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A Laboratory-Scale Sulfuric Acid Decomposition Apparatus for Use in Hydrogen Production Cycles

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ABSTRACT

As part of the US DOE Nuclear Hydrogen Initiative, Sandia National Laboratories is developing the high temperature process for conversion of sulfuric acid to produce sulfur dioxide as part of the thermochemical Sulfur-Iodine (S-I) cycle that produces hydrogen from water. The Sandia process will be integrated with other sections of the S-I cycle in the near future to complete a demonstration-scale S-I process. In the Sandia process, sulfuric acid is concentrated by vacuum distillation and then catalytically decomposed at high temperature (850°C) to produce sulfur dioxide, oxygen and water. Major problems in the process, corrosion and failure of high-temperature connections of process equipment, have been virtually eliminated through the development of an integrated acid decomposer constructed of silicon carbide and quartz. The unit integrates acid boiling, superheating and decomposition into a single unit operation and provides for exceptional heat recuperation. The design of acid decomposition process, the new acid decomposer, other process units and materials of construction for the process are described and discussed.

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1. INTRODUCTION

Concern over environmental pollutants resulting from the use of fossil fuels has led to the investigation of alternative energy sources. Hydrogen, because it is a zero emissions fuel with high energy content, is a particularly attractive option. Efficient methods for large-scale production of hydrogen include thermochemical cycles where water is split into hydrogen and oxygen through a series of chemical reactions combined with a heat source. All chemicals used in the process are recycled with only water being consumed. Although many thermochemical cycles have been developed and proposed for hydrogen production, the Sulfur Cycles-Sulfur-Iodine (S-I) cycle and Hybrid Sulfur Cycle are considered particularly promising because of high theoretical efficiency and technical maturity.

Under the U.S. DOE Nuclear Hydrogen Initiative (NHI) program, Sandia National Laboratories (SNL), General Atomics Corporation (GA) and the French Commissariat a l'Energy Atomique (CEA) are collaborating to construct a demonstration-scale S-I process. Each participant is responsible for design and construction of a different section of the process. The three sections will be integrated in the near future. SNL is responsible for the section of the S-I process where sulfuric acid is catalytically decomposed into sulfur dioxide (SO_2), oxygen (O_2) and water (H_2O) at high temperature (850°C). Sulfur dioxide and water are used in separate section of the S-I process and oxygen is a byproduct.

Fig. 1 depicts the S-I cycle for hydrogen production. Sulfuric acid (H_2SO_4) is catalytically decomposed at high temperature to produce SO_2, O_2, and H_2O (Sulfuric Acid Decomposition Section). The sulfur dioxide is reacted with iodine (I_2) and H_2O to produce hydrogen iodide (HI) and sulfuric acid. Hydrogen iodine is then decomposed to produce H_2 and I_2 (HI Decomposition). Decomposition of sulfuric acid takes place at temperature (~ 850°C) in the presence of a catalyst such as platinum or certain metal oxides. Heat can be provided to the process through various sources including nuclear and solar energy.

