperature metal components and the high-temperature ceramic components of the reactor. Plastic materials, such as Teflon, are only allowable at temperatures up to 300°C. The use of metal gaskets would create issues of corrosion and possible loosening under cyclic operating conditions. Additional issues include maintaining small pressure differentials between the helium side of the reactor and the sulfuric acid side as well as creating a design that is amenable to maintenance.

2. Westinghouse Composite Reactor

2.1. Westinghouse Design Concept

The Westinghouse solution to this design challenge is a top-fed, multi-step reactor that pre-heats, concentrates, and decomposes sulfuric acid. The reactor will operate under moderate pressure differentials (<1 MPa) between the heated gas and liquid sides. Ceramic material will be utilized for the high temperature and heat transfer portions of the reactor and lined metal in the low temperature distribution headers of the reactor. All seals are located in low temperature portions of the reactor, allowing for the use of Teflon or a similar material. A general schematic of the composite reactor is shown in Figure 2. The design allows for a relatively low cost of construction by using carbon or stainless steel for the pressure boundary of the vessel.

The decomposition tubes consist of a ceramic bayonet tube with an inside ceramic support tube, as shown in Figure 3. The bayonet tubes are contained in a vessel with internal insulation and structured packing to facilitate heat transfer from the helium to the bayonet tube. Inside the bayonet tube, a double-walled insulated ceramic support tube surrounded by a ceramic tube to create a gas downflow annulus sits on the bottom of the bayonet tube and supports a ceramic liquid catch ring with sloped sides and a hole in the middle. A ceramic gas distribution plate then sits on top of the liquid catch ring, which in turn supports ceramic packing material. On top of the packing material is a set of ceramic gas riser tubes filled with packing. At the bottom of the bayonet tube, ceramic packing material sits in the annulus between the bayonet and gas down flow ring and supports a catalyst to be used in the decomposition reaction. The entire assembly is made of ceramic, such as SiC, and is handled as a single unit.

The incoming liquid H_2SO_4 feed flows between the ceramic gas riser tubes where it is preheated by the upward flowing gases from the decomposition products. The liquid is directed downward into the liquid catch ring via the gas distribution plate where it flows down through the support tube. At the bottom of the support tube, the liquid can enter into the bayonet via holes or perforations in the support tube. The H_2SO_4 is further concentrated to 85-90 wt% then vaporizes and is demisted by the ceramic packing as it flows upward. As the H_2SO_4 vaporizes, it is decomposed into SO_3 and H_2O. Upon reaching the catalyst, the SO_3 is further decomposed into SO_2 and O_2. At the top of the bayonet tube, the gas will flow downward into the inner annulus where heat is recuperated into the incoming feed stream.

The primary advantages to the Westinghouse design lay in its amenability to assembly, inspection, and maintenance as well as the requirement for only one seal location. Additionally, the seal is not under a hydrostatic head that could result in a leak into the helium side.

2.2 Sandia National Laboratory Concept

The Sandia National Laboratory (SNL) solution to the design challenge is a reactor in which the decomposition reaction takes place within individual tubes of a multi-tube reactor that are pump-fed 78 wt% H_2SO_4 at 50 to 150°C. As in the Westinghouse design, ceramic material will be utilized for the high temperature and heat transfer portions of the reactor and lined metal in the low temperature portions of the reactor. Three seal locations are required, and all are located in low temperature portions of the reactor, allowing for the use of Teflon or a similar material. A general schematic of the decomposition reactor is shown in Figure 4. The design also allows for a relatively low cost of construction by using carbon or stainless steel for the pressure boundary of the vessel.

