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Pressurized Direct Contact Heat Exchanger Experiments for H_2SO_4 Decomposition

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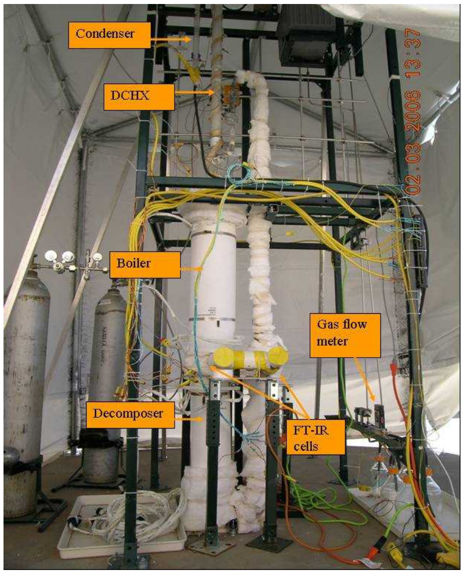

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ABSTRACT

Two sulfuric acid decomposition tests were performed with a DCHX (direct contact heat exchanger) to experimentally demonstrate the performance of this exchanger for recovering heat and undecomposed acid. The purpose of this test series was to demonstrate the potentially more efficient heat and mass transfer characteristics of a DCHX and validate computational models for subsequent use in the design of the acid decomposer for the Sulfur-Iodine integrated laboratory scale experiments. Both tests used a Hastelloy boiler and decomposer to vaporize and catalytically decompose the vapors, respectively, into oxygen, sulfur dioxide and steam. The first test was performed at ambient pressure to gain operational experience with the equipment prior to performing a pressurized test. Off-the-shelf glass components were used for handling hot liquid acid and practically no corrosion products formed. For the second test in which the apparatus was pressurized, the glass components were replaced with thick-walled ceramics, Teflon, and superalloy metallic fittings. Although this superalloy based apparatus will be changed to a SiC based configuration in the next series of experiments, these test do provide initial data for evaluation of DCHX operation that will be used in the design of the next generation ceramic system. The uncondensed gas produced by decomposition was 34% oxygen and 63% sulfur dioxide. This is nearly the ideal composition of 33.3% oxygen and 66.7% sulfur dioxide, which indicates that the decomposition reaction proceeded as expected and confirmed the viability of the real time diagnostics. In addition, by incorporating a DCHX, acid decomposition reached 90% conversion due to the recycle of the reactor effluent stream. Previously, without DCHX-recycling, acid conversion was only ~50%. The significant improvement in conversion approaches the theoretical limit of complete acid conversion. This report documents the completion of the NHI milestone on pressurized H_2SO_4 decomposition tests with a DCHX for the Sulfur-Iodine (S-I) thermochemical cycle project.

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I. Introduction

Catalytic decomposition of sulfuric acid has been studied and demonstrated previously in the context of developing the Sulfur-Iodine Thermochemical hydrogen production (Parker et al., 1982; General Atomics, 1986). An attractive energy source for this process is heat produced by a nuclear reactor. The maximum temperatures anticipated for the next generation of nuclear reactors is on the order of 900 C. At this temperature the decomposition of sulfuric acid is thermodynamically limited to be approximately 75%. However, this limitation is for a once-through processing of acid through an ideal decomposer. By recycling undecomposed acid, a steady operation can be achieved that approaches nearly 100% acid conversion.

A novel proposal for acid recycling that simultaneously recovers heat and unreacted acid was presented by Ozturk et al. (1994, 1995). In this approach, the gaseous effluent from the decomposer flows upstream and countercurrent to a falling liquid stream of acid in a Direct Contact Heat Exchanger (DCHX). A DCHX should provide excellent heat and mass transfer between the gas and liquid stream. However, we found no reports experimentally verifying the performance of this approach. Equally important, we found no analysis or experiments on problems that one may encounter integrating a DCHX into a process for decomposing sulfuric acid.

In this work we report on a sulfuric acid decomposition apparatus that tests the performance of a DCHX. Section II provides a description of the apparatus and details of the equipment, including interconnections, system assembly, approach, and the diagnostic instrumentation. In addition, the test sequence and operations are described. Section III describes the method used to process the data to obtain the acid conversion fraction. The results are presented and discussed in Section IV. Section V concludes with a review of the important results and plans for future work.

II. Description of Apparatus

Two acid decomposer configurations were developed and tested. The first configuration was used for an ambient or unpressurized test. In this test virtually no corrosion products formed in the system. This was a significant achievement and confirmed that several engineering innovations implemented to control corrosion in a superalloy system were successful. As explained below, metallic components were required for the second configuration in which the apparatus was pressurized. These components introduced more opportunities for corrosion, but still allowed data to be obtained on acid decomposition with a DCHX configuration.

II.1. Unpressurized Apparatus

A photograph of the unpressurized apparatus inside the tent is shown in Figure 1. A schematic of the apparatus is shown in Figure 2, with greater detail for the DCHX (Direct Contact Heat Exchanger) section shown in Figure 3. The yellow-shaded circles with numbers correspond to thermocouple numbers at the locations indicated in Figures 2 and 3. A peristaltic pump is used to deliver 42 mol% (80 wt%) acid to the top of the DCHX. The DCHX is a 5 cm inside diameter, 80 cm long, glass column with ground glass joints at the ends of the column. Glass components were chosen because they are off-the-shelf items that are highly acid resistant. (The only custom-made glass components are the glass loop, check valve, and DCHX top adapter.) This choice expedited the construction of the DCHX and connections to the rest of the apparatus. The column is packed with 5 mm glass Raschig rings. Liquid acid is dispersed as it falls through the packing while being heated by the rising hot gas effluent from the decomposer. In addition, unreacted SO_3 in the gas effluent stream is condensed into the liquid stream. The falling liquid acid is shown as blue drops in Figures 2 and 3. Because there are no intervening barriers between the liquid and gas streams, there is direct contact between the gas and liquid streams, and thus excellent heat and mass transfer. The liquid effluent from the DCHX passes through a check valve to prevent backflow. The liquid then collects in a glass loop. In this loop, two liquid columns form which prevent gas from rising up from the boiler. Once the loop is full, additional liquid added to the loop forces liquid in the other leg of the loop to drip down into the boiler through an alumina tube. Sediments collect at the bottom of the loop which reduces the chance for interfering with the operation of the check valve.

Hot liquid acid from the loop is introduced into the boiler where the acid is vaporized. The boiler is shown without the enclosing heater in Figures 4. The boiler is a 7.6 cm (3 in) diameter, 74 cm (29 in) long Hastelloy C276 pipe packed with 8 mm size silicon carbide (SiC) pellets that were provided by Ceramatec (Salt Lake City, Utah). An eight inch long glass sleeve is inserted at the top of the boiler to prevent liquid from contacting the upper walls of the boiler. The SiC pellets and top part of the glass sleeve are shown in Figure 5. To minimize the region in the boiler that requires heating, we adopted an idea used previously (General Atomics, 1986), and inserted concentrically into the boiler a solid alumina cylinder. A picture of the cylinder is shown in Figure 6. Thus, the acid flow is in the annular region between the alumina and the boiler wall. Approximately 3862 gm of SiC pellets are required to fill the boiler. A schematic of the boiler is given in Figure 7.

The boiler is designed to disperse the liquid acid as it falls through the SiC bed and vaporize before reaching the boiler walls. The boiling point of sulfuric acid is 337 C (Lide, 2001), and the boiler is designed to heat the fluid to ~500 C, with the wall temperature well above 600 C. Thus, all the acid solution is vaporized upon exiting the bottom part of the boiler and entering the decomposer. A split-tube heater encloses the boiler and provides up to 2200 W of power. In addition, a band heater surrounds the boiler top flange. Thermocouples are used to monitor the boiler as shown schematically in Figures 2 and 7. Measurements from thermocouples numbered 3 and 5 are used as control variables for the band and split-tube heater controllers, respectively. All thermocouples are K-type and temperature readings are stored every 5 seconds.

The bottom of the boiler is flanged and machined smooth. The boiler can be joined to either a FT-IR (Fourier Transform Infrared) cell (as shown in Figure 4), or directly to the decomposer (as shown in Figure 2) by compressing a gold O-rings to create a tight corrosion-resistant seal between the flanges. With the FT-IR cell installed, the gas concentrations of SO_2, SO_3, and H_2O prior to passing through the catalyst can be measured. For the tests in this report, the FT-IR cell upstream of the decomposer was removed because of problems with the window cracking. We attempted to use the downstream FT-IR cell to measure the gas concentrations after passing through the catalyst bed. However, due to alignment and sealing problems no FT-IR data were obtained.

The decomposer is a Hastelloy C276 pipe with a 3.34 cm (1.315 in) outside diameter, and a wall thickness of 3.38 mm (0.133 in) and is shown in Figure 5. The unit has a "U" shape and is therefore called a U-tube. A schematic of the decomposer with the location of thermocouples is shown in Figure 8. In the left leg of the U-tube, 90 grams of 1% Pt on zirconia catalyst are suspended to form a packed bed between thermocouples numbered 13 to 18. The catalyst is in form of 4.8 mm diameter and length cylindrical pellets, and is available from CRI Catalyst Company in Houston, Texas. To improve the measurements of the gas stream and catalyst bed temperatures, thermocouple wells 1.25 cm (0.5 in) long made from 3.18 mm (0.125 inch) Hastelloy tubing were welded radially inwards from the pipe walls, and thus extend ~9 mm into the flow. Hot gas from the decomposer flows up the right leg of the U-tube and enters an FT-IR cell for composition analysis.

Undecomposed acid vapor and water produced by decomposition enter the bottom of the DCHX as shown in Figures 2 and 3. The produced uncondensed gases, which are H_2O, SO_2 and O_2, flow out the top of the DCHX. Effluent gases from the DCHX are cooled to condense water, then dried by passing through a bed of $CaSO_4$, then filtered through a bottle containing glass wool. The flow rate of the remaining gas consisting of SO_2 and O_2 is measured with a mass flow meter, and the gas composition is analyzed with a gas chromatograph (GC). Data from the flow meter are stored every 5 seconds, and a gas sample is analyzed by the GC every 3 minutes just prior to venting gas to the atmosphere. A small bottle partially filled with water is used to monitor for gas bubbles, which provides a simple visual flow and leak check. The vent tube is 244 cm (8 ft) or more above ground level to ensure adequate dispersal of SO_2.

Samples for corrosion testing are placed at the bottom of the boiler and below the catalyst bed. The samples are held in perforated Hastelloy C276 tubes, as shown in Figure 9. The locations of these samples are shown in Figures 7 and 8.

