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**PRELIMINARY RESULTS FROM
BENCH-SCALE TESTING OF A SULFUR-IODINE
THERMOCHEMICAL WATER-SPLITTING CYCLE**

by

**D. O'KEEFE, C. ALLEN, G. BESENBRUCH, K. McCORKLE,
J. NORMAN, and R. SHARP**

JULY 1980

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ABSTRACT

Portions of a bench-scale model of a sulfur-iodine thermochemical water-splitting cycle have been operated at General Atomic Company as part of a comprehensive program to demonstrate the technology for hydrogen production from nonfossil sources. The hydrogen program is funded by the U.S. Department of Energy, the Gas Research Institute, and General Atomic Company. The bench-scale model consists of three subunits which can be operated separately or together and is capable of producing as much as 4 std liters/min ($6.7 \times 10^{-5} \text{ m}^3/\text{s}$ at standard conditions) of gaseous hydrogen. One subunit (main solution reaction) reacts liquid water, liquid iodine (I_2) and gaseous sulfur dioxide (SO_2) to form two separable liquid phases: 50 wt % sulfuric acid (H_2SO_4) and a solution of iodine in hydriodic acid (HI_x). Another subunit (H_2SO_4 concentration and decomposition) concentrates the H_2SO_4 phase to the azeotropic composition, then decomposes it at high temperature over a catalyst to form gaseous SO_2 and oxygen. The third subunit (HI separation and decomposition) separates the HI from water and I_2 by extractive distillation with phosphoric acid (H_3PO_4) and decomposes the HI in the vapor phase over a catalyst to form I_2 and product hydrogen. This paper presents the results of on-going parametric studies to determine the operating characteristics, performance, and capacity limitations of major components.

1. INTRODUCTION

The recent realization that the earth's fossil fuel resources cannot inexhaustibly supply society's needs has prompted investigating many alternative fuel sources. One alternative fuel source is hydrogen from water splitting. Hydrogen, when combined with solar or nuclear heat sources is a renewable, portable fuel from water, which can be stored as a gas, liquid, or hydride, depending on the application. A hydrogen economy appears to have many benefits, and researchers around the world have recently devoted considerable effort to developing viable processes for the economic large-scale production of hydrogen fuel from water. The General Atomic Company (GA) sulfur-iodine process is a thermochemical water-splitting approach currently being developed and assessed.

The program to investigate thermochemical water splitting using the high-temperature gas-cooled reactor (HTGR) as a heat source has been underway at GA since October 1972. Current program participants are the Gas Research Institute (GRI), which carries on the sponsorship of the American Gas Association (AGA), the U.S. Department of Energy (DOE), and GA. Northeast utilities Service Company and Southern California Edison Company previously participated.

The GA sulfur-iodine cycle was first described in the open literature by Russell (Ref. 1). Reference 2 is a recent overview of the entire program effort. The chemical basis for thermochemical water splitting is contained in a review paper on catalysis (Ref. 3), and Refs. 4 and 5 survey the chemical studies performed to establish the process direction. Reference 6 gives specific details on the program process engineering. Reference 7 reports on the materials investigation.

An abbreviated chemical description of the sulfur-iodine cycle is as follows:



The HI_x represents the mixture of several polyiodides formed in the main solution reaction (Eq. 1). The H_2SO_4 and HI_x are separated by gravity, since the acid solutions are almost completely immiscible. The upper phase contains almost all of the H_2SO_4 , and the lower phase contains most of the HI_x . However, several process engineering steps are needed to perform the reactions described above.

The Fig. 1 block diagram shows the links between these transformations. GA process engineering efforts estimate the obtainable energy efficiency, guide further chemical investigations, and help develop the flowsheet material and energy balances for realistic cost estimates on specific equipment designs. Presently, overall cycle thermal efficiency for the GA process, as determined from the flowsheets, is estimated at 47%. This paper discusses the status of the bench-scale testing of the GA sulfur-iodine cycle. Prior to these efforts, the process was demonstrated in the recycle mode in a closed loop cycle demonstrator (Ref. 8).

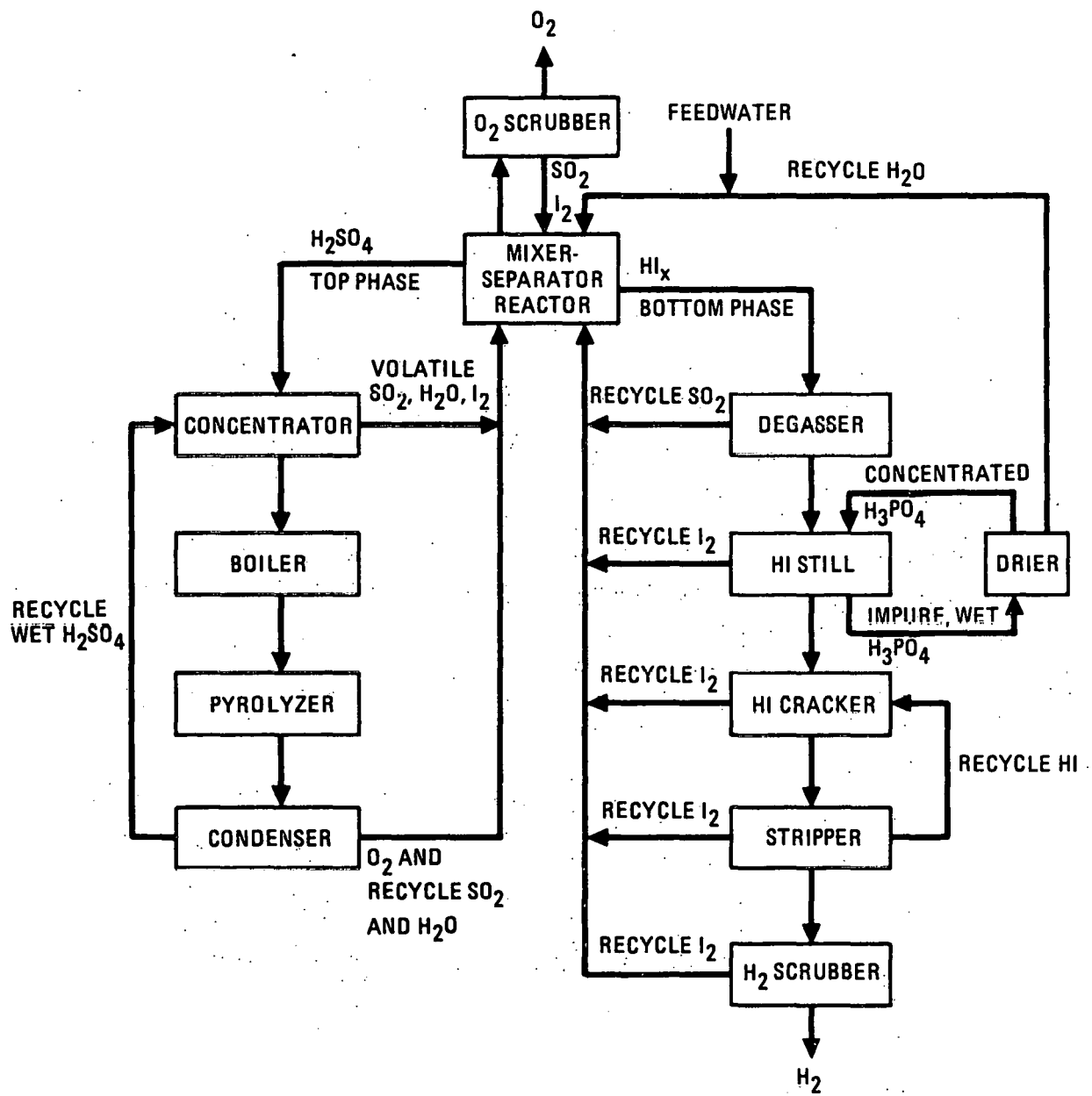


Fig. 1. Sulfur-iodine cycle process model

2. DESCRIPTION OF THE GA BENCH-SCALE TESTING UNIT

In 1977, under DOE contract, GA started the design and construction of a bench-scale unit to perform the sulfur-iodine thermochemical water-splitting cycle as one continuous operation. Except for water fed in and hydrogen and oxygen taken out as products, all materials are internally recycled. The purpose of bench-scale work is generally to study the actual processing steps and their interactions by conducting key continuous flow reactions and separation steps previously done by batch. Bench-scale investigations also report on fluid handling, key operation behavior, and the effects of incomplete physical separations and possible side reactions. In the later study stages, the three bench-scale subunits will be integrated and operated as one unit.

In bench-scale testing, no attempt is made to prove the cycle energy efficiency. The energy efficiency is estimated in the separate conceptual flowsheeting effort. However, the bench-scale components selected can potentially perform efficiently on a large scale. For instance, a flow reactor, rather than a stirred vessel, has been selected for the main solution reactions. Also, the bench-scale is currently not aimed at proving construction materials. Wherever possible, materials, such as inert plastics and glass, are used. However, some specific metals found in the materials screening tests will be added later. All hardware is mounted on Unistrut and Flexframe supports.

For these investigations, the process is divided into three subunits. After these subunits have been proven to operate satisfactorily alone, they can be linked together. The design goal of the bench-scale system is a H_2 production rate of ~ 4 liters/min ($6.7 \times 10^{-5} \text{ m}^3/\text{s}$) at standard conditions. The main features of the three subunits are briefly described below. References 9 and 10 give more detailed information on the bench-scale design.

2.1. SUBUNIT I, HI-H₂SO₄ PRODUCTION AND SEPARATION

The main solution reaction is carried out in this subunit. I₂, H₂O, and SO₂ are injected in a cocurrent reactor where the two acid phases are formed. The products are then passed into a gas separator, where excess SO₂ is removed for recycle, and eventually into a liquid-liquid separator, where the two phases are separated and collected. Figure 2 is the simplified bench-scale flowsheet for Subunit I.

The main solution reaction (Eq. 1) is carried out at ≤ 250 kPa and at a temperature slightly above the melting point of I₂. The reactants SO₂ and H₂O are metered with flow control valves and their flowrate is measured using conventional rotameters. The reactant I₂ is melted and delivered as a liquid. I₂ is metered using a Teflon flow control valve, and the flowrate is measured by observing the weight loss of the iodine charge with a load cell attached to the I₂ vessel.

The main solution reactor was designed to provide adequate reactant mixing and residence time in controlled temperature conditions. The reactor consists of an internal finned tube, which alters fluid flow directions a number of times. This flow is driven by an excess gaseous SO₂ flow. The liquid residence time is long compared to the gas residence time (i.e., many seconds compared to fractions of a second). The reactants are supplied to the reactor by a train injection system, where the SO₂ enters at the bottom of the train and both H₂O and I₂ (liq) are sequentially injected into the flowing SO₂. The reactor is jacketed for temperature control. After discharge from the reactor, the reaction mixture flows to a thermostated chamber, which serves as a gas-liquid de-entrainment system. The two liquid phases, which have been de-entrained from the SO₂ by gravity, are discharged from the bottom of the separator.