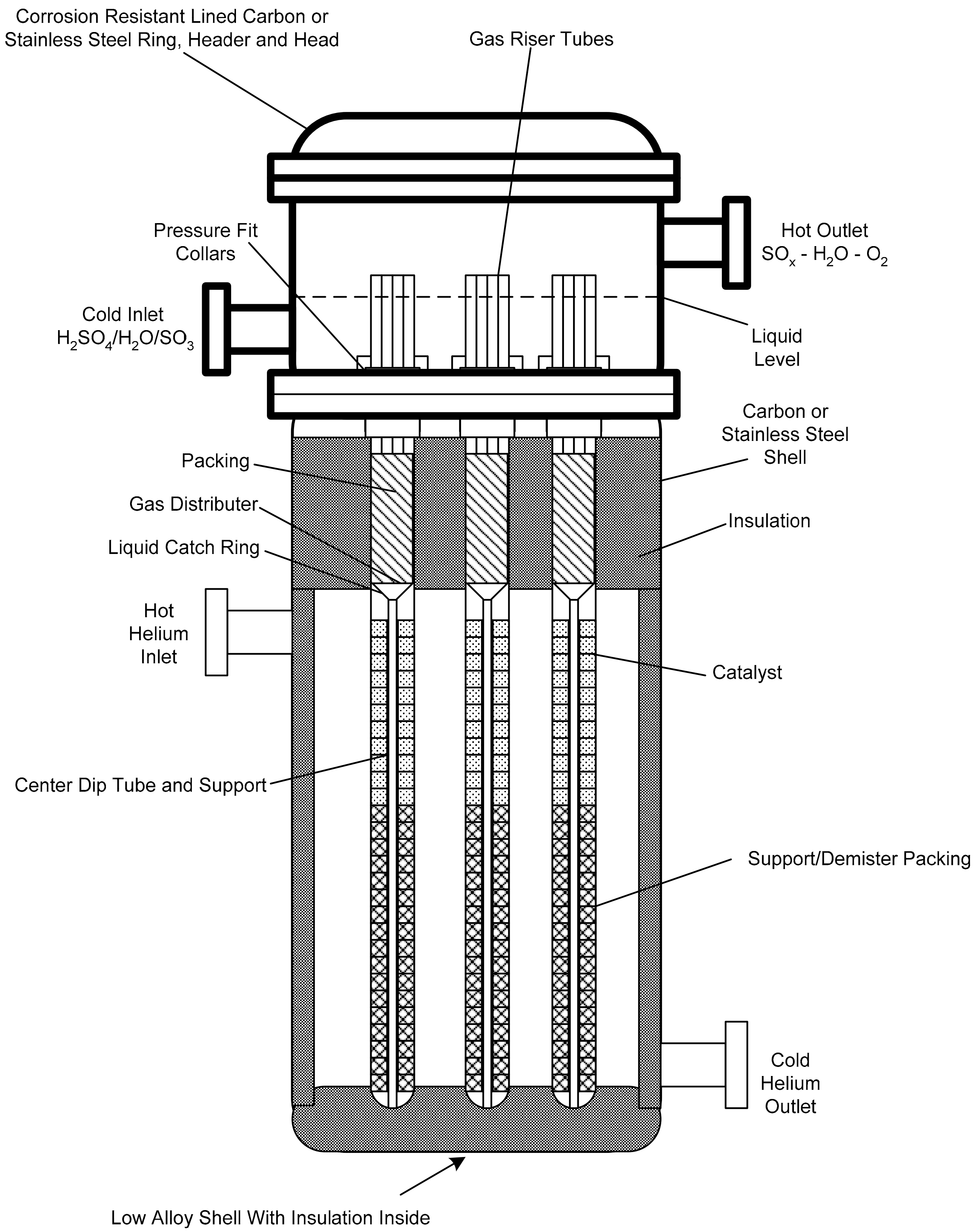

Figure 2 – Overall Schematic of Westinghouse Composite Reactor

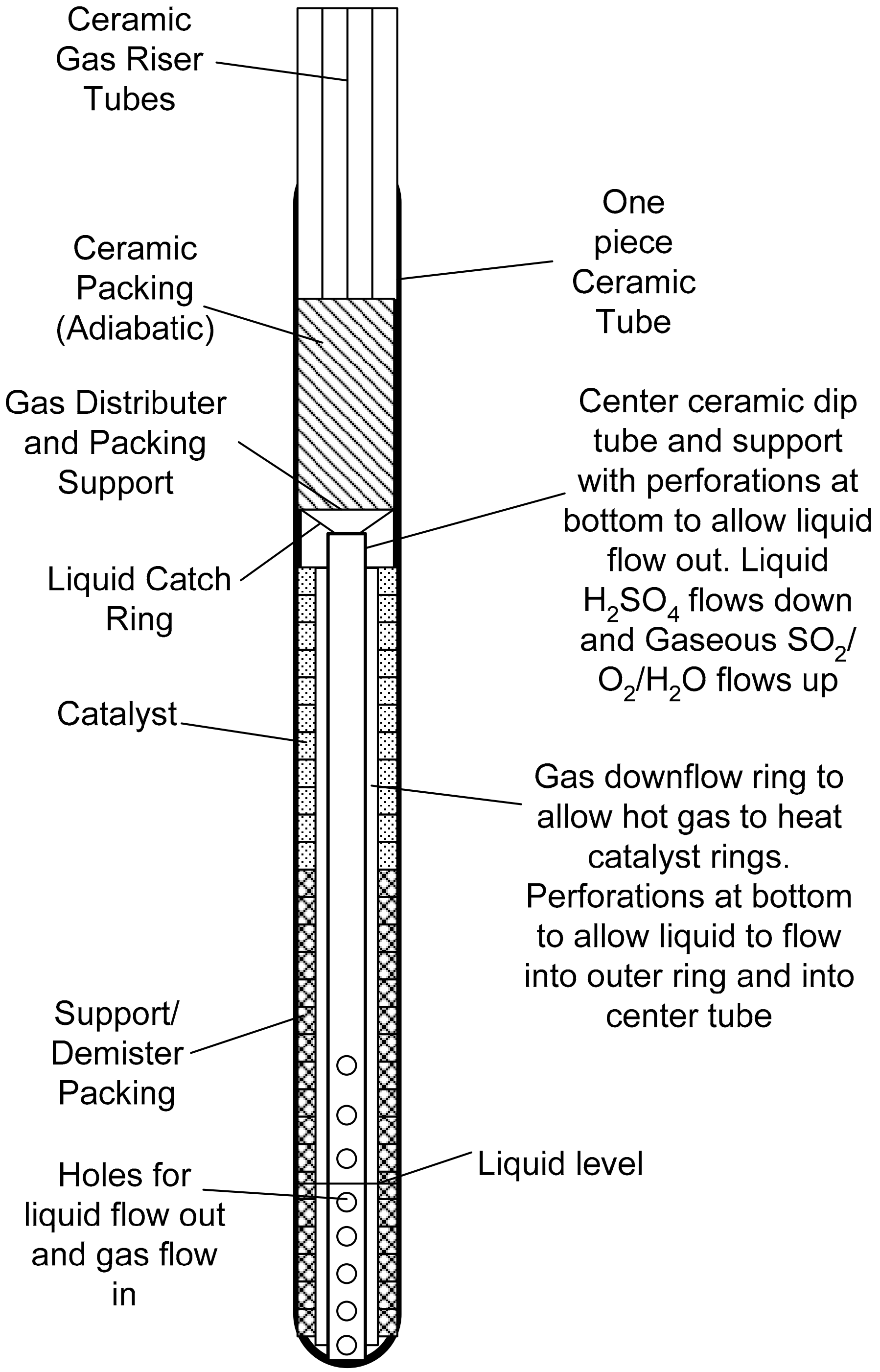

Figure 3 - Detail of Individual Westinghouse Composite Operation Tube

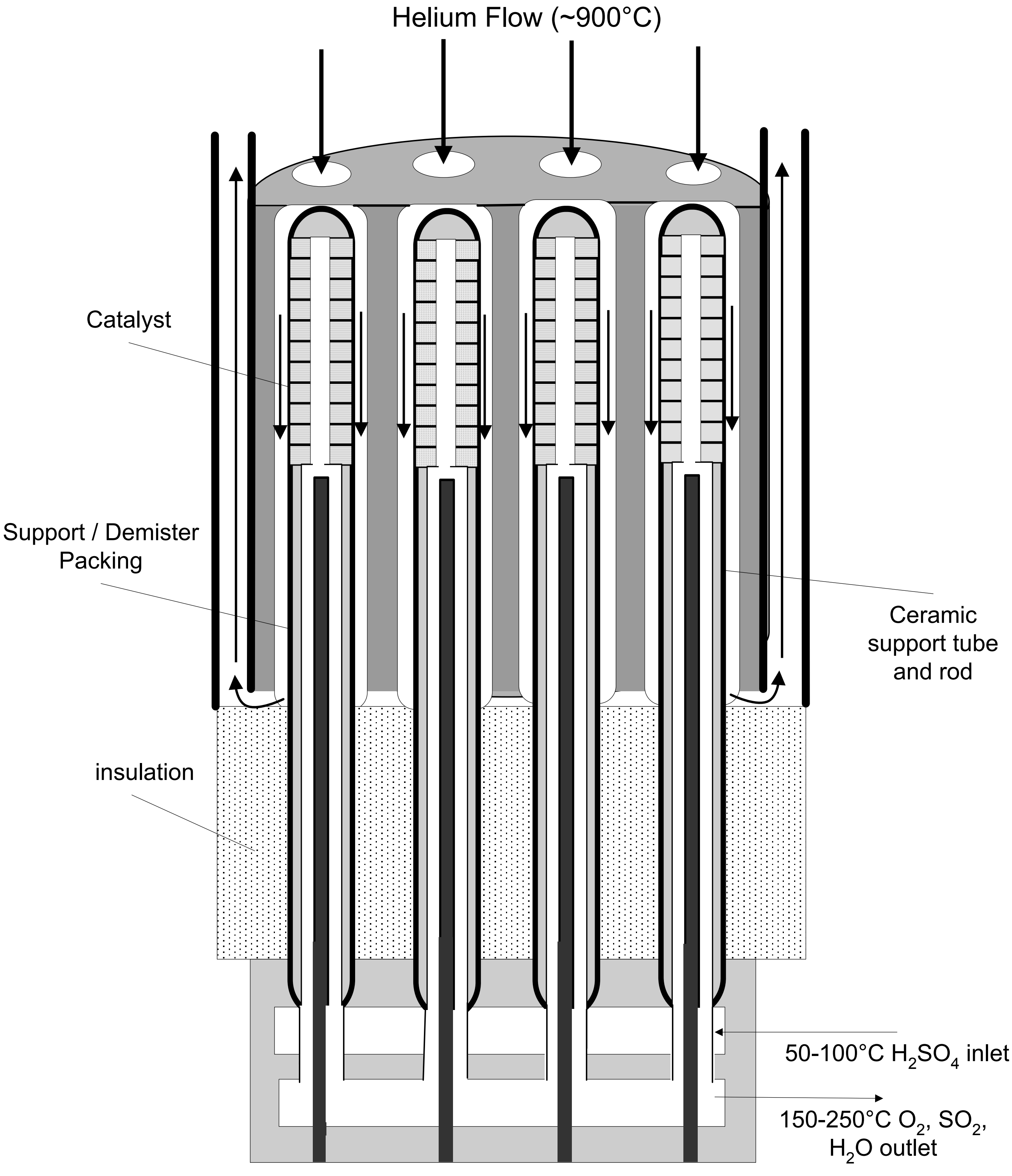

Figure 4 – Overall Schematic of H_2SO_4 Decomposition Reactor

The decomposition tubes consist of a ceramic bayonet tube with an inside ceramic support tube. A rod in the center of the exit tube creates an inner annulus to facilitate heat transfer, as shown in Figure 5. The bayonet tubes are contained in a vessel with internal insulation and