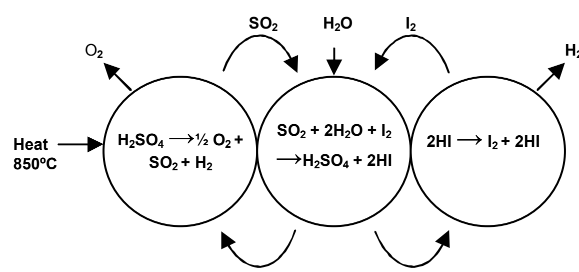

Fig. 1. S-I cycle for hydrogen production2HI

The first successful operation of the S-I process was performed by General Atomics, Corp in the late 1970's. The process was performed at the bench-scale level using mainly glass components and capable of producing 4 l/min H_2 (1, 2). Improvements in design to increase process efficiency were later proposed by Ozturk et al. (1994, 1995) and included the incorporation of a direct contact heat-mass exchanger (DCHX) into the process. The DCHX functioned to recover unreacted acid and recuperate heat from the products of acid decomposition through direct mixing and subsequent separation of input and output streams to the acid decomposer. A potential problem with the DCHX design is connection to other unit operations. The DCHX would have to be connected to the process at temperatures of 300°C and 800°C for input and output streams respectively. This could be problematic due to possible thermal expansion mismatching at the connections. Additionally, because the DCHX processes hot concentrated sulfuric acid, corrosion could also pose a problem. Recently, Gelbard and Pickard (2005) describe the operation of a sulfuric acid decomposition apparatus constructed of nickel and iron-silicon alloys. Glass liners and heated surfaces were used to minimize corrosion.

In this work, we describe the design and construction of a demonstration-scale apparatus for decomposition of sulfuric acid to sulfur dioxide. The apparatus is designed for a production rate of 100 to 200 l/hr H_2. At the heart of the apparatus is a novel sulfuric acid decomposition unit constructed of silicon carbide and quartz. This unit eliminates past problems with corrosion and failure of high temperature connections and allows for excellent heat recuperation. The process also utilizes an acid concentration step before acid decomposition. Preconcentration of the acid will allow for evaluation of the parameters space for operation of the acid decomposer and provide information for process scale up. The Sandia process will be connected with the two other sections of the S-I process in the near future for operation of a complete demonstration S-I process.

II. DESIGN CRITERIA

Under the DOE NHI program, certain criteria for design, construction and operation of the demonstration-scale process have been established. These include:

- A hydrogen production rate of 100 l/hr with the capability of short-term operation up to 200 l/hr,
- Allow for integration with the other sections of the S-I process,
- Scalability of the technical approach both technically and economically.

These criteria along with lessons learned from experimental work at SNL have been used to determine specific criteria for the acid decomposition section. In experiments performed at SNL, technical challenges have been identified that must be overcome for successful operation of a sulfuric acid decomposition process. These include the elimination of corrosion and high temperature connections of equipment. Severe corrosion was observed for almost all metals used in acid decomposition tests. These included 316 stainless steel, Hastelloy, Saramet and Inconnel alloys. Corrosion often resulted in plugging of process streams. Additionally, failure of connections between process equipment was observed at high temperature (>400ºC).

Based on the criteria for the S-I process and results from experiments at SNL, the criteria specific to the sulfuric acid decomposition section include:

- Acid decomposition temperature up to 900ºC and pressure up to 6 bar,
- SO_2 generation rate of 100 l/hr with the capability to increase to 200 l/hr,
- Heat recuperation where possible in this laboratory-scale process,
- Minimization or elimination of corrosion and high-temperature seals,
- Receive sulfuric acid at nominally 20 mole percent from the Bunsen section of the process.

III. RESULTS

III.A. CONSTRUCTION MATERIALS

Construction materials identified for use in the presence of sulfuric acid and sulfur dioxide at high temperature included Teflon, Viton, silicon carbide, alumina, quartz and glass.

Although Teflon has been reported to be excellent for use with sulfuric acid (6), Teflon is relatively permeable to sulfur dioxide (7). Additionally, Teflon is limited to approximately 260ºC, where at this temperature it begins to decompose. At a temperature of 150ºC, the strength of Teflon begins to rapidly decrease and at 250ºC Teflon retains only 20% of its strength. For these reasons, the use of Teflon is limited to lower temperature applications. Another elastomer, Viton is also reported to be resistant to sulfuric acid corrosion. Viton is an excellent sealing material and is widely used for O-rings and gaskets, but it is limited to approximately 180°C in the presence of sulfuric acid.