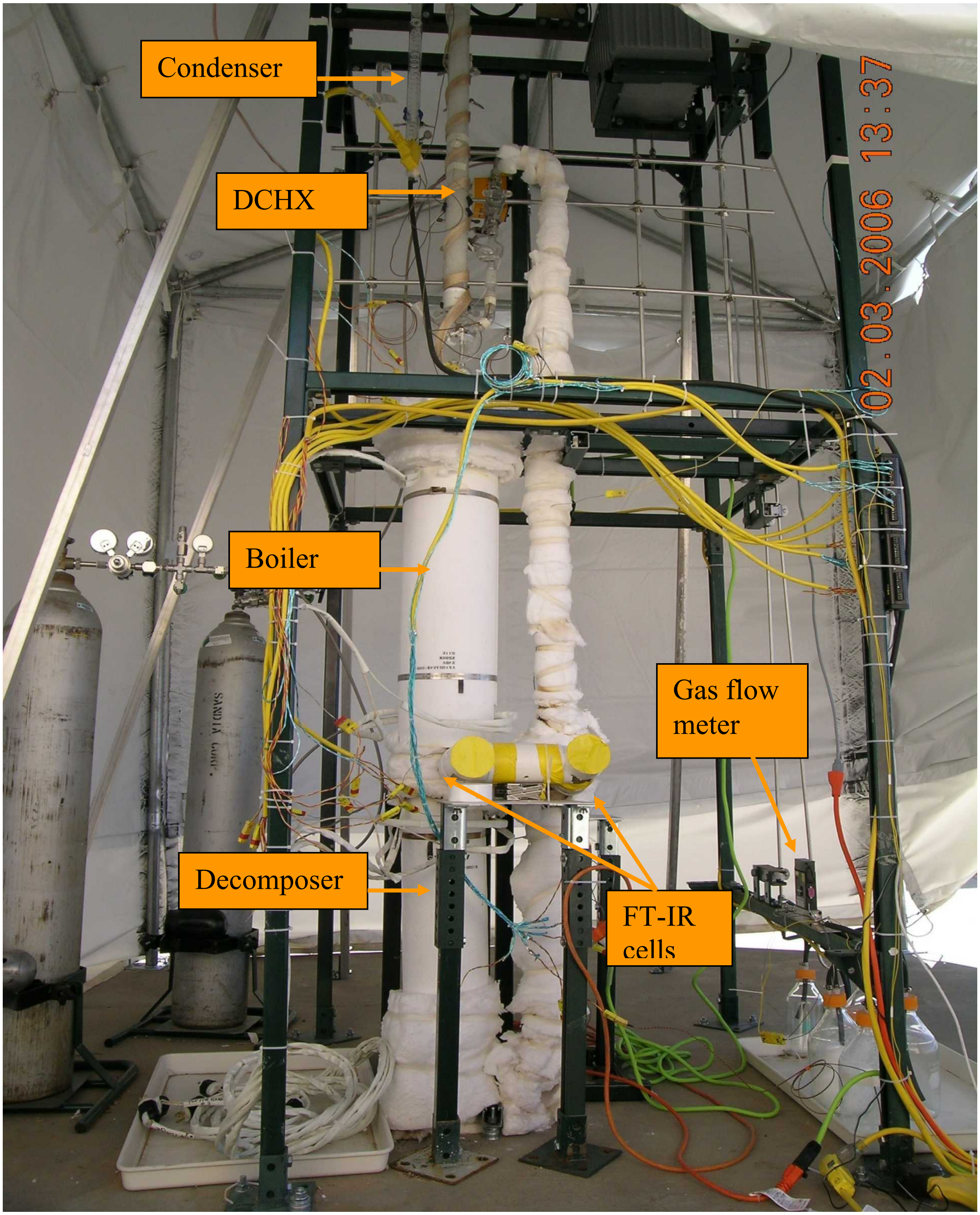

Figure 1. Unpressurized experimental apparatus with glass DCHX, cooler, gas-trapping loop, and check valve.

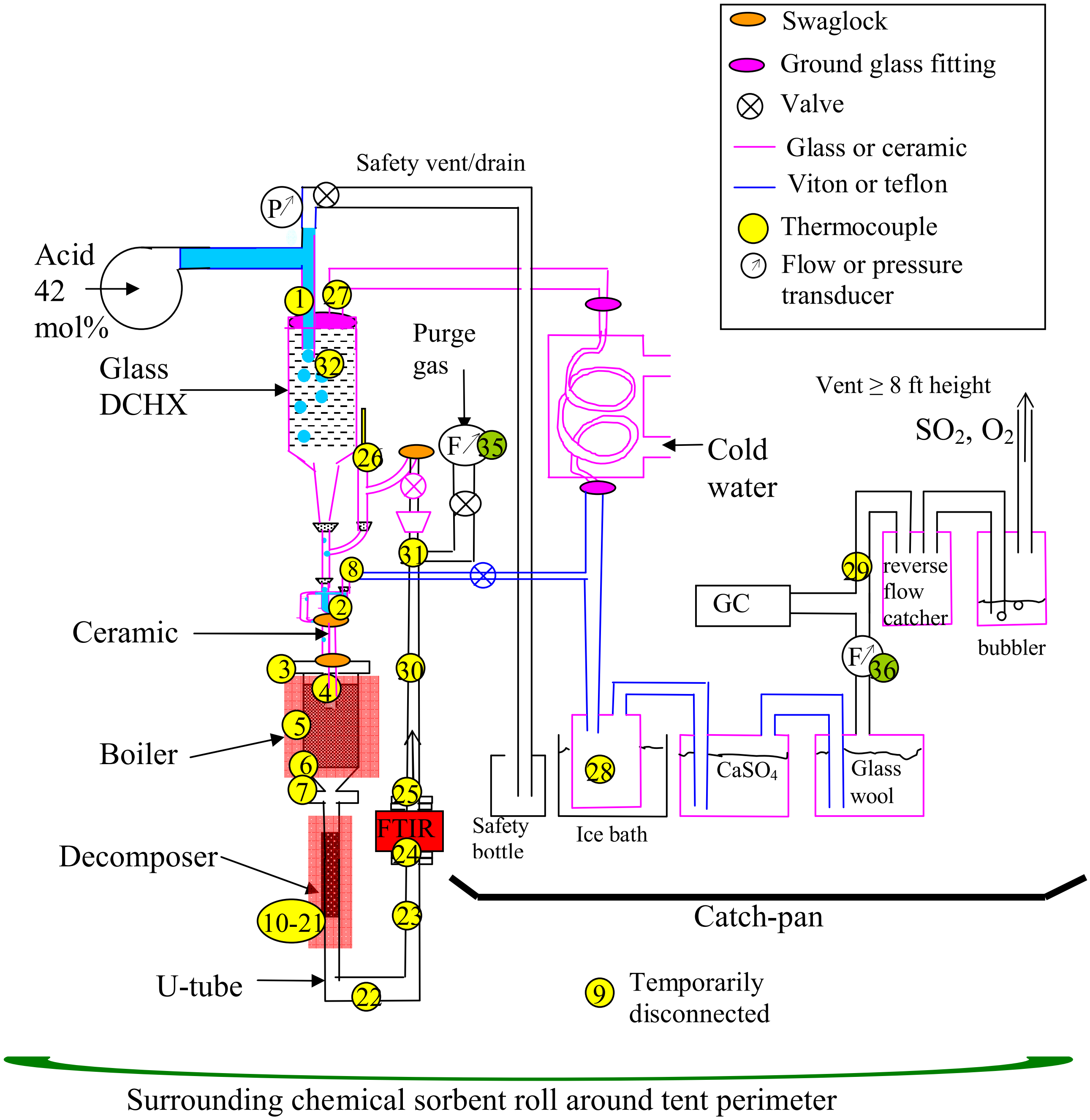

Figure 2. Schematic of unpressurized apparatus consisting of a DCHX, boiler, and catalytic decomposer. Red shaded regions of the boiler and decomposer represent split-tube heaters.

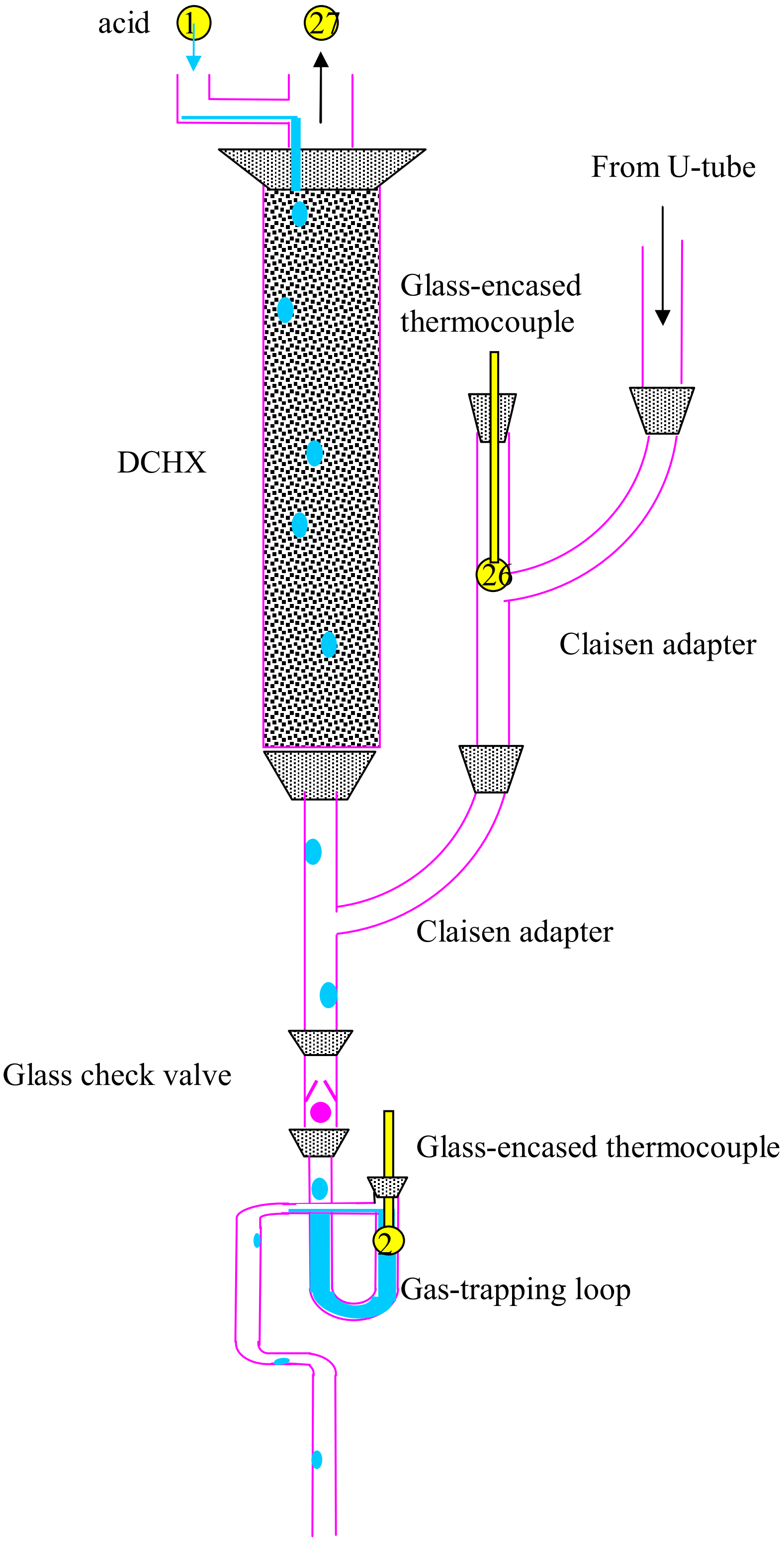

Figure 3. Glass components used in unpressurized test and were to be housed in a pressure vessel.