structured packing to facilitate heat transfer from the helium to the bayonet tube. The entire assembly is made of ceramic, such as SiC.

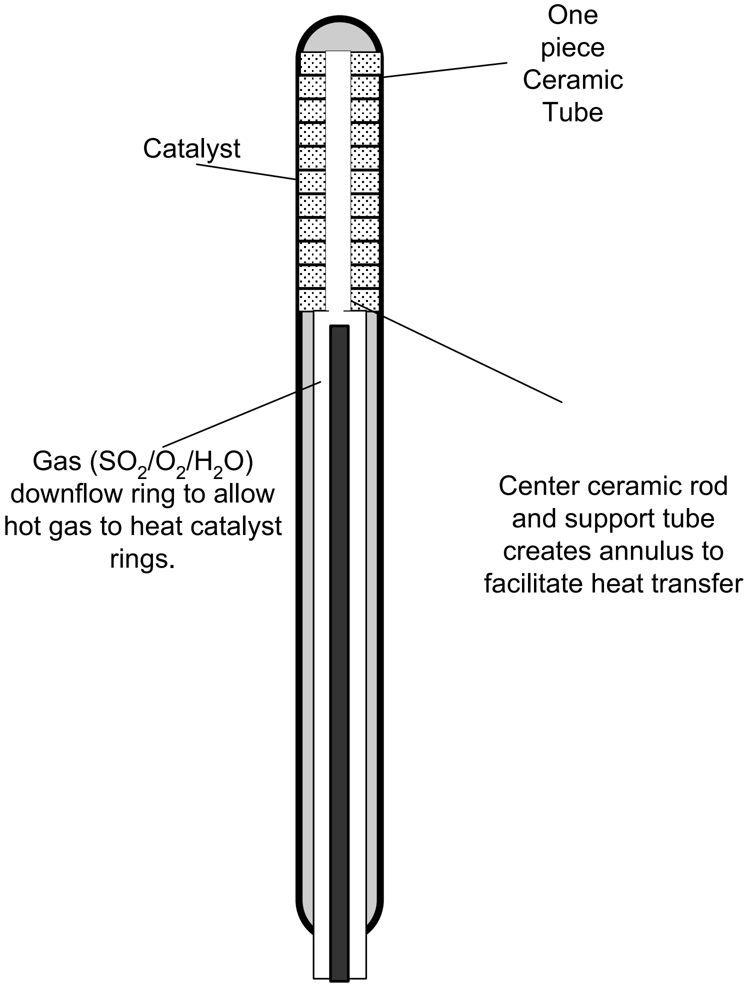

Figure 5 – Detail of Individual SNL Design Tube

The primary drawback to the SNL design is the necessity for three seals – a helium/reactant seal and two seals to maintain separation of the inlet and outlet streams (see Figure 6). The temperature in these areas is less than 300°C, therefore various commercially available seals can be utilized. Additionally, active cooling coils could be used for further cooling if desirable.