Silicon carbide and silicon carbide alloys are highly resistant to attack by sulfuric acid (8). Saint-Gobain, the manufacturer of Hexoloy, a silicon carbide alloy, reports a corrosion rate for Hexoloy in 98 weight percent sulfuric acid at 100ºC of 1.8 mg/cm2/yr (Saint-Gobain Ceramics, 2007). In corrosion screening studies performed at SNL, Hexoloy coupons were exposed to 80 mole percent sulfuric acid at 150ºC for 6 weeks. No corrosion of the coupons was observed through examination by transmission electron microscopy. Hexoloy also exhibits a very high thermal conductivity (125.6 W/mK at room temperature), high compressive strength and is widely availability in different configurations. The drawbacks of silicon carbide and silicon carbide alloys include their moderately low tensile strength, difficulties in machining, because of their very high hardness, and relatively high cost.

Quartz is inexpensive, can be formed into almost any shape, exhibits a very high softening point (1,500ºC), low coefficient of thermal expansion and is extremely resistant to corrosion by acids (9). The only major drawback of quartz is it susceptibility to breakage.

Glass, like quartz, is inexpensive and extremely resistant to corrosion by acids. Glass lined steel pipe is commonly used in production facilities, including sulfuric acid plants, where corrosive conditions exist (9). The corrosion rate of glass used in glass lined piping (Pfaulder, Inc) exposed to 40 weight percent sulfuric acid at 180ºC is reported to be 0.1 to 0.5 mm/year. There are numerous manufacturers of glass line pipe and equipment. The major drawback with glass lined steel equipment is the potential for cracking the glass liner resulting in exposure of the steel surfaces to the acid.

Taking into consideration the properties and limitations of the corrosion resistant construction materials identified and the design requirements for each section of the sulfuric acid decomposition process, materials to be used in each section of the process were selected as follows:

- All process streams carrying sulfur dioxide and water with or without any other components are constructed of glass lined steel pipe (Glasteel pipe, Pfaulder, Inc.)
- Process streams carrying sulfuric acid and no other components are constructed of Teflon (PTFE) tubing or Teflon lined steel tubing for sections under high pressure. The PTFE tubing used in this work (Saint Gobain, Inc.) was tested to temperatures up to 200°C and pressures of 300 psia without failure. Teflon, PTFE and PFA, was also used for corrosion resistant linings in process vessels.
- The sulfuric acid concentrator was constructed of Teflon (PTFE) and silicon carbide.
- The sulfuric acid decomposer was constructed of silicon carbide and quartz manifolded together with PTFE Teflon. Quartz was used as the material for the inner heat transfer tube because it was much more economical for this small-scale process than manufacture of a specialized silicon carbide piece. Because, Teflon (PTFE) is easily machined into complex forms and can be used up to temperatures of 260ºC, it was selected as the materials to manufacture the acid decomposer manifold. The maximum operating temperatures of the manifold is approximately a200°C.
- For temperatures below 180°C, Viton o-rings were used in seals for the acid decomposer manifold and for sealing certain plumbing section to unit operations.
- Alumina is not as resistant to acid corrosion as silicon carbide but is used in small-scale corrosion resistant pumps (Fluidmetering, Inc.) that were selected for this work.

III.B. PROCESS FLOWSHEET

A schematic diagram of the sulfuric acid decomposition process is given in Figure 3. Dilute sulfuric acid, nominal 20 mole percent, is fed to the acid concentrator where water is removed under vacuum at approximately 160ºC. The water is condensed collected in a stainless steel tank and subsequently transferred to the Bunsen section of the S-I process. The concentrated acid, 30 to 40 mole percent, is collected in a Teflon lined stainless steel tank. Acid from this tank is used to feed the acid decomposer. Heat for the decomposition reaction is provided by ceramic fiber heaters (Watlow, Inc.). The output from the acid decomposer consists of a mixture of SO_2, O_2, $H_2O_{(v)}$ and a fraction of undecomposed H_2SO_4 at 100 to 200ºC. The temperature of the output stream is dependent on the temperature of the inlet stream, feed acid concentration and flow rate and acid decomposition temperature. The outlet mixture is passed through an acid demister, a 12" long section of glass lined pipe packed with ½" Raching rings, and the undecomposed acid is collected in a Teflon lined stainless steel tank and recycled back to the acid decomposer. The SO_2, O_2 and $H_2O_{(v)}$ are passed through a water cooled condenser where water is condensed, removed and collected in a Teflon lined tank. Both the water and gases are sent to the Bunsen section of the S-I process for further processing.