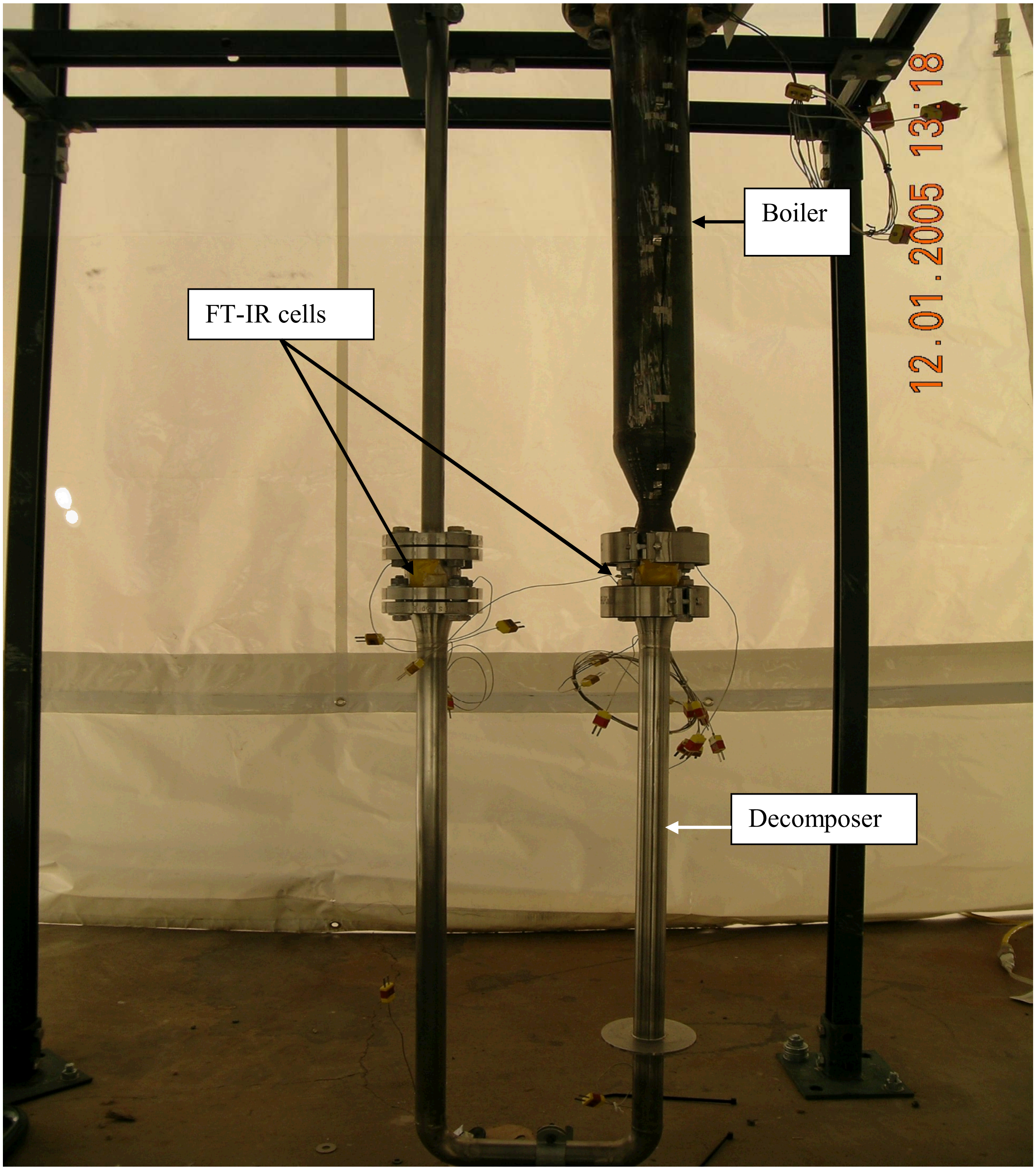

Figure 4. Boiler, decomposer, and FT-IR cells without split-tube heaters or insulation. The flange connections on the FT-IR cells match those of the boiler, decomposer, and return leg of the U-tube. Thus either or both FT-IR cells can be included or excluded from the apparatus. Band heaters are on the flanges for the FT-IR cell between the boiler and decomposer. The split-tube heater rests on the support ledge near the bottom of the decomposer.

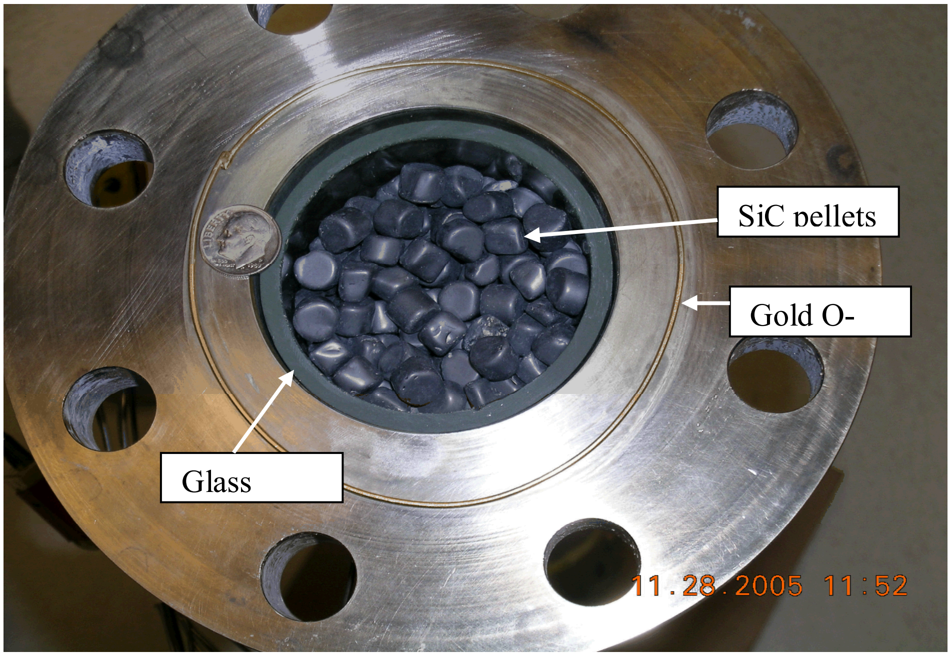

Figure 5. Top of Hastelloy boiler showing SiC pellets, glass sleeve, and gold O-ring.

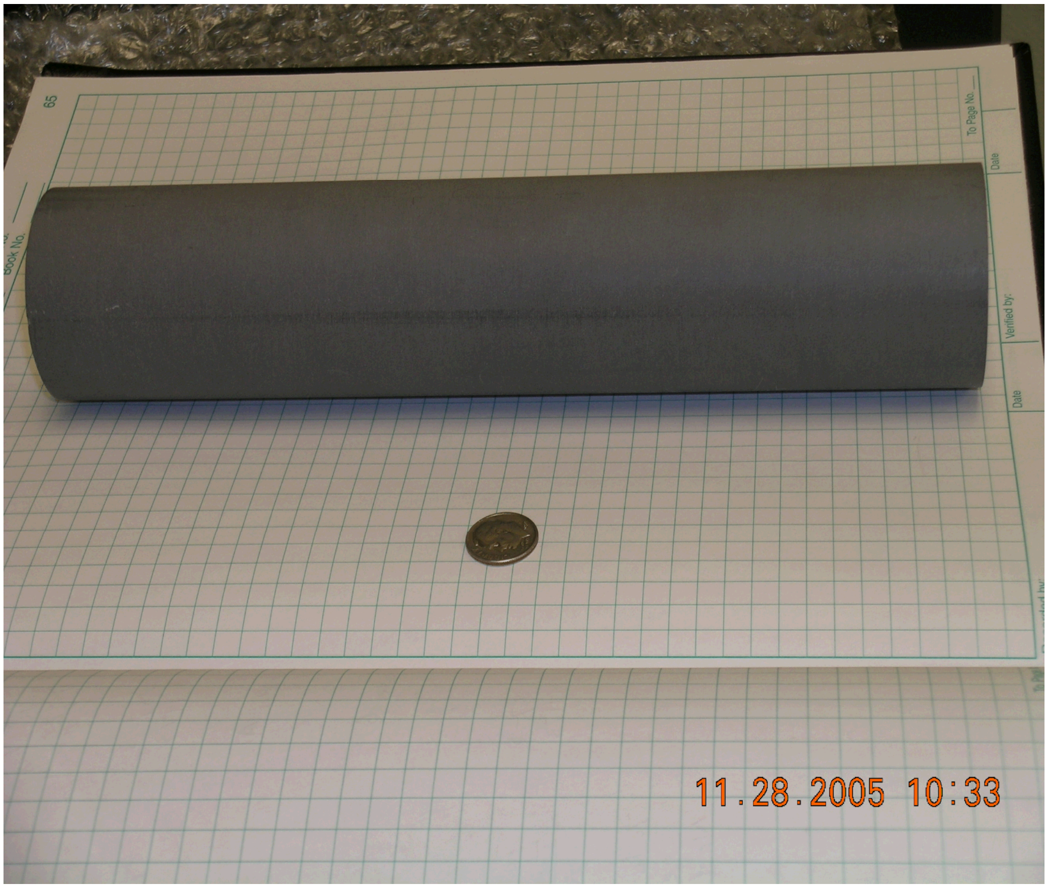

Figure 6. Alumina cylinder insert. The solid cylinder is 24 cm (9.5 in) long, 5.1 cm (2 in) diameter, and weighs 1324 gm.

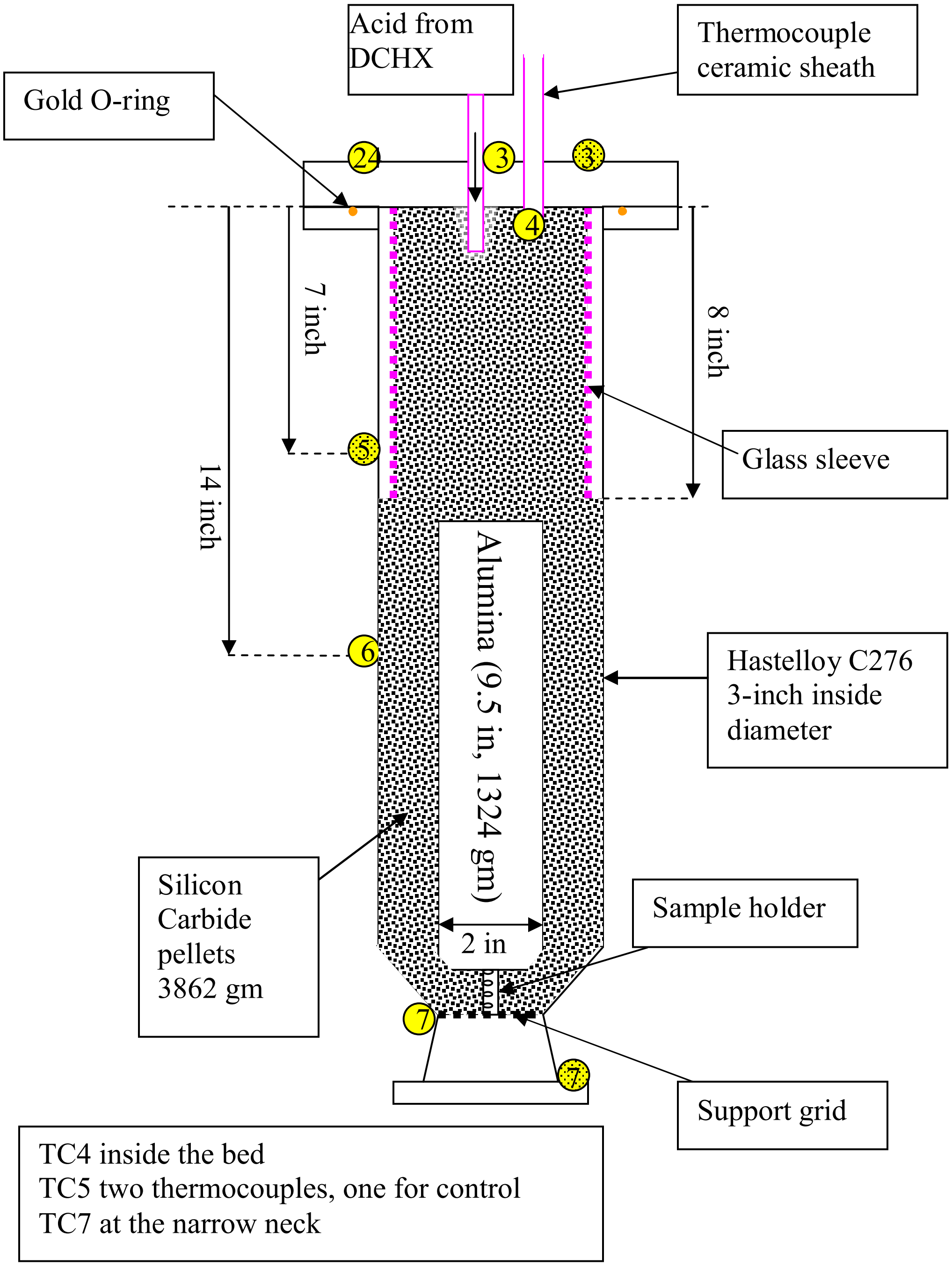

Figure 7. **Schematic of boiler packed with silicon carbide pellets, alumina cylinder, and sample holder for corrosion testing of materials.**