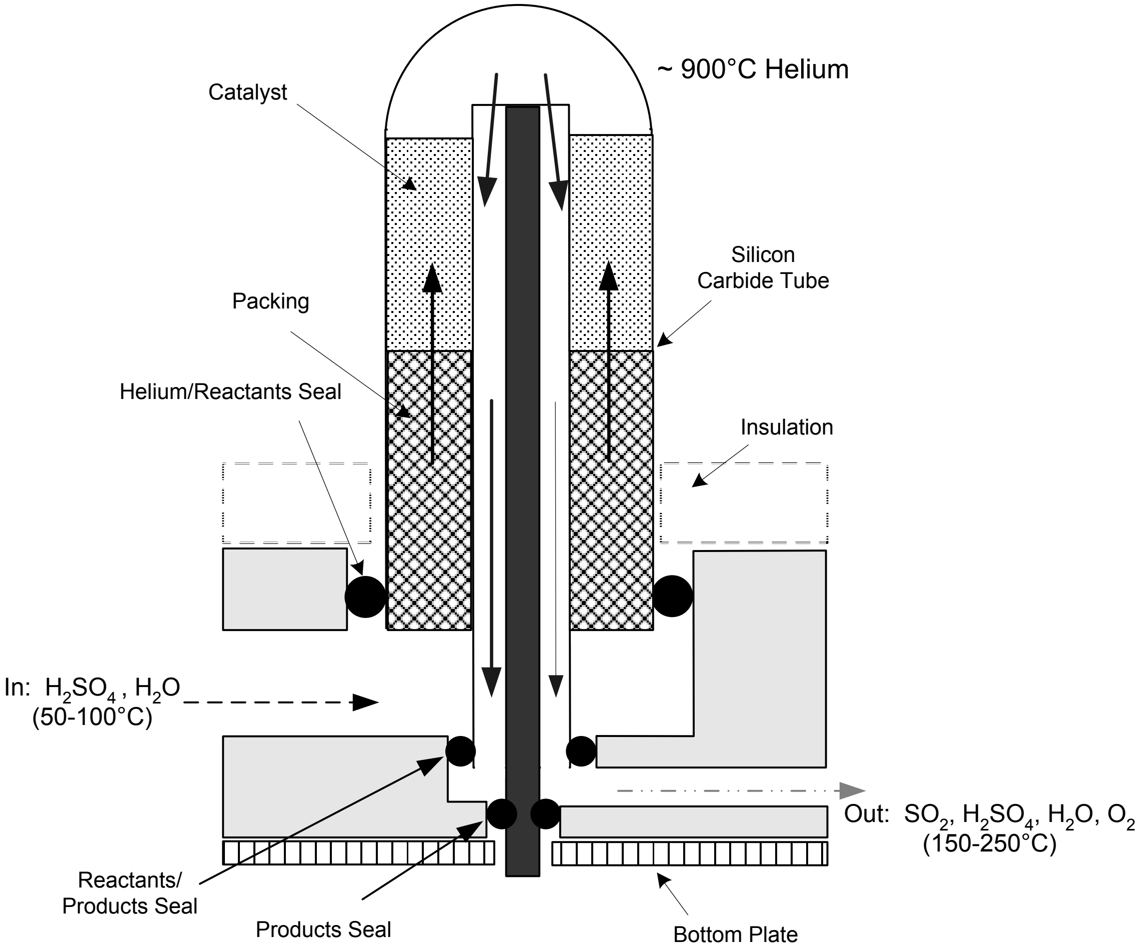

Figure 6 – Detail of Seal Locations

3. Development of Thermodynamic Model

3.1. T-H Diagram

Development of an accurate thermodynamic model was necessary for detailed modeling of the decomposition reactor. Such development is difficult due to the scarcity of vapor pressure data for highly concentrated H_2SO_4 systems. The highest temperature vapor pressure data available are those of Wüster(1), which reach a maximum temperature of 480°C for a range of concentrated solutions. Detailed development of the thermodynamic model is discussed in Connolly, et al.(2) The final T-H diagram shown in Figure 5 was developed using ChemCAD data up to the ASPEN predicted bubble point of 492°C, ASPEN data from 492°C to the dew point at 584°C, extrapolated CEA data from 492°C to 607.6°C and CEA data above 607.6°C. The merging of the data at the bubble and dew points is markedly smooth, indicating good correlation between the three data sources. Calculation of the T-H line for the helium is straightforward. Figure 7 confirms that there is no pinching between the helium and the sulfuric acid systems.

