

**GA-A24902
(and SAN2004-681)**

ENGINEERING MATERIALS REQUIREMENTS ASSESSMENT FOR THE S-I THERMOCHEMICAL CYCLE

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**GENERAL ATOMICS PROJECT 40017
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Abstract

This report summarizes the containment materials requirements for the chemicals to be used in the Sulfur-Iodine (SI) thermochemical cycle for hydrogen production. Detailed flowsheet descriptions of the Bunsen Reaction, the Sulfuric Acid Concentration and Decomposition and the HI Decomposition outlining the critical reaction conditions have been provided. A review on the current understanding of the corrosion resistant materials applicable to the three sections was also conducted. Based on the requirements and the available technical information, a list of material candidates for each section was identified. In addition, a materials development and qualification plan, along with the facilities and data base requirements, was established to help select the suitable materials of construction. Furthermore, it was concluded that priority should be placed on the effort to develop materials used in the HI reactive distillation and sulfuric acid decomposition processes based on the more severe technical challenges involved.

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1. Introduction

Thermochemical S-I cycles offer a promising approach to the high efficiency production of hydrogen from nuclear power, but possess substantial materials challenges. These materials challenges include corrosive agents such as hydrogen iodide and sulfuric acid at high temperature. This report summarizes our assessment of the primary materials options and known performance in the expected environments, identifies gaps in the existing performance data, and recommends a plan for future materials testing to support the development of the S-I thermochemical cycle.

This report is also provided as input to the Oak Ridge National Laboratory (ORNL) Materials Requirements Document that will define overall materials testing requirements for the Nuclear Hydrogen Initiative.

2. S-I THERMOCHEMICAL CYCLE OVERVIEW

The Sulfur Iodine (SI) water splitting cycle for hydrogen production consists of three coupled chemical reactions as shown in Fig. 2-1. First, sulfuric acid and hydrogen iodide are generated in the central low temperature reaction, a.k.a. the Bunsen reaction. The reaction products, sulfuric acid and hydrogen iodide are then decomposed separately at high and intermediate temperatures in the other two reactions. There are significant chemical separations associated with each chemical reaction. Water is the primary solvent in the system with iodine being an important solvent in the Bunsen reaction.

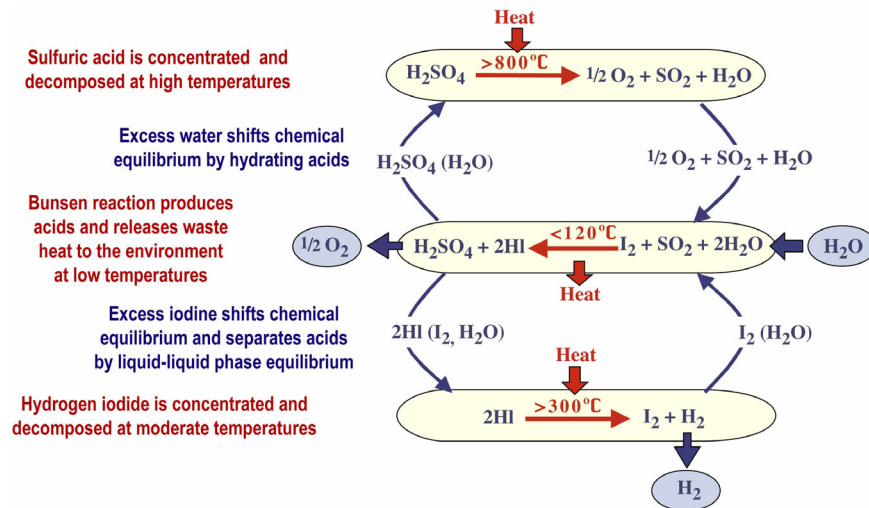


Fig. 2-1. The coupled chemical reactions of the S-I cycle.

The baseline design for the current SI work is the system configuration described in "High Efficiency Generation of Hydrogen Fuels Using Nuclear Power," General Atomics Report GA-A24285. The SI cycle flowsheet is divided into three sections:

- *Section 1 – Sulfuric Acid and Hydriodic Acid Generation.* This section receives the decomposed sulfuric acid from Sec. 2 and uses the Bunsen reaction to produce hydrogen iodide for Sec. 3. The diluted sulfuric acid is returned to Sec. 2.
- *Section 2 – Sulfuric Acid Concentration and Decomposition.* This section concentrates the sulfuric acid received from Sec. 1, and then decomposes it into sulfur dioxide, oxygen and water. The decomposed products are returned to Sec. 1.

- *Section 3 – Hydrogen Iodide Decomposition.* This section receives hydrogen iodide from Sec. 1 and decomposes it to produce hydrogen and iodine. The iodine and un-reacted hydrogen iodide is streamed back into to Sec. 1.

These three sections present extremely corrosive working environments. In order to realize a stable, safe and functional hydrogen production plant, careful selection of materials used to manufacture the reaction chambers, heat exchangers and other components for each section must be taken. The general guidelines to select materials suitable for SI cycle components can be summarized as follows:

- The materials must have good thermal conductivity, as heat exchangers play an integral part through out the SI cycle.
- Selected materials must be corrosive resistant to the working environment.
- Components manufactured from the materials must have suitable mechanical properties to provide structural integrity.
- The materials must have good fabricability, weldability, and availability to make building of a hydrogen production plant practical.

Among these requirements, corrosion resistant is the most critical factor as commercial success hinges on finding materials that work. The other factors can be dealt with accordingly once this hurdle is overcome. The goal of the project is to identify the optimal materials and processing methods suitable for constructing the various components of the hydrogen plant economically.

3. Materials Requirements for the S-I Cycle

The baseline version S-I Cycle considered in this report is based on HI decomposition through reactive distillation as described below. An alternate version of the S-I cycle, using phosphoric acid to separate water and iodine from HI_x and isolate HI for decomposition, is currently considered as a backup to the reactive distillation cycle. A description of the materials requirements for this backup cycle is provided in Sec. 3.6.

3.1 Baseline S-I Cycle Flowsheet

3.1.1. Section 1 – Sulfuric Acid and Hydriodic Acid Generation

Figure 3-1 provides a flowsheet for Sec. 1 of the SI cycle and its corresponding material balance with pressures, temperatures, compositions, and mass flows is detailed in Table 3-1. The bulk of the Bunsen reaction: $\text{I}_2 + \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 2\text{HI}$ takes place in the heat exchange reactor (R101) at 7 bar. This reaction also occurs in the primary oxygen scrubber (C101), the secondary oxygen scrubber (C104), and the H_2SO_4 boost reactor (C103). The pressures of C101, C104 and C103 remain at 4 bar, 1 bar and 1.85 bar, respectively.

