Sulfur Iodine Process Summary for the Hydrogen Technology Down-Selection

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Idaho National Laboratory

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Purpose

This report summarizes the sulfur-iodine (SI) thermochemical water splitting process for the purpose of supporting the process for evaluating and recommending a hydrogen production technology to deploy with the Next Generation Nuclear Plant (NGNP). This package provides the baseline process description as well as a comparison with the process as it was implemented in the Integrated Lab Scale (ILS) experiment conducted at General Atomics from 2006-2009.

Sulfur Iodine Baseline Process Summary

As part of an earlier Nuclear Energy Research Initiative (NERI) study sponsored by the U.S. Department of Energy, a team headed by GA and supported by Sandia National Laboratories (SNL) and the University of Kentucky evaluated 115 different thermochemical cycles that produce hydrogen [Brown, 2003]. The sulfur-iodine (SI) cycle was determined to be the best cycle for coupling to a high temperature reactor (HTR) because of its high efficiency and potential for further improvement. The Japanese Atomic Energy Agency (JAEA) has also selected the SI process for further development and has successfully completed bench-scale demonstrations of the SI process at atmospheric pressure [Kubo, 2005]. JAEA also plans to proceed with pilot-scale demonstrations of the SI process and eventually plans to couple an SI demonstration plant to its High Temperature Test Reactor (HTTR) [Terada, 2005], [Iyoku, 2005]. As part of an international NERI project, GA, SNL, and the French Commissariat L'Energie Atomique performed laboratory–scale demonstrations of the SI process at prototypical temperatures and pressures. This demonstration was performed at General Atomics in San Diego, CA and concluded in April 2009.

Water thermally dissociates at significant rates into hydrogen and oxygen at temperatures approaching 4000°C. As indicated in Figure 1, the SI process consists of three primary chemical reactions that accomplish this same result at much lower temperatures. The process involves decomposition of sulfuric acid and hydrogen iodide, and regeneration of these reagents using the Bunsen reaction. Process heat is supplied at temperatures equal to or greater than 700°C to concentrate and decompose sulfuric acid. The exothermic Bunsen reaction is performed at temperatures near 120°C and releases waste heat to the environment. Hydrogen is generated during the decomposition of hydrogen iodide, using process heat at temperatures greater than 300°C. Figure 2 shows a simplified process flow diagram of the SI cycle. The product hydrogen gas is produced at a pressure of 4.0 MPa.
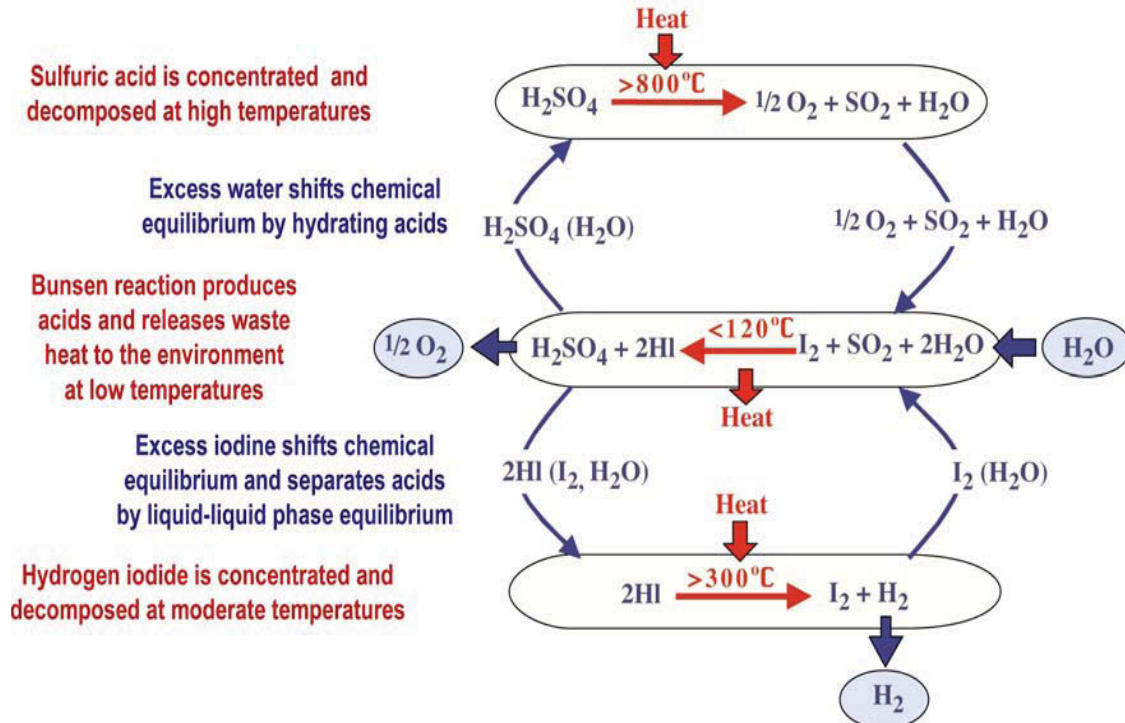
Figure 1 The SI Thermochemical Water Splitting Process
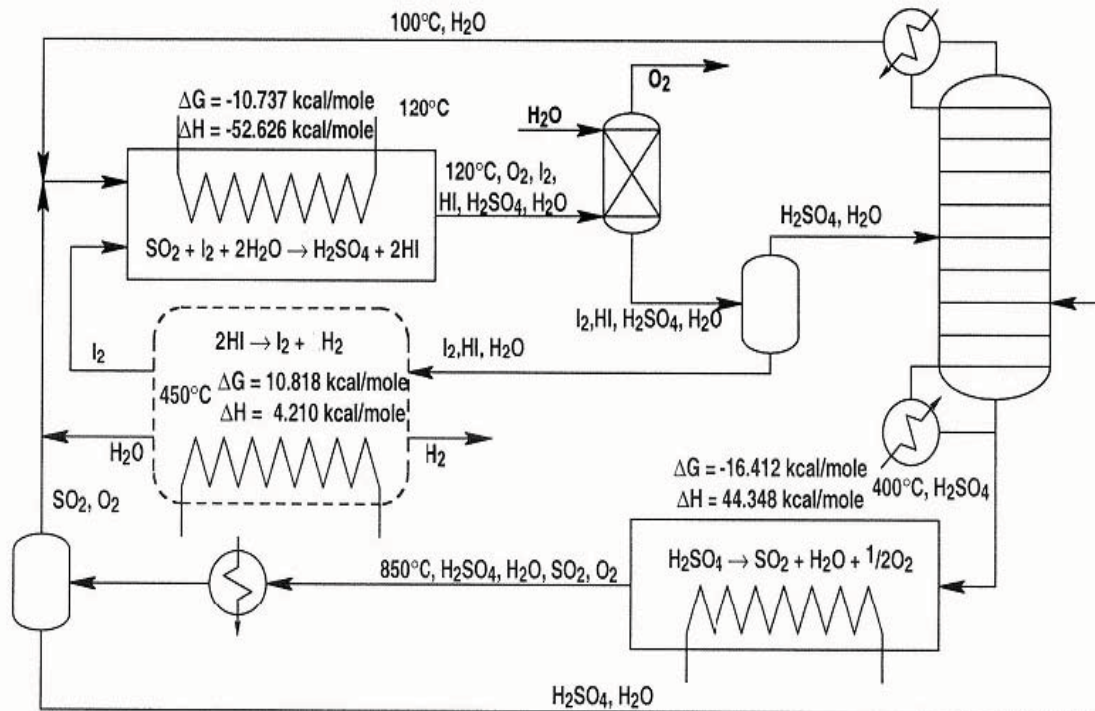
Figure 2 Simplified SI Process Flow Schematic

Hydrogen Production System

The Hydrogen Production System design is based on the design described previously [Brown, 2003]. The current design reflects optimization of the flowsheets to increase the hydrogen production rate and to improve efficiency.

Sulfur-Iodine Process Description

The S-I thermochemical cycle consists of three chemical reactions that result in dissociation of water into hydrogen at oxygen;

Bunsen Reaction:	$I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4$	(T ~ 120°C)
H_2SO_4 Decomposition:	$H_2SO_4 \rightarrow SO_2 + H_2O + \frac{1}{2}O_2$	(T > 800°C)
HI Decomposition:	$2HI \rightarrow I_2 + H_2$	(T > 350°C)
Net	$H_2O \rightarrow H_2 + \frac{1}{2}O_2$	

All three reactions are operated under conditions of chemical equilibrium. Energy inputs to the process are heat to the endothermic H_2SO_4 and HI decomposition reactions and electrical energy required for pumping process fluids and heat pumps. Heat at about 120°C is rejected from the exothermic Bunsen reaction. With the exception of water, all reactants are regenerated and recycled.

The Hydrogen Production System design is organized into subsystems according to these three chemical reactions. These subsystems are referred to as Sections 1, 2, and 3. Section 1 (Bunsen reaction) includes all the process equipment associated with production of the aqueous sulfuric acid phase and the hydrogen iodide ($HI/I_2/H_2O$) phase. Section 1 also includes equipment to purify the oxygen before release. Section 2 concentrates the aqueous sulfuric acid phase and then decomposes the concentrated acid. The decomposition products and the water removed from concentrating the acid are returned to Section 1. Section 3 concentrates and decomposes hydrogen iodide. Section 3 also includes equipment to purify the product hydrogen gas.

The flowsheets for Sections 2 and 3 have been analyzed and optimized using AspenPlus process-simulation software. Because the thermodynamic data for the thermophysical properties are still limited for the $HI/I_2/H_2O$ vapor equilibrium, the equilibrium conditions for Section 1 are based on previous calculations [Norman, 1982] Approximately two-thirds of the fresh water required for hydrogen production is supplied to Section 3 and the remainder is supplied to Section 1. The product hydrogen gas is produced at a pressure of 4.0 MPa.

Section 1 (Bunsen Reaction)

The flowsheet for Section 1 is shown in Figure 3 and the stream compositions are shown in Table 1. This flowsheet is essentially the same as that described previously

[Brown, 2003] and is based on experimental data obtained in the 1980s and later validated during the Integrated Lab Scale experiment during 2006-2009. A key component in Section 1 is the flow reactor R101, which functions as a heat exchanger. Because the kinetics of the Bunsen reaction are very fast, the rate of heat transfer controls the reaction rate. The mixture exiting R101 consists of three immiscible phases, of which two are liquid and one is gas. These phases are separated in component S101. The lower phase, which consists of $HI/I_2/H_2O$ in the approximate molar ratios 2/8/10, is stripped of dissolved SO_2 and H_2SO_4 in the packed column C102. Prior to stripping, the pressure is lowered in order to use a recycle O_2 stream as the stripping agent. The SO_2 is directly stripped by the O_2 stream. As the SO_2 is depleted, the reaction equilibrium shifts to produce more SO_2 from H_2SO_4 reacting with HI, which results in simultaneous removal of SO_2 and H_2SO_4. The stripped lower phase exits C102 and is transferred to Section 3, where it is processed to produce the hydrogen product gas. The upper phase exiting S101 (aqueous H_2SO_4) is transferred to boost reactor C103, which is a packed column. A portion of the upper phase exiting C102 (O_2 and SO_2) is also transferred to C103. In this column, the sulfuric acid is concentrated by contacting it with I_2 and SO_2. The molar ratio of H_2SO_4 to H_2O entering C103 is about 1:6 and is increased to about 1:4 at the exit of C103.

The remaining equipment in Section 1 is associated with processing the O_2 stream. The SO_2 is scrubbed from the O_2 stream in packed column C101. A small amount of iodine is added to C101 in order to minimize the amount of water required to remove SO_2 via the Bunsen reaction. The water streams to C101 are supplied from Section 2 and are cooled prior to entering C101 in order to remove the heat of reaction and minimize the amount of heat that is removed by R103. The SO_2 remaining in the upper phase that exits boost reactor C103 is scrubbed from the oxygen in packed column C104. Because all of the SO2 exiting C102 cannot be used in boost reactor C103, a portion of this stream is transferred to packed column C105 to scrub the SO_2 from the oxygen. This SO_2 is then transferred to R101. Energy recovery turbines are used to recover the work available from the compressed gasses and to provide the O_2 stripping gas at an appropriate pressure.