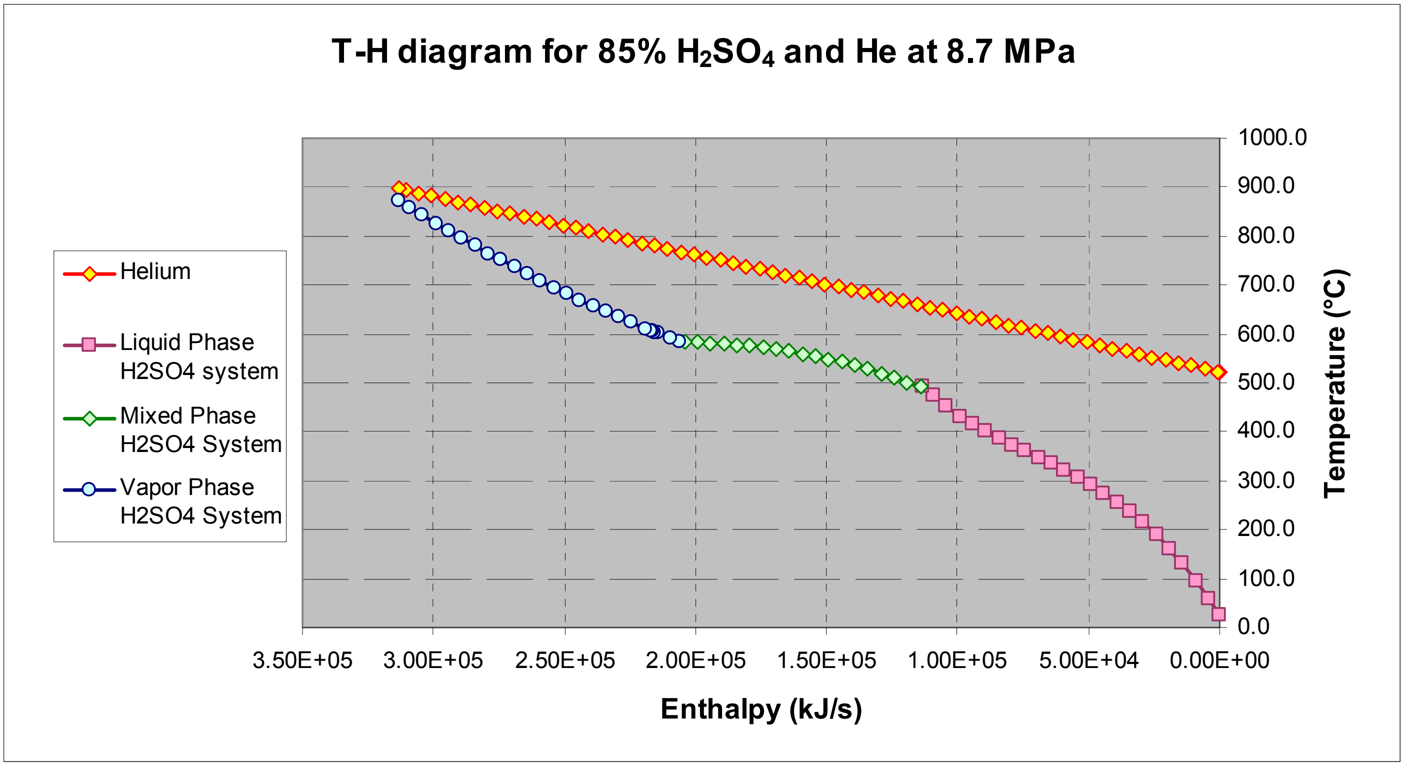

Figure 7 - T-H Diagram for Decomposition Reactor at 8.7 MPa

4. Decomposition Reactor Model

4.1. Design Equations

Previous detailed modeling and analysis has been performed for the non-recuperative Westinghouse design by Connolly, et al.(2) Current analysis involves detailed modeling and sizing of the recuperative concept by Westinghouse in order to form a basis for comparison. The model for the decomposition reactor is set up to balance the enthalpy and the heat transfer between the helium side, the outer annulus in which the decomposition reactions take place, and reaction products flowing downward through the inner annulus. The system consists of six total possible variable temperatures – the inlet and outlet temperatures for the helium side, the outer annulus, and the inner annulus. The temperature at the top of the inner (T_{inIA}) and outer (T_{outOA}) annuli must be the same and is set at 872°C by the WSP flow sheet. The inlet temperature of the helium stream (T_{inHe}) is also set by the WSP flowsheet. Thus, the three unknown temperatures – outlet temperature of inner annulus (T_{outIA}), outlet temperature of the helium (T_{outHe}), and the temperature of the feed (T_{inOA}) – serve as the variables for the system. Hence, three equations relating these temperatures via enthalpy and heat balances are required to model the system. The flow of helium on the shell side and the reaction products through the inner annulus are both downward and the feed in the outer annulus flows upward, which results in countercurrent flow between the helium and the outer annulus and also between the outer annulus and inner annulus, as shown in Figure 8.

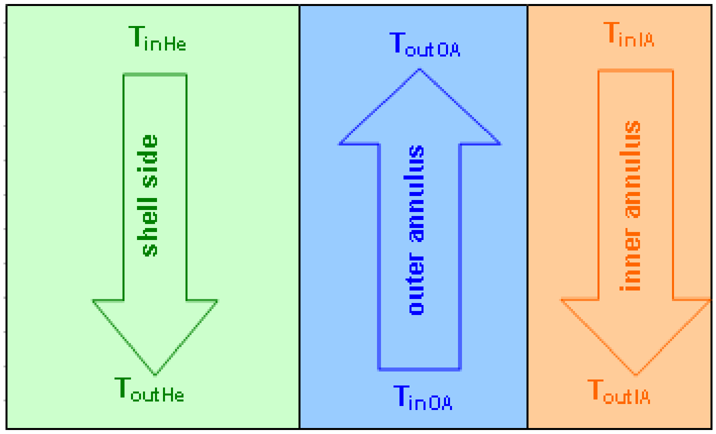

Figure 8 - Flow Pattern Through Decomposition Reactor

The first design equation (Equation 2) consists of an enthalpy balance on all three systems. The enthalpy leaving the helium must be exactly equal to the enthalpy that is gained by the H_2SO_4 system in the outer and inner annuli assuming that the overall operation is adiabatic. Enthalpy increases with temperature and the temperature of the system decreases with the direction of flow for the helium and the inner annulus but increases with the direction of flow in the outer annulus. The change in enthalpy, ΔH, is defined as $H_{out} - H_{in}$, thus the enthalpy change on the shell side and in the inner annulus will be negative and the enthalpy change in the outer annulus will be positive. The enthalpy balance is thus:

$$\dot{m}_{He}\Delta H_{He} + \dot{m}_{H2SO4}(\Delta H_{OA} + \Delta H_{IA}) = 0$$ **Equation 2**