The output from the main heat exchange reactor (R101) consists of three phases, which are separated in S101 and then processed separately. The gas phase (117A) consists of residual SO_2 in O_2 and this SO_2 is removed by the O_2 scrubber (C101). The majority of O_2 is vented but a portion is recycled and is used to strip any SO_2 remaining in the dense HI_x liquid (119A), the second product phase from R101, in C102. The processed HI_x liquid is sent to Sec. 3 for decomposition. The stripped SO_2 is then used to react with the water in the light liquid phase 118A, the third phase from R101, in the H_2SO_4 boost reactor (C103). The sulfuric acid stream enters this boost reactor at a mole fraction of 15% and exits at 20%. The iodine stream (110) exiting from the boost reactor bottom contains the HI formed in the boost reactor along with the water required to solutionize the HI. This stream is pumped (P103) to the heat exchanger reactor. The overhead liquid product of the boost reactor (131/140) is passed on to Sec. 2, where the H_2SO_4 is concentrated and decomposed.

Any SO_2 remaining in the sulfuric acid is returned to Sec. 1, along with water flashed from the sulfuric acid (101A). The gaseous product (131/139) of the boost reactor is scrubbed in the secondary scrubber, along with the exhaust (136) from the SO_2 absorber (C105). The gaseous product (129) of the secondary O_2 scrubber exits the process along

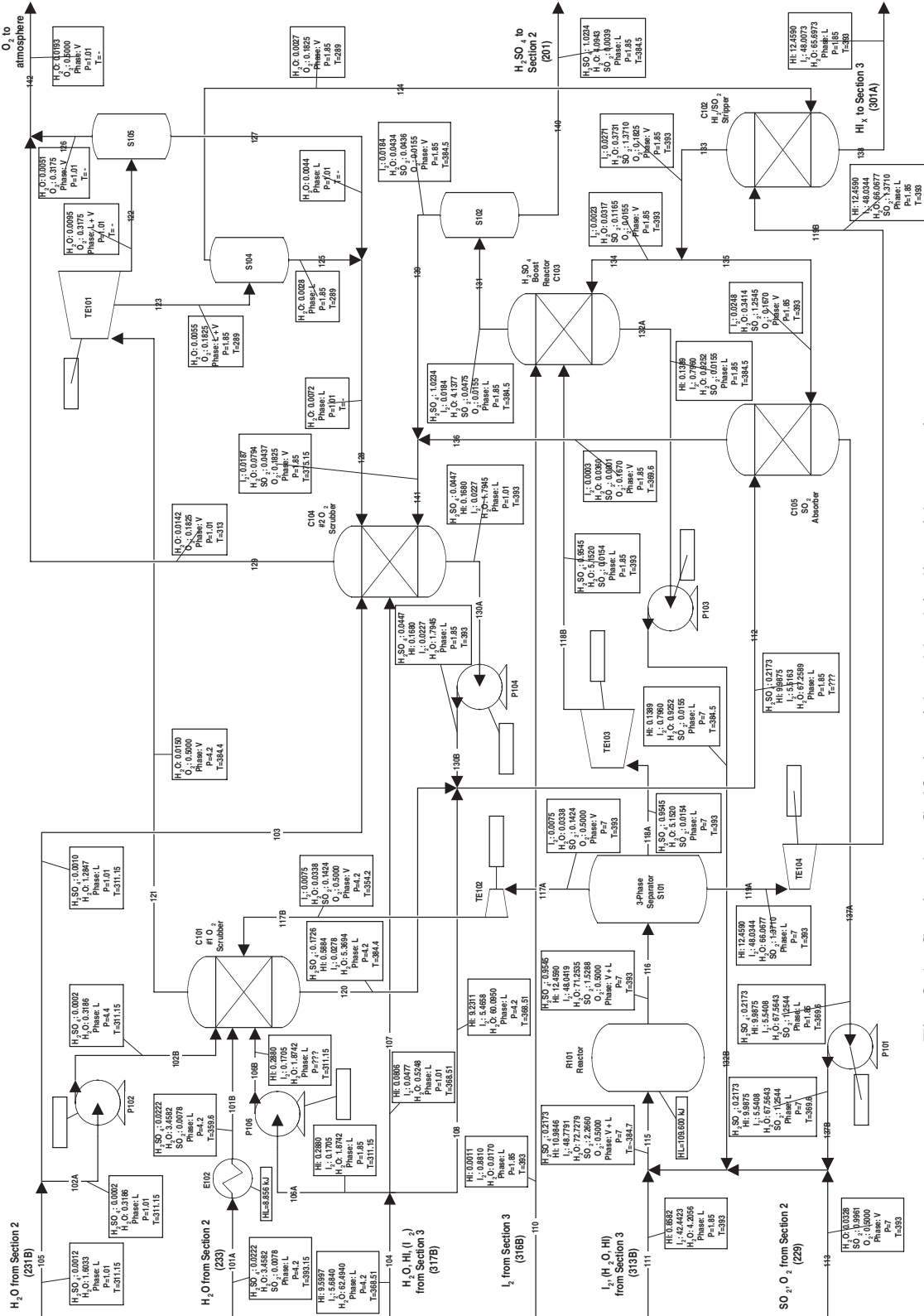


Fig. 3-1. Section 1 Sulfuric acid and hydriodic acid generation.

Table 3-1. Material Balance for Section 1 — Sulfuric Acid and Hydriodic Acid
Generation

Stream	H ₂ SO ₄	HI	I ₂	H ₂ O	SO ₂	O ₂	Total	Phase	P Bar	Temp K
101A	0.0222	0.0000	0.0000	3.4582	0.0078	0.0000	3.4882	L	4.2	393.15
101B	0.0222	0.0000	0.0000	3.4582	0.0078	0.0000	3.4882	L	4.2	359.6
102A	0.0002	0.0000	0.0000	0.3186	0.0000	0.0000	0.3188	L	1.01	311.15
102B	0.0002	0.0000	0.0000	0.3186	0.0000	0.0000	0.3188	L	4.4	311.15
103	0.0010	0.0000	0.0000	1.2847	0.0000	0.0000	1.2857	L	1.01	311.15
104	0.0000	9.5997	5.6840	62.494	0.0000	0.0000	77.7777	L	4.2	368.51
105	0.0012	0.0000	0.0000	1.6033	0.0000	0.0000	1.6045	L	1.01	311.15
106	0.0000	0.2880	0.1705	1.8742	0.0000	0.0000	2.3327	L	1.85	311.15
107	0.0000	0.0806	0.0477	0.5248	0.0000	0.0000	0.6531	L	1.01	368.51
108	0.0000	9.2311	5.4658	60.095	0.0000	0.0000	74.7919	L	4.2	368.51
110	0.0000	0.0011	0.8810	0.017	0.0000	0.0000	0.8991	L	1.85	393
111	0.0000	0.8582	42.4423	4.2056	0.0000	0.0000	47.5061	L	1.85	393
112	0.2173	9.9875	5.5163	67.2589	0.0000	0.0000	82.9800	L	1.85	
113	0.0000	0.0000	0.0000	0.0328	0.9961	0.5000	1.5289	V	7	393
115	0.2173	10.9846	48.7791	72.7279	2.2660	0.5000	135.4749	V+L	7	
116	0.9545	12.4590	48.0419	71.2535	1.5288	0.5000	134.7377	V+L	7	393
117A	0.0000	0.0000	0.0075	0.0338	0.1424	0.5000	0.6837	V	7	393
117B	0.0000	0.0000	0.0075	0.0338	0.1424	0.5000	0.6837	V	4.2	354.2
118A	0.9545	0.0000	0.0000	5.1520	0.0154	0.0000	6.1219	L	7	393
118B	0.9545	0.0000	0.0000	5.1520	0.0154	0.0000	6.1219	L	1.85	393
119A	0.0000	12.4590	48.0344	66.0677	1.3710	0.0000	127.9321	L	7	393
119B	0.0000	12.4590	48.0344	66.0677	1.3710	0.0000	127.9321	L	1.85	393
120	0.1726	0.5884	0.0278	5.3694	0.0000	0.0000	6.1582	L	4.2	384.4
121	0.0000	0.0000	0.0000	0.0150	0.0000	0.5000	0.5150	V	4.2	384.4
122	0.0000	0.0000	0.0000	0.0095	0.0000	0.3175	0.3270	L+V	1.01	-
123	0.0000	0.0000	0.0000	0.0055	0.0000	0.1825	0.1880	L+V	1.85	289
124	0.0000	0.0000	0.0000	0.0027	0.0000	0.1825	0.1852	V	1.85	289
125	0.0000	0.0000	0.0000	0.0028	0.0000	0.0000	0.0028	L	1.85	289
126	0.0000	0.0000	0.0000	0.0051	0.0000	0.3175	0.3226	V	1.01	-
127	0.0000	0.0000	0.0000	0.0044	0.0000	0.0000	0.0044	L	1.01	-