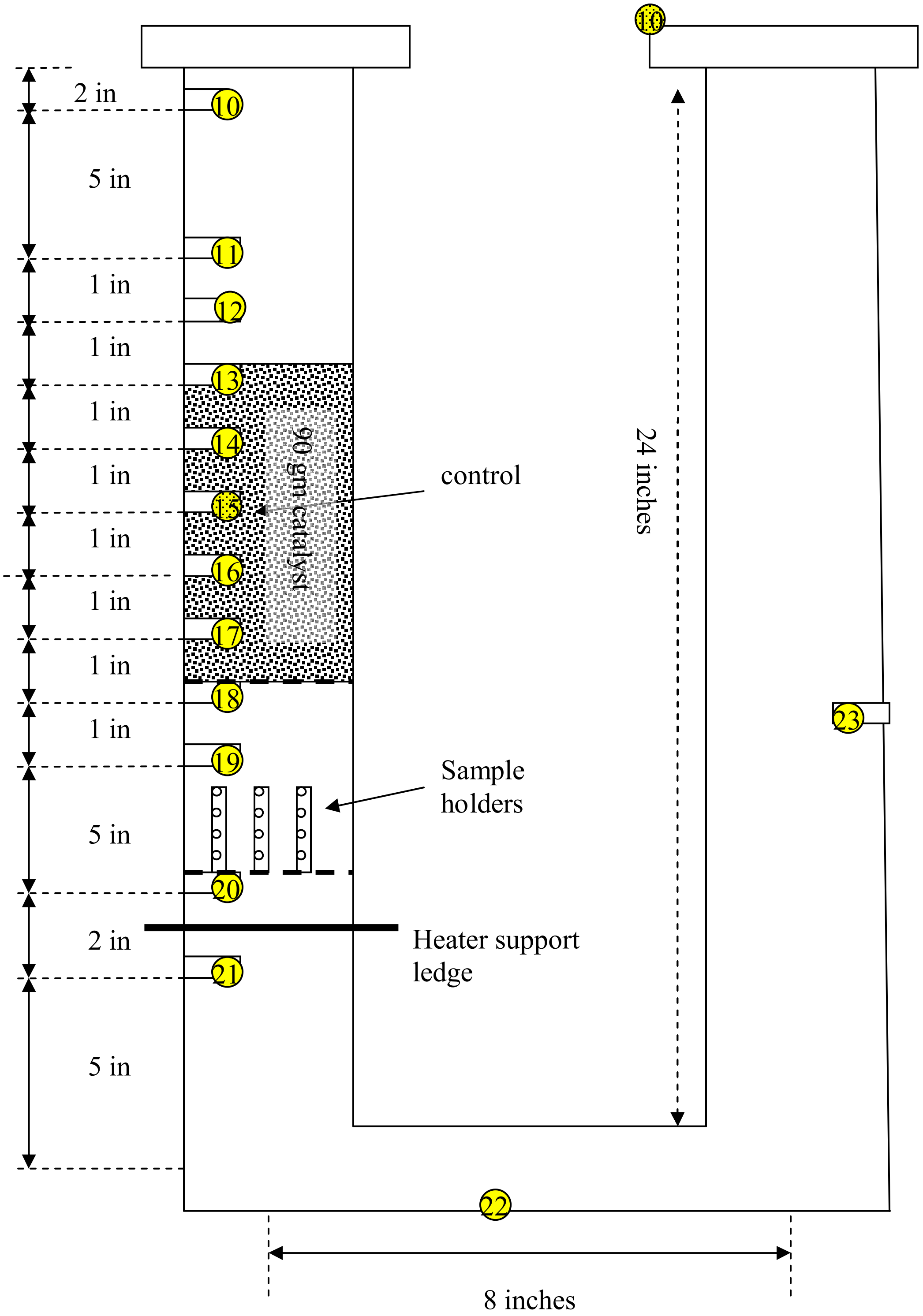

Figure 8. Schematic of decomposer U-tube showing the location of thermocouples, catalyst bed, and samples for corrosion testing.

II.2. Pressurized Apparatus

To perform pressurized tests in the acid decomposition apparatus, the glass components in the upper section had to be replaced with available thick-walled ceramics, Teflon, and metal components that could withstand pressurization. Significant corrosion was unavoidable with metallic components exposed to hot liquid acid, but the DCHX operations could still be tested.

The pressurized version of the apparatus is shown in Figure 10 and a schematic is given in Figure 11. It is similar to the unpressurized version in Figures 1 and 2, respectively. The boiler and decomposer are the same for both versions. However, the components above the boiler have been redesigned as shown schematically in Figure 12. The hot gases from the decomposer enter a Hastelloy-T and then rise up through the DCHX. We tried using alumina and mullite tubes for the DCHX, but a tight seal could not be obtained with the Hastelloy fitting. Instead a silicon carbide tube packed with denstone was used for the DCHX. A ceramic gas-trapping loop and/or check were not available for the test. Therefore these components were made from a looped Teflon tube and a Teflon check valve. To reduce the heat conducted to these components, alumina tubes were joined at both ends of the Teflon components. If the temperature exceeded the operating temperature of Teflon under pressure (~150 C), the experiment would have been stopped. The Teflon temperature was monitored by thermocouples numbered 2 and 8, as shown in Figure 12. The Teflon loop serves as a gas trap, similar to the glass loop described for the unpressurized test. In Figure 10, one can see that the Teflon loop is filled up to the top of the loop, similar to that shown in Figure 12.

A pressure relief valve set at 29 psia (2 atm absolute) was used to control the pressure, and is shown in Figure 10 and 11 between the bottles with $CaSO_4$ and glass wool. In parallel with this valve, a manually operated valve was installed to allow for purging the apparatus of SO_2 at the end of an experiment.

Figure 9. Perforated Hastelloy tubes used to hold samples for corrosion testing. The larger diameter tube was place at the bottom of the boiler, and the smaller diameter tubes were placed below the catalyst bed. The samples shown are pieces of silicon carbide.

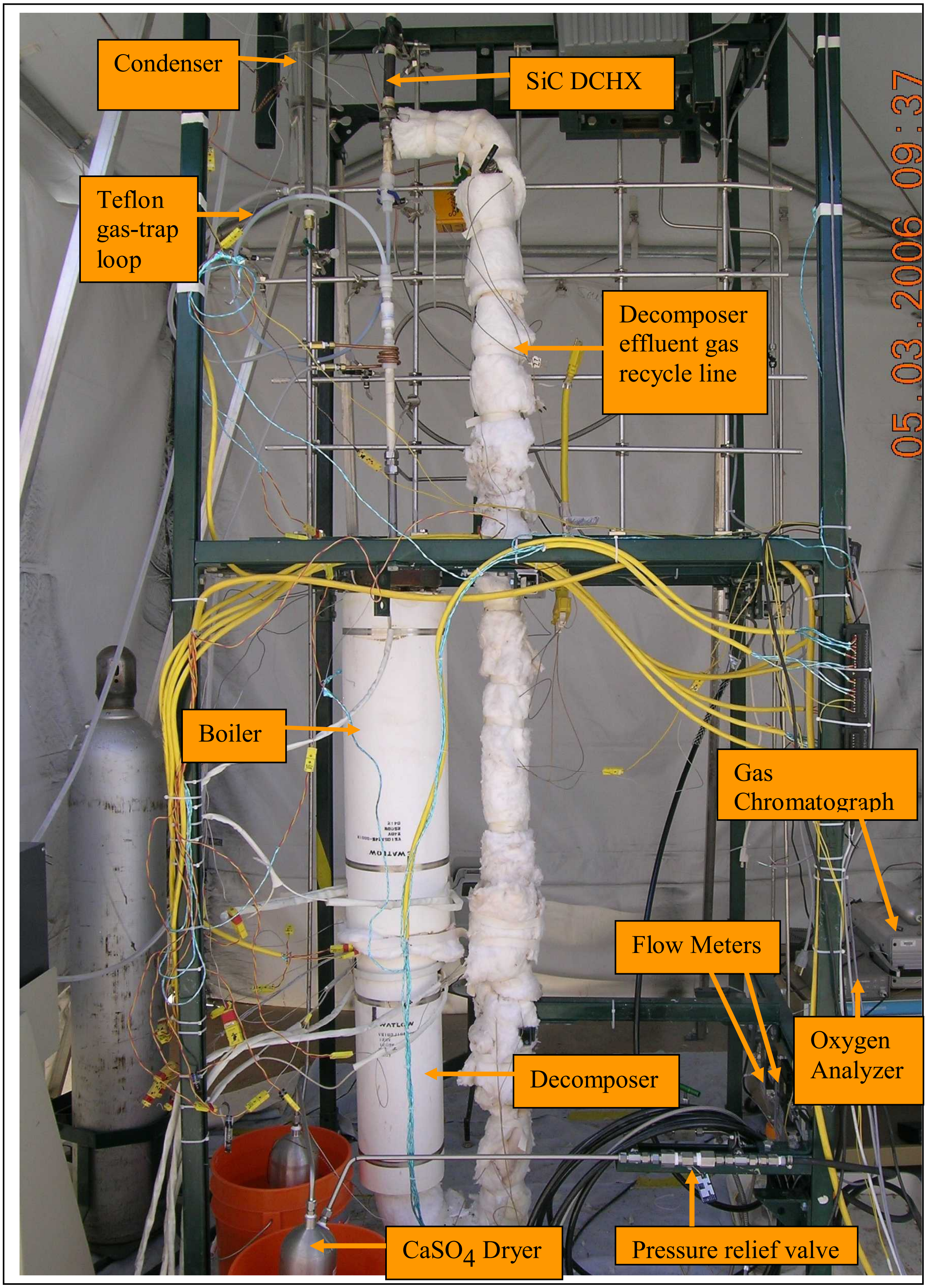

Figure 10. Picture of pressurized apparatus. The Teflon gas-trap loop is filled with acid up to the top of the loop.

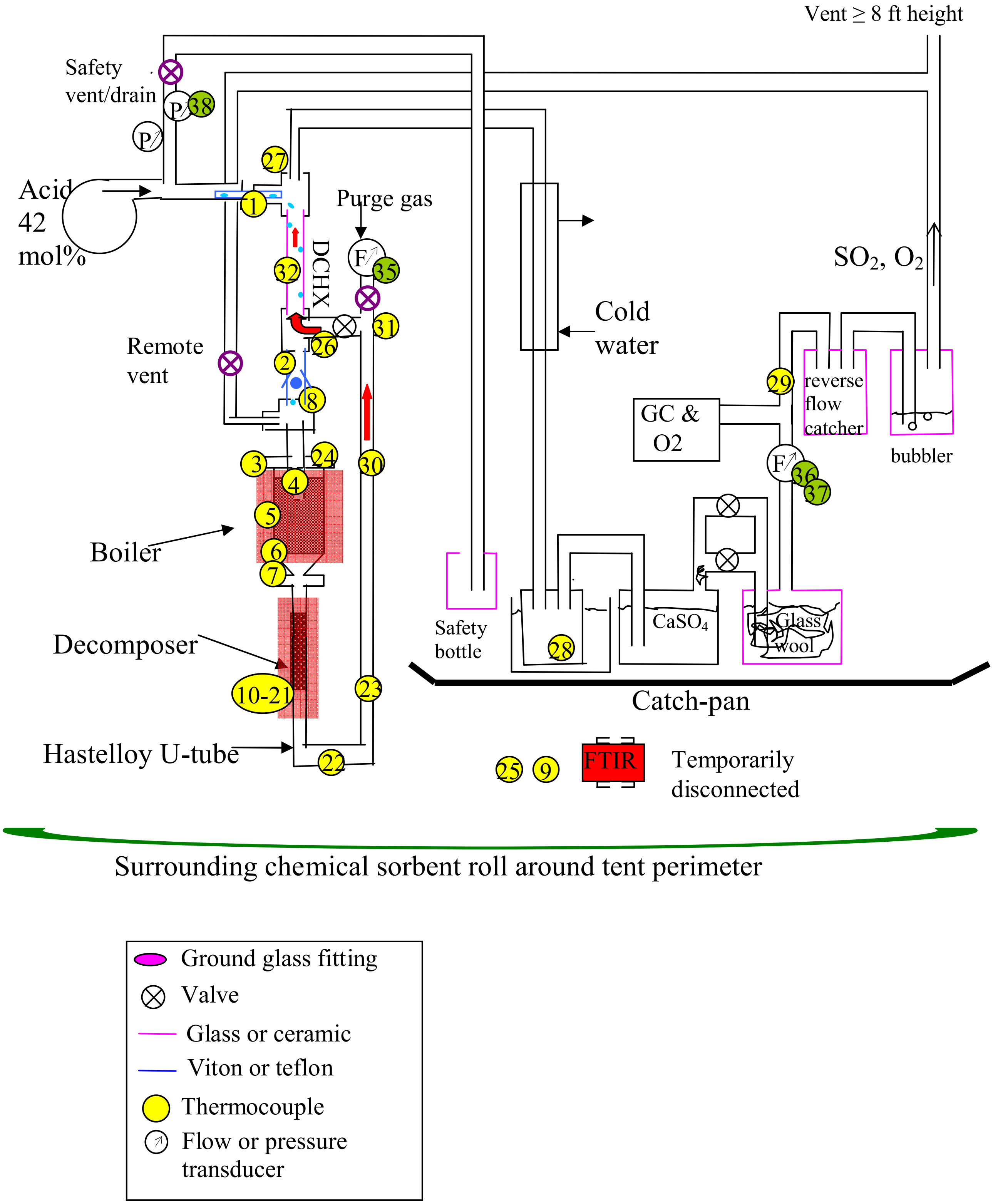

Figure 11. Schematic of pressurized apparatus.