Because the design point at the outlet of component R101 is essentially fixed in terms of temperature, compositions of both liquid phases, and the partial pressure of SO2, the only free variable is the system pressure. The system pressure must be below the operating pressure of Section 2 so that the gases can flow from Section 2 without compression. The pressure must also be sufficiently high for efficient operation of the SO_2 stripping column. Operating R101 at higher pressures does provide the benefit of a lower SO_2 to O_2 ratio at the exit of this reactor, which leaves less SO_2 to be removed in the first oxygen scrubber (C101). The operating pressure for R101 has been set at 0.7 MPa.
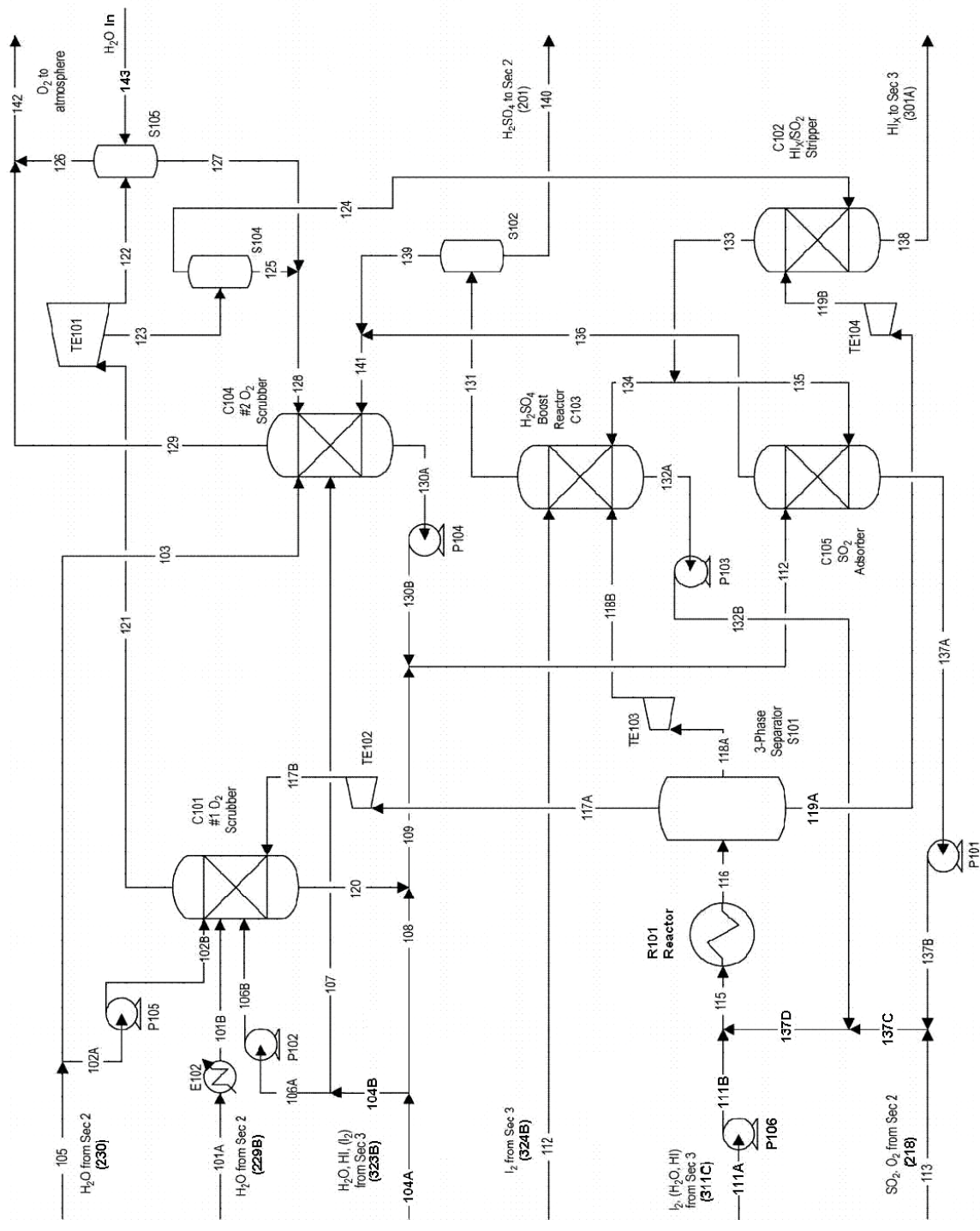
Figure 3 SI Process Section 1 Flow Stream Description

Table 1 Section 1 stream components

Stream ID	Species Present						Phase	Pressure (Bar)	Temp. (°C)
	H₂SO₄	HI	I₂	H₂O	SO₂	O₂			
101A	X			X	X		L	12.00	40.6
101B	X			X	X		L	12.00	86.5
102A	X			X	X	X	L	1.01	38.0
102B	X			X	X	X	L	4.40	38.0
103	X			X			L	1.01	38.0
104A		X	X	X			L	7.00	120.4
104B		X	X	X			L	7.00	120.4
105	X			X	X	X	L	L	-272.1
106A		X	X	X			L	7.00	120.4
106B		X	X	X			L	12.00	120.4
107		X	X	X			L	1.01	95.4
108		X		X			L	4.20	95.4
109	X	X	X	X	X	X	L	1.85	119.9
111A		X	X	X			L	7.00	118.8
111B		X	X	X			L	12.00	119.9
112		X	X	X			L	7.00	115.6
113				X	X	X	V	7.00	40.1
115	X	X	X	X	X	X	V+L	7.00	115.6
116	X	X	X	X	X	X	V+L	7.00	119.9
117A			X	X	X	X	V	7.00	119.9
117B			X	X	X	X	V	4.20	81.1
118A	X			X	X		L	7.00	119.9
118B	X			X	X		L	1.85	119.9
119A		X	X	X	X		L	7.00	119.9
119B		X	X	X	X		L	1.85	119.9
120	X	X	X	X	X	X	L	4.20	111.3
121				X		X	V	4.20	111.3
122				X		X	L+V	1.01	111.3
123				X		X	L+V	1.85	15.9
124				X		X	V	1.85	15.9
125				X			L	1.85	15.9
126				X		X	V	1.01	15.9
127				X			L	1.01	15.9
128				X			L	1.01	15.9
129				X		X	V	1.01	39.9
130A	X	X	X	X			L	1.01	119.9
130B	X	X	X	X			L	1.85	119.9
131	X		X	X	X	X	L	1.85	111.4
132A		X	X	X	X		L	1.85	111.4
132B		X	X	X	X		L	7.00	111.4
133			X	X	X	X	V	1.85	119.9
134			X	X	X	X	V	1.85	119.9
135			X	X	X	X	V	1.85	119.9

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136			X	X	X	X	V	1.85	96.5
137A	X	X	X	X	X		L	1.85	96.5
137B	X	X	X	X	X		L	7.00	96.5
137C		X	X	X			L	1.85	119.9
137D			X	X	X	X	V	1.85	111.4
140	X			X	X		L	1.85	111.4
141			X	X	X	X	V	1.85	102.0
142				X		X	V	1.01	24.9
143				X			L	1.01	24.9

Section 2 (Sulfuric Acid Decomposition)

The flowsheet for Section 2 is shown in Figure 4 and the stream compositions are shown in Table 2. Section 2 concentrates and decomposes the aqueous sulfuric acid phase that is transferred from Section 1. All of the heat from the secondary Helium Loop System (HLS) from the reactor is transferred to Section 2. As previously discussed, the sulfuric acid vaporizers and decomposers are operated at a pressure slightly lower than that of the secondary helium coolant in order to prevent chemical contamination of the Secondary HLS while minimizing pressure differentials across these components.

The H_2SO_4/H_2O stream from Section 1 (201) is concentrated in three successive vacuum flashes. The first flash (S201) is adiabatic but heat is added in the other two flashes. The first flash cools the stream significantly below the temperatures of Section 1 so that heat released in R103 can be used to evaporate water in the second flash (S202) of Section 2. The third vacuum flash (S203) uses heat recovered from Section 3. The vapors from the three flashes are cooled and the condensate returned to Section 1 (229B), as are the condensed vapors from the vacuum pump (228B). The concentrated acid is pumped from vacuum conditions to the pressure of the decomposition subsection using P201 and passed to the counter-current vapor-liquid recuperator (H206).

The hot liquid from the recuperator is heated and vaporized in three stages. The first two evaporators (H207 and H208A) are flow-through evaporators, with the stream progressively vaporized as it passes through the counter current heat exchangers. The condensate from the decomposer product is added between the first and second vaporizers. Any minerals that enter with the deionized water feed to the process and any mobile corrosion products from the entire system will eventually be deposited in the sulfuric acid decomposition process. If the final evaporation occurred while the stream was flowing through tubes, the minerals and corrosion products could deposit on the heat transfer surfaces and contribute to fouling or even plugging. For this reason, the third vaporizer (H208B) is a pool-type unit.

The sulfuric acid vapors are decomposed in two steps;

$$H_2SO_4 \leftrightarrow SO_3 + H_2O \qquad\qquad (T > 450°C)$$
$$SO_3 \rightarrow SO_2 + \tfrac{1}{2}O_2 \qquad\qquad (T > 800°C)$$
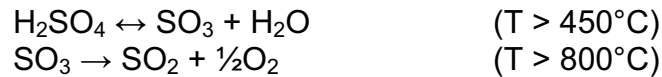
The first reaction is very fast and equilibrium is maintained, shifting to more complete decomposition as the temperature is raised or as SO_3 is removed by the second reaction. The first reaction begins to occur in the final vaporizer (H208B), but most of the vaporization occurs primarily in H209, which is a standard counter-current heat exchanger.

The second reaction requires a catalyst. The catalytic reaction occurs in two decomposers (H210A and H210B). Conceptually the decomposers are counter-current heat exchangers with catalyst on the heat transfer surfaces. The differences between the two decomposers are in how they are heated. H210B is heated with helium from the Secondary HTS (HE1). Decomposer H210A, which operates at slightly lower temperatures, is heated with both secondary helium (HE2) and the decomposer product (213A). In addition, both helium and decomposer product are used in parallel to heat the gas-gas recuperator (H209) and vaporizers 2 and 3 (H208A and H208B). Only the decomposer product is used to heat the first vaporizer (H207). Finally, the decomposer is used to provide the heat requirements for Section 3 (H213A). Some condensation occurs in this final heat exchanger. The product gases (215A) are separated (S207) from the condensate and pass to the gas-liquid recuperator (H206). The condensate (214) is recycled to the second vaporizer (H208A). The condenser (H213A) and separator (S207) are physically located above the vaporizers (H208A and H208B) such that the gravitational head exceeds the pressure drop through the decomposition system, which eliminates the need for a pump capable of operating at these extreme conditions.

The two-phase product from the decomposition system (215B) is separated and power is recovered separately from the two phases. Each phase is cooled to as low a temperature as practical before they are transferred to Section 1. Condensate from the cooling process is transferred separately to Section 1.

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Table 3
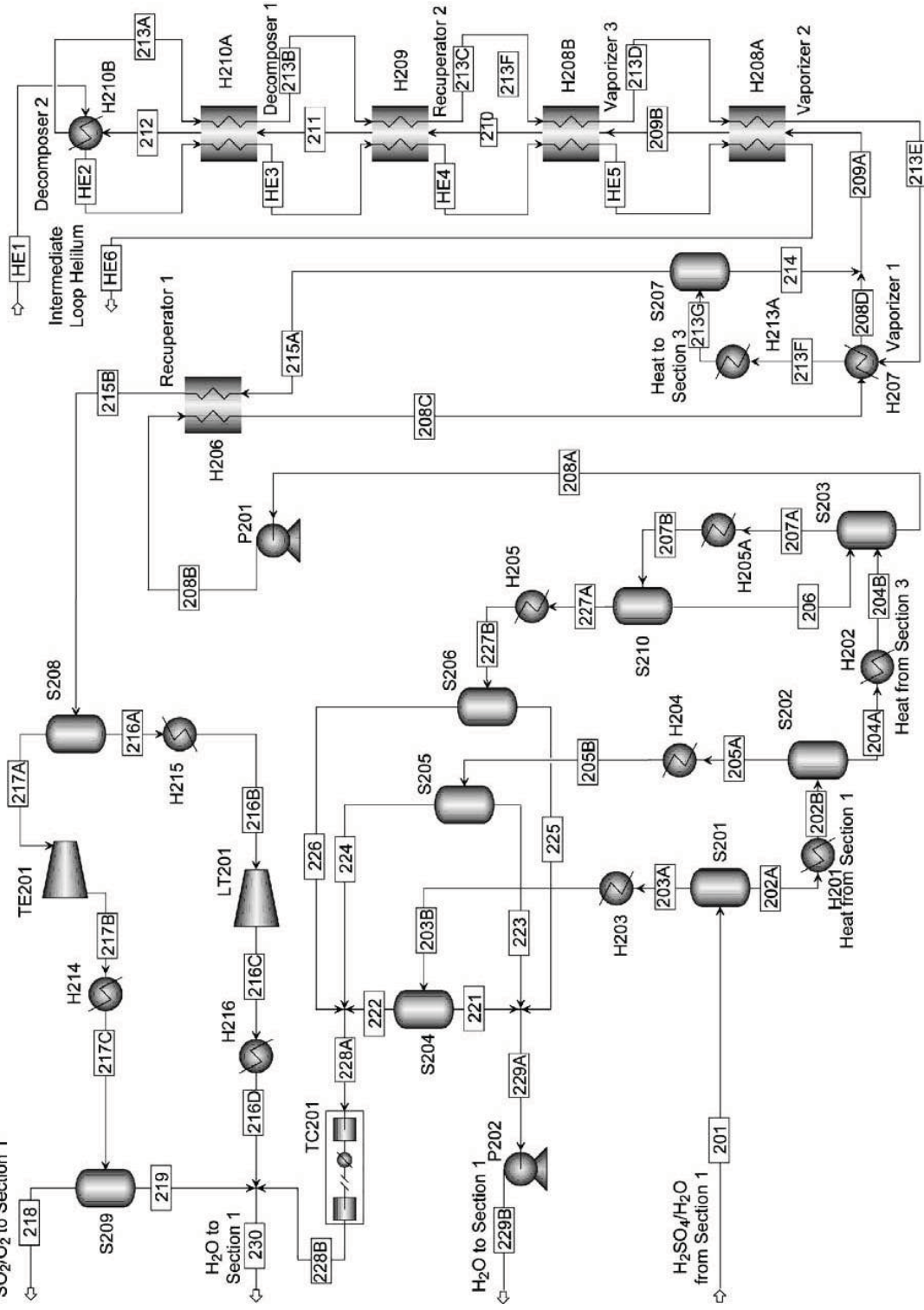
Figure 4 SI Process Section 2 Flow Stream Description