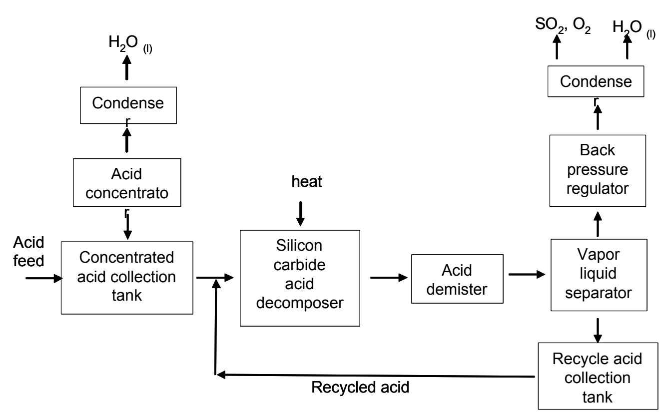

Fig. 2. Schematic diagram of the sulfuric acid decomposition process.

The acid decomposition pressure is controlled by a pneumatically controlled back pressure regulator placed at the outlet of the vapor/liquid separator. The unit is constructed of Teflon and glass filled Teflon and can operate up to pressures of 90 psia (Equilibar, Inc.).

The acid concentrator serves multiple purposes. It was observed in experiments at SNL with a 27” acid decomposer that when operating with 20 mole percent acid significant chugging of acid in the lower section of the decomposer occurred. This resulted in liquid acid contacting some of the catalyst and due to the thermal shock severe degradation of approximately 15% of the catalyst occurred. Although chugging was also observed while operating a 54” decomposer with 20 mole percent acid, no degradation of the catalyst was observed. However, in this initial phase of the work, it may be prudent to operate with higher acid concentrations at least until the acid decomposer is more fully characterized.

The acid concentrator also has economical and design implications for process scale up. The processing of more concentrated acid in the acid decomposer results in a higher yield of SO_2 per pass of acid through the apparatus. For scale up to a system with multiple acid decomposition units, this corresponds to fewer units required for a desired SO_2 production rate. Significantly more data on the process and a detailed economic analysis are required before any conclusions can be made for process scale up and process economics.

III.C. ACID CONCENTRATOR

Several different designs were considered for the acid concentrator. Based the design specifications, the need to construct the unit out of corrosion resistant materials, and avoid problems inherent with concentrating viscous solutions, a wiped film type of concentrator was selected. Fig. 3 is a diagram of the apparatus. The body of the concentrator is constructed of Hexoloy (Saint-Gobain Ceramics), a silicon carbide alloy. The end pieces and Teflon wiper are made from Teflon. Viton O-rings are used to seal the end pieces to the Hexoloy body. The apparatus in approximately 3.5 inches in diameter and 16 inches tall with a heated surface area of 82.2 in^2.

A four blade Teflon wiper driven by an electric motor force acid to the heated inner walls of the apparatus, thereby increasing the efficiency of the concentration process. Water vapor exits through the top of the unit whereas concentrated acid exits through the bottom of the unit. The water vapor is cooled and condensed and is sent to the Bunsen section for reuse. The concentrated acid is collected in a Teflon lined tank for feed to the acid decomposer.