Table 3-1. Material Balance for Section 1 — Sulfuric Acid and Hydriodic Acid
Generation (Continued)

Stream	H ₂ SO ₄	HI	I ₂	H ₂ O	SO ₂	O ₂	Total	Phase	P Bar	Temp K
128	0.0000	0.0000	0.0000	0.0072	0.0000	0.0000	0.0072	L	1.01	-
129	0.0000	0.0000	0.0000	0.0142	0.0000	0.1825	0.1967	V	1.01	313
130A	0.0447	0.1680	0.0227	1.7945	0.0000	0.0000	2.0299	L	1.01	393
130B	0.0447	0.1680	0.0227	1.7945	0.0000	0.0000	2.0299	L	1.85	393
131	1.0234	0.0000	0.0184	4.1377	0.0475	0.0155	5.2425	L	1.85	384.5
132A	0.0000	0.1389	0.7960	0.9252	0.0155	0.0000	1.8756	L	1.85	384.5
132B	0.0000	0.1389	0.7960	0.9252	0.0155	0.0000	1.8756	L	7	384.5
133	0.0000	0.0000	0.0271	0.3731	1.3710	0.1825	1.9537	V	1.85	393
134	0.0000	0.0000	0.0023	0.0317	0.1165	0.0155	0.1660	V	1.85	393
135	0.0000	0.0000	0.0248	0.3414	1.2545	0.1670	1.7877	V	1.85	393
136	0.0000	0.0000	0.0003	0.0360	0.0001	0.1670	0.1670	V	1.85	369.6
137A	0.2173	9.9875	5.5408	67.5643	1.2544	0.0000	0.0000	L	1.85	369.6
137B	0.2173	9.9875	5.5408	67.5643	1.2544	0.0000	0.0000	L	7	369.6
138	0.0000	12.459	48.0073	65.6973	0.0000	0.0000	0.0000	L	1.85	393
139	0.0000	0.0000	0.0184	0.0434	0.0436	0.0155	0.0155	V	1.85	384.5
140	1.0234	0.0000	0.0000	4.0943	0.0039	0.0000	5.1216	L	1.85	384.5
141	0.0000	0.0000	0.0187	0.0794	0.0437	0.1825	0.3243	V	1.85	375.15
142	0.0000	0.0000	0.0000	0.0193	0.0000	0.5000	0.5193	V	1.01	—

with the vent (126) from the primary O₂ scrubber. The combined vent (142) contains one-half mole of oxygen for every mole of hydrogen produced in the overall process. In a mature hydrogen economy, the oxygen will likely be vented to the atmosphere but for initial plants, the oxygen co-product may be sold. The liquid products of the two oxygen scrubbers (120/130B) are combined with a portion (108) of the HI/H₂O recycled from Sec. 3 (104). This combined stream (112) is used to adsorb much of the SO₂ stripped from the HI_x.

3.1.2. Section 2 – Sulfuric Acid Concentration and Decomposition

A flowsheet for Sec. 2 of the SI system is shown in Fig. 3-2. Table 3-2 provides a detailed material balance with pressures, temperatures, compositions, and mass flows for all its components. This cycle can be further refined into two parts: *i*) concentration and *ii*) decomposition of sulfuric acid.