The remaining two equations are provided by balancing the heat transfer into and out of the inner and outer annuli. The enthalpy change in the outer annulus is balanced by the heat transfer into the outer annulus from the helium and the inner annulus, as shown in Equation 3 where $U_{OA/IA}$ and $U_{He/OA}$ are the overall heat transfer coefficients between the inner and outer annuli, and the helium side and the outer annulus, respectively. Heat transfer correlations were used as described in Connolly et al.(2) A_1 corresponds to the area available for heat transfer between the shell side and the outer annulus, and A_2 corresponds to the area available for heat transfer between the outer and inner annuli. The standard log mean temperature differences for each system are represented by ΔT_{LM}.

$$\dot{m}_{H2SO4}\Delta H_{OA} = U_{OA/IA}A_2\Delta T_{LMOA/IA} + U_{He/OA}A_1\Delta T_{LMHe/OA}$$ **Equation 3**

In the inner annulus, the change in enthalpy is simply balanced with the heat transfer from the inner annulus into the outer annulus, as shown in Equation 4.

$$\dot{m}_{H2SO4}\Delta H_{IA} = - U_{OA/IA}A_2\Delta T_{LMOA/IA}$$ **Equation 4**

The values for the change in enthalpy are computed simply by regressing the data for the T-H diagrams to give temperature dependent functions of H. Similarly, the overall heat transfer coefficients are simply functions of the physical properties of the materials present in the system (which are temperature dependent) and the tube geometries.

4.2. Model Development

The current model for the decomposition reactor partitions the total required reactor tube length into 20 equal sections and balances the three previously stated design equations for each section. The model allows the user to vary tube diameters, clearances, and lengths as well as mass flow rates until the heat transfer requirements are met and pressure drops are kept below approximately 20 pounds per square inch (psi). The optimization limits for various tube geometries were obtained from either literature values or previous calculations.

The primary optimization parameter was the minimization of the total number of required tubes while still maintaining acceptable pressure drop losses and necessary heat transfer. The number of tubes was chosen as the primary optimization variable because initial cost estimates show that the internal components of the reactor will comprise the majority of the total reactor cost due to the necessity for corrosion resistant materials at high temperatures and pressures.

4.3. Optimization Calculations

To increase the heat transfer on the helium side of the reactor, it was proposed that using structured ceramic packing rather than the standard baffled approach would increase the heat transfer coefficient and eliminate the need for using a correction factor in the log-mean temperature difference. The assumed structured packing used for calculation purposes was Flexeramic® Type 38. This type of packing is typically used in mass transfer applications, however the effects on heat transfer and pressure drop are relevant.

The final optimized model utilizes 750 bayonet tubes distributed within two vessels with inner diameters of 3.2 meters, as shown in Table 1. The height of the tubes is 7.4 meters. The pressure drops on the shell side, outer annulus, and inner annulus were 18.9 psi, 9.2 psi, and 1.4 psi, respectively.

The temperature profile for the decomposition reactor is shown in Figure 9. Note that the zero point on the x-axis corresponds to the top of the tube. The temperatures in the inner and outer annuli are the same at the top of the reactor. Note that both the inlet feed temperature and the reaction products temperature are below 300°C at the bottom of the reactor. External heat transfer via the helium is only utilized until the helium reaches 500°C, as required by the other components of the HyS process.

4.4. Pressure Drop Calculations

Various methods of predicting the pressure drop through the different sections of the decomposition reactor were required. Specific equations for the pressure drops are available in Appendix A. The pressure drop through the bayonet portion was calculated using the Ergun equation with characteristic length and velocity relations as reported in Mills(3). The pressure drop in the support tube was calculated using a friction factor correlation for the transitional regime and a pressure drop equation for flow through circular pipes as reported in Welty(4).

The method of calculating pressure drop on the shell side depends on the design approach. For the packed design, the method for dry pressure drop in structured ceramic packing detailed by Uresti-Melendez and Rocha(5) was utilized. The total pressure drop for the shell side, outer annulus, and inner annulus as a function of tube length is shown in Figure 10.

Table 1 - Optimization Table for Recuperative Decomposition Reactor

Inside shell diameter	3.7	m
number of bayonet tubes required	750	
number of vessels	2	
total length of tubes	6.7	m
clearance between tubes	0.035	m
ID of support tube (inner wall)	0.020	m
thickness of support tube	0.004	m
insulation thickness	0.010	m
OD of support tube (outer wall)	0.056	m
distance in inner annulus	0.0025	m
ID of inner annulus	0.061	m
thickness of inner annulus	0.006	m
OD of inner annulus	0.073	m
distance in outer annulus	0.030	m
ID of outer annulus	0.103	m
thickness of outer annulus	0.021	m
OD of outer annulus	0.144	m
Pitch/OD outer annulus	1.242	
Catalyst void volume (ε)	50%	
catalyst/packing particle diameter (d_p)	0.010	m
heat transfer area on outside inner annulus	0.08	m^2
area available on shell side (per finger per section)	0.15	m^2
mass flow rate H_2SO_4 (m_S)	0.100	kg/s
mass flow rate Helium per finger (m_H)	0.213	kg/s
pressure drop on shell side	18.9	psi
pressure drop in outer annulus	9.2	psi
pressure drop in inner annulus	1.4	psi