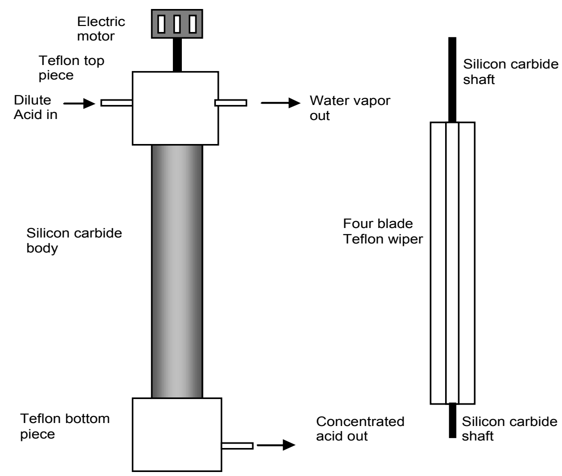

Fig. 3. Sulfuric acid wiped film concentrator

III.D. SILICON CARBIDE ACID DECOMPOSER

At the heart of the acid decomposition section is the silicon carbide integrated silicon carbide integrated acid boiler/superheater/catalytic decomposer. The apparatus is similar to a bayonet type heat exchanger () is a significant modification in the process and eliminates previous concerns with corrosion and high temperature connections. 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 a closed top. The two tubes are connected at the bottom using a manifold with O-ring seals.

The acid feed enters the annular space between the inner heat exchanger tube and outer heat exchanger tube. Heat is supplied to the surface of the outer tube. As the acid travel up the annular space it is heated to boiling in the lower part of the apparatus and superheated to 850ºC in the middle section of the apparatus. A catalyst is placed in the annular space in the top section of the apparatus. The acid is decomposed as it passes through the catalyst bed and the products of the decomposition, SO_2, O_2 and $H_2O_{(v)}$, enter the inner heat exchanger tube at the top, travel down the inner tube and exit at the bottom. As the gasses travel down the inner tube they release their energy to the acid in the annular space and heat is recuperated from the process. A very steep temperature gradient exists in the apparatus. Feed acid at the bottom enters at approximately 100ºC, the temperature of acid exiting the acid concentrator. In laboratory experiments using an apparatus constructed out of 27” heat exchanger tubes, the temperature increases to 850ºC at the top of the apparatus. The exiting stream from the inner heat exchanger tubes is between 150 and 200ºC indicating the high efficiency of heat recuperated in the apparatus. The length of the acid decomposer unit, heated length, quantity of catalyst, flow rate, and pressure will determine the total quantity of SO_2 that can be generated.

Based on experiments performed at Sandia, for the integrated laboratory scale experiments a 54 in unit is capable of producing sufficient SO_2 for hydrogen production rates of 200 L/hr or more. The unit has been successfully operated with 20, 30 and 40 mole percent sulfuric acid. However, testing with 20 mole percent acid indicated significant fluctuations of the liquid acid level in the acid boiling section of the unit. In experiments with a 27" acid decomposer, this "chugging" behavior resulted in liquid acid contacting the catalyst resulting in significant degradation of the catalytic pellets. Although no degradation of the catalyst was observed in the 54" unit, it may be advisable to operate the unit at higher acid concentrations.

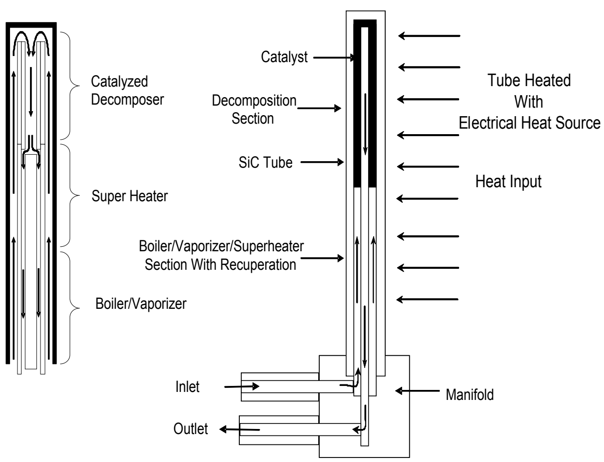

Fig. 3 Silicon carbide acid decomposer.