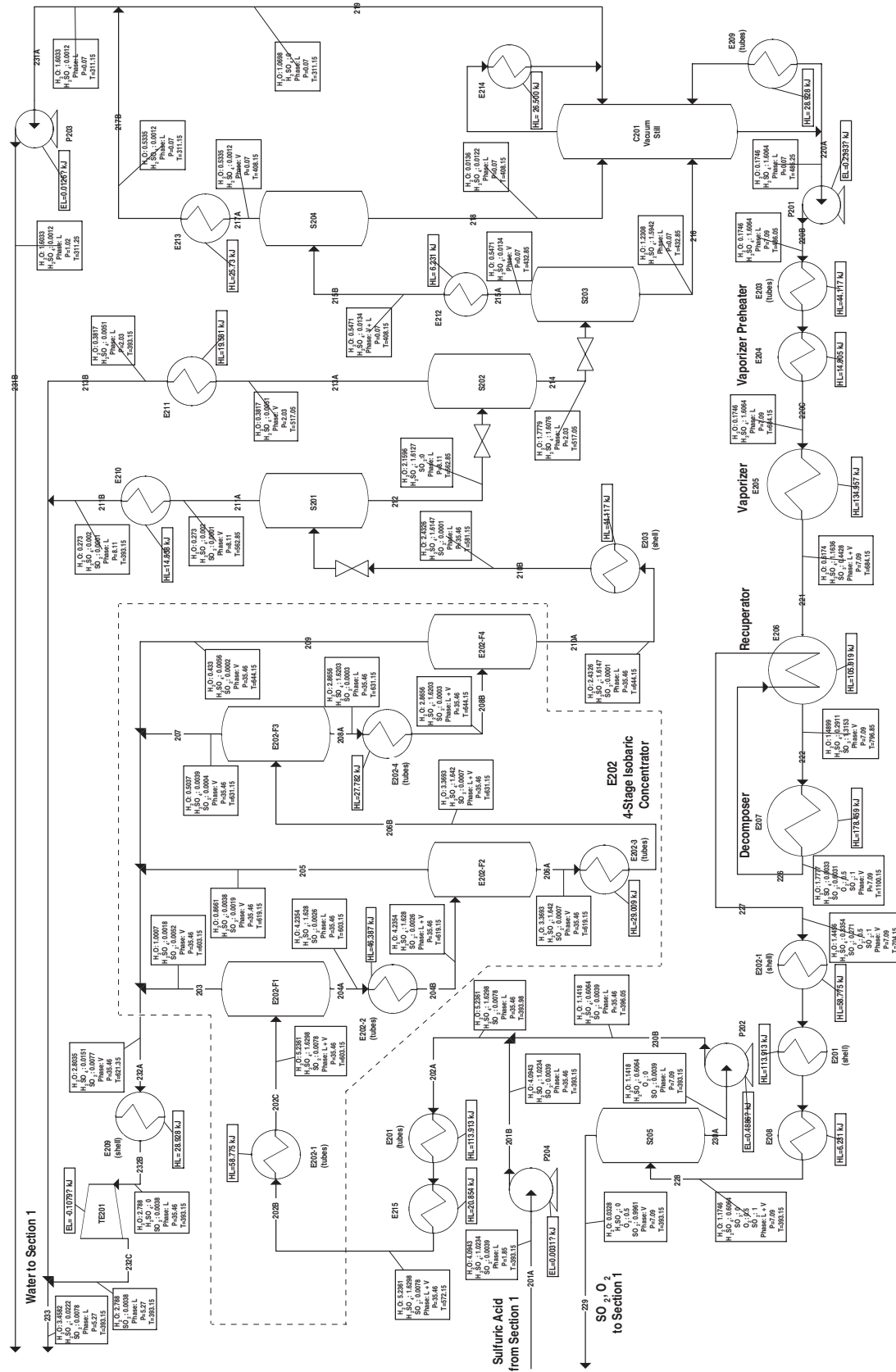


Fig. 3-2. Section 2 Sulfuric acid concentration and decomposition

Table 3-2. Material Balance for Section 2 — Sulfuric Acid Concentration
and Decomposition

Stream	H ₂ O	H ₂ SO ₄	SO ₃	O ₂	SO ₂	Total	Phase	Press. Bar	Temp K
201A	4.0943	1.0234	0	0	0.0039	5.1216	L	1.85	393.15
201B	4.0943	1.0234	0	0	0.0039	5.1216	L	35.46	393.15
202A	5.2361	1.6298	0	0	0.0078	6.8737	L	35.46	393.98
202B	5.2361	1.6298	0	0	0.0078	6.8737	L + V	35.46	572.15
202C	5.2361	1.6298	0	0	0.0078	6.8737	L + V	35.46	603.15
203	1.0007	0.0018	0	0	0.0052	1.0077	V	35.46	603.15
204A	4.2354	1.628	0	0	0.0026	5.866	L	35.46	603.15
204B	4.2354	1.628	0	0	0.0026	5.866	L + V	35.46	619.15
205	0.8661	0.0038	0	0	0.0019	0.8718	V	35.46	619.15
206A	3.3693	1.6242	0	0	0.0007	4.9942	V	35.46	619.15
206B	3.3693	1.6242	0	0	0.0007	4.9942	L + V	35.46	631.15
207	0.5037	0.0039	0	0	0.0004	0.508	V	35.46	631.15
208A	2.8656	1.6203	0	0	0.0003	4.4862	L	35.46	631.15
208B	2.8656	1.6203	0	0	0.0003	4.4862	L + V	35.46	644.15
209	0.433	0.0056	0	0	0.0002	0.4388	V	35.46	644.15
210A	2.4326	1.6147	0	0	0.0001	4.0474	L	35.46	644.15
210B	2.4326	1.6147	0	0	0.0001	4.0474	L	35.46	581.15
211A	0.273	0.002	0	0	0.0001	0.2751	V	8.11	562.85
211B	0.273	0.002	0	0	0.0001	0.2751	L	8.11	393.15
212	2.1596	1.6127	0	0	0	3.7723	L	8.11	562.85
213A	0.3817	0.0051	0	0	0	0.3868	V	2.03	517.05
213B	0.3817	0.0051	0	0	0	0.3868	L	2.03	393.15
214	1.7779	1.6076	0	0	0	3.3855	L	2.03	517.05
215A	0.5471	0.0134	0	0	0	0.5605	V	0.07	432.85
215B	0.5471	0.0134	0	0	0	0.5605	V + L	0.07	408.15
216	1.2308	1.5942	0	0	0	2.825	L	0.07	432.85
217A	0.5335	0.0012	0	0	0	0.5347	V	0.07	408.15
217B	0.5335	0.0012	0	0	0	0.5347	L	0.07	311.15
218	0.0136	0.0122	0	0	0	0.0258	L	0.07	408.15
219	1.0698	0	0	0	0	1.0698	L	0.07	311.15
220A	0.1746	1.6064	0	0	0	1.781	L	0.07	485.25
220B	0.1746	1.6064	0	0	0	1.781	L	7.09	486.05
220C	0.1746	1.6064	0	0	0	1.781	L	7.09	684.15

Table 3-2. Material Balance for Section 2 — Sulfuric Acid Concentration and Decomposition (Continued)

Stream	H ₂ O	H ₂ SO ₄	SO ₃	O ₂	SO ₂	Total	Phase	Press. Bar	Temp K
221	0.6174	1.1636	0.4428	0	0	2.2238	L + V	7.09	684.15
222	1.4899	0.2911	1.3153	0	0	3.0963	V	7.09	796.85
223	1.7	0.081	1.261	0.1322	0.2644	3.4386	V	7.09	875.05
224	1.757	0.024	1.0776	0.2524	0.5048	3.6158	V	7.09	955.05
225	1.7725	0.0085	0.8405	0.3787	0.7574	3.7576	V	7.09	1027.05
226	1.7777	0.0033	0.6031	0.5	1	3.8841	V	7.09	1100.15
227	1.4456	0.3354	0.271	0.5	1	3.552	V	7.09	704.15
228	1.1746	0.6064	0	0.5	1	3.281	L + V	7.09	393.15
229	0.0328	0	0	0.5	0.9961	1.5289	V	7.09	393.15
230A	1.1418	0.6064	0	0	0.0039	1.7521	L	7.09	393.15
230B	1.1418	0.6064	0	0	0.0039	1.7521	L	35.46	396.05
231A	1.6033	0.0012	0	0	0	1.6045	L	0.07	311.15
231B	1.6033	0.0012	0	0	0	1.6045	L	1.02	311.25
232A	2.8035	0.0151	0	0	0.0077	2.8263	V	35.46	621.35
232B	2.788	0	0	0	0.0038	2.7918	L	35.46	393.15
232C	2.788	0	0	0	0.0038	2.7918	L	5.27	393.15
233	3.4582	0.0222	0	0	0.0078	3.4882	L	5.27	393.15

3.1.2.1. Concentration. The incoming sulfuric acid from Sec. 1, along with the internally recycled sulfuric acid, is concentrated to 40 mole % in a high-pressure four-stage isobaric concentrator (E202). The feed to Sec. 2 (201A) and the recycle stream (230A) are first pumped up to the operating pressure of the isobaric concentrator at 35 atm and are then preheated together before entering the concentrator. As the sulfuric acid solution flows through four serially connected and heated chambers within the concentrator, water is boiled off within each chamber resulting in an increase in the temperature and the acid concentration of the solution. Upon completion, the concentrator produces a liquid phase with concentrated sulfuric acid and a vapor phase of steam. The small amount of sulfur dioxide that remains in the inlet sulfuric acid is removed with the water. The water vapor boiled off from each chamber is mixed above the chambers and leaves as a single stream. The sensible and latent heat in this stream can be re-used elsewhere in this section. The material balance table gives values for the intermediate streams within the isobaric concentrator but only the mixed vapor outlet and the concentrated liquid outlet are physically identifiable streams. The mixed vapor outlet is condensed and its sensible and latent heats are recovered via the re-boiler of the vacuum distillation column (C201).