Table 2 Section 2 stream components

Stream ID	Species Present						Phase	Pressure (Bar)	Temp. (°C)
	H_2SO_4	HI	I_2	H_2O	SO_2	O_2			
201	X	X		X		X	L	1.85	111.8
202A	X	X		X		X	L	0.1	66.4
202B	X	X		X		X	V+L	0.1	110
203A	X			X		X	V	0.1	66.4
203B	X			X		X	V	0.1	40
204A	X	X				X	L	0.1	110
204B	X	X				X	V+L	0.1	194.2
205A	X			X		X	V	0.1	110
205B	X			X		X	L	0.1	40
206	X	X				X	L	0.1	160
207A	X	X				X	V	0.1	189.9
207B	X	X				X	V+L	0.1	160
208A	X	X				X	L	0.1	189.9
208C	X	X				X	L	70.5	376.9
208D	X	X				X	L	70.5	401.9
209A	X	X				X	L	70.5	403
209B	X	X	X			X	V+L	70.5	563.9
210	X	X	X			X	V	70.5	626.9
213A	X	X	X	X	X	X	V	70.5	900
213G	X	X	X	X	X	X	V+L	70.5	401.9
214	X	X				X	L	70.5	401.9
215A	X	X	X	X	X	X	V	70.5	401.9
215B	X	X		X	X	X	V+L	70.5	250.9
216A	X	X		X	X	X	L	70.5	252.6
216B	X	X		X	X	X	L	70.5	120
216C	X	X		X	X	X	L	2	118.9
216D	X	X		X	X	X	V+L	2	40
217A	X			X	X	X	V	70.5	252.6
217B	X			X	X	X	V+L	7	128.3
217C	X			X	X	X	V+L	7	40
218	X			X	X	X	V	7	40
219	X			X		X	L	7	40
221							L	0.1	40
222	X			X		X	V	0.1	40
223	X			X		X	L	0.1	39.6
224	X					X	V	0.1	39.6
225	X	X				X	L	0.1	40
226							V+L	0.1	40
227A	X	X				X	V	0.1	160
227B	X	X				X	L	0.1	40
228A	X			X		X	V	0.1	40
228B	X			X		X	V+L	7	120
229	X	X		X		X	L	12	40.5

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HE1						V	70.6	924
HE6						V	69.6	557.5

Section 3 (Hydrogen Iodide Decomposition)

Two different processes have been investigated for HI decomposition. One process, referred to as extractive distillation, uses phosphoric acid to strip HI from the $HI/H_2O/I_2$ (HIx) mixture and to break the HI/H_2O azeotrope. The other process is referred to as reactive distillation and involves reacting the $HI/H_2O/I_2$ mixture in a reactive bed to effect the separation process and produce hydrogen. Extractive distillation is a proven process, but requires significant amounts of energy and many components to perform the extraction, distillation, concentration, reaction, and separation steps of the process (see Figure 5). The kinetics for reactive distillation are still relatively unknown, but the process can be performed in a single component without requiring concentration of the acid (see Figure 6). For the nth-of-a-kind SI-Based H_2 plant design, the HI decomposition flowsheet is based on the reactive distillation process. One disadvantage of reactive distillation is that there is significant recycle of HI back to Section 1, which increases equipment sizes for Section 1.
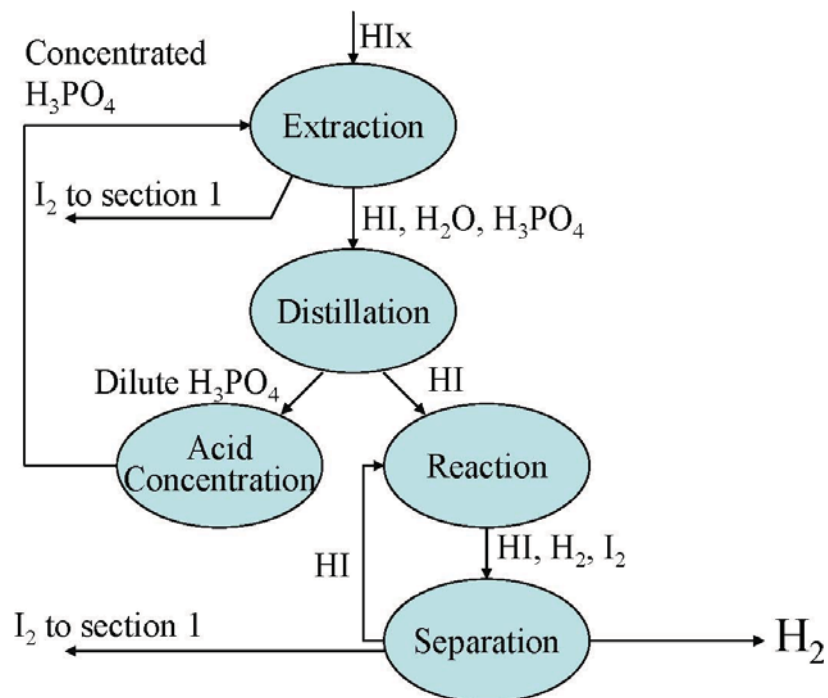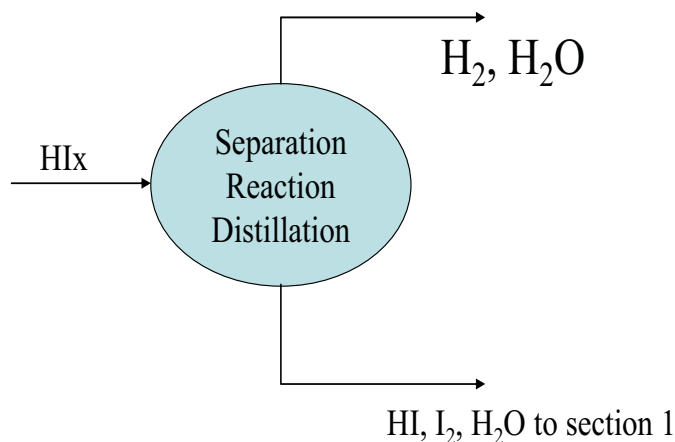

Figure 5 Extractive distillation process diagram

Figure 6 Reactive distillation process diagram

The flowsheet for Section 3 is shown in Figure 7 and the stream compositions are shown in Table 3. The reactive distillation process is performed within a packed-bed distillation column using activated carbon as a catalyst. Significant quantities of heat are required for Section 3, but there are also significant quantities of heat available for recovery within Section 3. Because much of the heat available for recovery is at a temperature lower than required for process operations, heat pumps (using water as the working fluid) are used to transfer the heat from the lower temperature source to the higher temperature sink. The distillation column has a high heat duty in the reboiler and has heat available from the condenser. The first heat pump transfers heat from the condenser to the reboiler at the expense of externally supplied shaft work. Much of the heat is used to break the binding energy of the $HI/I_2/H_2O$ complex. For recycled HI, the heat of mixing is recovered and a second heat pump is used to raise the temperature of this stream to that required for heating the distillation column feed. The remaining heat duty of Section 3 is recovered from the decomposer products of Section 2.

The heat pumps consist of a multi-staged steam compressor, a hot heat exchanger complex that transfers heat to the process and condenses steam, an expansion valve in which the condensate is partially flashed and the pressure is lowered, and a cold heat exchanger in which the condensate is evaporated. Mechanical energy drives the compressor and much of this mechanical energy adds internal energy to the steam. The hot heat exchanger network includes the interstage coolers of the compressor as well as the subsequent condenser.

Recovery of the heat of mixing of the $HI/I_2/H_2O$ is necessary for process efficiency but does require additional process steps (described below) to produce a stream of pure I_2 that is required for operation of the H_2SO_4 boost reactor in Section 1. The HIx from Section 1 (301A) is pumped up to the operating pressure of the reactive distillation column (C301) and heated to the required feed temperature in a series of heat exchangers (H301, H302, and H303). Most of the required heat is recovered from cooling hot streams, but a portion of the heat is obtained from Heat Pump 2. The distillation column operates with a vapor product (305) consisting of $HI/H_2/H_2O$. The cold side reflux condenser on C301 is HP1-QH, which is the heat input to Heat Pump 1. The

hot side of the reboiler on C301 is HP2-QC. The heavier liquid phase is nearly pure iodine. This phase is cooled, washed with water in C303, and returned to Section 1 for use in the H_2SO_4 boost reactor. The lighter liquid phase is cooled to the same temperature as the column overhead and then combined with the column overhead (306) to recover the heat of solution from the undecomposed HI. This heat is removed in H304, which is the hot side of HP2-QC and the heat input to Heat Pump 2. HP2-QH, the heat output of Heat Pump 2, is the hot side of H303 and the final preheat of the still feed. The two-phase stream leaving H304 is separated in S301. The vapor phase contains the hydrogen product gas. This stream is cooled in H308 and the condensate is removed in S302. The hydrogen is then washed with water in C302 to yield the final hydrogen product. The condensate from S302 consists of two liquid phases. The heavier phase is primarily iodine and is washed in C303 for use in the H_2SO_4 boost reactor of Section 1. The lighter phase is mostly water and is combined with the lower phase from C302, which is also mostly water. These two streams function as the wash for C303.

Pure water is not very effective at washing iodine out of hydrogen, but iodine is very soluble in HI. For this reason, a small amount of the distillation overhead (313A) is split from the main flow (305), cooled, and then added back to the wash column (C301) at an intermediate stage.

The liquid phase from S301 is split for heat recovery. Part of the heat is recovered into the column feed and the remainder is cooled in H305, which is the hot side of H202 in Section 2.
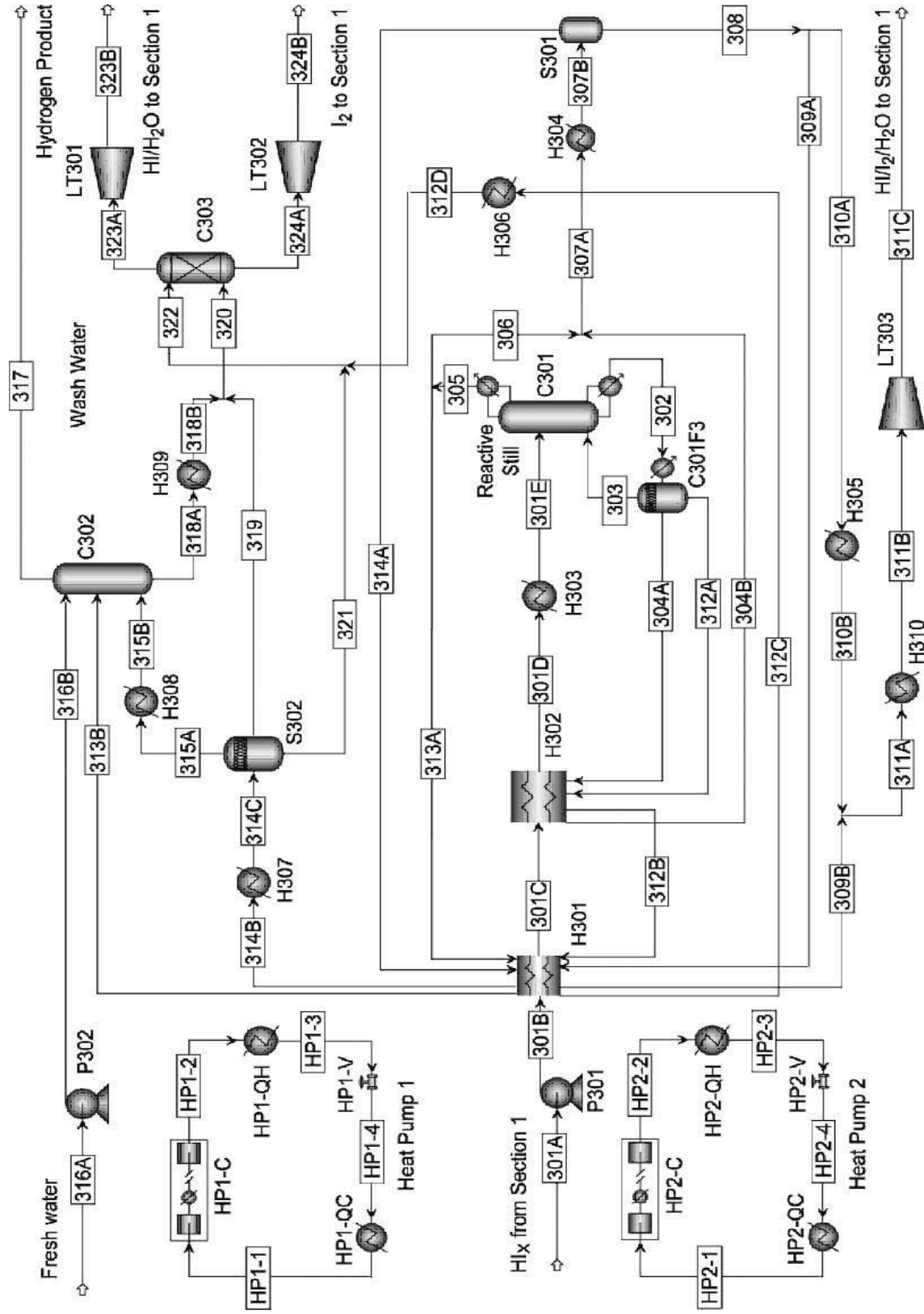
Figure 7 SI Process Section 3 Flow Stream Description