The liquid-liquid separator is very similar in design to the gas-liquid separator and separates the H₂SO₄ (sol'n) phase from the heavier HI_x (sol'n)

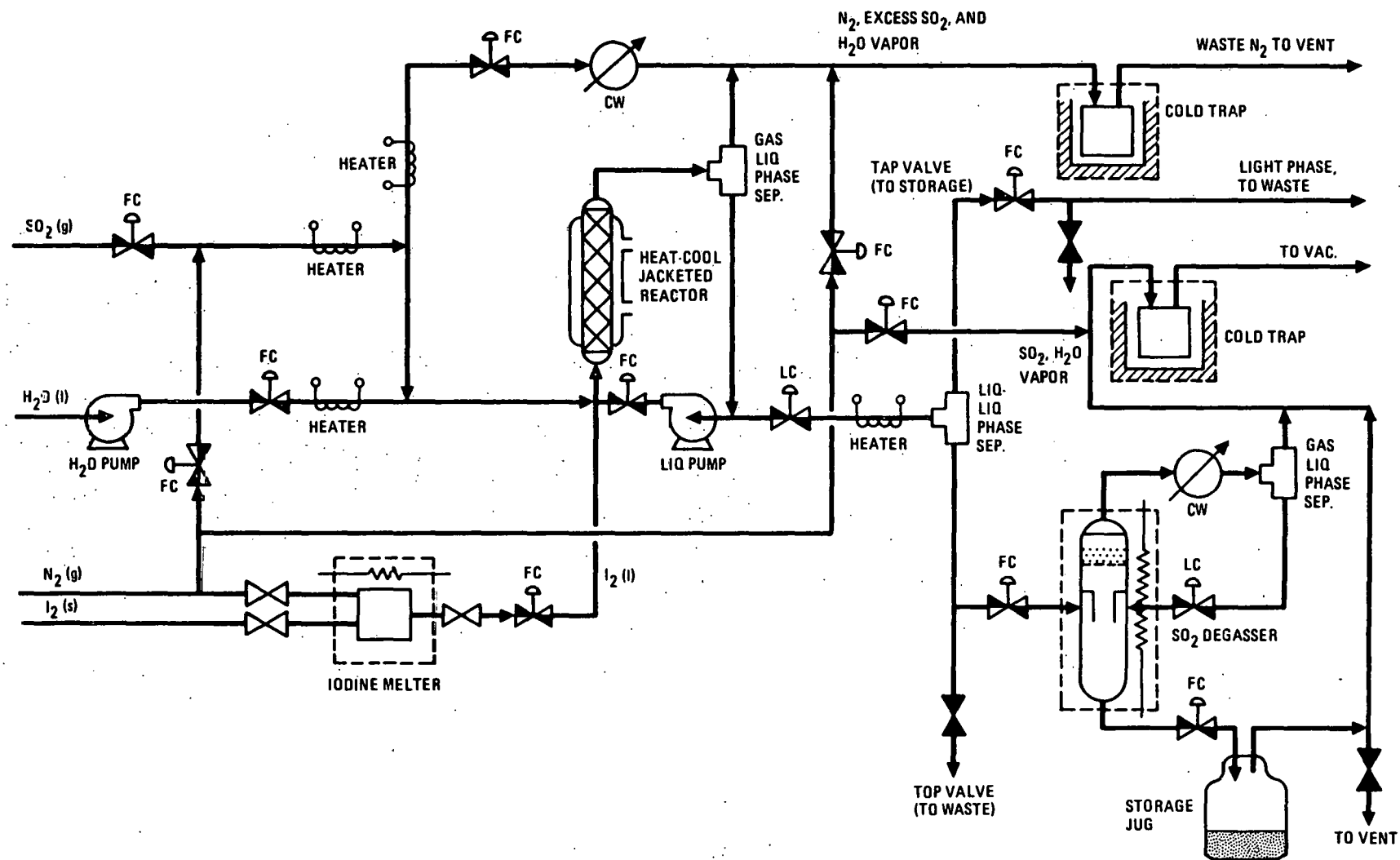


Fig. 2. Simplified bench-scale flowsheet for Subunit I (main solution reaction)

phase. The HI_x lower phase of the liquid-liquid separator is saturated with unreacted SO_2 . The SO_2 must be removed from this phase to avoid forming H_2O and sulfur by reacting with the product HI during the various lower phase treatments. A vacuum flask degasser is used to remove the SO_2 . After degassing, the liquid collects in the bottom of the drum, then is pumped to the next unit. Since I_2 and the HI_x are solids at room temperature (aqueous HI_x will precipitate I_2 as temperature is reduced), forced-air ovens are built around the units.

Figure 3 is a photograph of a portion of Subunit I as installed in the protective fume hood enclosure which houses the complete bench-scale unit.

2.2 SUBUNIT II, H_2SO_4 CONCENTRATION AND DECOMPOSITION

In this subunit, the H_2SO_4 phase from Subunit I is purified, concentrated, and pyrolyzed at temperatures up to 870°C . Uncracked H_2SO_4 is recycled to the concentration column; then wet $\text{SO}_2\text{-O}_2$ product can either be passed to a caustic scrub prior to metering and discharging or recycled to Subunit I without removing O_2 .

Figure 4 shows the simplified flowsheet design for the H_2SO_4 concentration and decomposition section.

The feed system for Subunit II provides flow metering of the light phase liquid effluent from Subunit I. The light phase flow from Subunit I is ~ 50 wt % H_2SO_4 aqueous solution at an absolute pressure from ambient to 3.1×10^5 Pa and at a temperature from ambient to 115°C . Variable amounts of SO_2 , HI , and I_2 on the order of 0.5 to 1.5 wt % each are dissolved in the solution, with some of the I_2 possibly occurring as a solid phase.

Removal of I_2 from the sulfuric acid is effected by countercurrently contacting the input liquid against heated water vapor at temperatures and times adequate to vaporize substantially all the I_2 from the liquid. The heated water vapor is generated from the liquid effluent of the counter-

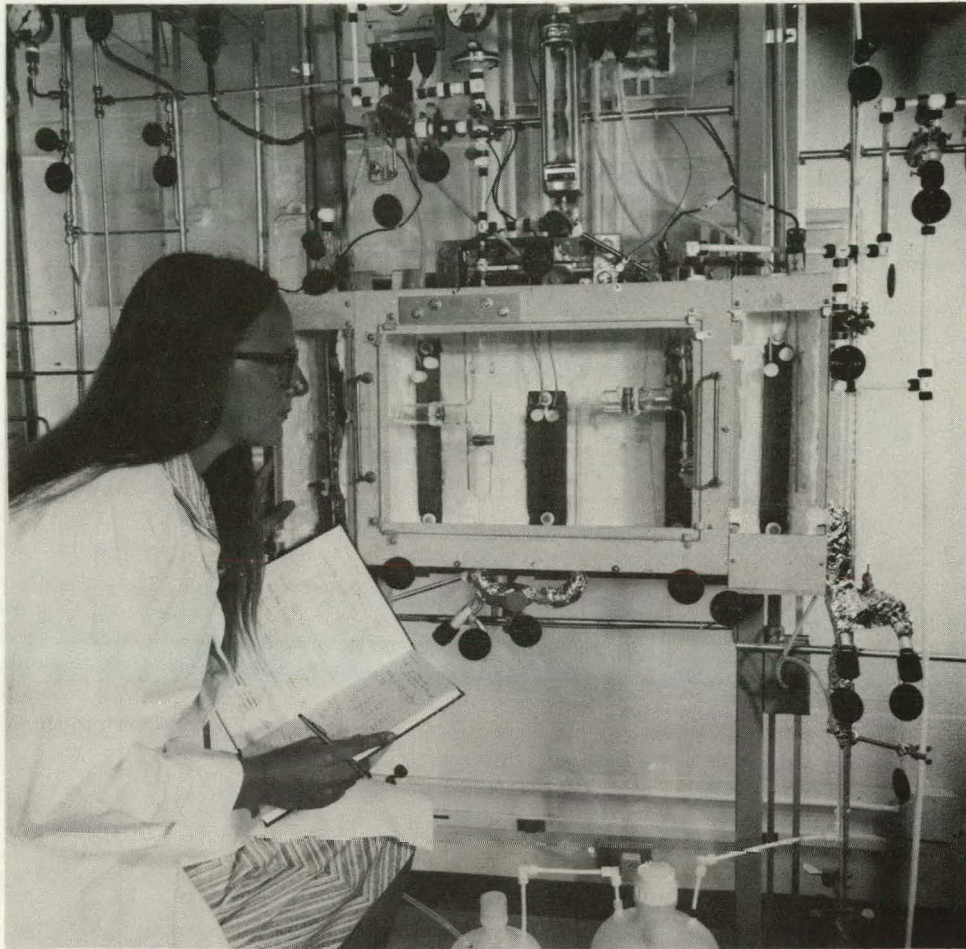


Fig. 3. Photograph of Subunit I as installed in protective fume hood enclosure showing the separator oven and ancillary equipment

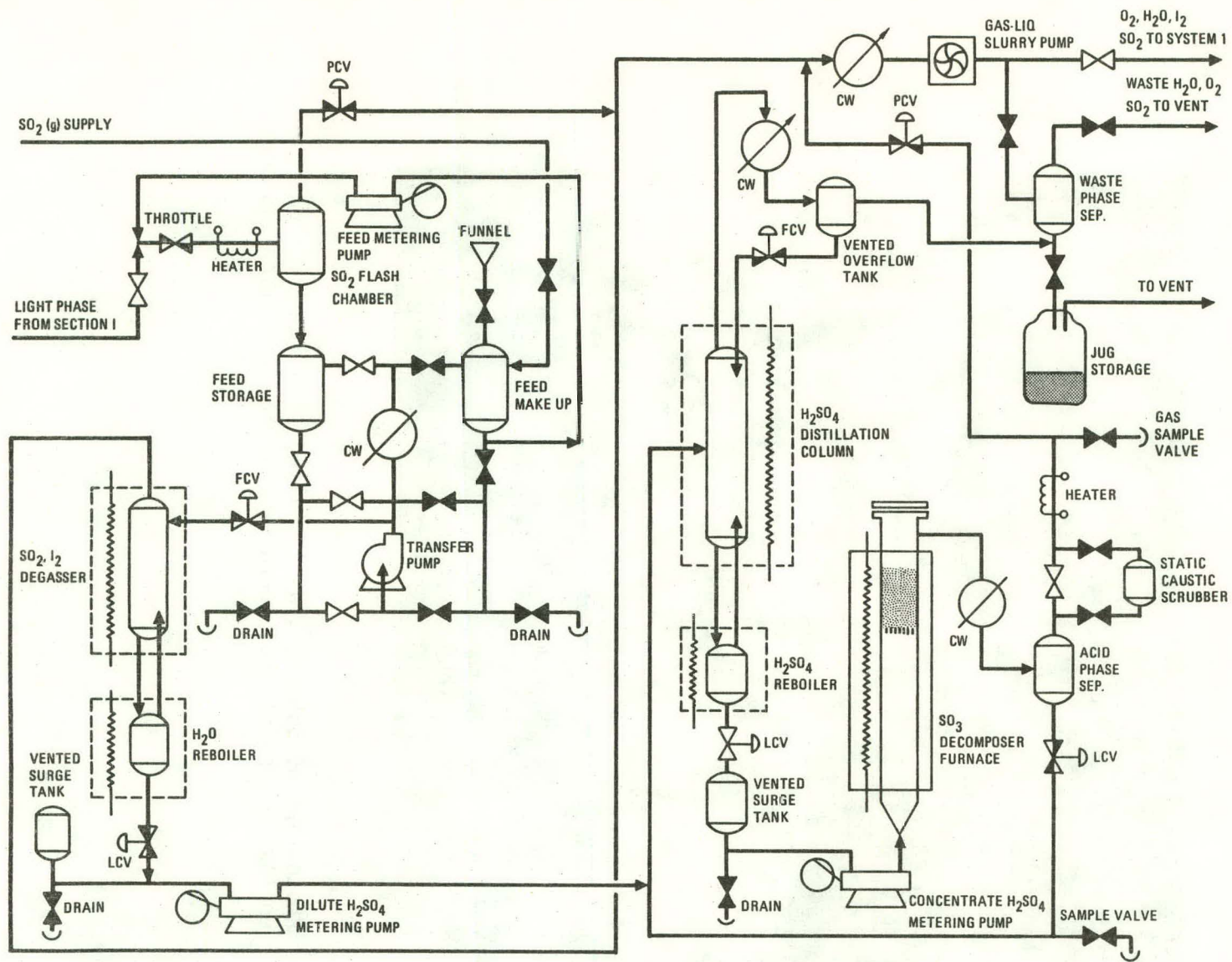


Fig. 4. Simplified bench-scale flowsheet for Subunit II (H_2SO_4 - H_2O separation and decomposition)

current contacting operation After cooling, the acid solution is metered at a controlled flowrate into a fractionation still. The still produces >96 wt % aqueous H_2SO_4 and H_2O vapor substantially free of H_2SO_4 in separate streams.