The liquid product of the isobaric concentrator (210A) is further concentrated in a series of three reduced pressure flashes at 8 bar, 2 bar and 50 Torr before entering the 50 Torr vacuum still (C201). Prior to the first flash, some heat is removed for use later in the process but the subsequent flashes are adiabatic. The feed to the vacuum still (216) is 56 mole % sulfuric acid. The vapor from the final adiabatic flash passes through a partial condenser. The condensed liquid from the partial condenser (218) is fed to the vacuum still at a position appropriate to its composition (47 mole % H_2SO_4).

The pressures of the distillation column and the isobaric concentrator were chosen such that the column re-boiler temperature is low enough to utilize the heat recovered from condensing the isobaric concentrator vapor stream. Hence, a balance must be struck between the pressure of the isobaric flash and the pressure of the distillation column in order to utilize this heat. As the pressure of the isobaric flash increases, the temperature of heat recovered from the vapor stream also increases. As the column pressure is decreased, the corresponding required temperature goes down. With all other considerations being equal, the operating pressures should be as low as practical. However, a higher helium temperature from the nuclear reactor might allow higher overall process efficiencies at higher pressures. A Japanese plant producing semiconductor grade sulfuric acid has demonstrated successfully operation at a column pressure of 50 Torr and thus this pressure was chosen for our vacuum still. The corresponding isobaric flash pressure is 35 bar.

The overhead from the still, which is nearly pure water, is returned to Sec. 1. The bottom product of the distillation column (220A) is azeotropic sulfuric acid (~90 mole % H_2SO_4) liquid at 212°C. The concentrated sulfuric acid is pumped from the column pressure up to the 7 bar and then decomposed.

3.1.2.2. Decomposition. Before the sulfuric acid can be decomposed, it must first be heated and vaporized. Some of the heat required to preheat the stream prior to vaporization is recovered from the liquid product of the isobaric concentrator but the remainder of the heat required for heating, vaporizing, and decomposing the sulfuric acid is provided by the high temperature helium from the nuclear reactor. Some of the sulfuric acid decomposes into SO_3 and water as it is vaporized and this reaction proceeds further as the vaporized stream is heated in the recuperator.

The recuperator retrieves much of the heat that remains after sulfuric acid decomposition. Physically, the recuperator is similar to a shell and tube heat exchanger, with the hot fluid flows on the tube side and the cool fluid flows on the shell side. Most of the sulfuric acid has decomposed into SO_3 and water by the exit of the recuperator (222). The SO_3 is then permitted to decompose into SO_2 and O_2 . The material balance table for Sec. 2 (Table 3-2) shows the effect of performing the decomposition in four

stages but the flowsheet only shows a single piece of equipment. The four-stage decomposer/reactor was chosen to improve the process efficiency. As the number of stages is increased, more of the heat can be supplied to the reactor at lower temperatures.

The reactor outlet stream (226) is cooled in the recuperator, transferring heat to its feed, as mentioned previously. The SO_3 reacts with water reforming H_2SO_4 . The reaction products are further cooled and the heat is recovered for use within this section in the product cooler. The product cooler is physically divided into three heat exchangers. Part of the recovered heat is used for the first stage of the isobaric concentrator and the remainder is used to preheat the concentrator feed. Unrecoverable heat is lost to the cooling water. The liquid condensed in the product cooler is recycled to the isobaric concentrator and the gas phase, consisting primarily of SO_2 and O_2 is recycled to Sec. 1. The entire sulfuric decomposition reaction occurs at 7 bar.

3.1.3. Section 3 – Hydrogen Iodide Decomposition

The flowsheet and materials balance information for Sec. 3 are presented in Fig. 3-3 and Table 3-3. The HI_x ($\text{HI} + \text{I}_2 + \text{H}_2\text{O}$) product from Sec. 1 is first pumped up to 22 bar and then recuperatively heated to the feed temperature of the reactive distillation column (C301) in a network of heat exchangers (E301/E302/E303). This heat is recovered from the two liquid products of the distillation column: the bottom stream (305A) contains most of the iodine, and the side outlet (306A) made up from mostly water and hydrogen iodide.

The overhead product of the column is scrubbed in a packed column (C302) with water to remove the residual hydrogen iodide from the hydrogen. The high pressure (22 bar) and low temperature (25°C) of the scrubber result in a relatively low water content (0.14 mole %) in the hydrogen product. Fresh de-ionized water is used to scrub the product hydrogen.