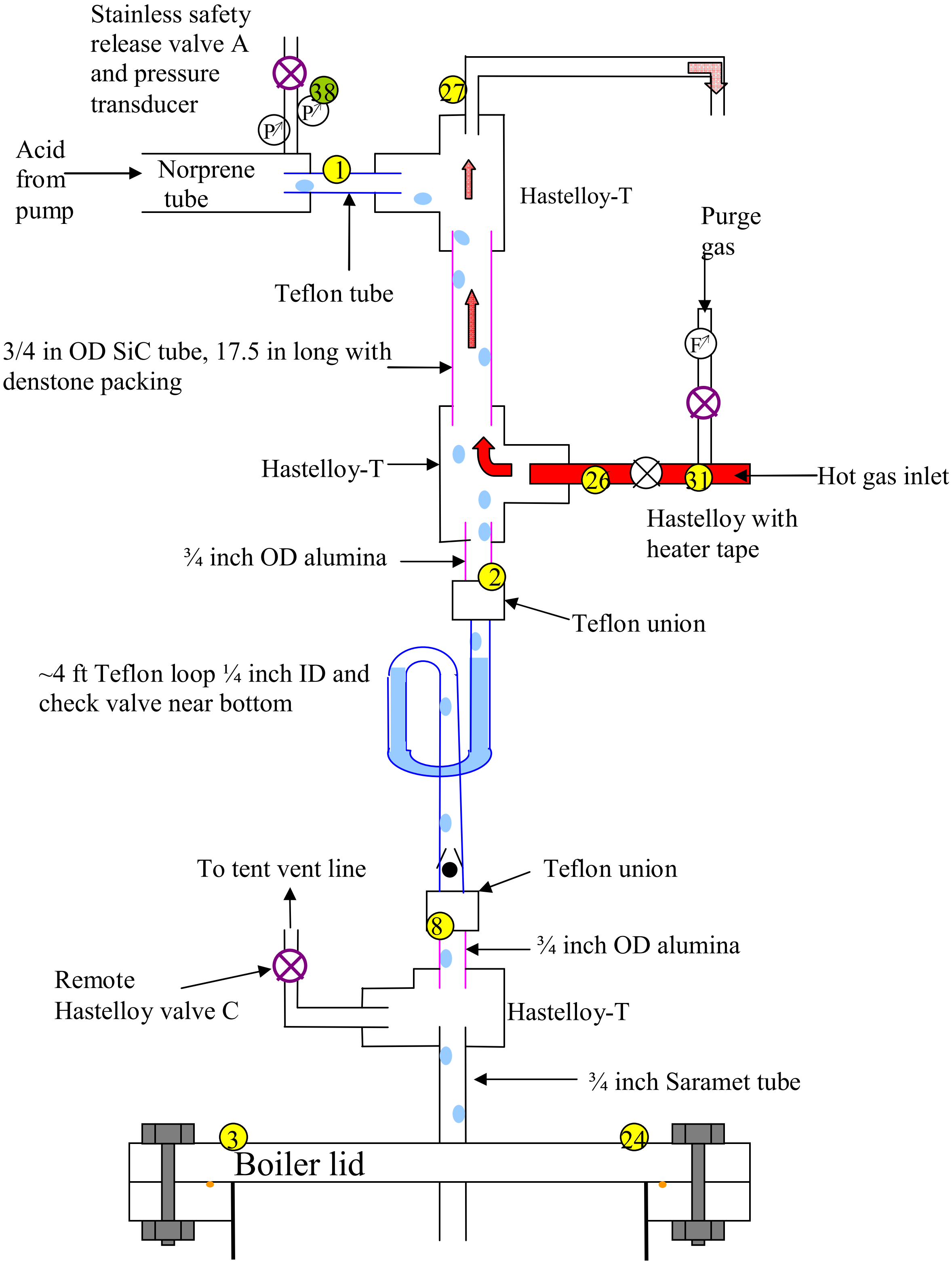

Figure 12. Schematic of pressurized DCHX.

III. Data Analysis

A key parameter to be determined from the experiment is defined as η, the fraction of acid converted to H_2O, SO_2 and O_2 as a function of pressure and temperature. In the experiments, the effluent gases are cooled to less than 20 C, and the flow rates of only the uncondensed gases (SO_2 and O_2) are measured. For each mole of decomposed acid one mole of SO_2 and half a mole of O_2 are produced. Therefore,

$$\eta = \frac{1}{1.5}\left(\frac{f_{gas}}{f_{acid}}\right) \tag{1}$$

where

η = acid conversion fraction (dimensionless),
f_{gas} = molar flow rate of uncondensed effluent gas (mol/min), and
f_{acid} = molar injection rate of acid (mol/min).

In the limit of no conversion, there are no measured gases produced in the experiment, thus $f_{gas} \rightarrow 0$ and $\eta \rightarrow 0$. In the other limit of complete acid conversion, $f_{gas}/f_{acid} \rightarrow 1.5$ and therefore $\eta \rightarrow 1$.

This analysis neglects the removal from the gaseous effluent stream of SO_2 by dissolution in condensed acid. Measurements of pressurized SO_2 solubility in aqueous sulfuric acid have been reported at 25 C and 50 C at pressures up to 4 bars (Hayduk et al., 1988). The solubility is generally less than 0.1 SO_2 mole fraction, and is therefore a small correction. In addition, as noted in the paper, the "dissolution process required the use of the stirrer and that the amount of gas dissolved during the initial charging period was negligibly small." In these dissolution experiments, the time to dissolve the gas with stirring required at least one hour. In the tests in this work there is no stirring of the solution. Thus SO_2 dissolution in condensed acid is neglected.

The uncondensed gas molar flow rate can be determined from the measured uncondensed gas volumetric flow rate and the ideal gas law, and is given by,

$$f_{gas} = \frac{P\underline{V}}{RT} \tag{2}$$

where

$\underline{V}$ = measured volumetric uncondensed gas flow rate (liters/min),
P = pressure at which uncondensed gas flow rate is measured (~12 psia in Albuquerque, New Mexico),
R = ideal gas constant (1.206 liter-psia/mol-K),

T = gas temperature where the uncondensed gas flow rate is measured (typically 310 K for the tests), and

f_{gas} = uncondensed gas molar flow rate (mol/min).

Substituting Eq. (2) into Eq. (1) provides the expression needed to determine the acid conversion fraction from the data, and is given by,

$$\eta = \frac{1}{1.5}\left(\frac{P\underline{V}}{RTf_{acid}}\right). \qquad (3)$$

IV. Test Results and Discussions

IV.1. Ambient Pressure DCHX Experiment

The unpressurized acid tests began with a heatup sequence. Heaters were turned on in the morning and required approximately 4 hours to bring the apparatus to the operating temperature. For this experiment the center of the boiler and the center of the catalyst bed were initially at 650 C and 820 C, respectively. The acid pump was turned on at 13:35 and off after 1 hour and 13 minutes of acid injection. The mass of acid solution injected was 683.9 gm, and thus for 80 wt% acid, the acid injection rate was 0.0764 moles/min.

The temperatures in the DCHX streams, the boiler, and the catalyst bed are given in Figures 13, 14, and 15, respectively. The thermocouple numbers in the legends correspond to those given in Figures 2 and 3. Except at the top of the boiler bed and the decomposer, all temperatures were measured by thermocouples attached to the outside of the equipment.

The tubing from the decomposer to the DCHX was heated to ensure that the decomposer effluent stream remained above 350 C to prevent acid condensation. From the temperature given by thermocouple 31 in Figure 13, it took approximately 15 minutes from the time acid injection started until hot vapors from the decomposer arrived at the DCHX. At 13:50 there is a significant increase in the vapor temperature. An additional 10 minutes was required for these vapors to heat up and pass through the DCHX to raise the temperature of the vapor stream measured by thermocouple 27. The liquid stream was heated by the rising vapors, but the temperature rise of the exiting liquid stream from 23 to 32 C is too small to discern from the plot. The small temperature increase may be due to the large heat losses associated with small scale flows. Nonetheless, clearly a DCHX that is 80 cm long and 5 cm wide is large enough to capture the heat from the decomposer effluent stream.

The heated acid from the DCHX entered the boiler through an alumina tube. As given in Figure 14, the temperature at the top of the SiC bed in the boiler dropped significantly after 25 minutes of acid injection due to the arrival of much colder acid. The temperature at the bottom of the boiler remained above 400 C, and thus the acid was completely vaporized upon leaving the boiler.

The decomposer temperatures are given in Figure 15. Initially there was a sharp increase in catalyst temperature. This phenomenon was observed previously (Gelbard et al., 2005), and may be due to acid reacting with water or contaminants in the catalyst section. However, the catalyst section quickly drops to below 700 C. At this low temperature SO_3 is not decomposed. A malfunctioning heater controller or defective heater was thought to be the reason why the heater did not quickly reheat the decomposer. To bring the decomposer temperature up to at least 750 C, power from the boiler heater was alternately switched to the decomposer heater. That is why the decomposer temperature oscillated for the remainder of the test. After the test the reason for the problem with the decomposer heater was traced to the facility wiring, where only 110 volts was available from a 208 outlet.

The effluent gas flow rate is shown in Figure 16. The increase in flow rate beginning at 13:50 correlates well with the increased vapor temperature leaving the DCHX at this time shown in Figure 13. The gas flow rates, however, oscillated considerably for the remainder of the acid injection period. In previous tests, these oscillations were attributed to problems with a pressure relief valve not opening and closing smoothly. However, in this test no such valve was used and the pressure varied greatly. An alternative explanation for the oscillations is that acid was dripping into the boiler and these drops were rapidly vaporized and created large pulses of gas.