The H_2SO_4 decomposition system cools the >96 wt % H_2SO_4 effluent of the H_2SO_4 concentration system from its normal boiling point to $42^\circ C$. After cooling, the acid is metered at a controlled flowrate into a vertical-tube decomposition chamber, where vaporization of the liquid takes place; then catalytic decomposition of the vapor occurs to within 98% of equilibrium decomposition. The system provides nominally isothermal decomposition temperatures from 530° to $1030^\circ C$ at ambient pressure for varying catalyst bed volumes having empty tube nominal slug flow contact times of <10 s.

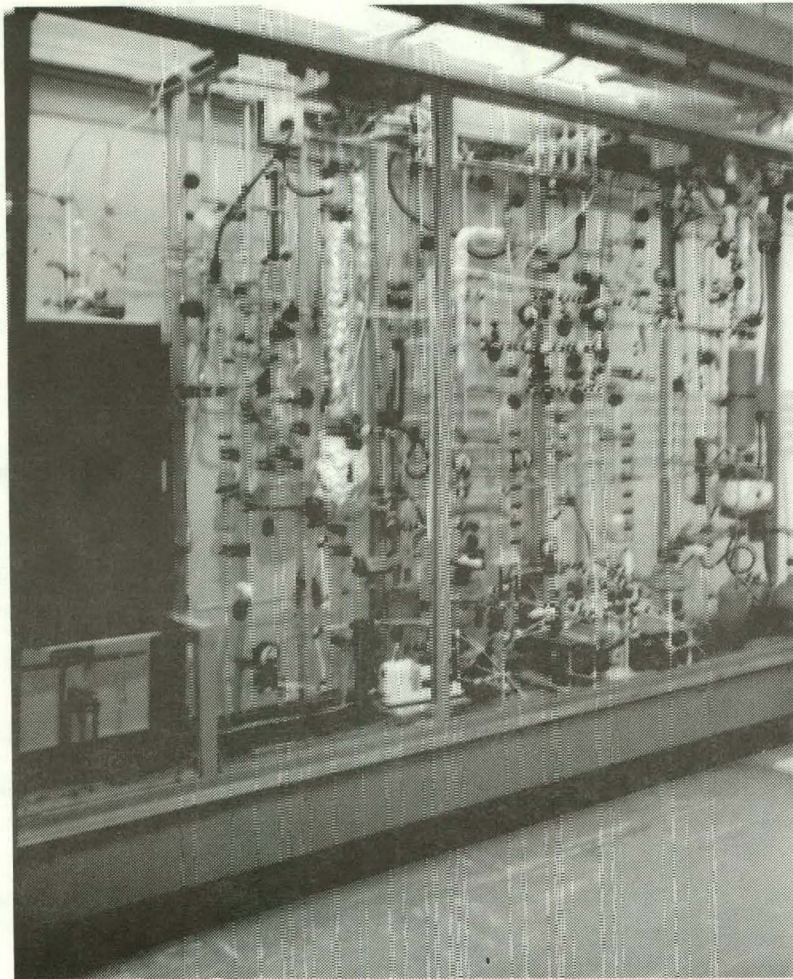
The offgas system collects gas from the SO_2 removal step, the HI- I_2 removal system, and the H_2SO_4 decomposition system through control valves which permit regulating the pressure differential between the offgas system and the other subsections of the overall unit. The system can discharge to the Subunit I feed inlet SO_2 stream or to a gaseous waste vent.

For the gaseous effluent of the H_2SO_4 decomposition system, the offgas system removes substantially all SO_2 from the O_2 in a form amenable to subsequent quantitative chemical analysis, and it meters the flow of the SO_2 -free gaseous effluent or the whole gaseous effluent of the H_2SO_4 decomposition system when the SO_2 removal capability is bypassed.

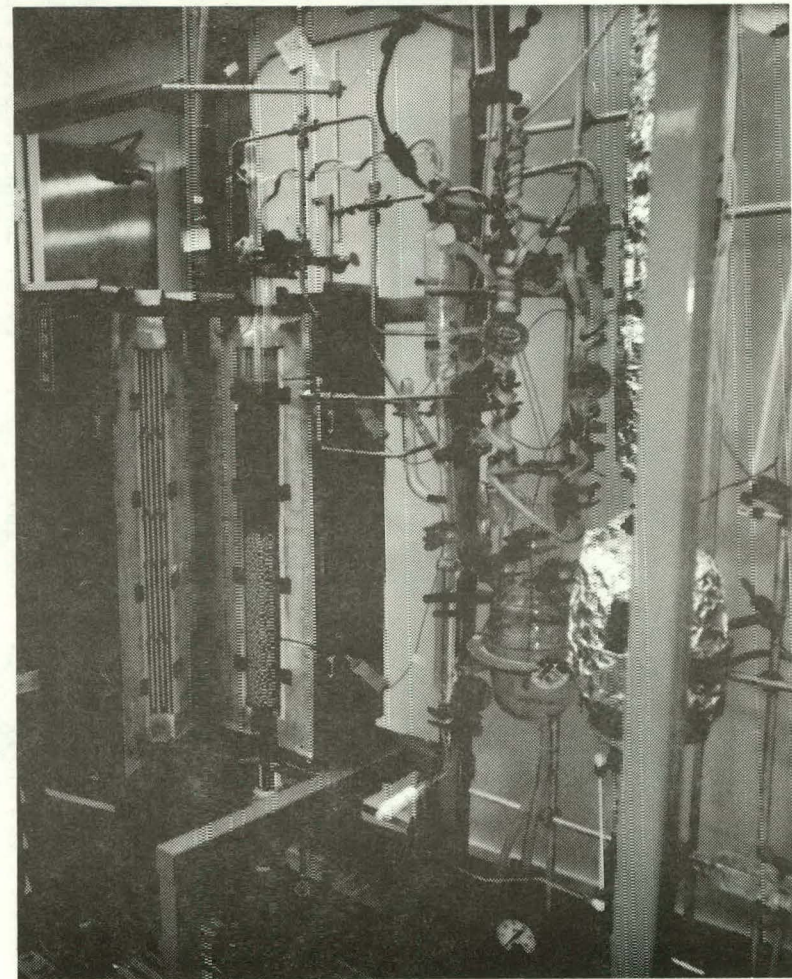
Figures 5a and 5b are selected photographs of the Subunit II equipment installed in the protective fume hood.

2.3 SUBUNIT III, HI SEPARATION AND DECOMPOSITION

Mainly, this subunit separates HI from the lower phase product of the main solution reaction (containing HI, I_2 , and H_2O) by treating with concentrated H_3PO_4 . The HI is then catalytically decomposed as a gas at moderate



(a)



(b)

Fig. 5. Bench-scale Subunit II: (a) overview, (b) SO₃ decomposer with catalyst in place

temperature. Figure 6 shows the flowsheet for Subunit III. The following paragraphs give the basic functions of the principle equipment items.

The feed system provides metered flow of heavy phase liquid effluent from Subunit I at 600 Pa to an ambient discharge pressure. The heavy phase from Subunit I has a mole ratio composition of $\text{HI}/3.8\text{I}_2/5.5\text{H}_2\text{O}/0.01\text{H}_2\text{SO}_4$ from ambient temperature to 97°C . The nominal H_2SO_4 content of actual heavy phase represents a mixture of sulfur species not yet completely defined but which is predominately H_2SO_4 .

The I_2 separation system receives heavy phase from the feed system and separates the I_2 as liquid from the heavy phase by countercurrent contact with 100% H_3PO_4 at a rate sufficient to substantially remove all water from the liquid I_2 that is separated from the heavy phase. The system water scrubs substantially all entrained H_3PO_4 from the I_2 before the I_2 liquid leaves the I_2 separation system. Scrubbing operation conditions are maintained such that both the water and the iodine are liquids. The raffinate of the water scrub operation is introduced into the H_3PO_4 -HI- H_2O phase of the I_2 separation operation, and the combined flow is conducted to the feed subsystem of the HI distillation step.

The HI distillation column accepts H_3PO_4 -HI- H_2O solution from the I_2 separation step and provides a gaseous effluent of HI vapor that is substantially free of water vapor. The HI is accompanied by a variable amount of I_2 vapor flow. The I_2 vapor flow is still undefined but is certainly substantially smaller than the flowrate of the combined HI- I_2 effluent from the HI distillation step. Approximately 85 wt % H_3PO_4 effluent, which is substantially free of HI and at a temperature less than 77°C , leaves the HI distillation step and is conducted by gravity to the H_3PO_4 concentration step. HI- H_2O is separated by extractive distillation, using H_3PO_4 as the extraction agent. Distillation overhead reflux is 100% H_3PO_4 .

In the H_3PO_4 concentration column, the 85 wt % H_3PO_4 effluent of the HI distillation step is heated to sufficient temperature, $<222^\circ\text{C}$,