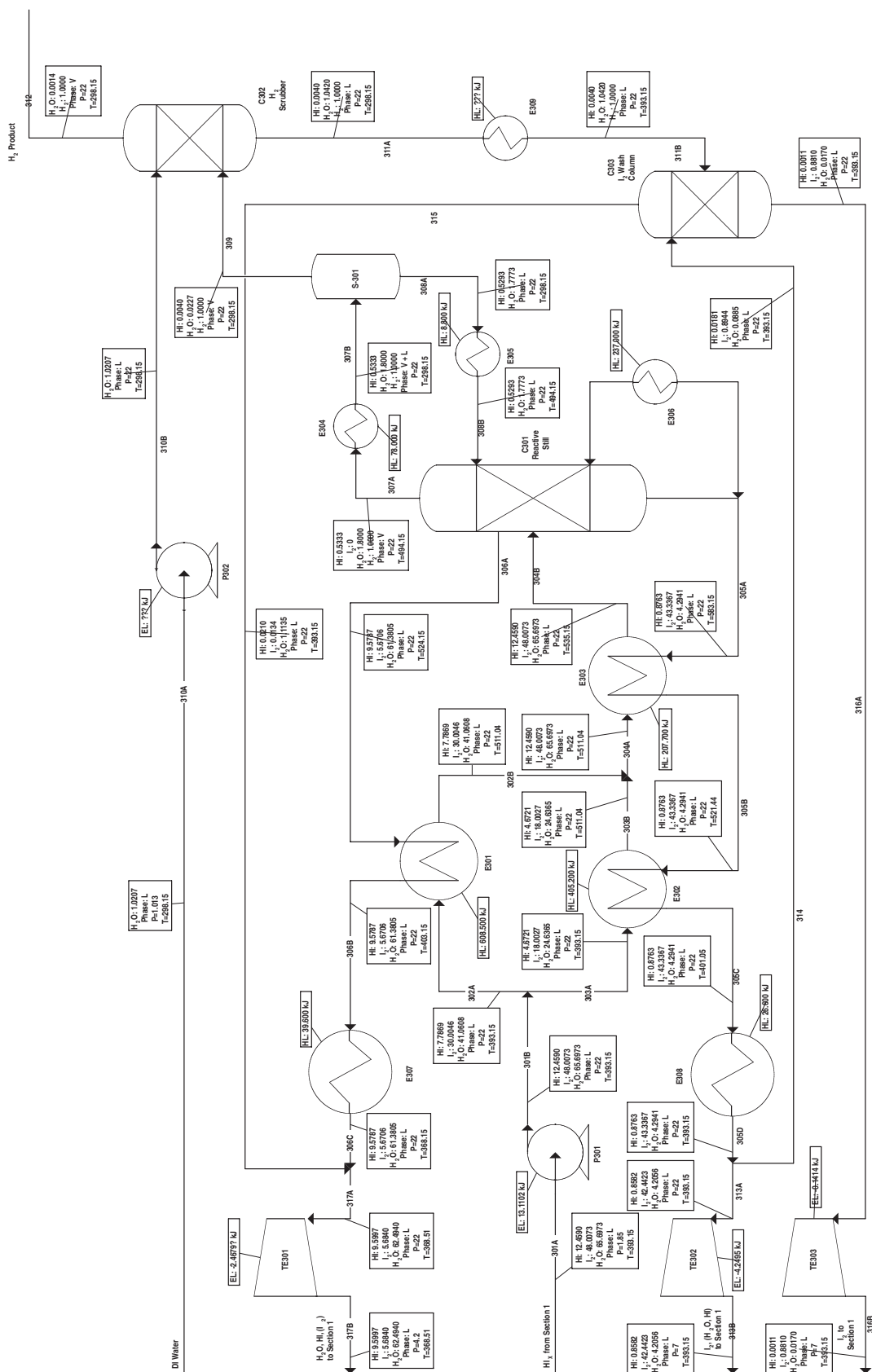


Fig. 3-3. Section 3 Hydrogen iodide decomposition

Table 3-3. Material Balance for Section 3 — Hydrogen Iodide Composition

Stream	HI	I ₂	H ₂ O	H ₂	Total	Phase	Press. Bar	Temp K
301A	12.4590	48.0073	65.6973	0.0000	126.1636	L	1.85	393.15
301B	12.4590	48.0073	65.6973	0.0000	126.1636	L	22	393.15
302A	7.7869	30.0046	41.0608	0.0000	78.8523	L	22	393.15
302B	7.7869	30.0046	41.0608	0.0000	78.8523	L	22	511.04
303A	4.6721	18.0027	24.6365	0.0000	47.3113	L	22	393.15
303B	4.6721	18.0027	24.6365	0.0000	47.3113	L	22	511.04
304A	12.4590	48.0073	65.6973	0.0000	126.1636	L	22	511.04
304B	12.4590	48.0073	65.6973	0.0000	126.1636	L	22	535.15
305A	0.8763	43.3367	4.2941	0.0000	48.5071	L	22	583.15
305B	0.8763	43.3367	4.2941	0.0000	48.5071	L	22	521.44
305C	0.8763	43.3367	4.2941	0.0000	48.5071	L	22	401.05
305D	0.8763	43.3367	4.2941	0.0000	48.5071	L	22	393.15
306A	9.5787	5.6706	61.3805	0.0000	76.6298	L	22	524.15
306B	9.5787	5.6706	61.3805	0.0000	76.6298	L	22	403.15
306C	9.5787	5.6706	61.3805	0.0000	76.6298	L	22	368.15
307A	0.5333	0.0000	1.8000	1.0000	3.3333	V	22	494.15
307B	0.5333	0.0000	1.8000	1.0000	3.3333	V+L	22	298.15
308A	0.5293	0.0000	1.7773	0.0000	2.3066	L	22	298.15
308B	0.5293	0.0000	1.7773	0.0000	2.3066	L	22	494.15
309	0.0040	0.0000	0.0227	1.0000	1.0267	V	22	298.15
310A	0.0000	0.0000	1.0207	0.0000	1.0207	L	1.013	298.15
310B	0.0000	0.0000	1.0207	0.0000	1.0207	L	22	298.15
311A	0.0040	0.0000	1.0420	0.0000	1.0460	L	22	298.15
311B	0.0040	0.0000	1.0420	0.0000	1.0460	L	22	393.15
312	0.0000	0.0000	0.0014	1.0000	1.0014	V	22	298.15
313A	0.8582	42.4423	4.2056	0.0000	47.5061	L	22	393.15
313B	0.8582	42.4423	4.2056	0.0000	47.5061	L	7	393.15
314	0.0181	0.8944	0.0885	0.0000	1.0010	L	22	393.15
315	0.0210	0.0134	1.1135	0.0000	1.1479	L	22	393.15
316A	0.0011	0.8810	0.0170	0.0000	0.8991	L	22	393.15
316B	0.0011	0.8810	0.0170	0.0000	0.8991	L	7	393.15
317A	9.5997	5.6840	62.4940	0.0000	77.7777	L	22	368.51
317B	9.5997	5.6840	62.4940	0.0000	77.7777	L	4.2	368.51

It is uneconomic and unnecessary to remove all of the water and hydrogen iodide from the still's bottom but it is necessary to provide a small amount of pure iodine for the boost reactor in Sec. 1. The scrub water (311A) is used to wash a portion of the bottoms in a packed column. The column was modeled as a single LLE stage using the model for HI/I₂/H₂O previously discussed.

3.2 Current Materials Status

3.2.1. Section 1 – Sulfuric Acid and Hydriodic Acid Generation

A literature review performed in 2002 identified some candidate materials i.e., ceramics (SiC, Si₃N₄, Al₂O₃), glass, fluorocarbons, Tantalum (Ta) and Zirconium (Zr) or Ni alloys. Starting in March 2003, preliminary electrochemical tests were performed on Ta, Zr 702 and Hastelloy B3 (Ni-Mo), at a temperature of 95°C. The behaviour of these materials in the two individual acids as a function of concentrations was studied. In addition, the combined effect of both acids by adding traces of one to the other was also investigated. Corrosion rates appear to be about 100 times higher in HI_x than in H₂SO₄. Furthermore, the rate is 10X and 1000X higher for Zr and Hastelloy B3 respectively than for Ta in both acids.

In late 2003, further corrosion tests were performed with H₂SO₄ and HI_x for Hastelloy B3, zirconium and tantalum. The results clearly indicate an increase of corrosion with the simultaneous presence of both acids and that Hastelloy B3 must be avoided even with traces of HI_x. The best material currently identified for the Bunsen section is tantalum.

3.2.2. Section 2 – Sulfuric Acid Concentration and Decomposition

A survey of materials was performed that included industrial materials used in similar applications, materials experience from previous S-I cycle work, exotic materials such as platinum alloys, advanced ceramics materials, and emerging engineered materials in development. However, there are very limited data available on the corrosion performance of any of these materials in superheated sulfuric acid vapor. The result of the survey is summarized in Table 3-4.

3.2.2.1. Concentration. High-silicon iron and stainless steel alloys are known to be stable in liquid sulfuric acid at compositions up to the natural boiling point. Hastelloy B-2 has been shown to exhibit corrosion rates of less than 0.1 mm/yr. at acid concentrations up to 60%. High silicon steel also provides corrosion rates of less than 0.1 mm/yr. for concentrated acid, but has shown higher rates at lower acid concentration.