Table 3 Section 3 stream components

Stream ID	Species Present						
	H_2O	I_2	HI	H_2	Phase	Pressure (Bar)	Temp. (°C)
301A	X	X	X		L	1.85	119.85
301B	X	X	X		L	40.00	123.07
301C	X	X	X		L	40.00	247.17
301D	X	X	X		L	40.00	269.87
301E	X	X	X		V + L	40.00	282.46
302	X	X	X	X	L	40.00	289.69
303	X	X	X	X	V	40.00	289.06
304A	X	X	X		L	40.00	289.06
304B	X	X	X		L	40.00	257.17
305	X	X	X	X	V	40.00	262.17
306	X	X	X	X	V	40.00	262.17
307A	X	X	X	X	V + L	40.00	271.06
307B	X	X	X	X	V + L	40.00	257.17
308	X	X	X	X	L	40.00	257.17
309A	X	X	X	X	L	40.00	257.17
309B	X	X	X	X	L	40.00	139.01
310A	X	X	X	X	L	40.00	257.17
310B	X	X	X	X	L	40.00	139.01
311A	X	X	X	X	L	40.00	139.01
311B	X	X	X	X	L	40.00	120
311C	X	X	X	X	L	7.00	118.78
312A	X	X	X		L	40.00	289.06
312B	X	X	X		L	40.00	257.17
312C	X	X	X		L	40.00	139.01
313A	X	X	X	X	V	40.00	262.17
313B	X	X	X	X	V + L	40.00	139.01
314A	X	X	X	X	V	40.00	257.17
314B	X	X	X	X	V + L	40.00	139.01
314C	X	X	X	X	V + L	40.00	120
315A	X	X		X	V	40.00	120
315B	X	X		X	V + L	40.00	40
316A	X				L	1.01	25
316B	X				L	40.00	27.26
317	X			X	V	40.00	28.82
318A	X	X	X	X	L	40.00	42.97
318B	X	X	X	X	V + L	40.00	110
319	X	X	X	X	L	40.00	120
320	X	X	X	X	V + L	40.00	117.69
321	X	X	X	X	L	40.00	120
322	X	X	X	X	L	40.00	118.27
322D	X	X	X		L	40.00	120
323A	X	X	X	X	L	40.00	120.55
323B	X	X	X	X	L	7.00	120.39
324A	X	X	X	X	L	40.00	118.04
324B	X	X	X	X	L	7.00	115.57

HP1-1	X				V	44.77	257.12
HP1-2	X				V	71.60	288.46
HP1-3	X				L	71.60	287.4
HP1-4	X				V + L	44.77	257.12
HP2-1	X				V	41.21	252.13
HP2-2	X				V	79.50	295.69
HP2-3	X				L	79.50	294.6
HP2-4	X				V + L	41.21	252.13

Integrated Lab Scale Experiments

The Sulfur-Iodine (S-I) thermochemical cycle is one of the baseline production methods that is being investigated under the Nuclear Hydrogen Initiative (NHI). The current objective is to conduct an integrated lab scale (ILS) experiment in order to provide a technical basis for the assessment of the viability of the S-I cycle for nuclear hydrogen production. This will serve as a stepping stone for future pilot and engineering scale demonstrations. The overall ILS project objectives were as follows:

- Complete the open-loop component reaction experiments that demonstrate the key chemical processes in stand alone mode in engineering materials of construction.

- Perform closed-loop lab scale hydrogen production experiments under prototypic conditions to provide the technical basis for evaluating the S-I cycle for nuclear hydrogen production.

- Develop a process flowsheet for pilot scale plants that can be used to project process efficiency and preliminary costs.

The development of the S-I cycle ILS loop has been performed as an international effort involving the US Labs and Industry and the Commissariat à l'Énergie Atomique (CEA) of France. The S-I cycle consists of three reaction sections which are currently being developed by three different organizations. Sandia National Laboratory (SNL) developed the high temperature sulfuric acid decomposition section, General Atomics (GA) developed the HI decomposition (hydrogen generation) section, and the CEA developed the primary Bunsen reaction section. These three sections along with a fourth interface section have been integrated together to demonstrate closed loop operation of the S-I cycle. General Atomics was chosen by DOE to host the ILS loop.

Brief description of the ILS loop

The ILS loop is made up of four interconnecting sections:

Section I (Bunsen Reaction) $\qquad$ $SO_2 + 2H_2O + I_2 \rightarrow H_2SO_4 + 2HI$
Section II (Sulfuric Acid Decomposition) $\qquad$ $H_2SO_4 \rightarrow H_2O + SO_2 + 1/2O_2$
Section III (HI Decomposition) $\qquad$ $2HI \rightarrow H_2 + I_2$
Interface section – buffer tanks for storage and feed between the process sections

Each section is constructed on an individual skid (pallet) and all the associated process equipment is enclosed within. The walls and the tops of the skids are constructed from Lexan or similar material. The bases are made from steel and are shaped to contain any chemical spill. The four sections are linked together through connection pipes that transport the process chemical streams. A 3-D schematic of the ILS loop layout is shown in Figure 8. The three process sections are connected to each other via the interface skid, which holds the storage and feed tanks for the circulating reaction fluids. With this design, each individual section can operate on its own without the need for concurrent operation of another section to either supply or receive the process chemicals. This helps to ensure the safe operation of the individual sections.
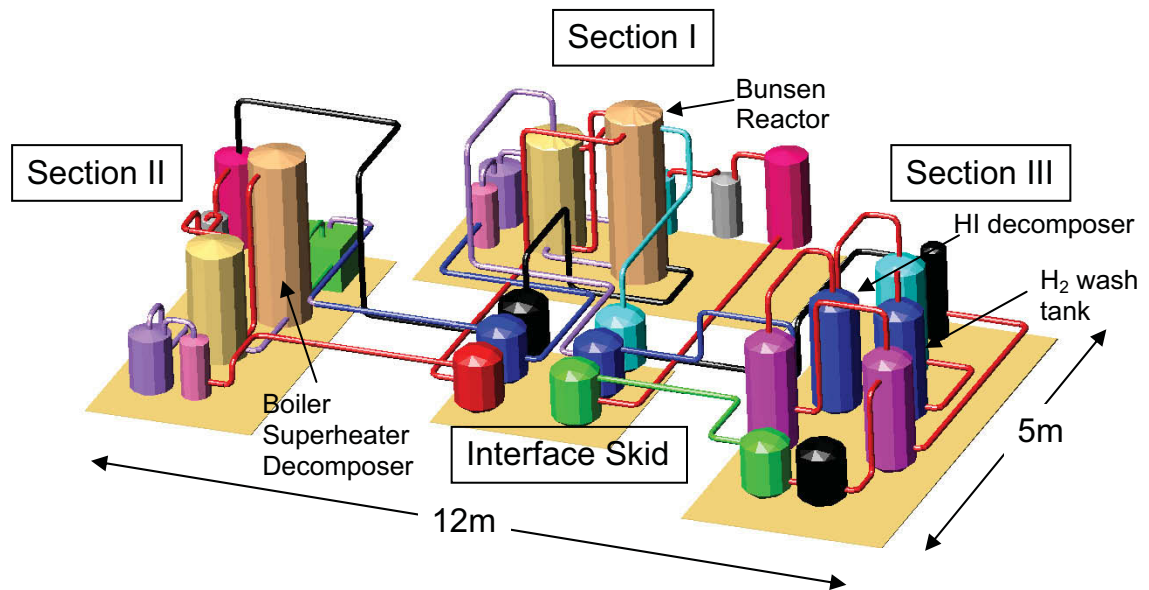
Figure 8 A schematic showing the four different skids of the ILS loop.

S-I Cycle Integrated Lab Scale Experiment Schedule

The ILS experiments proceeded in stages as follows:

- Year 1 FY06 -- R&D to support the construction and testing of the integrated lab scale sections
- Year 2 FY07– Testing of individual skid mounted sections at each site, ship and assemble sections at the GA integrated lab scale experiment site
- Years 3 & 4 FY08/09– Conduct integrated lab-scale hydrogen production experiment program

In addition to the development of process chemistry, materials testing and diagnostic development for each section, this project has involved specific lab scale integration activities to develop S-I control systems for closed loop operations, section interface components and the safety documentation and approvals to conduct the lab scale experiments. The overall integrated lab scale equipment is shown in Figure 9.

Figure 9 Integrated Lab Scale (ILS) experiment

Design Criteria for the ILS

The ILS experiment has been designed to meet the following criteria:

- Demonstrate the three component steps of the Sulfur-Iodine process
- Demonstrate the operation of the integrated equipment
- Generate hydrogen at a rate of 100 l/hr

- Equipment constructed from engineering materials
- Operated at nominal temperature and pressures (120-850 °C and up to 20 bar)
- Experimental enclosures constructed to ensure safe operation and containment of any possible leaks or spills
- Implement a control system which allows for the remote operation of the equipment and data logging of the process conditions

Bunsen Reaction Skid Description (Section 1)

The Bunsen section reacts water with iodine and sulfur dioxide to produce two acid phases, the light sulfuric acid phase and the heavy hydriodic acid phase. In addition to producing the two acid phases, the Bunsen section also separates oxygen from the sulfur dioxide produced by Section 2. The flowsheet for the Bunsen section skid, scaled to 1 mole/hr H_2 production, is shown in Figure 10.
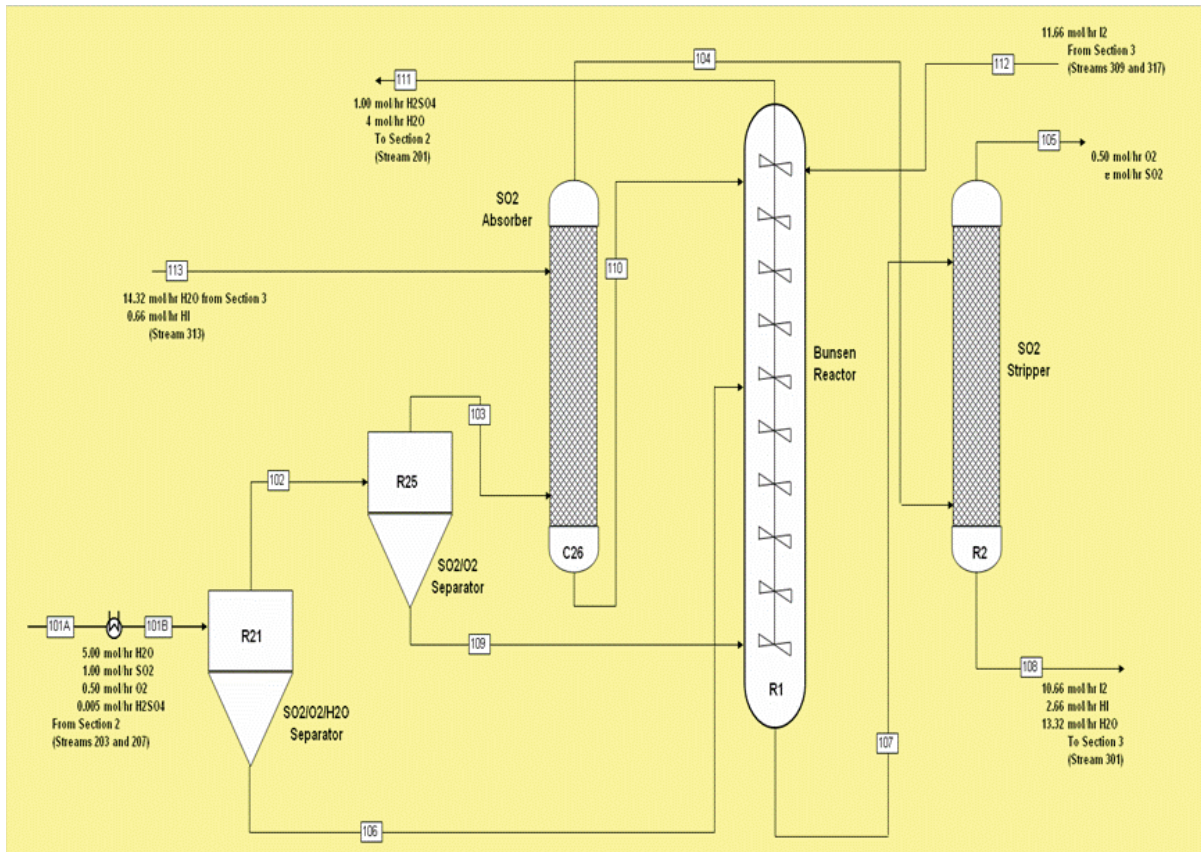
Figure 10 Bunsen section flowsheet

The Bunsen section equipment, shown in Figure 11.

Figure 11 Bunsen section skid

Process Description

In the Bunsen section iodine and SO_2 react with H_2O to form HI and H_2SO_4. The reaction is exothermic and takes place at medium temperature (~120 °C). The co-current heat exchanger –reactor approach was demonstrated by GA in 1981, and subsequently by JAERI in 2003, and has been the basis for most analyses. An alternative flow sheet is currently being considered by CEA involving a counter current three phase reactor. O_2, which does not participate to the reaction, is removed from the input gases. This requires compression and cooling to separate SO_2 and O_2. The Bunsen reaction is carried out in a single reactor. This approach has a higher theoretical efficiency than the original 1984 GA model. The basic flow sheet options, considered for the Bunsen section, are shown in Figure 12. CEA has added three alternative features to the former flow sheet:

•   Addition of a reactor for boosting the HI content of the dense liquid phase.
•   Grouping the main Bunsen reactor and the H_2SO_4 and HI boost reactors into a single counter-current reactor.
•   Separation of SO_2 and O_2 before introduction into the Bunsen reactor.