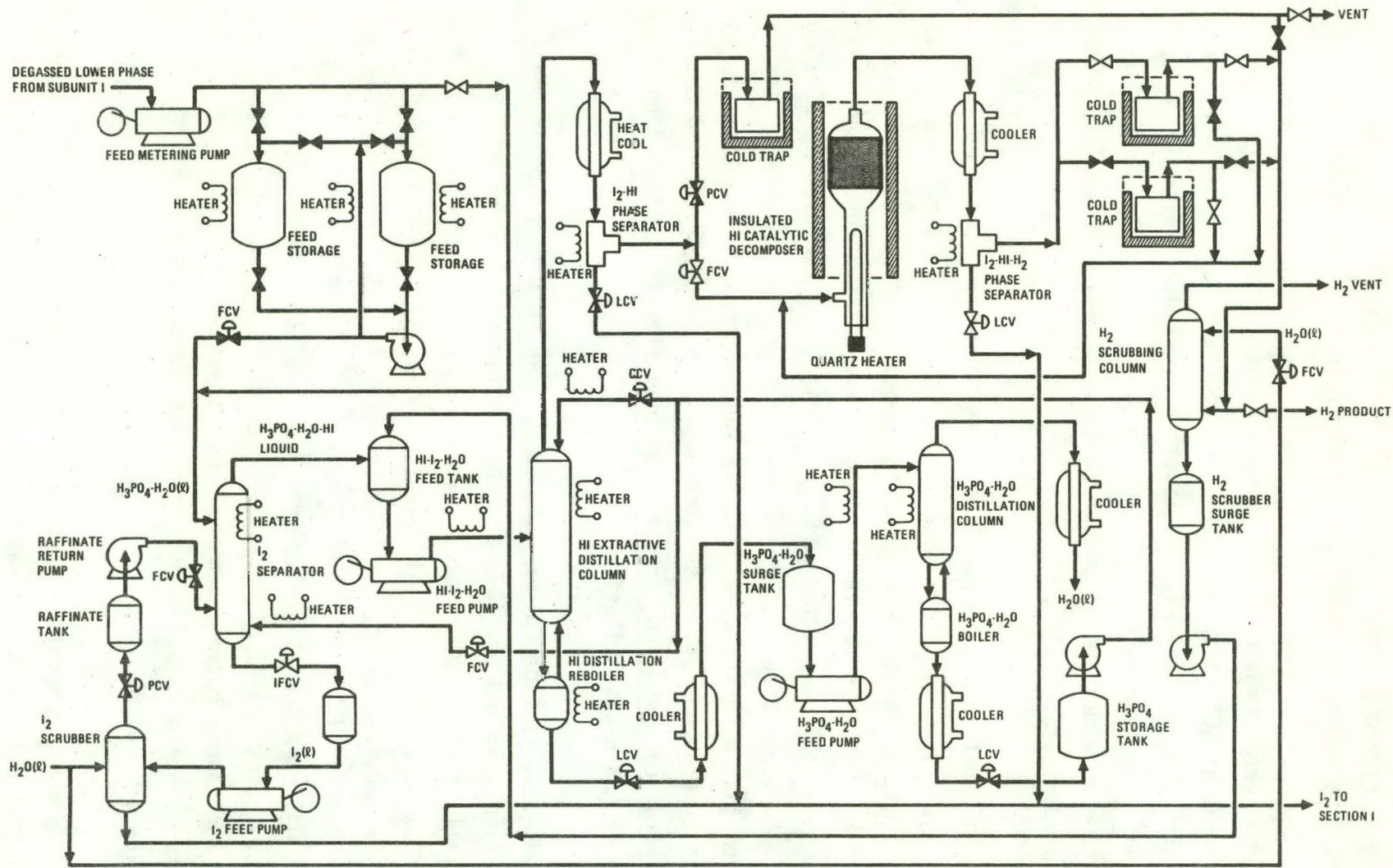


Fig. 6. Simplified bench-scale flowsheet for Subunit III (HI concentration and decomposition)

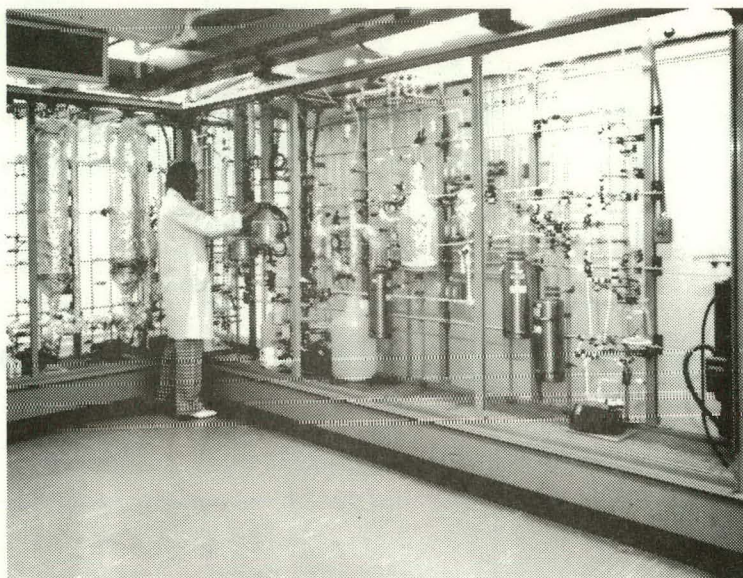
to substantially remove all water vapor from the H_3PO_4 . The water vapor is then discarded, and 100% H_3PO_4 is recycled to the I_2 separation system and to the HI distillation step at the metered rates specified in the design criteria for those subsections of bench-scale Subunit III. Effluent water vapor is condensed before being discarded to the waste H_2O collection vessel.

The HI and I_2 vapor effluent from the HI distillation step is cooled in a condenser to a temperature slightly exceeding the melting point of iodine, and condensed iodine separated from the residual vapor before the vapor is metered and sent to the vertical tubular heated chamber. Thermal decomposition of the HI vapor occurs in the heated chamber at a controlled temperature in the range 177° to 925°C at substantially ambient atmospheric pressure. The controlled temperature volume for HI decomposition is $\sim 4 \times 10^{-3} \text{ m}^3$, including catalyst volume, if any. The present integrated bench scale system employs gaseous HI decomposition. This will be replaced by a liquid hydrogen iodide process step which is now being tested as a separate bench-scale unit. This latter unit is discussed in this paper under the heading "Future Work."

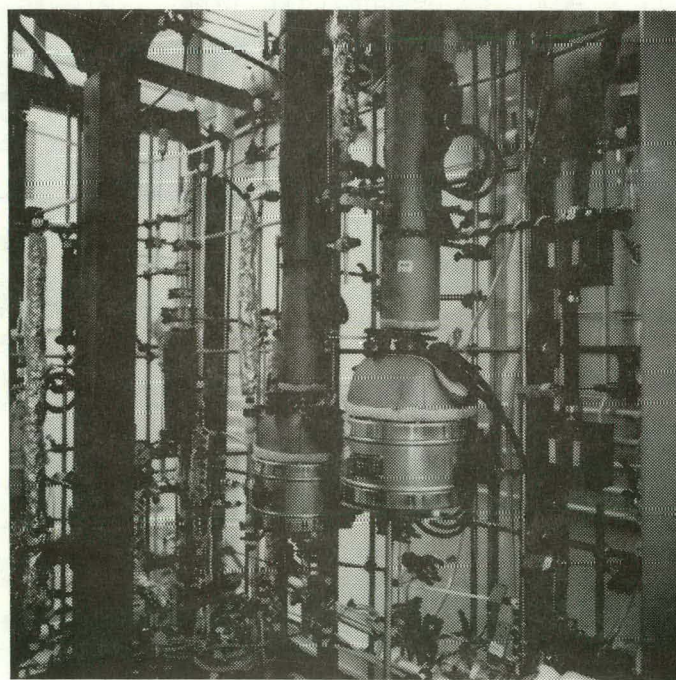
The HI decomposition gaseous products are first cooled to a temperature slightly above the melting point of iodine (114°C), and condensed iodine is separated from the residual gas vapor. The residual gas vapor from the I_2 condensation is then chilled with liquid nitrogen or dry ice to a sufficiently low temperature to remove substantially all condensable vapors from the H_2 product gas. Provision also is made to revaporize the HI condensed at liquid nitrogen or dry ice temperature for recycle at metered rates to the HI decomposition step.

The H_2 purification step provides countercurrent scrubbing with water to remove low concentrations of HI from the effluent H_2 of the HI recycle system.

Figures 7a and 7b are photographs of Subunit III as installed for operation.



(a)



(b)

Fig. 7. Bench-scale Subunit III: (a) overview, (b) HI extractive distillation column and H₃PO₄-H₂O distillation column

3. PRELIMINARY RESULTS OF BENCH-SCALE TESTING

At this writing, preliminary tests on Subunits I and II have been conducted; Subunit III has not yet been tested. The results of the available tests are described below.

3.1. RESULTS OF SUBUNIT I PRELIMINARY TESTS:

3.1.1. Cold Testing of the Engineering Characteristics of Subunit I

After assuring integrity by pressure leak testing, flow characteristics of the constructed unit were qualitatively determined. In some preliminary cold flow tests, $\text{CH}_3\text{-CCl}_3$ with a little dissolved I_2 was used to simulate molten I_2 , and N_2 was used in place of SO_2 . During the tests, the flow control, reactor flow, and separator characteristics were all observed. After these tests, the reactor fin system was changed to provide better mixing properties. Also determined was that the reactor operation depends on continuous visual monitoring and manual flow adjustment unless the system control is automated. Steady-state operation of the reaction under present circumstances is best assured by achieving and maintaining stable levels in the gas-liquid and liquid-liquid interfaces in the two separators. Level stabilization coupled with constant inlet flow of H_2O and I_2 allows attainment of steady state by manual operation. Also noted was that a considerable excess of SO_2 was needed to drive the liquids through the reactor fin system.

3.1.2. Hot Testing of the Ovens in Subunit II

The thermal characteristics of the ovens built around the gas-liquid and liquid-liquid phase separators have been tested. The first test revealed the temperature gradients in the ovens to be too large. To

solve this problem, forced air circulation and additional insulation were added to the ovens. In addition, a similarly thermally insulated chamber for the I_2 melt vessel was replaced by a heating mantle since keeping the I_2 melted was difficult using the external heating coils associated with the first design. In the new configuration, ~ 9 kg of fresh I_2 crystals (bulk density ~ 2.2 g/m³) in a glass vessel is initially melted in 30 min with a 1-kW external electrical heating mantle. Resolidified iodine with a higher bulk density takes somewhat longer to melt.

3.1.3. Initial Data Obtained from Operation of Subunit I

Several experiments yielding useful data have been conducted with Subunit I. Initially, two tests were conducted with relatively low weight ratios of I_2 to H_2O of ~ 2.5 . Analysis of the light phase after degassing indicated H_2SO_4 concentrations of between 42 and 44 wt %, whereas the design concentration is 50 wt %. Another test was then run employing a weight ratio of I_2 to H_2O of 5.3 and the concentration of the H_2SO_4 product phase increased to 49 wt %, which is close to design value. The design weight ratio of I_2 to H_2O is ~ 7.0 .

These experiments have verified the concept of a cocurrent reactor for the main solution reaction and, in general, the operability of the components in Subunit I. In addition, the experiments indicate that flowsheet design conditions can be met without great difficulty.

3.2. RESULTS OF SUBUNIT II PRELIMINARY TESTS

3.2.1. Cold Testing of the Engineering Characteristics of Subunit II

Equipment shakedown, including leak testing, instrument calibration, and verification of functional operability with water and inert gas, were conducted on this subunit. As with Subunit I, no fundamental process design problems were discovered during shakedown. Several minor equipment design problems, such as pump air lock and inoperable flow-indicators, were uncovered. The system was subsequently modified to incorporate the required changes.

3.2.2. Initial Data Obtained from Operation of Subunit II

At this writing, several experiments using synthetic feeds were conducted in Subunit II to check operation of the various components under actual conditions and to gather data needed for scale-up design. Several very simple component changes were made to insure efficient operation. In addition, the centrifugal pumps had to be replaced with inert gas pressurization to initiate system flows. Through what appears to be a nucleation controlled process, the centrifugal pumps caused precipitation of I_2 crystals and possibly sulfur from the fluids, with concomitant problems of partial flow blockage and feed concentration changes. This problem occurred when the synthetic feed solutions were stored a relatively long time (1 h or more). Apparently, storage for these lengths of time results in a supersaturation of I_2 and sulfur due to slight back reaction of the H_2SO_4 and HI in solution. This supersaturation should not be a problem in any large-scale continuous flow system, where the chemical storage times would be minimal.

3.2.2.1. Iodine Stripping Experiments. Experiments were carried out in bench-scale Subunit II to establish design parameters for the iodine removal from the upper phase sulfuric acid. Removal of the iodine from the upper phase will reduce potential corrosion problems during final concentration of the acid and allow the use of lower cost system construction materials.