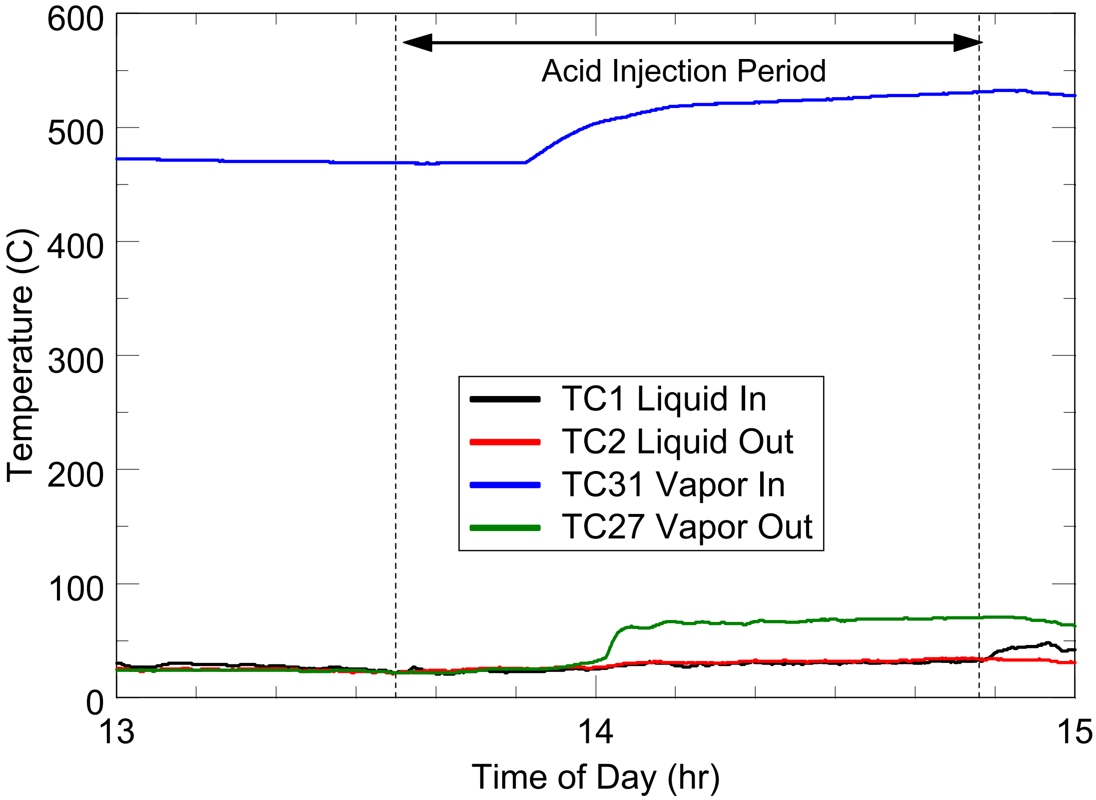

Figure 13. Temperature measurements for flow streams entering and exiting the DCHX.

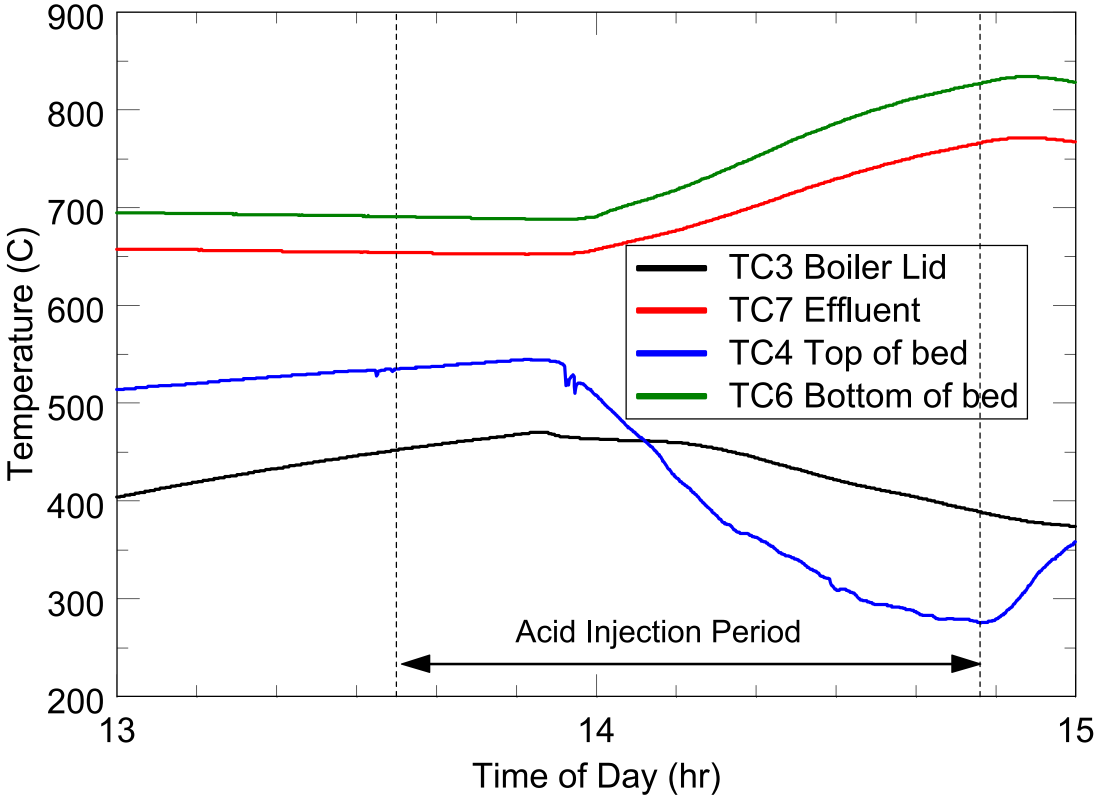

Figure 14. Boiler temperature measurements.

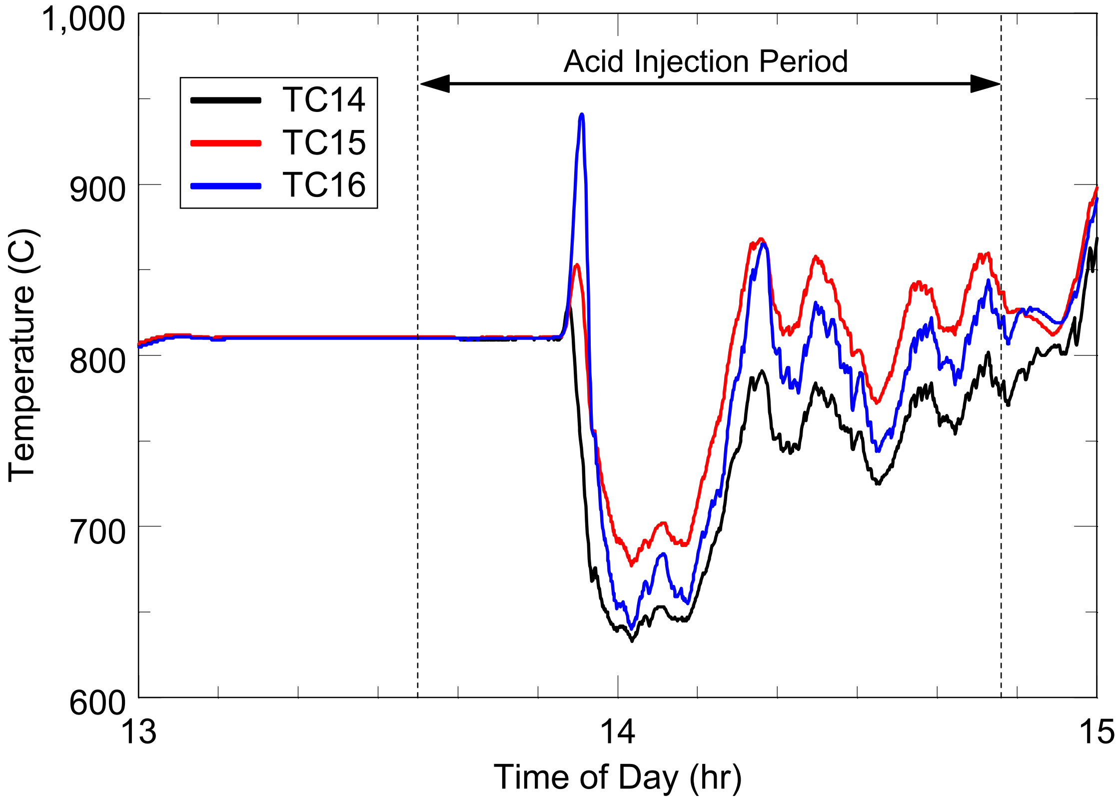

Figure 15. Temperatures in the decomposer catalyst bed.

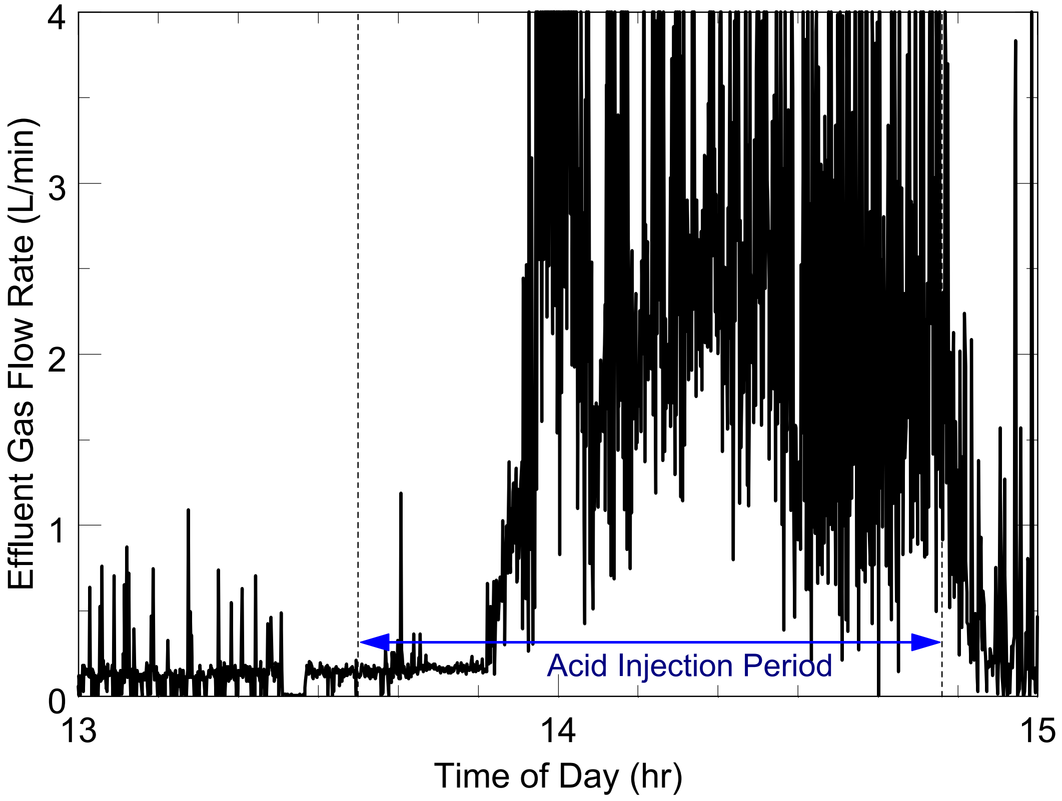

Figure 16. Total flow rates of SO_2 and O_2 out of the top of the DCHX.

IV.2. Pressurized DCHX Experiment

Several modifications and improvements were made to the diagnostics based on our experience with the unpressurized test. To capture rapid pulses of released gas, a second flow meter with a range of 0 - 20 L/min was added in series to the existing meter which had a range from 0 – 4 L/min. This second flow meter is shown in Figures 10 and 11. In addition, a real-time oxygen analyzer (Oxigraf Corporation, Mountain View, California) was added to the sampling stream, and is shown in Figure 10. This instrument sampled the gas very 5 seconds compared to the sampling frequency of 3 minutes for the GC (Gas Chromatograph), which provided the SO_2 concentration. To obtain good baseline oxygen and sulfur dioxide concentrations, the apparatus was flushed with nitrogen prior to acid injection.

The pressure and gas flow rate data for the test are given in Figure 17. The gas composition is shown in Figure 18 for both the gas chromatograph and the oxygen analyzer. The temperatures at the key positions for the DCHX, boiler, and decomposer are given in Figures 19, 20, and 21, respectively. The thermocouple numbers in these figures correspond to those given in Figures 12, 7, and 8, respectively.

The plan for the test was to continuously inject 80 wt% acid for two hours at 4 mL/min and measure the total gas flow rate and composition. As described below, instead of continuous acid injection there were four time periods over which the acid was injected, with venting and repressurization between each acid injection period. The acid injection periods are indicated in Figures 17, 18, and 22 as starting at the time shown with a vertical broken line, and terminating at the time shown with a vertical solid line. For the first three acid injection periods, a horizontal double arrow is also given in Figures 17 and 22. The fourth time period was too short to include a double arrow.