With this design, four basic operations (three reactors and a phase separator) are combined in a single device operating in the counter-current mode.
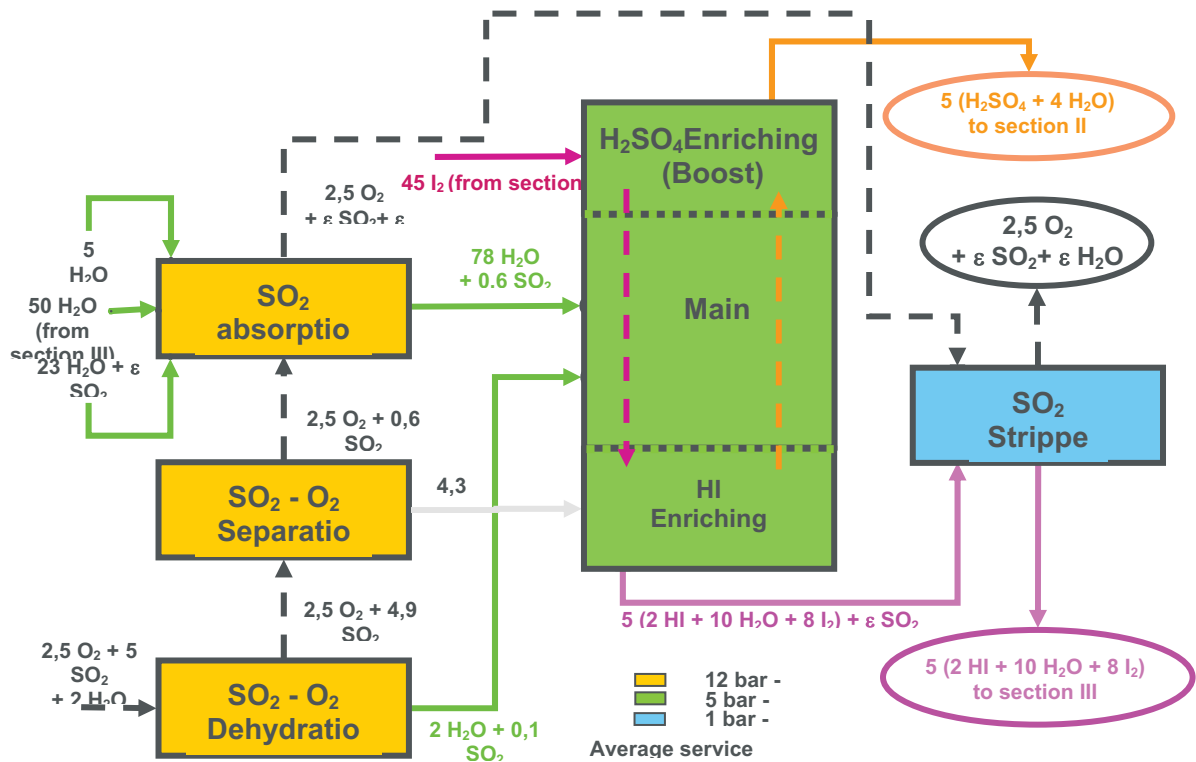

Figure 12 Bunsen Section. CEA proposed flow sheet.

Two criteria, reaction time and heat transfer, must be taken into account: Reaction time must be minimized to avoid side reactions but heat transfer needs sufficient exchange surface to extract the heat of reaction. The combination of these two constraints led to the choice of an apparatus consisting of a set of continuously stirred reactors installed vertically in series in the form of a mechanically stirred column-type liquid-liquid contactor (Kühni contactor).

Mixers in each section of the reactor maintain conditions required for the chemical reaction. They also promote heat transfer through the walls of the reactor, which is required for the exothermic reaction to proceed. The reactor also incorporates the phase separators. The remaining gas phase must be separated at the top the reactor. The separation of the two liquid phases can occur at either the top or bottom of the reactor, but the reactor construction is simpler if this separation takes place at the top. Due to the highly corrosive properties of the reactants, the materials used for the components of the reactor are glass coated steel, fluorinated polymer, zirconium and tantalum at specific locations.

The operating principles are the following:
SO_2 is fed at the bottom of the reactor and flows upward. The I_2 rich heavy phase flows downward. SO_2 reacts with I_2 and water forming H_2SO_4 and HI. H_2SO_4 separates from the iodine as a separate liquid phase, extracting additional water from the HIx as it does so. The light H_2SO_4 phase also rises against the downward flowing heavy phase.

The central reaction zone is the location of the main reactor. An aqueous phase fed into this zone mixes with the rising H_2SO_4 phase and flows upwards in contact with the downward flowing I_2 phase. Additional SO_2 is added with the water so that they both can react with I_2 generating H_2SO_4 and HI. Some SO_2, that entered at the bottom of the reactor remains as a separate vapor phase. H_2SO_4 that forms dissolves in the light phase and HI in the heavy one. The optimal additional water feed location depends on yet unknown thermodynamic and kinetic data.

As the H_2SO_4 phase and gaseous SO_2 phases continue moving upwards, they are in contact with increasingly purer I_2. The pure molten I_2 enters at the top of this section. The Bunsen reaction continues in this region with formation of both HI and H_2SO_4. H_2SO_4 dissolves in the light phase and HI in the heavy one. The dissolution of HI in I_2 favors the extraction of water from the H_2SO_4 phase and its incorporation into the heavy phase.

Since the Bunsen reaction takes place in the liquid phase, it is necessary to dissolve the SO_2 in the reaction medium and maintain the highest possible SO_2 partial pressure. The reaction temperature selected is 120°C, which results in a high SO_2 vapor pressure - close to 30 bars. To favor dissolution, the reactor will operate at a pressure of 5 bars. These considerations suggest prior separation of the $SO_2 – O_2 – H_2O$ mixture from section 2. This takes place in three successive phases:

Dehydration of the recycled gas stream from the H_2SO_4 decomposition section: the gas stream is isobarically cooled to 25°C.

$SO_2 – O_2$ separation: The dried gas is adiabatically compressed to 12 bars and cooled to 25°C. Most of the SO_2 is condensed and separated from the oxygen which contains some residual SO_2.

Stripping residual SO_2 from the gas stream: The oxygen leaving the previous stage is washed with water in a counter-current packed column.

Design of the ILS Bunsen Section
The pilot unit has been sized for the production of 5 moles of hydrogen per hour (112 NL.h^{-1}). The overall reaction is the following:

$$45 \, I_2 + 5 \, SO_2 + 80 \, H_2O = 5 \, (2 \, HI + 10 \, H_2O + 8 \, I_2) + 5 \, (H_2SO_4 + 4 \, H_2O)$$
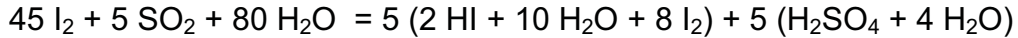
The pilot unit, proposed for the Bunsen reaction, must enable tests to be carried out for characterization of the process in stand-alone mode and be suitable for integration in a system constituting a demonstrator for the entire S-I loop. These constraints have the following consequences:

In stand-alone mode, the quantities of molecular iodine used are substantial. The flow per unit mass for decomposition represents 1.28 $kg.h^{-1}$ and the excess stream close to 11.5 $kg.h^{-1}$. Recycling of the iodine is therefore essential to carry out the tests under acceptable conditions. A distillation column has been designed to allow online iodine recycling. Aqueous HI is batch treated (inverted Bunsen reaction) to recover iodine.

Ease of integration in the S-I loop: The equipment supplying the loop with reagents must be designed to accept the recycled streams from the acid decomposition sections. The outlet products must be compatible with the decomposition sections.

Sulfuric Acid Decomposition Skid Description (Section 2)

The sulfuric acid skid, shown in Figure 13, has been installed and tested at a production rate comparable to 300 l/hr H_2 production.

Figure 13 Sulfuric acid decomposition skid

The sulfuric acid decomposition section (skid 2), concentrates, heats and catalytically decomposes the acid to sulfur dioxide, oxygen, and water. The sulfur dioxide and water produced in the process is combined with iodine and water in the Bunsen section (skid 1) to produce hydrogen iodide and sulfuric acid. The sulfuric acid is recycled back to the sulfuric acid decomposition skid. For the sulfuric acid decomposer skid to operate in the ILS, the following design objectives must be met:

- generate sulfur dioxide equivalent to a hydrogen production rate of >100 liter/hr (equivalent to >100 liter/hr hydrogen) from input acid at concentrations of 20 mol% or higher,
- maintain a decomposition temperature of 850 ºC and pressures up to nominally 3 bar,
- perform safely with redundent safety systems for containing SO_2 releases, and
- utilize corrosion-resistant materials of construction to allow extended operations.

Decomposition Skid Details

A schematic of the H_2SO_4 decomposition skid developed for the ILS experiments at GA is shown in Figure 14. Dilute acid from the Bunsen skid enters the concentrator where the acid is concentrated from 20 mol% to about 40 mol%. The concentrated acid is collected into the Concentrated Acid Tank, and the water vapor is condensed and collected in Water Tank 1. The acid is then combined with unreacted acid from the bayonet and introduced into the base of the bayonet. In the bayonet the acid is heated to 850 °C and partially decomposed. The gaseous decomposition products of SO_2, O_2, and H_2O flow out the inner channel and most of the heat content is recuperated to the incoming acid. Undecomposed acid is condensed, collected in the Recycle Acid Tank, and recycled back to the bayonet. The gas stream is then cooled to condense liquid water into Water Tank 2. A gas stream consisting of SO_2 and O_2, and a liquid water stream from Water Tanks 1 and 2 are the products of the H_2SO_4 decomposition skid. These two streams are sent to the Bunsen skid.
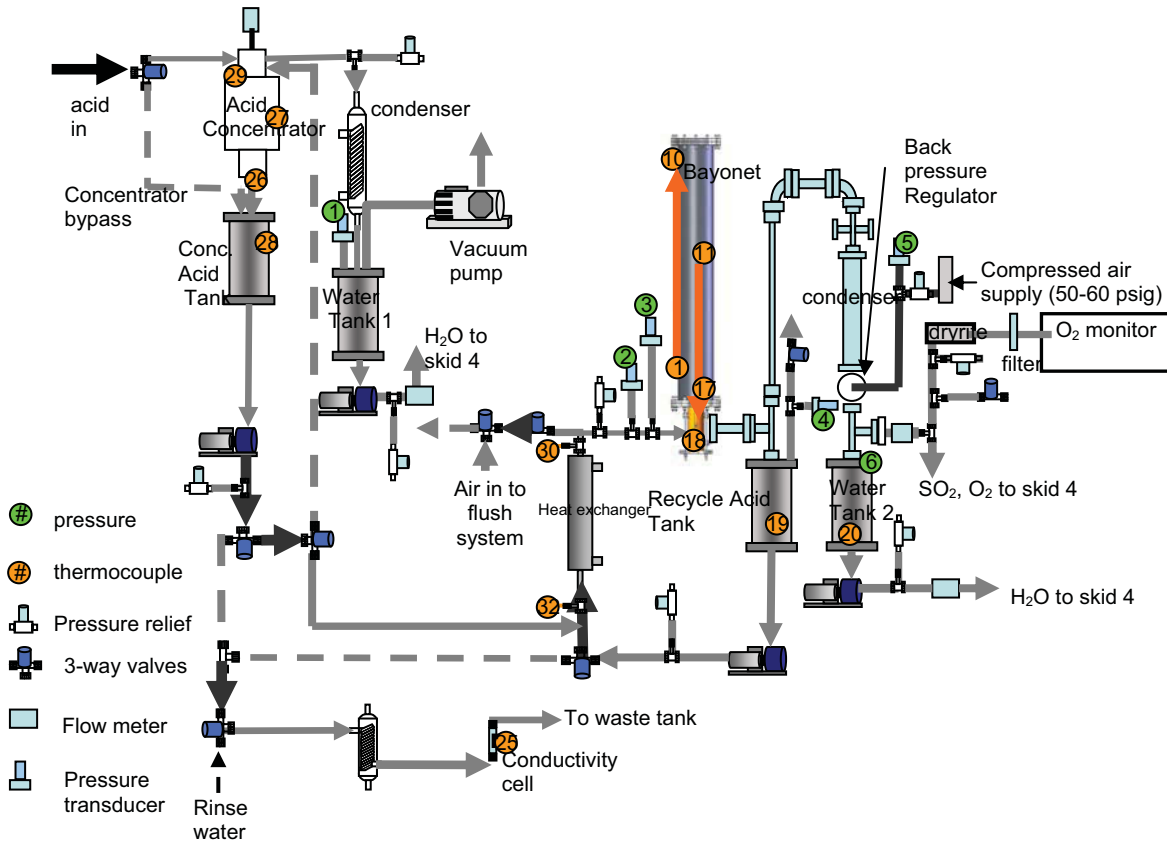
Figure14 Schematic layout of the H$_2$SO$_4$ decomposition section skid.
(The orange and green shaded circles correspond to the locations of thermocouples and pressure transducers, respectively. The shapes of the bayonet, concentrator, water tank 1, water tank 2, recycle acid tank, and the concentrated acid tank in this Figure are drawn to be similar to the actual units shown in Figures 15 and 16).

The entire H$_2$SO$_4$ decomposition skid is contained within a Lexan enclosure that has a 4 ft by 4 ft base, and is 8 ft high. The two access sides of the skid are shown in Figures 15 and 16, respectively. The outer enclosure is connected to the GA ventilation system, which continuously draws 800 cfm from within the enclosure through a charcoal filter before releasing the gas to the atmosphere.