Experiments were carried out in the iodine stripping column of bench-scale Subunit II shown in Fig. 8. The iodine stripping column consists of a pyrex tube (60 cm long, 3 cm diam) filled with glass beads (3 mm diam). The column is externally heated and insulated. Sulfuric acid (~50 wt %) containing ~1.2% HI and 0.6% I_2 is fed to the top of the heated column. Iodine is removed from the liquid by steam stripping with the water evaporating from the liquid. This changes the HI/ I_2 equilibrium, allowing the hydrogen iodide to react with the H_2SO_4 to form I_2 , SO_2 , and H_2O via Eq. 1. The I_2 and SO_2 so formed are further stripped from the liquid. The experiments were carried out at various temperatures and three

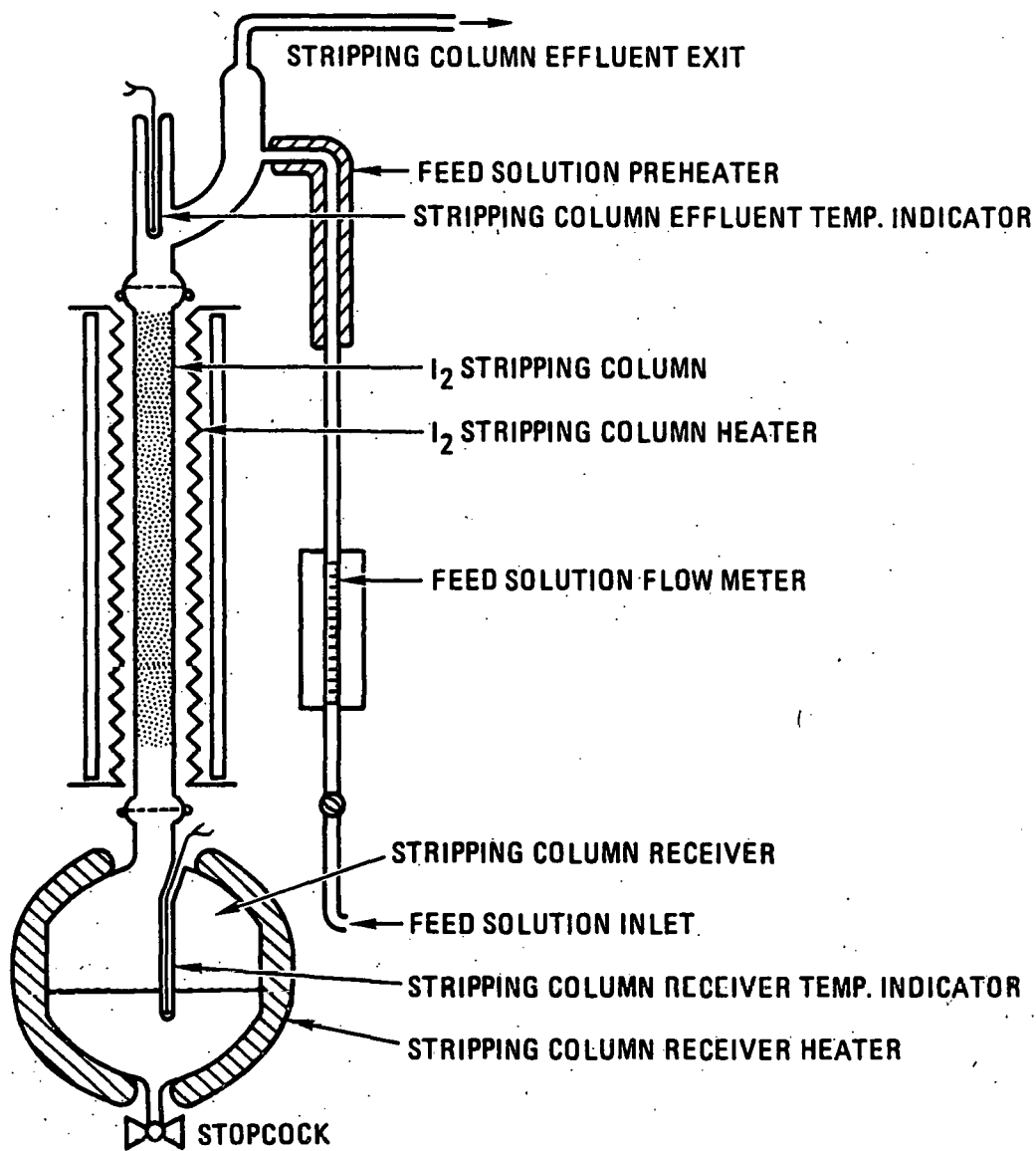


Fig. 8. Schematic of iodine stripping column in use in Subunit II

different feed flow rates. The results are given in Table 1 and plotted in Fig. 9.

The concentrator temperature was calculated from the known boiling point data (Ref. 11) for sulfuric acid and its measured concentration in the stripping column receiver. Because no thermocouple exists central to the column in this particular design and because inner and outer regions of the column have large temperature differences, this calculation is necessary for the present runs. The acid concentration was obtained by standard laboratory titration methods; the small amounts of I_2 (both in the form of I_2 and HI) were measured by neutron activation analysis.

The results indicate that at flowrates of 10 and 17 $cm^3 H_2SO_4/min$ very good stripping of the iodine can be achieved at relatively low temperatures. At a flowrate of 5 cm^3/min , bypass flow apparently occurs in the column, and the results are somewhat erratic. Each of these I_2 stripping tests were run for several hours. Very low I_2 concentrations were achieved, but presently, exact permissible levels of I_2 concentrations are not known. Nevertheless, these data will be useful in scale-up design for the process.

When the -79 curve and the -83 curve of Fig. 9 are compared, the concentration of I_2 in the effluent increases by a factor of 3.5 when the flowrate is increased by a factor of 1.7, with constant temperature at the bottom of the column. Since the constant temperature is a boiling condition, the column bottom concentration is the same at both flowrates, and the liquid-to-vapor flowrate mole ratio of the column is practically unchanged. With constant feed input composition at the top, the operating vapor equilibrium line behavior on a mole fraction plot should be nearly unchanged. For the observed large shift in the bottom liquid concentration with flowrate, simple interphase diffusion as the dominant mass transfer resistance mechanism is unlikely. The effect of gas flowrate on the height of a transfer unit is, in general, small, as is the effect of liquid flowrate. As an example, see page 236, Ref. 12, for the effect

TABLE 1
RESULTS OF I₂ STRIPPING EXPERIMENTS

| Sample No. | Column Temperature (°C) | Feed Flowrate (cm ³ /min) | H ₂ SO ₄ Concentration (wt %) | I ₂ Concentration ^(a) (ppm) |
|--------------|-------------------------|--------------------------------------|---|---|
| 3260-90-1750 | 135 | 5.0 | 57.9 | 23.54 |
| 3260-90-1815 | 141 | 5.0 | 60.5 | 15.13 |
| 3260-90-1895 | 132 | 5.0 | 56.4 | 15.33 |
| 3260-90-1550 | 138 | 5.0 | 59.5 | -- |
| 3260-90-1620 | 140 | 5.0 | 60.0 | 14.86 |
| 3260-90-1303 | 152 | 5.0 | 65.7 | -- |
| 3260-90-1333 | 158 | 5.0 | 67.5 | -- |
| 3260-90-1403 | 148 | 5.0 | 64.0 | 2.89 |
| 3260-90-1430 | 143 | 5.0 | 62.5 | 0.76 |
| 3260-90-1930 | 197 | 5.0 | 78.9 | 0.99 |
| 3260-90-1053 | 228 | 5.0 | 93.3 | -- |
| 3260-90-1123 | 228 | 5.0 | 93.4 | 0.0 |
| 3260-79-1030 | 148 | 10 | 63.9 | 1.86 |
| 3260-79-1230 | 141 | 10 | 60.6 | 4.82 |
| 3260-79-1407 | 133 | 10 | 56.9 | 14.35 |
| 3260-83-1058 | 160 | 10 | 68.3 | 0.66 |
| 3260-83-1326 | 164 | 17 | 69.6 | 3.26 |
| 3260-83-1508 | 185 | 17 | 75.9 | 1.15 |
| 3260-83-1645 | 150 | 17 | 64.2 | 7.88 |

(a) I₂ concentration includes I₂ in the form I₂ and HI.

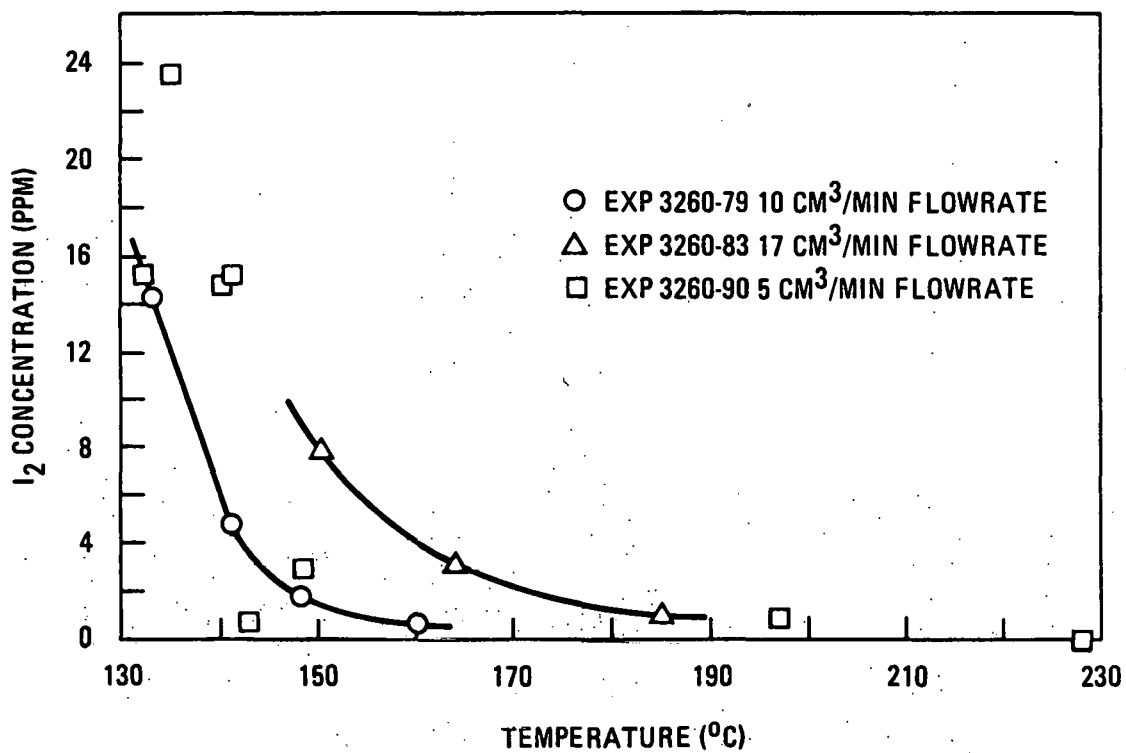


Fig. 9. I₂ concentration versus column temperature for Subunit II for 5, 10, and 17 cm³/min feed flowrates

of flowrates on desorption of O_2 from H_2O .

Probably, the I_2 concentration in the liquid effluent is controlled by the rate of reaction between HI and H_2SO_4 to generate free, volatile I_2 . Also, probably, the average residence time of the fluid flowing through the column is an important parameter with respect to this reaction. Further experiments to test the foregoing hypothesis are planned.

3.2.2.2. H_2SO_4 Concentration Experiments. The H_2SO_4 concentration process provides >96 wt % H_2SO_4 to the SO_3 decomposer. Since extensive vapor-liquid equilibria data already exist for $H_2SO_4-H_2O$ (e.g., Ref. 11), the only data taken in these bench-scale studies is practical-operational with respect to accepting the upstream output rate and meeting the downstream input concentration specification.

For a feedrate of $5 \text{ cm}^3/\text{min}$ of 60 wt % H_2SO_4 (equivalent to 1 std liter/min H_2), the equipment was able to supply H_2SO_4 in excess of 96 wt % without the originally specified glass feed preheater. With an Inconel feed preheater installed, the concentrated H_2SO_4 output rate (equivalent to 3 std liters/min H_2) could be tripled, but the metal contamination of the product, judged qualitatively by color change, was deemed unacceptable. As a practical solution, the required additional heat was supplied via an emersion heater in the still pot. This arrangement operated satisfactorily for feedrates of 60 wt % acid equal to $10 \text{ cm}^3/\text{min}$. The upper limit of feedrate that the current installation can carry without dropping the output concentration below 96 wt % H_2SO_4 is presently being investigated.