III.E. ADDITIONAL PROCESS EQUIPMENT

All process tanks are Teflon lined stainless steel with the exception of the water collection tank from the acid concentrator that is constructed of stainless steel with no lining (Alloy Products, Inc.). All valves used in the process are solenoid operated with all wetted surfaces constructed of Teflon (Teqcom, Inc.). Pumps used in the process are piston type pumps with a ceramic body and piston and Teflon seals (Fluidmetering, Inc.)

The two chilled water cooled condensers, one for condensing water from the acid concentrator and the other for condensing water from the product gasses stream, were constructed with coiled PTFE tubing placed inside a PVC or glass lined pipe housing. Because small amounts of sulfur dioxide would diffuse through the tubing into the cooling water and produce sulfurous acid, all cooling water was passed through an acid neutralizer placed before the inlet of the chilled water circulator. The neutralizer contained high temperature processed magnesium oxide.

IV. SKID MOUNTED ACID DECOMPOSITION PROCESS

A picture of the completed sulfuric acid apparatus is given in Fig 4. The frame is stainless steel strut mounted to a steel bottom piece designed for transport with a forklift. The entire process is enclosed with 1/4" thick Lexan. The Lexan shield serves to contain process fluid in the event of a leak and direct ventilation through the skid. As an additional safety step, components processing sulfur dioxide including the acid decomposer, vapor/liquid separation tank, storage tanks and various analytical and control equipment will be contained in an inner enclosure also constructed using stainless steel strut and Lexan. An activated carbon filter is placed inside the inner enclosure to remove any sulfur dioxide in the event of a leak.

Fig. 4. The sulfuric acid decomposition apparatus. The silicon carbide decomposer (SID) is shown on the left side of the photograph with heaters removed.

Power connections for the skid process are through a junction box mounted on the side of the skid. The process requires electricity at 110V and a total of approximately 12,000 watts of power to operate heaters, pumps and control systems. In addition to power, the process requires compressed air or nitrogen at 100 psi to 130 psi to regulate the system operating pressure.

V. PROCESS MONITORING AND CONTROL

All process monitoring and control equipment and power supplies are mounted on panels attached to the side of skid. The process control equipment is shown in Fig 5 mounted to the side of the skid. The control units can be remotely operated by computer or used to operate individual process units directly at the skid. Under normal operation, the system will be remotely operated. During equipment installation, testing and maintenance or in the event of a problem with the computer control system the individual skid mounted control units can be used to operate the individual skid components.

Fig.5 Process control and monitoring equipment mounted on the side of the acid decomposition skid.

The concentrations of SO_2 and O_2 in the products stream are determined using an Oxygen analyzer, I-30 (Oxigraf, Inc.). This instrument can detect O_2 concentrations to an accuracy of 0.1%. Once the oxygen concentration is known, the concentration of sulfur dioxide in the output stream can be calculated based on the stoichiometery of the sulfuric acid decomposition reaction.

Thermocouples (Omega, Corp.) and pressure transducers (Kulite Semiconductor Products, Inc.) are placed throughout the process for monitoring and controlling the process. Gas and liquid flowmeters (Cole-Parmer Instrument Company) have Teflon and Viton wetted surfaces. Gas flowmeters are of the rotor type and liquid flowmeters are optical in design. Tank level indicators are of the float type, all Teflon construction and operate using a magnetically activated reed switch (Innovative Products, Inc.).

All process instrumentation including pumps, valves, thermocouples, pressure transducers, flow meters and tank level indicators will be connected to Allen-Bradley process control interfaces (Rockwell International) that are connected to a computer through a single Ethernet line.

VI. CONCLUSIONS

Sandia National Laboratories has completed design, construction and initial testing of the acid decomposition section of the process. The process consists of two main processing steps; acid concentration and acid decomposition. The acid concentrator is a wiped-film type unit constructed of silicon carbide and Teflon. A novel design for the acid decomposer has been developed and has eliminated past problems with corrosion and failure of high temperature connections. The SNL process section is scheduled to be connected with the other sections of the S-I process in the near future for operation of a demonstration-scale S-I process.

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