Within the outer enclosure the components are segregated into two different areas of the skid; those containing liquid acid solutions shown in Figure 14, and those containing SO$_2$ shown in Figure 15. Previous tests at SNL showed that SO$_2$ is highly permeable through Teflon and Viton. To minimize the possible releases of SO$_2$ two design features were added to the system. First, glass-lined steel was used on the outlet side of the bayonet to the product outlet to minimize the release of SO$_2$ from the unit itself. Second, an inner Lexan enclosure was constructed within the primary outer enclosure to confine any SO$_2$ permeating from the system. As shown in Figure 16, the bayonet and other SO$_2$ containing

components were arranged within an inner confinement enclosure. Other components that contain only acid solutions are arranged within the primary outer skid enclosure. Any gas leakage from the apparatus within the inner enclosure is contained. The inner enclosure has a separate activated charcoal filter system to absorb small gas leaks. A blower can be remotely operated to vent the inner enclosure to the outer enclosure, which then is vented to the GA ventilation system. Both the inner enclosure volume and the primary outer enclosure volume contain SO_2 monitoring systems that allow for continuous readout both at the skid and at the control panel. A third SO_2 monitor is mounted on the outside of the skid to detect leakage outside the enclosures. Furthermore, two handheld SO_2 monitors are used when running an experiment or servicing the skid,
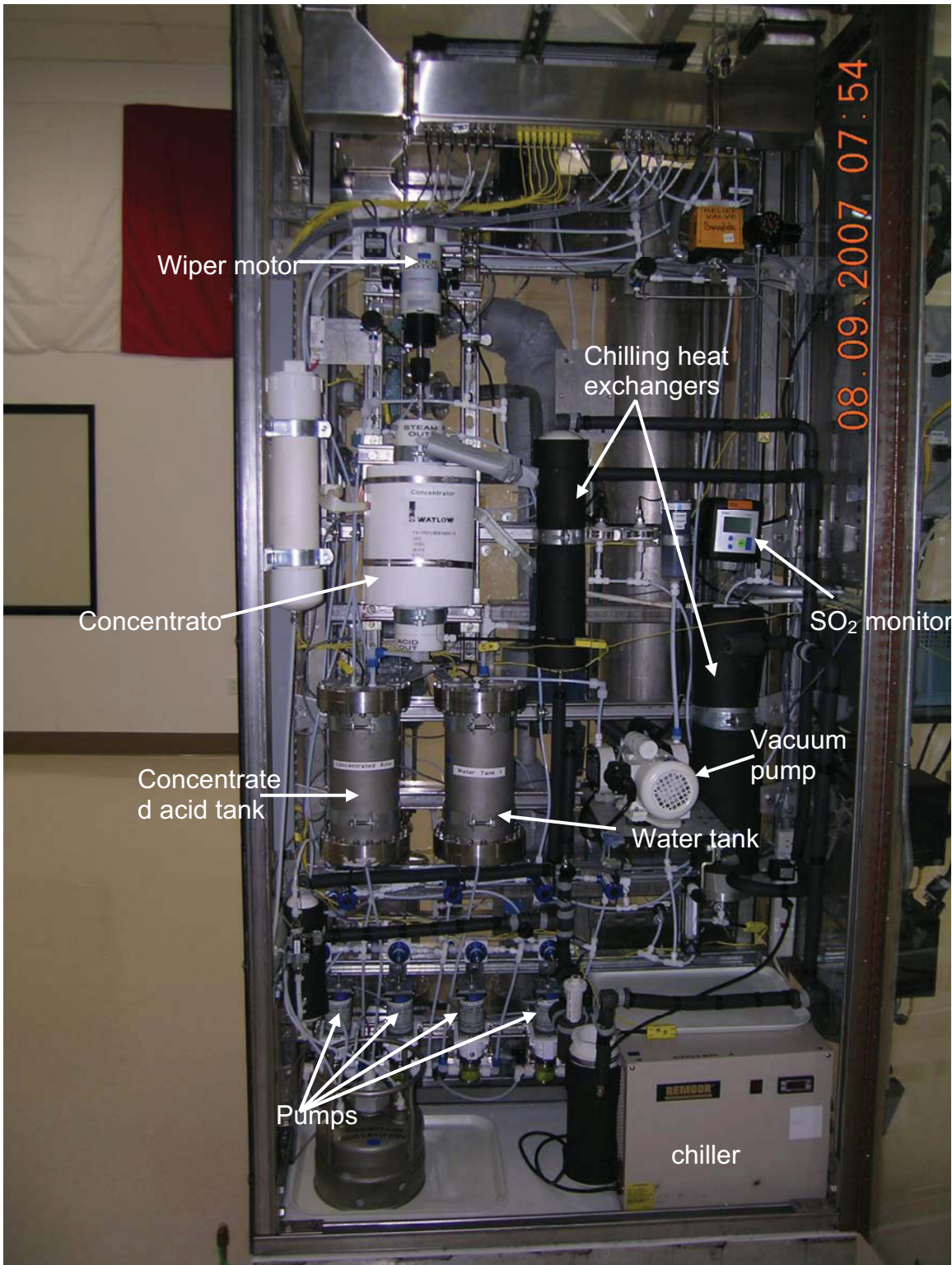
Figure 15 The liquid acid side of the acid decomposition skid assembled at GA.
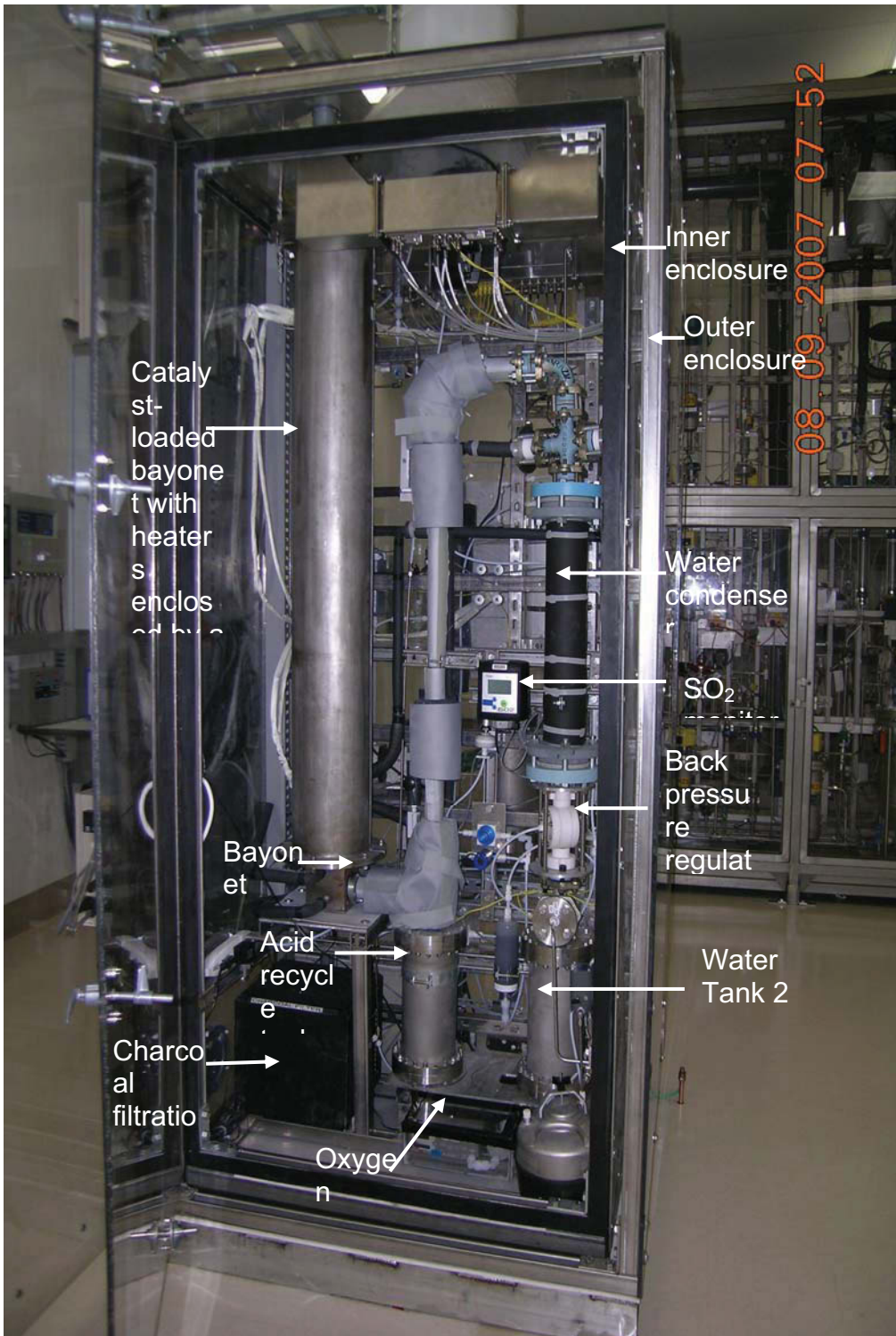
Figure 16 The SO$_2$ side of the acid decomposition skid assembled at GA.

Catalyst-loaded bayonet with heaters enclosed by a

Bayonet

Acid recycle

Charcoal filtratio

Oxygen

Inner enclosure

Outer enclosure

Water condenser

SO$_2$ monitor

Back pressure regulat

Water Tank 2

08.09.2007 07:52

Acid Concentration

Sulfuric acid enters the skid at approximately 20 mol%. Acid heating and acid concentration are accomplished in an electrically heated heat exchanger constructed of a SiC pipe with Teflon end caps. A schematic diagram of the concentrator in Figure 14 is given below in Figure 17.
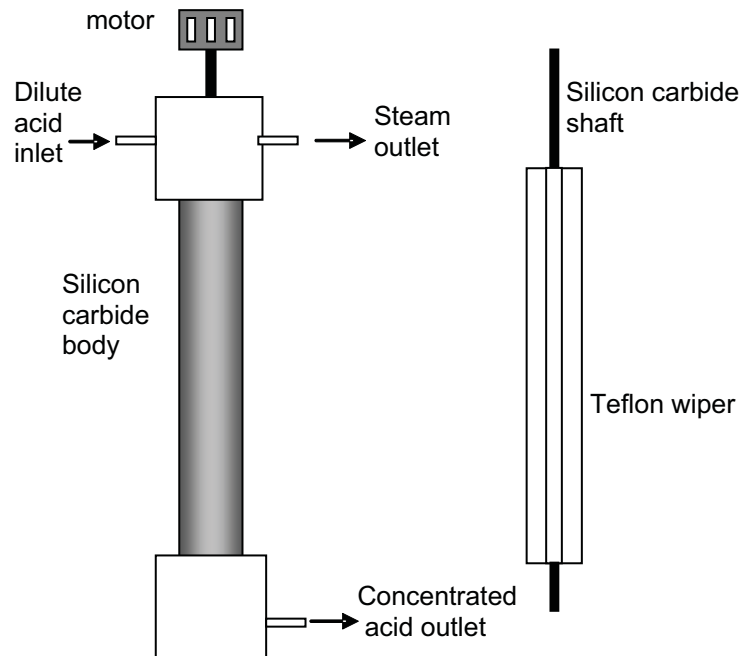

Figure17   Schematic of concentrator, excluding the surrounding electric heater.

The concentrator is a wiped-film type unit with a rotating inner Teflon wiper to maintain liquid contact with the heated walls. The concentrator is under vacuum which removes water vapor and concentrates the acid to approximately 40 mol%. Dilute acid enters the top of the concentrator and travels downward. The wiper, driven by a laboratory stirrer, increases contract of the liquid with the heated silicon carbide wall and increases the path length of the acid through the apparatus. For optimum efficiency, the concentration process is performed under sub-atmospheric pressure of approximately 1.0 psia. By lowering the pressure and therefore the boiling temperature of the acid, the energy required to heat the acid to its boiling point is decreased and input heat is mainly used for the heat of vaporization of the water from the dilute acid solution. Heat is supplied to the concentrator using a ceramic heater. Water is removed from the top of the apparatus as steam which is cooled to liquid water in a water-cooled condenser. The water is collected in a stainless steel pressure vessel labeled Water Tank 1 in Figures 16 and 16. A vacuum pump connected to the tank is used to maintain vacuum in the system including the acid concentrator pressure.

Bayonet Acid Decomposer

The bayonet is shown schematically and as disassembled components in Figure 18. The operations of the bayonet have been described in previous reports (Moore et al., 2007; Gelbard et al. 2007). The basic operating parameters for the unit are the acid flow rate, the inlet acid temperature, and the maximum temperature. The bayonet is heated using electrical heaters controlled to a maximum temperature at the outside top portion of the bayonet. The products of acid decomposition are sulfur dioxide, oxygen and water vapor. These are separated from undecomposed acid in the lower section of the inner SiC tube.

12 inch ruler

Outer SiC tube

Quartz baffle

Inner SiC tube

Teflon manifold

Stainless steel
block
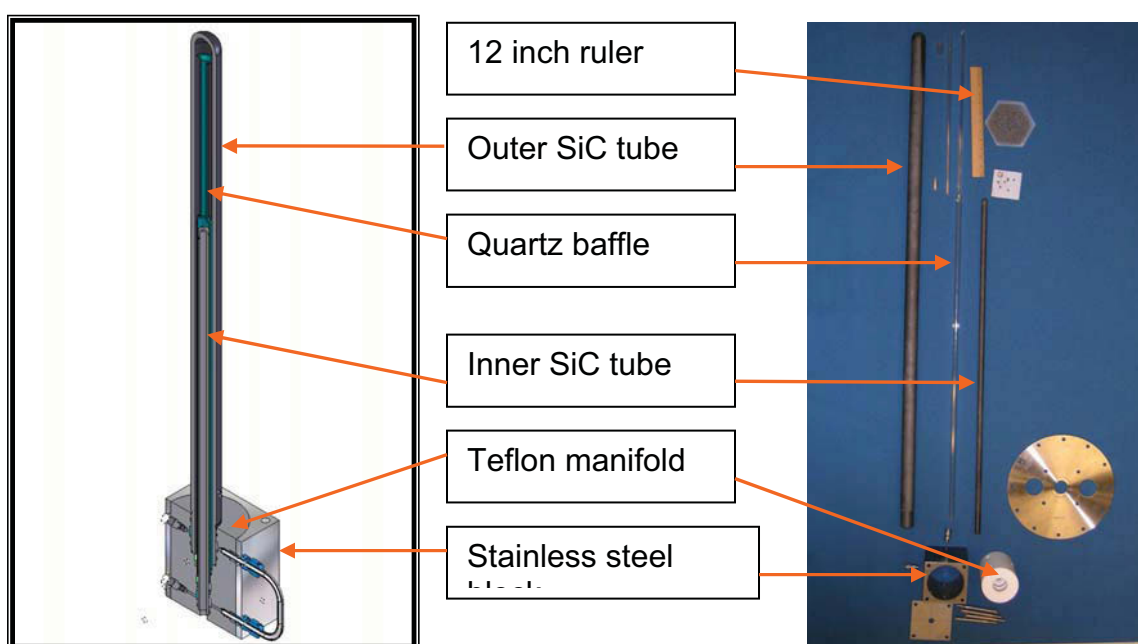
Figure 18 The SiC bayonet decomposer shown schematically on the left and the actual hardware on the right.