The H_2SO_4 output concentration is determined by titration of samples and by literature data from Ref. 11, which relates boiling point to temperature in the still pot. Concentration values obtained by titration measurement typically are ~1% lower than by still pot boiling temperature. The discrepancy is fairly constant and may be due to temperature measurement error or to the extremely hygroscopic H_2SO_4 diluting by adsorbing atmospheric moisture. Although no special dry box provisions were

employed with respect to sampling and titration, the discrepancy is small.

3.2.2.3. H₂SO₄ Decomposition Experiments. Experiments evaluated the decomposing of H₂SO₄ into SO₂, H₂O, and O₂ and observed any catalyst changes in the bench-scale apparatus. A platinum on zirconia catalyst, 0.3175 cm (1/8 in. diam) right cylinder pellets containing ~0.2 wt % platinum was used at temperatures between 800° to 900°C. The gas slug-flow residence time in the reactor was between 0.3 to 1 s. Figure 10 shows the gas decomposition results for the four runs obtained thus far. These data points were calculated both by measuring the amount of unreacted H₂SO₄ which condensed in the decomposer effluent and the oxygen output flowrate after caustic absorption of the SO₂. The two methods agree to within ±5%, with the condensed H₂SO₄ analysis being preferred as the more accurate; this latter method is the basis for Fig. 10. Catalyst bed temperature is taken to be the maximum reading of an axial temperature traverse of the bed taken during steady-state operation.

Sulfuric acid flowrates of 3.0 and 5.3 cm³/min (equivalent to 1.1 and 2.0 std liters/min H₂, respectively) were employed. The experimental results are within ±2% of the theoretical prediction using the maximum catalyst temperature and the equilibrium composition calculated from the JANAF tables (Ref. 13). The low point at ~875°C in Fig. 10 was obtained in a loading of the catalyst bed for which a significant portion of the bed was in the exit region where the temperature had substantially fallen off from the maximum near the axial center of the decomposer. This resulted in a significant back reaction of the decomposition products from the hotter region and thus a low conversion compared to theoretical. This problem was rectified by shortening the catalyst bed and using only the hottest region of the decomposer. The other data points in Fig. 10 were taken using such a configuration.

In the first decomposition run, zirconia pellets without platinum were used to support the catalyst in the hottest zone of the vertical furnace. The zirconia bed support at the boiling interface of the concentrated H₂SO₄ feed was chemically attacked sufficiently to make desirable

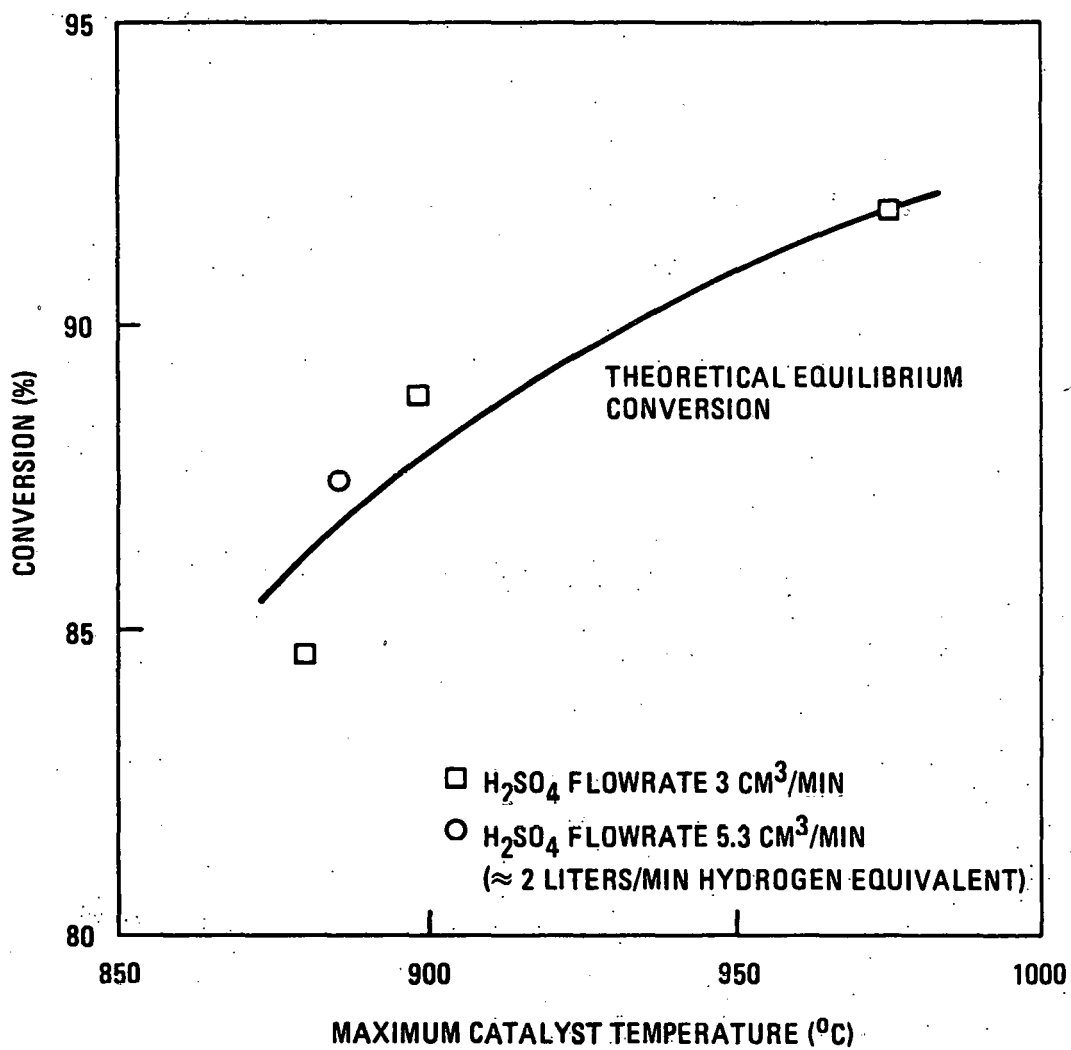


Fig. 10. Performance of bench-scale H₂SO₄ decomposition equipment.

the replacement with some other support material. Zirconia support pellets were thus replaced by a high silica (953 wt % SiO₂) aluminosilicate ceramic [1.27 cm (0.5 in.) diam spheres] with the tradename Denstone.* This support material showed only slight color change and surface roughening at the boiling interface after the first run and no discernible further change in subsequent runs. Additionally, a rust-pink band was seen deposited on the reactor tube wall after the first run with the Denstone support, although it was not discernible on the catalyst itself, and no change in catalyst activity was detected in any of the runs.

3.2.2.4. Joint Operation of the Components of Subunit II. Currently, the overall simultaneous operation of all Subunit II components was demonstrated at a flowrate equivalent to 2 std liters/min H₂. All process steps functioned as designed until after 12 to 14 h operation when apparent cyclic thermal ratcheting of the large rough-surfaced spherical Denstone support pellets against the quartz reaction tube of the decomposer caused tube breakage. Use of smaller particles of irregular shape (possibly cracked Denstone spheroids) is expected to eliminate this problem.

* A product of Norton Company.

4. FUTURE WORK ON BENCH-SCALE UNIT

Data gathering from Subunits I and II will continue to guide the integrated system operation, further demonstrate the flowsheet feasibility, and indicate improvements for scaling up to a larger demonstration unit. Functional testing of Subunit III will also begin. Additionally, extensive process improvements, suggested by the basic chemistry studies, are being considered for incorporation into the bench-scale system. These include replacing the gaseous hydrogen iodide decomposition equipment with a liquid HI decomposition section and adding a sulfuric acid concentration boost reactor. Currently, the sulfuric acid boost reaction bench-scale system has been constructed and some initial tests conducted. The HI liquid bench-scale system, on the other hand, has been designed, and the construction just begun. Both systems and the results for the sulfuric acid studies are described below. The two systems will be readied for eventual incorporation into the integrated bench-scale system.

4.1. SULFURIC ACID CONCENTRATION BOOST REACTION BENCH-SCALE SYSTEM

4.1.1. Sulfuric Acid Concentration Boost Reaction Concept

The concept of the sulfuric acid concentration boost reaction is detailed in Ref. 5. Briefly, the concept involves staging Eq. 1 to use the high iodine activity of pure molten iodine. In a countercurrent flow system, liquid iodine contacts the H_2SO_4 product of the standard $SO_2-H_2O-I_2$ reaction in the presence of high-activity SO_2 . This causes a redistribution of components and a general tendency for the reaction to create more H_2SO_4 and HI. The H_2SO_4 product contains small amounts of HI and I_2 and large amounts of H_2SO_4 and H_2O . In contact with pure liquid iodine, the HI tends to extract into the iodine phase with a small portion of the H_2O . The iodine tends to extract too, since HI

helps it dissolve in the H_2SO_4 phase. Also, this process only slightly lowers the H_2O activity, raises the iodine activity, and slightly raises the H_2SO_4 activity. This means that a reaction of I_2 with SO_2 and H_2O is then favored, because some HI has to be made to bring the reaction system back into equilibrium. This generation of HI is accompanied by a concomitant H_2SO_4 production. The iodine used to drive this counter-current reaction is later used in the prime reaction (or is converted to normal HI_x product). No additional H_2O reactant is required to accomplish this increased product yield, which is important since H_2O dominates recycle energy demands. Initial single-stage experiments indicate that the treatment of the nominally 50% H_2SO_4 aqueous lower phase formed via Eq. 1 results in attaining ~56% H_2SO_4 .

4.1.2. Description of Sulfuric Acid Concentration Boost Reaction Bench-Scale System

This process is clearly best carried out in a countercurrent reactor where highest activity I_2 , initially substantially free of HI and H_2O , contacts the sulfuric acid of the highest possible activity with the least HI present. Precisely this situation develops in an infinitely staged countercurrent column. While creating an infinite number of stages is beyond experimental abilities, a system with an experimentally substantial number of stages could be created.