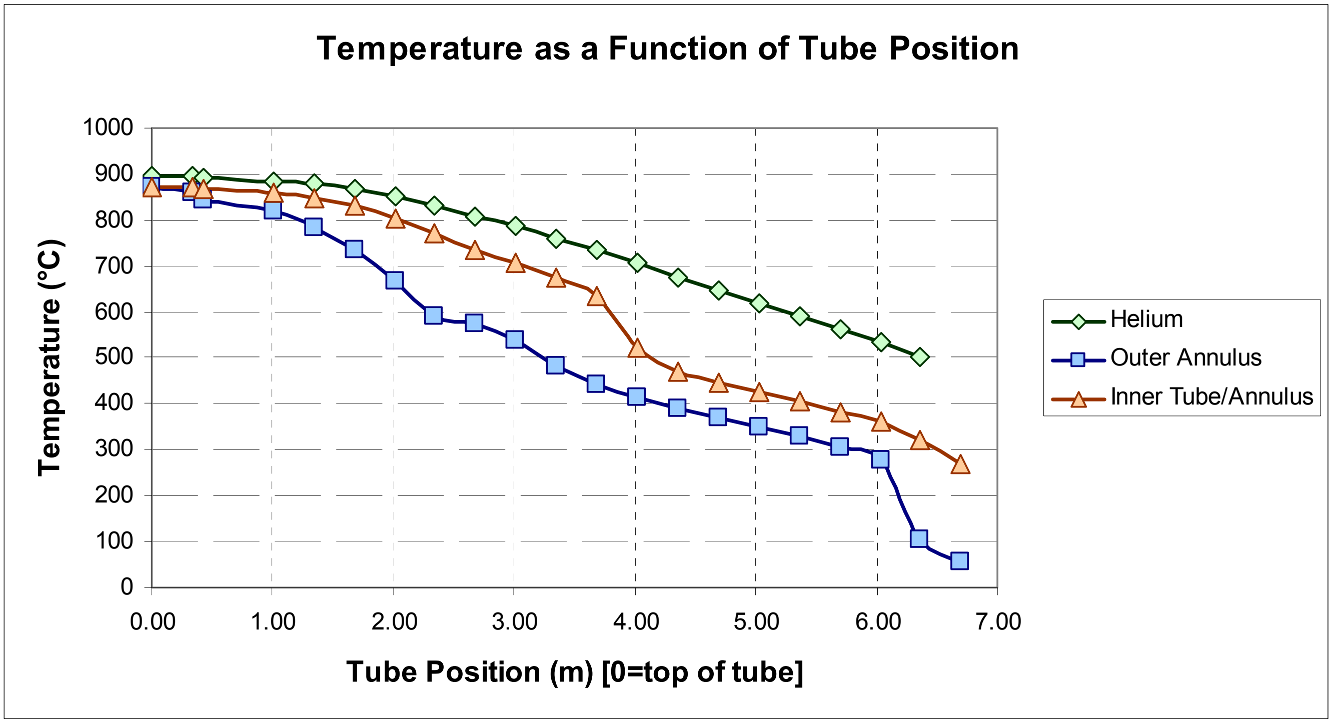

Figure 9 - Temperature Profile for Decomposition Reactor

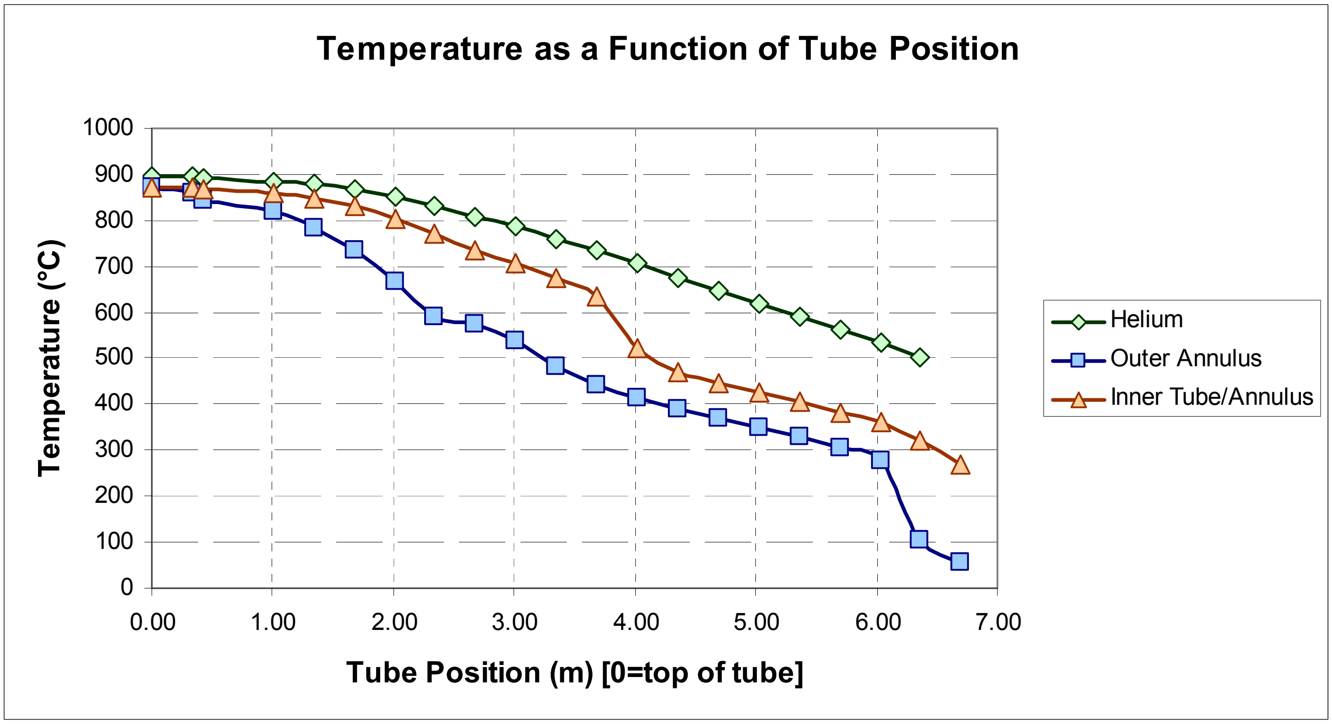

Figure 10 - Pressure Drop for Decomposition Reactor

5. Calculation of Vessel Size and Catalyst Volume

5.1. Vessel Sizing and Concentrator Height

The calculation of the inner diameter of the vessel is based on the total number of bayonet tubes as determined by the decomposition model. The tubes will have a triangular pitch arrangement with a minimum pitch-to-diameter ratio of 1.125. The user can input a desired number of vessels to obtain the required vessel diameter as shown in Table 2.