HI Decomposition Skid Description (Section 3)

The HI Decomposition section takes the heavy acid phase, which contains excess iodine and water in addition to the hydrogen iodide, from the Bunsen section. This skid separates the excess iodine and water from the feed by extractive distillation, utilizing phosphoric acid in a multi stage separation. The hydrogen iodide is decomposed at 450 deg ºC to produce the hydrogen product. The installed skid is shown in Figure 19.

Figure 19 HI Decomposition Skid

The HI decomposition skid takes the HIx feed (2:8:10 molar ratios of HI:Water:Iodine) from Section 1 and first removes the iodine in a liquid-liquid extraction process utilizing phosphoric acid. Next the HI is distilled from the remaining water-phosphoric acid solution and delivered to the reactor for decomposition to I_2 and H_2. As the reaction is limited to a 20% conversion thermodynamically, the unreacted HI must be separated and recycled in order to reach the desired H_2 production rates. Initially both reactive and extractive distillation processes were evaluated. Based on experimental results, extractive distillation was selected as the HI distillation approach for the ILS experiment. The objectives of the extractive distillation demonstration were to construct a system capable of withstanding the highly corrosive chemicals, at a hydrogen production of 100 l/hr or greater, and demonstrate extraction of HI and H_2O from HIx solution, and distillation of pure HI.

Task Overview - HI Decomposition Skid

The progress to date includes the design, construction and operation of both reactive and extractive distillation experiments, and construction and initial testing of the extractive distillation ILS skid. Glass systems were constructed for

both the reactive and extractive distillation experiments to enable a down selection between the two processes. The HI Decomposition Skid, as part of the DOE Integrated Lab Scale (ILS) experiment demonstrating closed-loop operation of the sulfur-iodine process, has been constructed and tested. The process system consists of 6 major components:

1. Iodine extraction
2. HI distillation
3. HI decomposition
4. Iodine and HI recycle
6. Phosphoric acid concentration

Each component has been tested at nominal temperature and pressure (120-450 deg C and 11 bar). In stand-alone mode, premixed feed solutions were used to validate the operation and performance of the different components. The skid has been demonstrated at 30 l/hr with no recycle of the HI, which is comparable to 300 l/hr with recycle. The recycle unit was not evaluated in this shakedown due to limited quantities of the premixed HI gas feed used for the reactor testing. A control system was also developed allowing for remote operation of the equipment. The control system has been designed to allow stand-alone operation as well as integration with the Supervisory Control System during integrated operation with the other process skids.

Design Criteria of the HI Decomposition Section

The HI Decomposition skid has been designed and constructed to meet the following criteria:

- Demonstrate the three component steps of the Sulfur-Iodine process
- Demonstrate the operation of the integrated equipment
- Generate hydrogen at a rate of 100 l/hr
- Construct equipment from engineering materials
- Operated at nominal temperature and pressures (120 to >450 °C and up to 20 bar)
- Construct experimental enclosure(s) to ensure safe operation and containment of any possible leaks or spills
- Design and implement a control system which allows for the remote operation of the equipment and for data logging of the process conditions

Process Flowsheet

The hydrogen iodide decomposition section for the ILS uses the extractive distillation method to produce hydrogen. The HI_x feed is contacted with a concentrated phosphoric acid stream, which separates the water and hydrogen iodide from the iodine. This iodine stream is returned to Section 1 for use in the

Bunsen reaction. The phosphoric acid/water/hydrogen iodide stream is then sent to a distillation column, where the phosphoric acid serves a second purpose by breaking the water/hydrogen iodide azeotrope that exists at approximately 15 mole% hydrogen iodide. This allows for a pure hydrogen iodide stream to be drawn from the top of the column. The reaction that occurs upon subsequent decomposition of hydrogen iodide is:

$$2HI \rightarrow H_2 + I_2$$
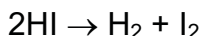
The reaction takes place in a catalytic reactor at 450 ºC. Activated carbon is used as the catalyst. The diluted phosphoric acid is concentrated and recycled back to the contactor with HIx.

The flowsheet for hydrogen iodide decomposition is shown in Figure 20. The flowsheet is scaled to one mole of hydrogen produced per hour. Equilibrium conversion of hydrogen iodide to hydrogen and iodine at $450^{\circ}C$ is approximately 21%. Thus, nearly 80% of the feed to the decomposition reactor must be recycled. Earlier flowsheets called for a membrane separator to recover the hydrogen product from unreacted hydrogen iodide, before recycling the hydrogen iodide back to the reactor. Currently no suitable membrane separator has been developed and therefore a membrane separator is not implemented in the ILS. Efforts for pursuing a membrane separator will continue, but in the interim a different design for separation of hydrogen iodide from hydrogen has been used in the ILS.

The gas-phase hydrogen iodide reactor loop operates at a pressure of 10-20 bar. The reactor product stream is cooled to $120^{\circ}C$ to condense and separate the iodine for recycle back to Section 1. The remaining hydrogen iodide/hydrogen stream is then sent to a vapor-liquid separator operating at -40 ºC, where the hydrogen iodide is condensed to a liquid. The vapor pressure of hydrogen iodide at this temperature is low enough that over 90% can be recovered in the liquid phase through a single pass in the separator. Once separated from hydrogen, the liquid hydrogen iodide is evaporated and the vapor is sent to the reactor. The residual hydrogen iodide remaining with the hydrogen product in the vapor phase is sent to a wash column. The vapor product of the wash column is the product hydrogen, and the water/hydrogen iodide liquid stream can be returned to Section 1 for use in the Bunsen reaction or sent back to the HI distillation column.
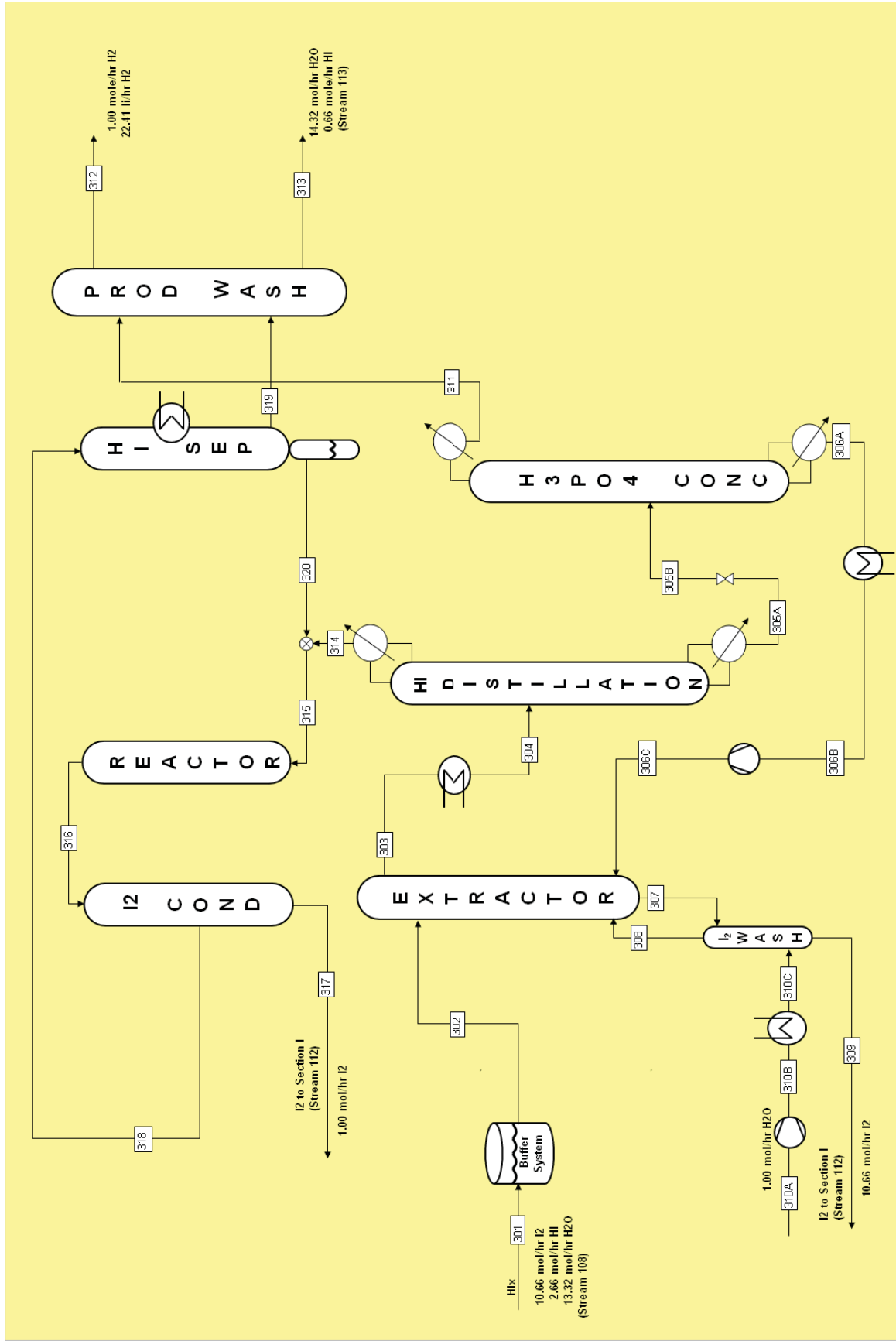
Figure 20 ILS Section 3 Flowsheet- Hydrogen Iodide Decomposition

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Interface Skid Description and Controls

A key issue regarding operation of the ILS is how the sections interact, both from materials exchange and from a supervisory control standpoint. Each section should be able operate independently during trials as well as operate together in an integrated mode. In addition, each section has waste management and ventilation treatment requirements.

One way to consolidate and simplify these issues is to collect all interface, storage and ventilation processing equipment onto a single, separate skid. Each section is provided with storage for both its inputs and outputs, and with treatment/storage/disposal capability as appropriate. A flowsheet illustrating the concept is shown in Figure 21.

The interface system between any two streams consists of two tanks, heated and pressurized as necessary, and pumps that are suitable for pumping the associated streams. Each group working on individual sections has recommended appropriate pumping technology. Dry and/or wet scrubbers are placed on the interface skid to process ventilation streams before release to the environment. The interface skid is a self-contained enclosure, with dedicated ventilation. In addition to storage tanks, the interface skid is equipped with a chemical scrubber. Sulfur dioxide or other chemicals not being used in integrated testing or chemicals that need to be vented during maintenance operations or other reasons are transferred to the scrubber.
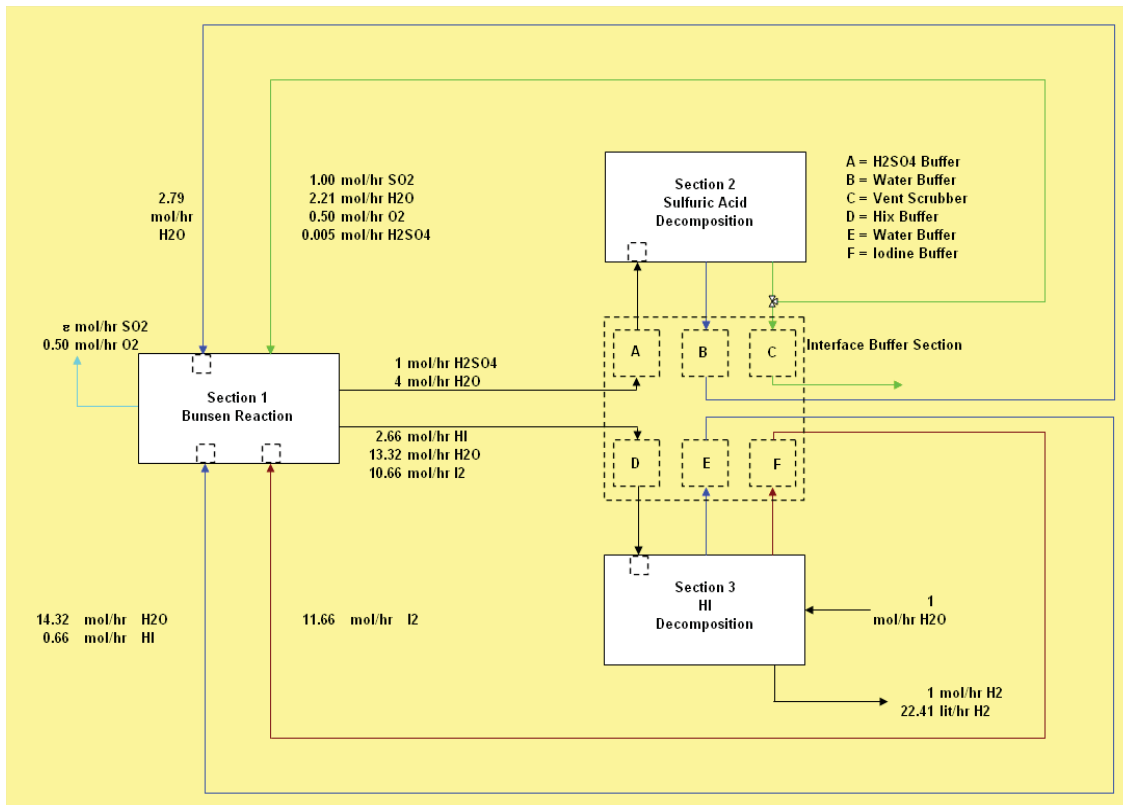

Figure 21 Interface skid flowsheet

The installed interface skid is shown in Figure 22

Figure 22 Interface Skid: I_2/HIx tanks and Water/H_2SO_4 tanks/Scrubber

ILS Interfaces Between Section 1 and Section 2

The primary interchange between Sections 1 and 2 is the delivery of dilute sulfuric acid from Section 1 to Section 2, and the return of a gas-phase SO_2 stream from Section 2 to Section 1. A secondary liquid H_2O stream will be sent to Section 1 from the condenser associated with the sulfuric acid condenser.