As part of the bench-scale studies, a staged countercurrent flow reactor column and ancillary equipment has been constructed. Figure 11 shows this system. It consists of the following: (1) a 10-stage stirred column in which the solutions passing from stage to stage are equilibrated by reaction and extraction, (2) a liquid I_2 feed system, (3) a 50% H_2SO_4 feed system, (4) an SO_2 feed system, (5) an SO_2 - H_2SO_4 gas/liquid phase separator, and (6) appropriate reactant and product holding vessels. Iodine is added to the top of the column and flows down the column, where it is taken off as an I_2 -rich phase. Approximately 50% H_2SO_4 is fed to the bottom of the column, causing the dilute light phase to flow up the column, being exposed to purer and purer I_2 as it traverses the

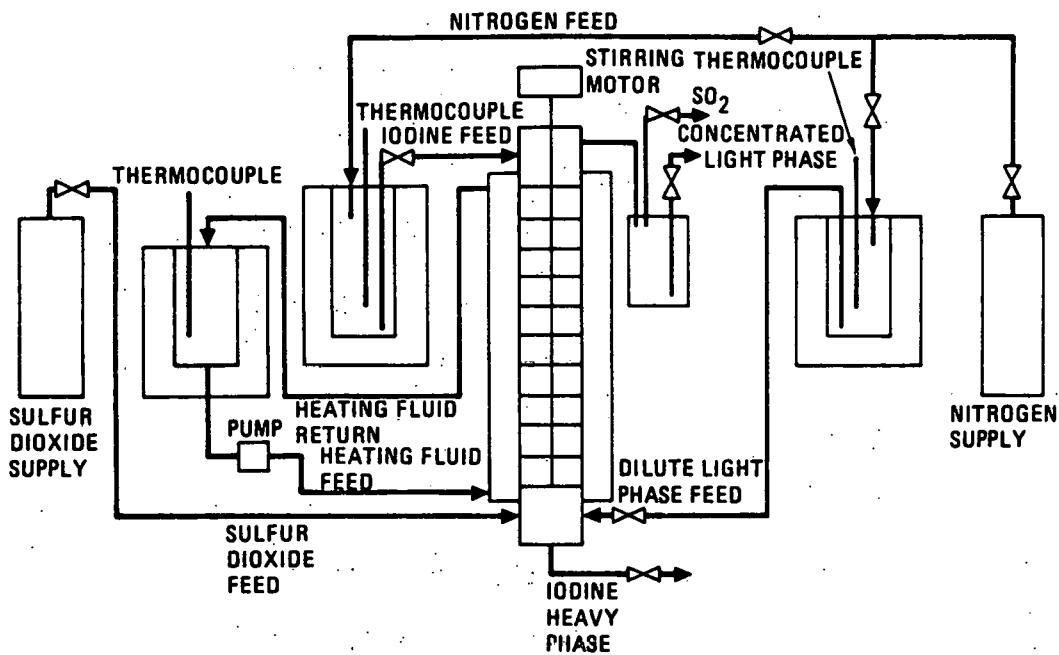


Fig. 11. Process flowsheet for reaction of iodine with upper-phase product

column. A saturating flow of SO_2 is added to the bottom of the column.

Figure 12 shows an individual stage of the column. The outer glass tube of this column, shown by diagonal cross hatching, has precision inner bore internal diameter, and the glass support ring is of close-fitting precision external dimensions. Between the glass support rings are Teflon separators provided with small openings for phase flow. Stirring is accomplished by centrifugal pumping of liquid from the opening area near a separator to the spinning pump exit. A baffle in the lower portion of the cell reduces swirl. The stirrer/centrifugal pump is operated by a regulated variable-speed motor. The stirring rates and torques are metered. Every column stage should be operated at equilibrium, although the column may be required to support a temperature gradient. Although operating in a temperature gradient (at the I_2 melting point at the top of the column and at the liquidus temperatures for I_2 solutions within the column) may be beneficial, all studies so far have been isothermal at a few degrees above the melting point of iodine for convenience.

4.1.3. Results of Bench-Scale Testing of H_2SO_4 Concentration Boost Reaction System

Several experiments have been run with this equipment; most were to establish flow control information and to test certain reactor modifications. The apparatus has been operated so that meaningful data with fully describable flow and stirring parameters are available. During these studies, 50% H_2SO_4 has been enriched in a number of experiments to 57% H_2SO_4 . The data indicate that about half of this increase was due to production of more H_2SO_4 , as confirmed by HI found in the I_2 phase. The other half comes from dehydration, which is valuable to the cycle energetics. Data do not yet indicate that steady-state operation on the H_2SO_4 boost reaction bench-scale unit has been attained. Figure 13 illustrates this by the results for a typical run at a flow ratio of 9.8 G I_2 /G 50% H_2SO_4 solution. Obviously, neither the concentration of HI in I_2 nor the H_2SO_4 concentration has leveled out over the 60 min

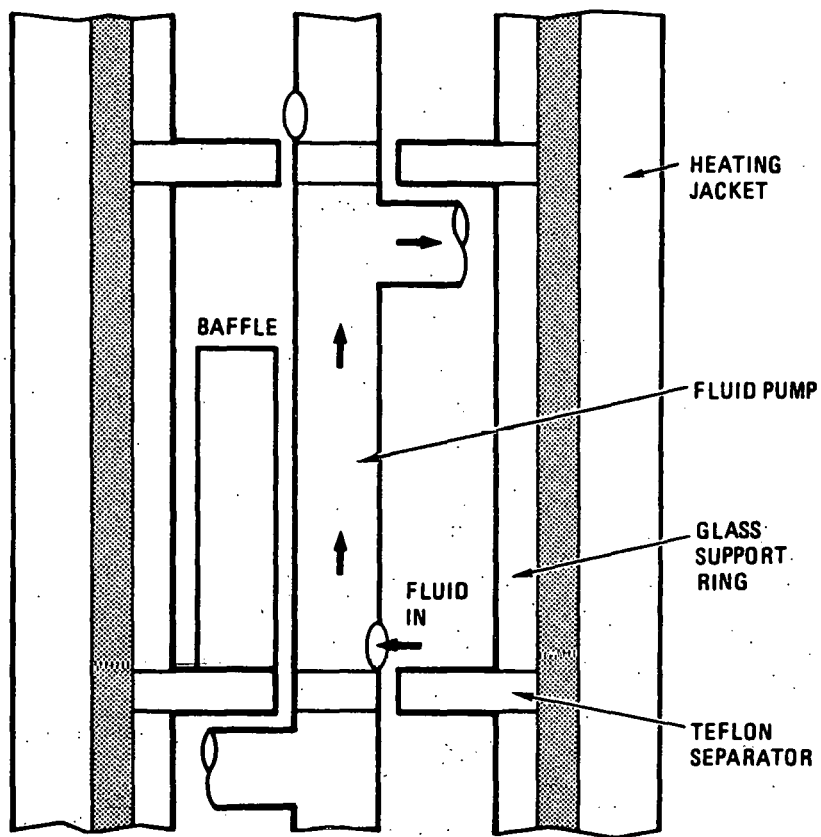


Fig. 12. Typical cell of H₂SO₄ boost column

run, and steady-state conditions have not been reached. This is also the case for lower flowrates, although steady state seems more assured at longer than 140 min. An even higher concentration of H_2SO_4 in the present bench-scale unit is, therefore, limited by the amount of liquid I_2 which can be processed at these flowrates. The flowrate ratio chosen to generate the Fig. 13 data is set by the main solution reaction, the requirement that the boost reaction be as effective as possible. As indicated in Fig. 13, experimental error is greater in measuring the H_2SO_4 concentration than the percent HI in I_2 .

4.2. LIQUID HYDROGEN IODIDE DECOMPOSITION BENCH-SCALE SYSTEM

4.2.1. Liquid Hydrogen Iodide Decomposition Concept

References 3 and 10 detail the advantages of decomposing HI in the liquid phase. This innovation results in enhanced conversion, since the chemical potential of the HI is maximized, while that of the I_2 is stabilized at a value determined by the partial pressure of I_2 . This pressure is orders of magnitude less than the H_2 pressure, because it dissolves in the HI liquid phase. Also, the process reactivity is at a high level, even for highly pregnant I_2 /HI solutions, because the liquid HI has intimate contact with the active surface of the catalyst. Nominally suggested operating temperatures are between $90^\circ C$ and the approximate critical temperature of pure HI (i.e., $150^\circ C$). Reference 10 describes the theoretical H_2 equilibrium pressure levels, the expected conversion levels, and some results of a catalyst survey conducted in the liquid HI environment. Expected conversion levels are between 50% to 55%, with the production of H_2 at pressure levels equal to conventionally accepted pipeline pressures (i.e., 50 atm) and higher. Incorporating liquid HI decomposition in the GA process flowsheet adds 3% to overall process efficiency due to the resulting recycle energy savings.

4.2.2. Description of Liquid Hydrogen Iodide Decomposition Bench-Scale System

Figure 14 is a schematic of the liquid HI bench-scale unit constructed.

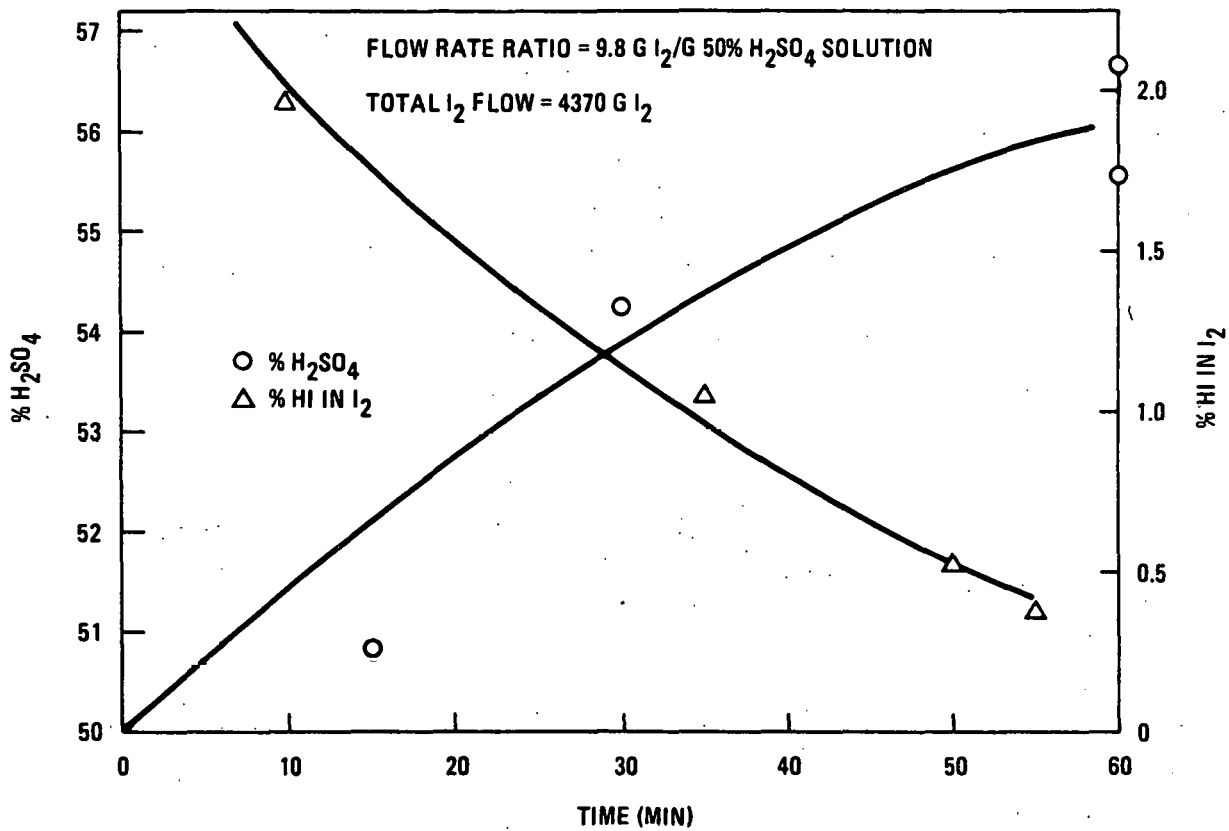


Fig. 13. Boost reaction approach to steady-state study (120°C nominal)