Table 3-4. Materials Options for Section 2: Sulfuric Acid Concentration and Decomposition

Process Regime	Conditions	Candidate Materials	Compatibility	Comments
H ₂ SO ₄ concentration	300—450 K, 50%	Glass lined steel, plastics, ceramics	Hastelloy B-2 < 0.1 mm/yr for concentrations up to 60%	Concentration may require multiple materials
	300—420 K, 50%-75%	Hastelloy B-2, C-276	High Si steel corrosion ~0.1 mm/yr for concentrated acid, higher for low concentrations	Options identified for all concentrations and temperatures
	450—700 K, 75%-95% H ₂ SO ₄ , iodine species, impurities	Incoloy 800H, AL610, high Si steel, Au or Pt plating		Evaluate coatings, plating B-2 promising at low concentration
H ₂ SO ₄ vaporization	600—800K	Structural: Incoloy 800H	800 H, 800 HT	High Si steel fabrication issues
	H ₂ O+SO ₃ , iodine, other contaminants	AL610, high Si steel SiC, Si ₃ N ₄ Hastelloy G, C-276	High Si steel (SiO ₂) < 5 mpy SiC ~ no corrosion in 1000 h test at 75% to 95% acid (JPN)	Coated materials (Pt) cost issue Ceramics promising, but have fabrication and joining issues Dry wall boiler design with ceramics may be option
			C-276 ~1 mm/yr at 476 h	Data needed with iodine contamination
H ₂ SO ₄ decomposition	800—1200 K	Structural: Incoloy 800 HT, Inconel 800 H (with aluminide coatings), AL 610	Incoloy, Inconel Bare — 2 to 4 mg/cm ² in 1000 h at 1173 K	Incoloy 800 HT may address intergranular corrosion C-SiC composites should be examined
	H ₂ O, H ₂ SO ₄ , SO ₃ , SO ₂ , O ₂	Ceramics, Pt or Au coatings on super alloy structural materials	Aluminide coatings — approx. 1 mg/cm ² in 1000 h at 1173 K	Pt coating may serve function of catalyst and reduce corrosion
		Catalysts: Pt, Cu, Fe ₂ O ₃	Intergranular corrosion observed for 800 H Noble metal coatings may provide corrosion protection	Corrosion benefits of noble metal coatings must be demonstrated

A similar selection of materials as presented for the concentration reaction may be acceptable in the vaporization cycle stage even though the presence of gaseous sulfuric acid complicates things due to the lack of available literature data on material performance in such environments. While high-silicon iron and stainless steel alloys are known to be stable in liquid sulfuric acid at compositions up to the natural boiling point, there is little information on the performance of these materials in the presence of gaseous sulfuric acid at elevated temperatures. It is possible that this situation could destabilize the protective oxide layer on the metal surface.

Both platinum and gold may also be capable of containing acid in this regime. The latter materials may be applied either alone, or in the form of a cladding over a stronger, structural alloy (such as a nickel-based material). Silicon carbide materials have been shown to provide extremely low corrosion rates in this environment, though the fabrication and joining of the engineering components required for this operation remain an issue.

3.2.2.2. Decomposition. GA Technologies had explored the use of Hastelloy C-276 for the boiler and superheater, and Incoloy 800H for the decomposer. They found C-276 to exhibit low corrosion rates in the boiler (330°C) and it decreased dramatically when passing to the gaseous phase in the vaporizer (600°C). In the case of Incoloy 800H used in the decomposer (850°C), the overall degree of corrosion was low. The attack that did occur was nearly entirely intergranular in nature (G.A. Tech, 1986). In addition, microcracking was observed which stems from rough machining marks in the sample. Highly localized attack, such as IGA, results in the formation of numerous stress concentrators on the metal surface, any one of which could potentially result in sudden, catastrophic failure of a pressure vessel. This fact does not, however, preclude the use of such alloys as a supporting structural material, such as the base layer of a clad material.

3.2.3. Section 3 – Hydrogen Iodide Decomposition

A survey of the materials candidates for Sec. 3 is shown in Table 3-5. Among the three ingredients of HI_x , iodine has the highest capacity to corrode. Past literature have shown there are three groups of materials, which works well in pure iodine at high temperatures. They consist of noble metals, refractory metals such as Ta, Mo and their alloys and Ni based alloys. Noble and refractory metals show no corrosion in pure iodine up to 300°C whereas the rate for Ni based alloys is less than 0.05 mm/yr. Some ceramic materials such as Al_2O_3 and ZrO_2 have also shown to work well in the presence of iodine but their use will be limited in the present context as they have very low thermal conductivity. The corrosion data of materials on hydriodic acid is very limited but refractory metals should be effective in this environment.

Table 3-5. Materials Options for Section 3 — Hydrogen Iodide Decomposition

Process Regime	Conditions	Candidate Materials	Compatibility	Comments
Reactor HI _X feed (HI + I ₂ + H ₂ O)	533 K, ~40 bar - Impurities, H₂S, S etc.	- Ta and alloys, Nb and alloys, Zircaloy, Mo - SiC	- Pure Mo and Ta < 0.1 mm/yr - Hydrogen embrittlement effects	- Processing effects unknown - Evaluate coatings, plantings - Fabrication and cost issues
Reactor bottom HI _X with high I ₂ concentration (<85%)	573 K, ~40 bar - Sulfur species contaminants.	- Ta and alloys, Nb and alloys, Zircaloy, Mo, W - SiC	- W, Mo and Ta < 0.01 mm/yr in pure iodine at 300°C. - Gold and Pt works well in pure iodine but performs poorly in HI_X	- SiC composites should be examined - Materials need to be compatible with the HI_X feed for reactor application
Non distillation HI _X with high I ₂ concentration (<85%)	390 K, ~40 bar - Contaminants from other sections	- Ta and alloys, Nb and alloys, Zircaloy, Mo, W - SiC and carbon composite - Ni-Mo, Ti alloys, Hastelloy B2	- Ni-Mo alloys < 0.05 in pure iodine - Ti and Hastelloy B2 compatible with HI_X below 150°C.	- Carbon composite can be consider for lower temperatures - Systems level design considerations in the integration of different materials

Previous immersion corrosion testing [P.W. Trestor and H.G. Staley, “Assessment and Investigation of Containment Materials for the Sulfur-Iodine Thermochemical Water-Splitting Process for Hydrogen Production,” Gas Research Institute Report 80/00981, May (1981)] of material coupons in HI_x solution with different concentrations and physical conditions had been carried out at General Atomics (GA). Detailed results can be found in Appendix A. Only a limited amount of data is available on materials tested at the high temperature and pressure conditions required by the version 1 HI_x decomposition cycle. The majority of the materials that performed well were refractory metals and their alloys with corrosion rate in the range of 0.02 mm/yr. Although refractory alloys all have very low corrosion rate in HI_x but Nb, Zr and Ta can absorb H_2 to some extent and may be sensitive to hydrogen embrittlement whereas Mo does not absorb hydrogen at all. This needs to be considered during the materials development stage. Other non-metallic materials, which have demonstrated corrosion resistance, include SiC, glass and vitreous carbon. SiC can be a very useful material as it has high thermal conductivity (Table 3-6) and heat exchanger made from it is readily available.