Acid pumping commenced at 12:52. From Figure 17, the pressure started increasing rapidly after about 15 minutes of acid injection. The pressure rose to over 38 psia with only a small release of gas on the order of 0.3 L/min. These two measurements indicated that either corrosion products had obstructed the flow, or that the relief valve was malfunctioning. In either case, for safety reasons the acid pump was shut down and the apparatus vented.

During the first period of acid injection very little gas was released by the relief valve and the oxygen concentration was negligible. These are shown in Figures 17 and 18, respectively. Therefore, the acid conversion fraction was also negligible as computed from Eq. (3) and shown in Figure 22. From Figure 18 we see that some gas did pass through the relief valve after the pump was turned off and that resulted in an increase in the oxygen concentration shown in Figure 18.

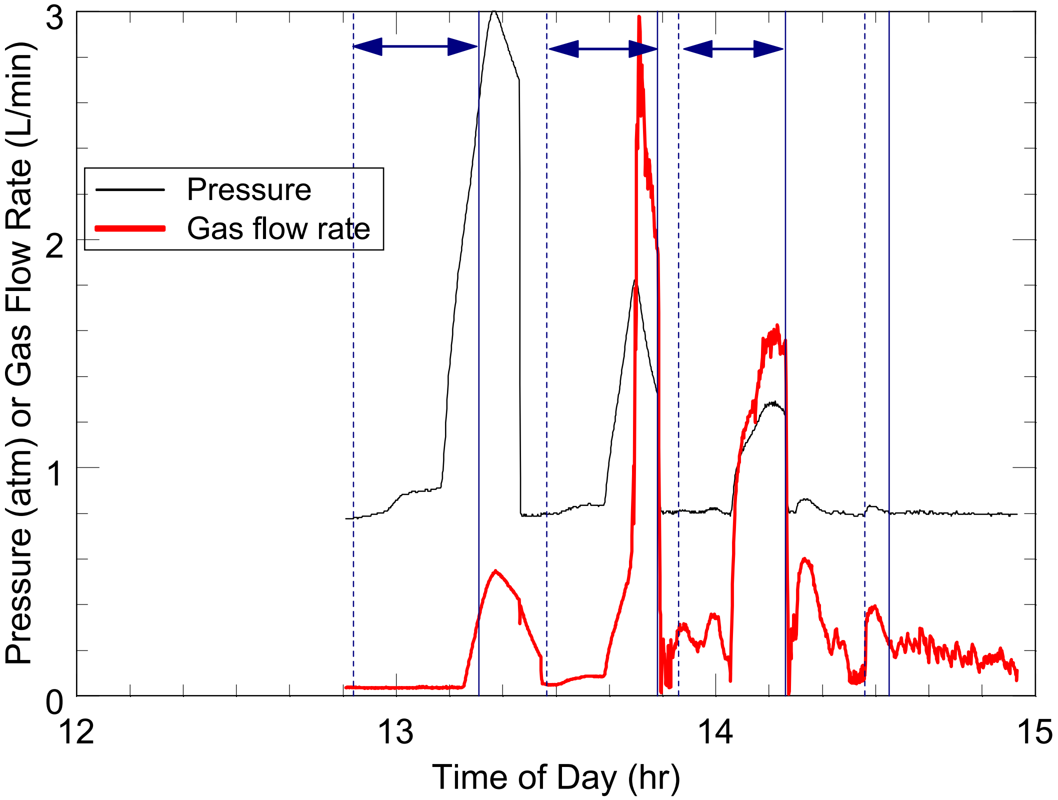

Figure 17. Pressure of liquid acid stream entered the DCHX and total gas flow rate of SO_2 and O_2 out of the DCHX. The acid pump was on in the time period indicated by the double-headed arrow. Between these periods the pump was off and the apparatus vented to the atmosphere.

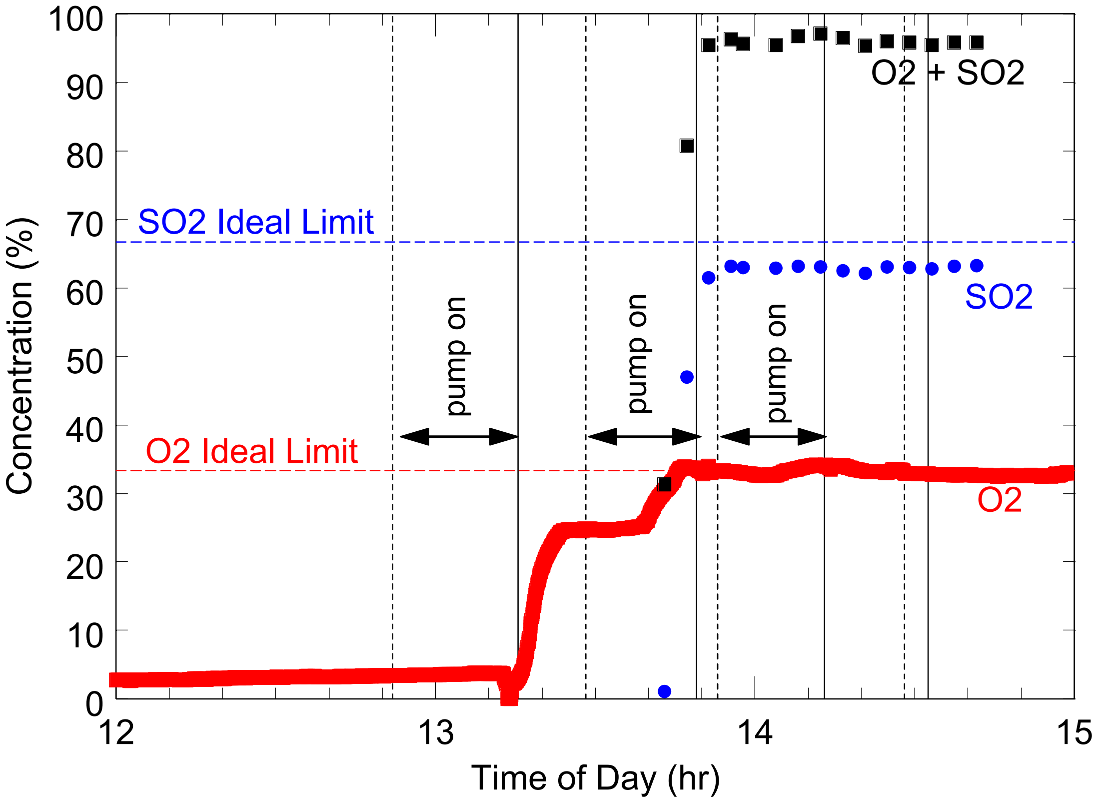

Figure 18. Effluent gas concentrations. The SO2 and O2 concentrations were measured with a gas chromatograph and an Oxigraf oxygen analyzer, respectively. The sum of these two gas concentrations approach the expected limit of 100%.

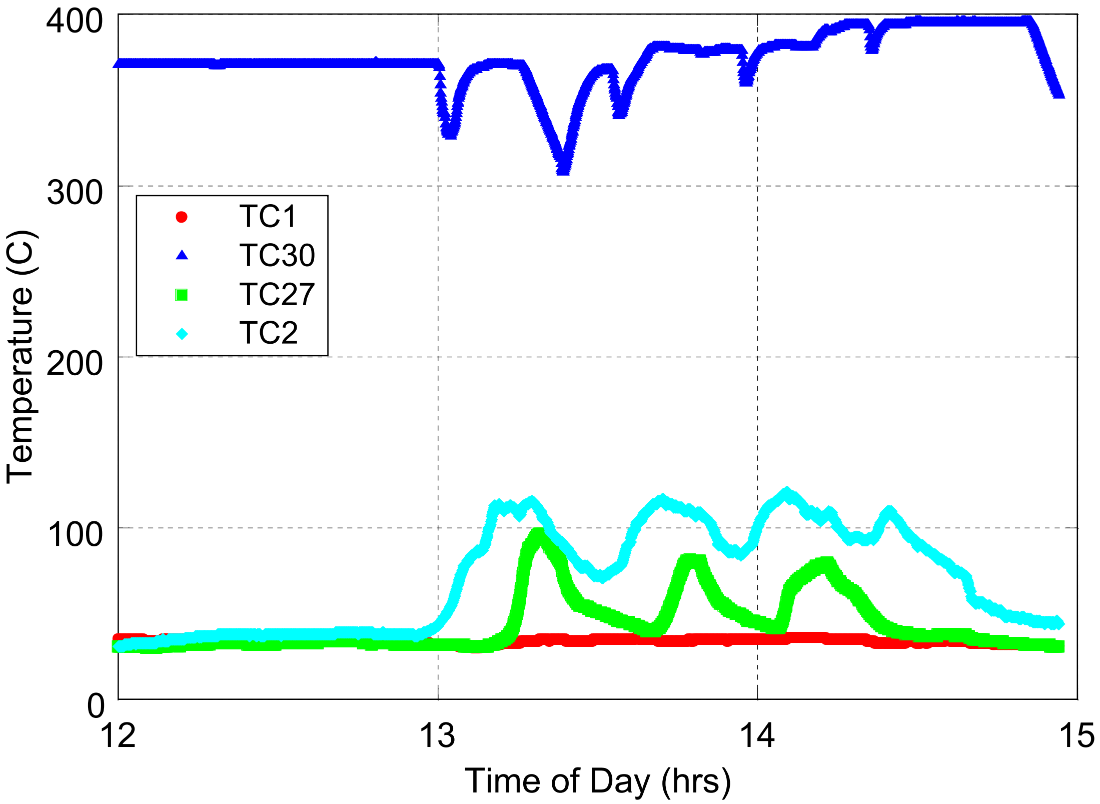

Figure 19. Temperatures of flow streams into and out of the DCHX for the pressurized test.

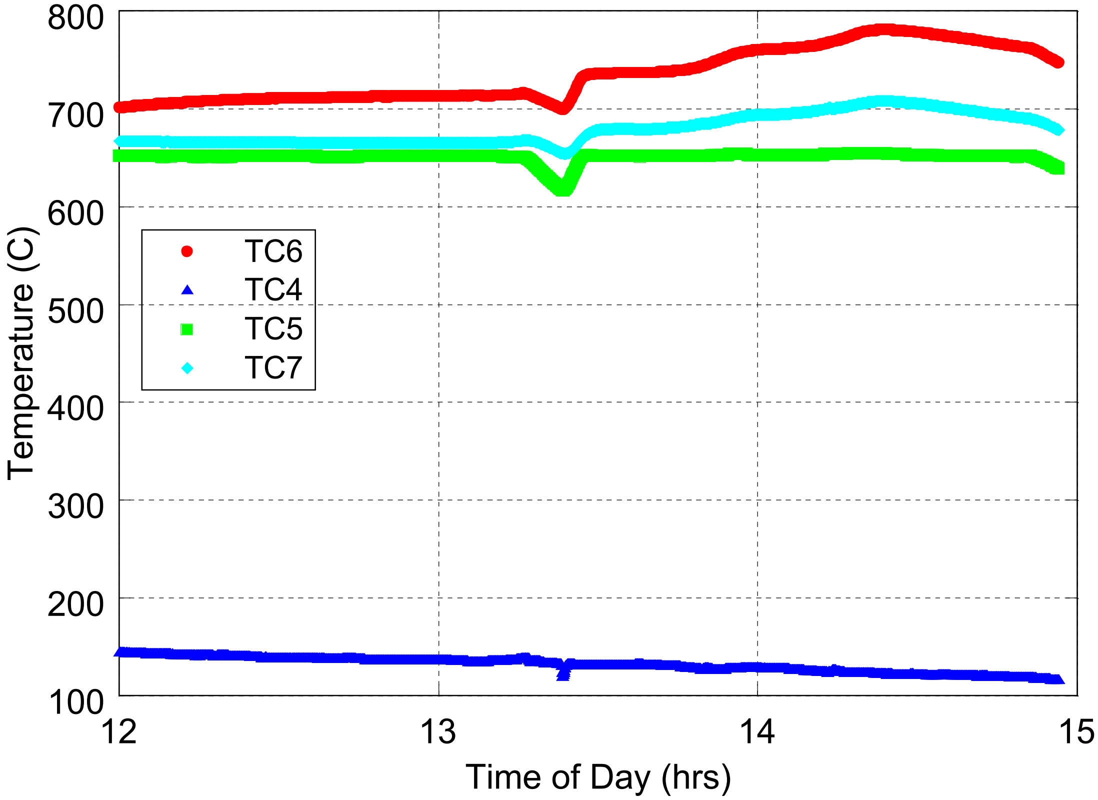

Figure 20. Boiler temperatures for the pressurized test.