Table 2 - Calculation of Vessel Diameter

Area of Unit Cell	0.0139	m^2
Area of Tube	0.0082	m^2
Total Cross-Sectional Area	20.92	m^2
Inside Diameter of Vessel	3.65	m
Number of Vessels	2	

5.2. Calculation of Required Catalyst Volume

The required catalyst volume to decompose the SO_3 into SO_2 was calculated to ensure that the annular space in the bayonet tubes were large enough to accommodate the catalyst. The calculation was based on kinetic data from Lin and Flaherty(6). The catalyst was assumed to be iron oxide. Assuming an SO_3 conversion of 50%, the required catalyst volume space is approximately 0.005 m^3 and the available volume in the annular region of the bayonet tubes where the temperature is above 600°C is 0.010 m^3. Thus, the volume in the annular region exceeds the required volume by an order of magnitude and achieving the necessary residence time should not pose an issue.

Appendix A: Pressure Drop Calculations

i. Packed Bed Flow(3)

$$\frac{\Delta P}{\Delta Z} = \frac{150 \mu v_c}{L_c{}^2} + \frac{75 \rho v_c{}^2}{L_c}$$

ii. Flow through Pipe(4)

$$\frac{1}{\sqrt{f_f}} = 4\log_{10}\frac{d_s}{e} + 2.28 - 4\log_{10}\left(4.67\frac{d_s/e}{\mathrm{Re}\sqrt{f_f}} + 1\right)$$

$$\Delta P = 2 f_f \frac{Z}{d_s} \rho v^2$$

iv. Packed Helium side (structured Packing)(5)

$$\frac{\Delta P}{\Delta Z} = \frac{0.0453\rho_g}{S\varepsilon^2(1-\varepsilon)(\sin\theta)^2} + \frac{6.6441\mu_g}{S^2\varepsilon(1-\varepsilon)\sin\theta}$$

Nomenclature

A_1 – area available for heat transfer between the helium side and the bayonet [m^2]
A_2 - area available for heat transfer between bayonet and support tubes [m^2]
c_p – heat capacity [J/kg/°C]
f_f – Fanning friction factor
h - heat transfer coefficient [$W/m^2/°C$]
H_{in} – enthalpy at the inlet temperature [kJ/kg]
H_{out} – enthalpy at the outlet temperature [kJ/kg]
h_s - heat transfer coefficient on shell side [$W/m^2/°C$]
k – thermal conductivity [W/m/°C]
L_c – characteristic length of packing [m]
$\dot{m}_{gas}$ – mass flow rate of vapor phase in concentrator [kg/sec]
$\dot{m}_{He}$ - mass flow rate of the helium [kg/sec]
$\dot{m}_{H2SO4}$ - mass flow rate of the H_2SO_4 [kg/sec]
$\dot{m}_{liq}$ – mass flow rate of liquid phase in concentrator [kg/sec]
$\dot{n}_{vap}$ – molar flow rate of evaporated water [mole/sec]
$Nu_{boiling}$ – Nusselt correlation for boiling phase
Nu_{gas} – Nusselt correlation for gas phase
Nu_{liq}– Nusselt correlation for liquid phase
Pr – Prandtl number = $\mu c_p/k$
psi – pounds/square inch
S – side dimension of structured packing corrugation [m]
T_{inHe} – inlet temperature to the helium side [°C]
T_{inIA} – inlet temperature to the inner annulus [°C]
T_{inOA} - inlet temperature from the outer annulus [°C]
T_{outHe} – outlet temperature on the helium side [°C]
T_{outIA} – outlet temperature from the inner annulus [°C]
T_{outOA} - outlet temperature from the outer annulus [°C]
$U_{He/OA}$ – overall heat transfer coefficient between the helium and the outer annulus [$W/m^2/°C$]
$U_{OA/IA}$ – overall heat transfer coefficient between the outer and inner annuli [$W/m^2/°C$]
v_c - characteristic velocity [m/s]
VF – vapor fraction
v_s - superficial velocity [m/s]
Z – height [m]

ε – void fraction of packing
μ_g - viscosity of gas [kg/m/s]
ΔH_D – change in enthalpy in the bayonet tube [kJ/kg]
ΔH_{gas} – change in enthalpy of vapor phase in concentrator [kJ/kg]
ΔH_{He} – change in enthalpy of the helium [kJ/kg]

ΔH_{liq} – change in enthalpy of liquid phase in concentrator [kJ/kg]
ΔH_S – change in enthalpy in the support tube [kJ/kg]
ΔH_{vap} – heat of vaporization of water [J/mol]
ΔT_{LM} – log mean temperature difference = $[(T_{inhot} - T_{outcold}) - (T_{outhot} - T_{incold})] / \ln[(T_{inhot} - T_{outcold})/(T_{outhot} - T_{incold})]$ [°C or K]
$\Delta T_{LMHe/OA}$ - log mean temperature difference between the helium side and inner annulus
$\Delta T_{LMOA/IA}$ – log mean temperature difference between the outer and inner annuli
$\Delta P/\Delta Z$ – pressure drop per unit height [Pa/m]
Φ - ratio of viscosity in the bulk fluid to viscosity at the wall
θ – angle with the horizontal for corrugation channel [radians]
ρ_L- density of liquid [kg/m^3]
ρ_g - density of vapor [kg/m^3]
μ – viscosity [kg/m/s]
ψ – density of water/density of liquid

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