The delivery of dilute sulfuric acid to Section 2 is accomplished with a system of buffer tanks. Specifications are for the tanks to have a volume of 20 liters. The tanks are constructed from Teflon lined steel. The turnover time per tank is 8 hours at a hydrogen production rate of 200 liters per minute. The buffer tanks have level sensors to allow for the inventory of each tank to be measured over the entire volume capacity of the tank. By monitoring the inventory volume as a function of time, the flow rate in each tank can also be determined.

The SO_2 vapor stream from Section 2 is either sent directly for use in Section 1 if the ILS is operating in an integrated mode, or it l is be processed through a chemical scrubber before venting. With the exception of small amounts on the CEA Bunsen process skid, SO_2 is not stored. For stand-alone operation of Section 1, SO_2 from commercially available pressurized cylinders is used.

ILS Interfaces Between Section 1 and Section 3

The primary interchange between Sections 1 and 3 is the delivery of HI_x solution from Section 1 to Section 3, and the return of a liquid-phase iodine stream from Section 3 to Section 1. A secondary liquid H_2O stream is sent to Section 1 from the condenser associated with the phosphoric acid condenser. Consequently, the net water input to the ILS is located in Section 3.

For the delivery of HI_x to Section 3, and for iodine delivery back to Section 1, a buffer tank system is used. Specifications are for the tanks to have 89-liter volumes and the ability to operate at pressures up to 2 bar, and at temperatures up to 130 ^{o}C. The tanks are constructed of glass-lined steel. The turnover time per tank is 16 hours at a hydrogen production rate of 100 liters per minute. The buffer tanks and storage tank have level sensors to allow for the inventory of each tank to be measured over the entire volume capacity of the tank. By monitoring the inventory volume as a function of time, the flow rate in each tank is determined. Additionally, all HI_x/iodine plumbing/piping is heat-traced to 120°C to prevent iodine freezing.

Summary Experimental Results

Phase I of this project involved integration of the three process sections into a complete S-I cycle. The initial integrated operation was performed in April of 2008 and is documented in the SAND Report titled "Results of Phase 1 Testing of the Sulfur-Iodine Integrated Laboratory-Scale Experiment". Phase II of the work includes completion of initial integrated shakedown operations, control verification tests (interface skid operations, production rate tests, shutdown tests), transient response tests (startup, shutdown, flow rate perturbations, mismatched flow rates), and cross talk tests (inter skid contamination and response) and process improvements or modifications as budgets permit. The results from phase I of the project along with additional stand-alone and integrated tests have identified issues for each process section that have been addressed in phase II work. These include redesign and replacement of major system components, corrosion control and modification of process monitoring. Several identified problems have led to very significant process modifications. However, for all three process sections, all major modifications have been completed.

The General Atomics hydrogen iodide section has undergone several modifications and has been successfully operated multiple times to produce hydrogen. The hydrogen iodide reactor has been replaced with a smaller unit to decrease the time for preheating the unit and reach equilibrium while operating. Using the smaller reactor, hydrogen has been produced at a rate of 10 to 75 L/hr. Problems with differential pressure cells used throughout the process for monitoring and control have been eliminated by replacing the units with higher quality units. Ta alloy corrosion problems were encountered due to hydrogen embrittlement of Ta vessels and piping. Most of these issues have been mitigated for the ILS with either modified operational conditions, or periodic replacement. Longer term solutions are being developed and will be tested in FY09.

The CEA has completed major modifications to the Bunsen section and the section is ready for additionally testing of the Bunsen reactor at this time. Completed modifications include: installation of a new Bunsen reactor equipped with Raching ring packing and differential pressure cells for enhanced process control and a redesign and modification of the system for transferring iodine from the chemical storage skid to the CEA skid. In

addition to these modifications, additional integrated testing with the SNL acid decomposition section has been completed and the transfer of chemicals between the CEA section and the SNL sections is now considered routine. The CEA tested the new Bunsen reactor at the end of April 2008 as part of the final integrated operations with the SNL process section.

In the SNL acid decomposition section, system modifications include incorporation of an acid neutralization step to the process cooling water system to prevent corrosion of the circulating water chiller used in the process, an increased efficiency of the acid concentrator and the addition of a pressure control system to maintain a constant pressure in the acid decomposer. The acid decomposition process has been successfully operated multiple times over the past 18 months in the stand-alone and integrated modes. In the last operations of the process, the effect of temperature on acid decomposition was determined at a pressure of 1 bar. The results indicate the production of sulfur dioxide begins to decrease between 750 and 800ºC with a decrease in gas production of 50% at 700ºC. No sulfur dioxide was detected at 650ºC.

The GA hydrogen iodide decomposition section and SNL acid decomposition section of the S-I process are ready for additional integrated testing. All modifications were completed and successful stand-alone tests have been performed with the new equipment as well as integrated operations with the Bunsen section

The results from the integrated tests in April, 2008 provided some initial results for the integrated system, but these results also indicated major equipment modifications were required for the CEA hydrogen production process and the GA hydrogen iodide decomposition process. Although in the CEA process hydrogen iodide was produced, it was determined that additional modifications were required and a modified Bunsen reactor has been installed. Once the operational parameters for the Bunsen reactor were identified integrated tests with all three process sections were continued. In addition to replacement of the reactor, a new iodine pumping system, using pressure to transfer iodine from the chemical storage skid to the Bunsen reactor, has been installed and successfully operated. The hydrogen decomposition reactor in the General Atomics hydrogen decomposition process has been replaced with a smaller unit and the process has been successfully operated multiple times to produce hydrogen at a rate of 75 L/min. The SNL acid decomposition process section has undergone several modifications to improve process efficiency and integrated operation. The most significant improvement is the installation of a backpressure regulator and buffer tank between the SNL section and the CEA section to prevent pressure fluctuations in the SNL acid decomposition reactor that can result in breakage of the unit. The SNL process has been successfully operated multiple times with sulfur dioxide produced at a rate of 100-300 L/hr.

Uncertainties and Risk Reduction

The sulfur-iodine cycle, coupled to a high temperature nuclear reactor, shows promise of economic hydrogen production in the future. Before nuclear hydrogen becomes commercial, the current uncertainties must be reduced. The technical uncertainties lie in several areas: chemistry, solution thermodynamics, chemical kinetics, and materials science. The economic uncertainties lie in the areas of capital and operating cost estimates, future costs of alternative clean (and dirty) hydrogen sources and the politics of global warming.

TECHNICAL UNCERTAINTIES

Chemistry

The chemistry of the Sulfur-Iodine process is well understood and there are few potential side reactions. The side reactions, which could be problematic, are the formation of sulfur or hydrogen sulfide in Section 1. Sulfur dioxide can be disproportionate to form either elemental sulfur or hydrogen sulfide along with sulfuric acid. These reactions are in competition with the much more rapid Bunsen reaction but are energetically more favorable. Any hydrogen sulfide that is formed will eventually be recycled back to the oxygen scrubbers in Section 1 where conditions are favorable to the formation of elemental sulfur from hydrogen sulfide and sulfur dioxide. Thus the ultimate questions concerning side reactions are how much sulfur, if any, will be formed, where will it go and what will happen to it? Elemental sulfur is molten at the exit temperatures of Section 1. Any sulfur accompanying the sulfuric acid to Section 2 would accumulate in the H_2SO_4 vaporizer where it would react with the SO_3 forming SO_2. More likely, any elemental sulfur formed will accumulate in the iodine recycle stream.

If sulfur accumulates in the iodine, the sulfur removal will need to be demonstrated. Sulfur and iodine should be easily separable by distillation as their boiling points of differ by over 250°C. The sulfur would then be fed to the outlet of the sulfuric acid decomposer where the sulfur would be oxidized to SO_2 by O_2. Alternatively, the sulfur might be removed from the iodine by electrochemical oxidation. In either case, the maximum permissible concentration of sulfur in the iodine must be determined.

Solution Thermodynamics

The reactive distillation process for generating hydrogen appears to be viable but the current flowsheet is uncertain to the extent that the vapor-liquid equilibria of the system $HI/I_2/H_2O$ are based on models and not experimentally determined. There is also some uncertainty in the enthalpy of solution of this system. The missing data can either be determined by specific experiments or in integral form from operation of prototypical process steps.

The liquid-liquid equilibria for $HI/I_2/H_2O/H_2SO_4$ are also very limited. Additional data would allow extrapolation to operating conditions outside the current operating

envelope. Alternatively, one could simply extend the operating range through operation of prototypical process equipment.

Chemical Kinetics

The chemical kinetics of HI decomposition under the conditions of the reactive distillation column are unknown. If the kinetics are too slow for economic operation, a noble metal catalyst may be needed. The kinetics need to be examined in the absence of catalyst and in the presence of supported catalysts in both gas and liquid phases and liquid phase solution catalysts.

Material Science

Significant headway has been made at determining applicable materials of construction for the sulfur-iodine process. Materials applicable to Sections 1 and 2 have been, for the most part, adequately researched. The one area of Section 2 that presents some concerns is that of boiling heat transfer. The only materials resistant to concentrated sulfuric acid at the gas-liquid interface tend to be brittle materials such as siliconized cast iron and silicon carbide. Small heat exchangers have been made from such materials but such exchangers must be developed in the required sizes.

The containment materials for Section 3 will be similar to those in Section 1. The higher temperatures of Section 3 will be accommodated by the use of corrosion resistant insulating materials inside the chemical containment boundary. The heat transfer materials used in Section 1 may also be usable at the higher temperatures encountered in Section 3 but this needs to be verified.

ECONOMIC UNCERTAINTIES

The economic uncertainties are twofold: the projection of future hydrogen costs from alternative sources and the uncertainties in the capital cost of the nuclear hydrogen plant. We have no control over the future cost of hydrogen from alternative sources. The future cost of hydrogen from fossil sources will certainly increase. The increase may be dramatic if carbon sequestration is mandated or a carbon tax is imposed.

The uncertainties in the capital cost of the reactor and chemical plant are manageable. The cost estimate for the GT-MHR was performed very recently, with the aid of an A&E firm. The cost of the PH-MHR was derived from the GT-MHR cost by eliminating systems and should be equally firm. The cost presented for the H2-MHR was extrapolated from the PH-MHR cost and should be updated during the current DOE effort at defining a Very High Temperature Reactor (VHTR) as part of their Generation IV effort. The uncertainties in the cost of the chemical plant will be reduced as the chemical uncertainties are reduced and a pilot plant is designed.

RECOMMENDATIONS FOR RISK REDUCTION

There are two possible approaches to obtaining the data necessary to implement large-scale production of hydrogen using the sulfur-iodine process and thus overcoming the technical uncertainties indicated. The first is a science based approach utilizing a systematic and methodical examination of each area of uncertainty before proceeding further. The second is an engineering approach that builds on previous work in the area to provide specific targeted technology demonstrations. The science-based approach has the least risk but will delay the potential benefits to the nation of reduced pollution and increased reliability of the national energy supply. The engineering approach will provide clean hydrogen from nuclear energy in the shortest time frame and at the lowest overall development cost, but has some risks.

We believe that a combination of the two approaches is optimal. We recommend that the engineering development be carried out in five phases: (1) demonstration of the complete process chemistry in an integrated laboratory scale flow loop, (2) design, fabrication, and operation of an engineering demonstration loop, (3) design, fabrication, and operation of a small nuclear hydrogen production demonstration plant, (4) design, fabrication, and operation of the first commercial nuclear hydrogen demonstration plant based on a single reactor module, and (5) design, fabrication, and operation of the first full scale nuclear hydrogen production demonstration plant powered by multiple reactor modules.

The first three phases will require government participation but, assuming the demonstration plant is a success, the last two phases should be financed by industry. Laboratory studies, especially solution thermodynamics and material science investigations, should be carried out simultaneously with the engineering development, particularly during two demonstration phases. The material sciences investigations, in particular, can be "piggy backed" on to the operation of the demonstration loops at a minimal cost. During each phase engineering models of the process should be updated based on the latest scientific information and on operational data from the previous phase of scaleup. Table 4 gives the recommended scaleup steps and the degree to which process conditions and equipment construction would be typical of the final full-scale production plant. The efficiency will increase as the scale is increased due to the increased thermal integration possible with larger plants, the decrease in heat losses from larger equipment, and the concurrent development of higher temperature nuclear reactors.

Table 4 Recommended Scaleup steps for SI process

Recommended Scaleup Steps					
			Heat		Hydrogen
Materials		**Heat Source**	**Integration**	**Efficiency**	**(kg/day)**
Laboratory demonstration loop	Primarily glass/quarts with selected prototypical components	Electrical	None	Nil	0.2
Engineering demonstration loop	Prototypical	0.5 MW Electrical	Minimal	20%	60
Pilot plant	Prototypical	5 MW Electrical	Moderate	30%	900
Demonstration plant	Prototypical	50 MW_t Nuclear	Full	40%	12000
Commercial demonstration	Commercial	600 MW_t Nuclear	Full	42%	150000
Commercial production	Commercial	2400 MW_t Nuclear	Full	52%	760000

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