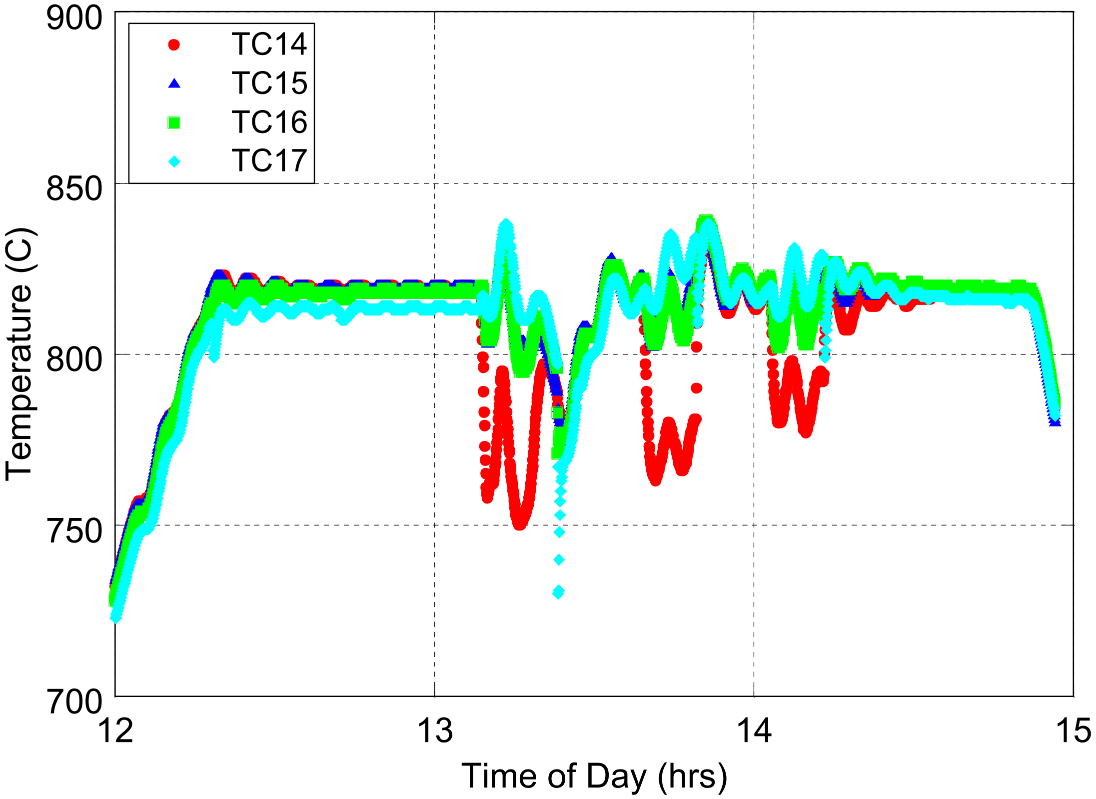

Figure 21. Temperatures in catalyst bed for the pressurized test.

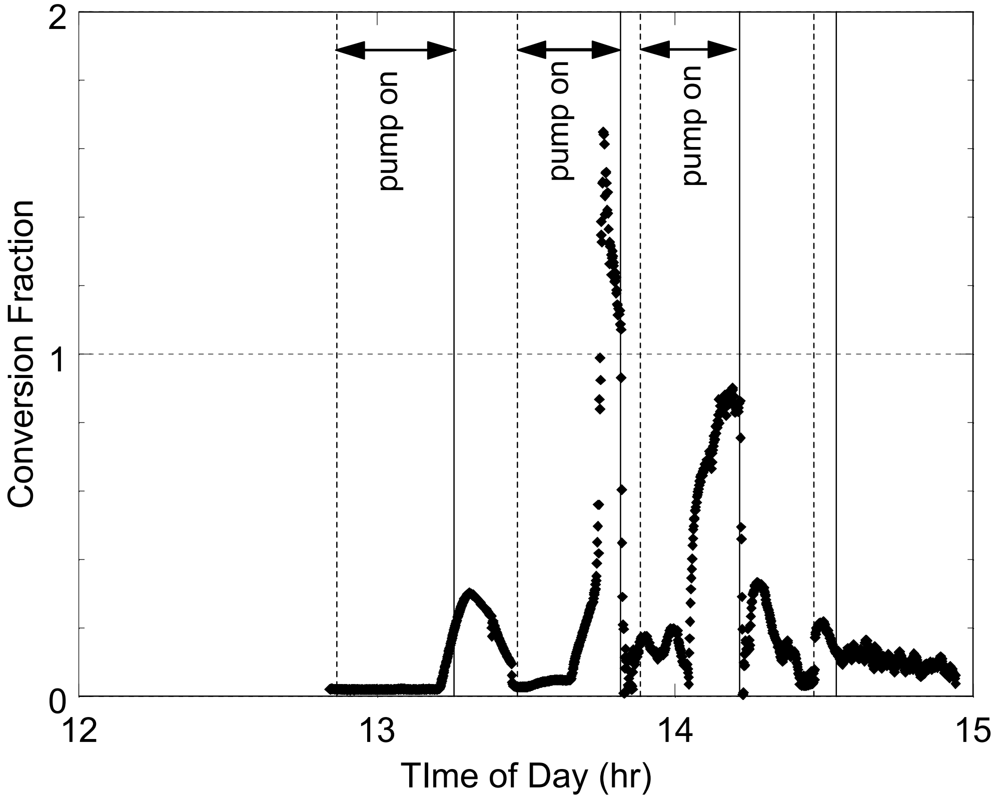

Figure 22. Acid conversion fraction for the pressurized test. (Values above unity correspond to when an obstruction cleared and there was an unrepresentative burst of gas released. These values are unphysical and should be disregarded.)

Two possible causes for overpressurization were considered: either an obstruction had developed or a relief valve had malfunctioned. Due to the use of a Saramet inlet tube to the boiler, there was a significant possibility of a corrosion obstruction developing at some point in the test. Since replacement acid-resistant ceramic fittings and seals had been ordered but were not available in the time frame of the test sequence, there would have been a considerable delay in testing. If the pressure increase was due to a malfunctioning relief valve, then we could proceed by replacing the valve. To check if the relief valve was the problem, the by-pass valve was opened in preparation for a second period of acid injection. If the pressure buildup persisted even with the by-pass valve opened, then the problem was not the relief valve.

Acid pumping resumed for a second time at 13:28 with the by-pass valve open, and the pressure starting building again. However, the pressure reached only ~25 psia and then quickly dropped. As shown in Figure 17, when the pressure dropped the gas flow increased dramatically, indicating that the early corrosion caused blockage had been cleared. The gas chromatograph samples the gas stream every three minutes and could not fully capture the SO_2 concentration of the released gas. However, the sampling time for the oxygen analyzer was 5 seconds which was fast enough to capture the transient. We see from Figure 18 that the oxygen concentration quickly reached 34%. This is in excellent agreement with the expected oxygen concentration of 33.3%. The abrupt release of gas resulted in a large value for the gas flow rate. This transient caused the acid conversion fraction shown in Figure 22 to exceed unity during this time period. Clearly, this transient data should be disregarded because the abrupt gas release is not accounted for in the expression used to determine the acid conversion fraction.

The acid pump was stopped at 13:53 and the by-pass valve was then only partially closed so that a higher pressure could be maintained. When acid pumping resumed for the third time, the pressure and flow started increasing, but the pressure reached only 1.25 atm before starting to decline again. This indicated that the manual by-pass valve was still opened too much. During this third time period of acid injection the gas flow rate closely followed the pressure, both increasing and leveling off at the same time. Thus the desired near free-flow conditions had been obtained, and the gas flow rate is more representative of acid processing operations. As shown in Figure 18, the oxygen and sulfur dioxide concentrations remained steady during this time period at ~34% and ~63%, respectively. The sum of these concentrations as given in Figure 18 account for nearly all the noncondensible gas released, which is what would be expected for acid decomposition. If the gas flow rates shown in Figure 17 are substituted into Eq. (3), then the acid conversion fraction near the end of this period reached 0.9 as shown in Figure 22. This is close to the ideal performance of the system with a DCHX in which the conversion fraction is 1.0. Thus the DCHX efficiently recycled undecomposed because previously (Gelbard et al., 1995) the conversion fraction was nominally 0.5.

Due to the equipment problems encountered, the duration of the experiment and the parameter space investigate were more limited that originally planned. However, the DCHX experiments did demonstrate the desired functions of the DCHX and do provide data for model validation which is important for the design of the integrated lab scale decomposer

V. Conclusions

The sulfuric acid decomposition tests with a DCHX provided the first experimental demonstration that such a unit can efficiently recover heat and unreacted acid from a catalytic acid decomposer. The unit is designed to provide near 100% conversion of acid to reaction products, even though the decomposer temperature was far less than would be required for near 100% conversion in a single pass configuration. In our experiment a conversion of approximately 90% was achieved, but a longer term experiment is needed to confirm that measurements reflect true steady state conditions.

In previous experiments corrosion was a major problem because no ductile metal was found that is corrosion-resistant to hot liquid sulfuric acid. To circumvent this problem, the acid is introduced into a packed bed of hot ceramic pellets. The acid vaporizes before reaching the heated metallic walls, and thus much corrosion is avoided. In addition, we found that by including a glass sleeve around the bed corrosion is further greatly reduced, even though the sleeve is not tightly fitted. To avoid cracking of the sleeve, a tougher ceramic may be used instead. Because not all the acid is decomposed to reaction products, some unreacted vapors need to be recycled for additional passes through the catalyst. Thus far there is no process available to separate unreacted vapors from the gaseous reaction products. Therefore, the separation is performed by cooling the effluent stream to condense unreacted acid. The condensed vapor results in hot liquid acid, for which the corrosion problem is most severe. As was shown in this work, this corrosion problem can be avoided by having the effluent stream cooled in glass or ceramic vessels connected to the metallic reaction vessel.

In these experiments, the uncondensed gas produced by decomposition was 34% oxygen and 63% sulfur dioxide. This is nearly the ideal composition of 33.3% oxygen and 66.7% sulfur dioxide, which indicates that the decomposition reaction proceeded as predicted. In addition, by incorporating a DCHX nearly 90% of the acid was decomposed. Previously, without DCHX-recycling of the reactor effluent stream the acid conversion was only ~50%. The significant improvement in conversion due to the recycle of effluent acid allows the DCHX apparatus to provide nearly complete conversion of the incoming acid stream.

Because real-time measurements of acid conversion are essential for controlling the process, we tried another instrument for gas concentration analysis. A gas chromatograph is the traditional instrument used for such applications. However, GCs are delicate instruments that require considerable maintenance and a compressed gas cylinder that need regular replacements. Furthermore, the sampling frequency of a GC is on the order of minutes. Previously an optical probe for oxygen was tested that does not require compressed gas and has a sampling time on the order of seconds (Gelbard et al., 2005). The unit worked well in mixtures with nitrogen, but was deactivated by the sulfur dioxide. In this work we demonstrated that a new laser light absorption instrument (Oxigraf Oxygen Analyzer) can be used to measure the oxygen concentration without interference from sulfur dioxide, on the order of seconds, and without requiring compressed gases.

These experiments provided the first demonstration of direct contact heat and mass exchange for acid decomposition. The data will now be used validate computational models which will be used to design the next generation acid decomposer for the integrated laboratory experiments. The new design is a highly integrated SiC bayonet heat exchanger that integrates the boiler, superheater, decomposer and recuperation in a single structure (Moore et al., 2006). The new design minimizes the number of connections and seals, and allows commercially available components to be used in the condenser and piping. The data from this series of test will be used to define the DCHX for these next series of tests.

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