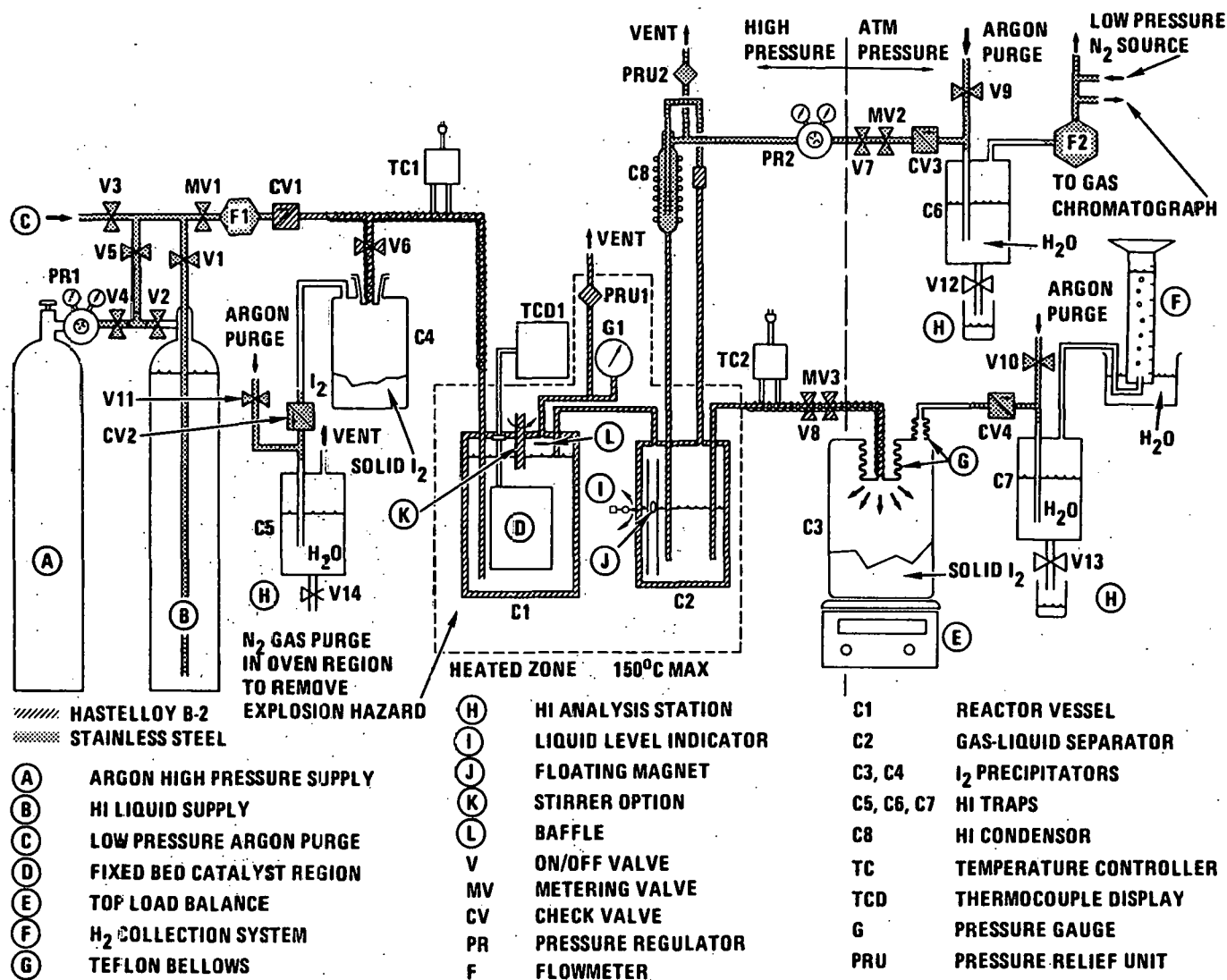


Fig. 14. Schematic of liquid HI decomposition bench-scale system

to demonstrate liquid HI decomposition at actual operating temperature and pressure (90° to 150°C and 30 to 80 atm). Previous studies were performed by batch, as reported in Refs. 3 and 10, and the results were extrapolated to the actual process conditions.

The liquid HI bench-scale unit is mainly constructed of stainless steel and Hastelloy Alloy B-2. Stainless steel is used for system parts exposed to nearly pure HI liquid or vapor at room temperature. Hastelloy Alloy B-2 is employed for system parts containing mixtures of HI and I₂ liquid at temperatures up to 150°C. These materials were chosen based on metallurgical studies performed at lower temperatures in simulated environments in the glass batch system used for the first-generation catalyst studies (Refs. 3 and 10) and in separate high pressure, high temperature batch tests in Hastelloy Alloy B-2 small volume ampules.

Dry liquid HI purchased in commercial pressure bottles is vapor transported to a stainless steel pressure bottle B. In doing so, the HI is assured of being almost free of the I₂, which slowly accumulates to significant levels in storage and transportation. The almost pure liquid HI is then transported to the reactor C1 through appropriate control valves and flowmeters by pressurizing with argon gas to the required pressure. The reactor vessel is a 1-liter Parr Instrument Corporation chemical bomb made of Hastelloy Alloy B-2 with the required top penetrations, as shown. Vessel C-2, which serves as a gas-liquid separator, is a smaller Hastelloy Alloy B-2 Parr chemical bomb. Both these vessels are sealed with Teflon gaskets.

Vessels C3 through C7 are all atmospheric pressure vessels constructed of glass. As indicated in Fig. 14, C3, C6, and C7 trap the unreacted HI and the product I₂. Vessels C4 and C5 are also HI and I₂ traps, but they are used only in a back-flush operation upon shutdown of the equipment. Vessel C8 condenses HI vapor and returns it to the gas-liquid separator, alleviating the problem of contact between a highly rich corrosive HI gas environment and the pressure regulator PR2. The pressure regulator reduces the pressure upstream of control valve MV2 to good

flow control levels. All valves contacting HI/I₂ liquid are fabricated of Hastelloy Alloy B-2; Autoclave Engineers, Inc. is the supplier. Figure 14 indicates appropriate check valves, pressure relief units, and heat tracing.

The HI traps have the facility for removing aliquots for titration while the I₂ formed is weighed on an electronic top load balance which can display the weight change on a chart recorder. Hydrogen flow is measured with the appropriate size rotameter once the HI component of the vapor is trapped. A gas chromatograph intermittently analyzes the H₂ gas stream. A low-pressure N₂ purge dilutes the H₂ gas to below the explosive limit for release into the fume hood. The H₂ collection system F measures the amount of H₂ dissolved in the liquid HI/I₂ phase.

The reactor vessel (C1), the gas-liquid separator (C2), the bourdon gauge (G1), and pressure relief unit (PRV1) are housed in a forced convection oven with control from room temperature to 200°C. All high-pressure sections are contained within a high-impact-resistant plastic enclosure for operator protection. The oven is purged constantly with N₂ gas to dilute any leaked H₂ to below the explosion limit.

In many ways, the bench-scale unit construction is unique, mainly because of the corrosive fluids and the relatively high temperatures and pressures. Highest pressures and temperatures expected are 100 atm and 150°C, respectively. A preheat on the incoming HI, controlled by temperature controller TC1, is required to speed up attaining steady-state conditions within the oven. The amount of power required to attain steady state is estimated to be only ~50 W for the maximum flows used. This accounts for the estimated heat capacity effect, vaporization of the HI (liq.), and the heat of reaction.

The reactor internal design is unique. The reaction makes a large amount of H₂ gas internal to the catalyst bed in the presence of the liquid HI and liquid I₂. Under such conditions, a certain loss of contact with the catalyst would be expected of the HI liquid in a one pass-through

reactor design. Instead, the internal design, which will be tested first, involves a fixed catalyst bed with appropriate space around its sides and bottom. Hopefully, such a configuration will result in facile escape of the H_2 gas bubbles from within the catalyst bed, with a resulting self-stirred motion of the surrounding liquid up through the bottom of the bed. This design will be tried initially, and the design will be optimized once results are obtained. The reactor vessel has a high-pressure magnetic drive stir option. The catalyst will be contained in a Hastelloy Alloy B-2 wire mesh cage for the above studies. The one pass-flow-through reactor will also be assessed by placing a machined Teflon plug into the reactor with the appropriate location of the cavity for the catalyst. For the flexibility required, the above reactor has been designed oversize. All components in the system have been designed to produce 4 std liters of H_2 /min, and it is compatible with incorporation into the integrated bench-scale system later.

5. CONCLUSION

This report presents preliminary results from the bench-scale testing of the GA sulfur-iodine thermochemical water-splitting cycle. These studies have verified the flowsheet design criteria for the specific subsections tested. Some modifications, not anticipated, were made in the system fluids handling. Most changes involved simple component redesign to handle the required flows and to obtain compatibility with specific corrosive environments. The most notable change, which will possibly impact future scaleup designs, is the discovery of a potential solids nucleation problem in certain H_2SO_4 solutions carrying small quantities of I_2 and HI. The problem is believed to be associated with the combined relatively long storage times of the synthetic feed solutions and the agitation of greatly oversized centrifugal pumps. These are inherent problems associated with the size of the bench-scale unit. Furthermore, the synthetic feed stock solutions were arbitrarily chosen close to the saturation limits of HI and I_2 . These levels should be lower in the actual process.

Two innovations of the GA sulfur-iodide process, the sulfuric acid concentration boost reaction and the liquid HI decomposition process steps, were constructed as bench-scale units after batch testing. The H_2SO_4 boost reaction bench-scale unit operation indicated that sulfuric acid concentrations approached 57%. This translates as additional 3% overall process efficiency, as calculated from the process flowsheets.

Overall, these precursory studies on isolated subsection operation within the bench-scale unit have further proven the technical viability of the GA sulfur-iodine process flowsheet design.

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ABSTRACT

Portions of a bench-scale model of a sulfur-iodine thermochemical water-splitting cycle have been operated at General Atomic Company as part of a comprehensive program to demonstrate the technology for hydrogen production from nonfossil sources. The hydrogen program is funded by the U.S. Department of Energy, the Gas Research Institute, and General Atomic Company. The bench-scale model consists of three subunits which can be operated separately or together and is capable of producing as much as 4 std liters/min ($6.7 \times 10^{-5} \text{ m}^3/\text{s}$ at standard conditions) of gaseous hydrogen. One subunit (main solution reaction) reacts liquid water, liquid iodine (I_2) and gaseous sulfur dioxide (SO_2) to form two separable liquid phases: 50 wt % sulfuric acid (H_2SO_4) and a solution of iodine in hydriodic acid (HI_x). Another subunit (H_2SO_4 concentration and decomposition) concentrates the H_2SO_4 phase to the azeotropic composition, then decomposes it at high temperature over a catalyst to form gaseous SO_2 and oxygen. The third subunit (HI separation and decomposition) separates the HI from water and I_2 by extractive distillation with phosphoric acid (H_3PO_4) and decomposes the HI in the vapor phase over a catalyst to form I_2 and product hydrogen. This paper presents the results of on-going parametric studies to determine the operating characteristics, performance, and capacity limitations of major components.

1. INTRODUCTION

The recent realization that the earth's fossil fuel resources cannot inexhaustibly supply society's needs has prompted investigating many alternative fuel sources. One alternative fuel source is hydrogen from water splitting. Hydrogen, when combined with solar or nuclear heat sources is a renewable, portable fuel from water, which can be stored as a gas, liquid, or hydride, depending on the application. A hydrogen economy appears to have many benefits, and researchers around the world have recently devoted considerable effort to developing viable processes for the economic large-scale production of hydrogen fuel from water. The General Atomic Company (GA) sulfur-iodine process is a thermochemical water-splitting approach currently being developed and assessed.

The program to investigate thermochemical water splitting using the high-temperature gas-cooled reactor (HTGR) as a heat source has been underway at GA since October 1972. Current program participants are the Gas Research Institute (GRI), which carries on the sponsorship of the American Gas Association (AGA), the U.S. Department of Energy (DOE), and GA. Northeast utilities Service Company and Southern California Edison Company previously participated.

The GA sulfur-iodine cycle was first described in the open literature by Russell (Ref. 1). Reference 2 is a recent overview of the entire program effort. The chemical basis for thermochemical water splitting is contained in a review paper on catalysis (Ref. 3), and Refs. 4 and 5 survey the chemical studies performed to establish the process direction. Reference 6 gives specific details on the program process engineering. Reference 7 reports on the materials investigation.