Table 3-6. Thermal Conductivity of Materials of Interest

Materials	Thermal Conductivity (W/mK)
Glass	1
Hastelloy	16
Titanium	18
Zirconium	20
Stainless steel	30
Tantalum	48
SiC	116

3.3. Materials Selection, Development, and Qualification

The choice of materials for construction will have significant effect on the initial investment and the operating cost of the hydrogen plant and plays an important role in determining the ultimate price of hydrogen. To successfully build a SI Cycle plant, the materials used for construction need not only to meet the performance and safety requirements but must also satisfy the economical realities in order to make hydrogen production viable. The first consideration is the initial capital cost of to produce the process equipment. It is directly affected by the price of the selected material and the cost of fabricating process equipment with it. The equipment costs are indirectly affected by the physical properties of the material (strength, thermal conductivity, etc.) and the required corrosion allowance. Of equal importance are operating cost considerations such

as useful life of the components; their replacement cost based on the corrosion allowance and their efficiency in performing non-corrosive retardant role such as heat transfer. In addition, there can also be an added cost due to the fact that in a thermochemical hydrogen plant, corrosion products may re-circulate with the process chemicals and will accumulate somewhere in the process train and thus requiring maintenance effort to remove them. Given the cost factors associated, careful selection of the optimal material for the right application is of utmost importance.

3.3.1. Section 1 – Sulfuric Acid and Hydriodic Acid Generation

Although the Bunsen reaction conditions contains SO_2 , H_2SO_4 , and possibly reaction byproducts of Sulfur and H_2S in addition to HI_x , the overall reaction environment (120°C and 1 atm) is much less corrosive than Sec. 3. In addition, preliminary testing has suggested HI_x to be 100X more corrosive than H_2SO_4 . It is safe to assume those materials suitable for building components for Sec. 3 should in theory be applicable here. Hence, the materials selection and development process for Sec. 1 will be covered under that for Sec. 3. Once the proper construction materials candidates for HI decomposition cycle are determined, they will be subjected to corrosion testing using the Bunsen reaction environment to confirm their applicability.

3.3.2. Section 2 – Sulfuric Acid Concentration and Decomposition

3.3.2.1. Materials Selection. Successful implementation of a system for sulfuric acid concentration and decomposition represents a significant challenge from a materials selection vantage. The materials must possess sufficient thermal conductivity to allow for the ready delivery of thermal energy to the sulfuric acid solution. In addition, they will have to withstand the chemical and mechanical environment within each individual reaction in this section. For the acid concentration process, the material components utilized must be:

- Corrosion resistant in sulfuric acid with concentrations ranging from 15% to 95% and temperatures from 300 to 600 K.
- Sufficient mechanical strength to contain the elevated pressure between 1 to 50 bar during concentration and superheating of the acid and acid vapor.

For the acid vaporization process, the material components utilized must be:

- Corrosion resistant in sulfuric acid with concentrations above 95% and temperatures from 600 to 800 K
- Sufficient mechanical strength to contain the elevated pressure between 2 to 50 bar during concentration and superheating of the acid and acid vapor.

For the acid vaporization process, the material components utilized must be:

- Corrosion resistant in gaseous sulfuric acid, water, oxygen, SO₂ and SO₃ at temperatures between 600 to 1100 K.
- Sufficient mechanical strength to contain the elevated pressure between 3 to 50 bar during concentration and superheating of the acid and acid vapor.

3.3.2.2. Materials Development. After the materials candidates are determined, their long-term stability, processing related issues and other performance related issues will be examined. For the materials to be applicable in Sec. 2, they need to have:

- Long-term mechanical stability.
- Resistance to hydrogen embrittlement and stress corrosion cracking.
- Ability to resist electrochemical attack.
- Corrosion integrity of processed materials, e.g. weld joints, machined surface etc.
- Resistance to small concentration of iodine (and small quantity of bromine depending on the overall process).
- Capability to develop technique to manufacture components from the materials candidate.
- Ease and reliability of processing materials into large sections of different geometry.
- Ease of materials to be joined and processed e.g. welding, machining etc., be readily formable into the desired shape – thus machinability, weldability, etc.
- Possibility in applying the material candidate as a corrosion resistive coating.

3.3.2.3. Materials Qualification. To qualify the selected material candidate(s), prototype(s) of the intended components need to be built and tested under normal and accelerated corrosion conditions. The prototype needs to demonstrate:

- Acceptable serviceability.
- Ease of long term performance monitoring.
- Environmentally compatible.

3.3.3. Section 3 – Hydrogen Iodide Decomposition

3.3.3.1. Materials Selection. The preliminary material selection criteria will be based on the immersion corrosion performance of the candidates under conditions similar to those inside the reactive still (Sec. 3.1.3). Qualified candidate(s) should satisfy the following requirements:

- General corrosion rate TBD ($\sim <0.02$ mm/yr).
- Absence of pitting corrosion.
- Absence of crevice corrosion.
- Absence of intergranular corrosion cracking.

To accomplish this, a special high temperature, high-pressure vessel apparatus has to be assembled for the experiment. A more detailed layout is given in the next section.

3.3.3.2. Materials Development. Once the suitable candidate materials are determined, we need to investigate their performance under more critical working environment and probe their long-term corrosion resistance. Their performance will be gauged based on:

- Dynamic corrosion rate TBD ($\sim <0.03$ mm/yr) i.e. testing with agitation or aeration.
- Minimal hydrogen embrittlement effect.
- Minimal stress corrosion cracking.
- Corrosion integrity of processed materials .e.g. weld joints, machined surface etc.
- Minimal thermal fatigue effects.

In addition to the requirements cited above, the applicability of the chosen materials to component manufacturing will also need to be addressed. These include:

- Ability and cost for the materials to be formed or machined into different form and shape such as pipe, shell heat exchanger, connectors etc.
- Capability to develop technique to manufacture components from the materials candidate.
- Ease and reliability of processing materials into large sections of different geometry.
- Ease of materials to be joined and processed e.g. welding, machining etc.
- Material compatibility with environmental regulation for disposal.
- Galvanic and general compatibility with other parts of the system.
- Ease of monitoring on long term performance of the components.
- Possibility in applying the material candidate as a corrosion resistive coating.

3.3.3.3. Materials Qualification. To qualify the selected material candidate(s), prototype(s) of the intended components need to be built and tested under normal and accelerated corrosion conditions. In addition to demonstrating the corrosion integrity and a capacity to be readily manufactured, the prototype also needs to show:

- Acceptable serviceability.
- Ease of long term performance monitoring.
- Environmentally compatible.

3.4. Materials Testing and Data Base Requirements

Although the literature data does provide a general indication as to the behavior of the materials discussed above in high temperature sulfuric acid, more information is needed for selection of engineering materials for the S-I process. Effects brought about by the processing conditions or impurities present within the acid stream are not addressed by the literature. In addition, there are very limited data available on the corrosion performance of any of these materials in superheated sulfuric acid vapor. As such, it is imperative that each material be evaluated under conditions, which simulate as closely as possible, those that will be present within the reaction vessel itself.

The combination of elevated temperatures and pressures with the highly aggressive environment make the application of traditional electrochemical experimentation difficult, if not impossible. As such, immersion coupon tests remain the only truly viable means to assess the performance of materials to these conditions. Hence, the materials selection process will greatly rely on the materials immersion tests in a setting as close to the real working environment as possible. In the development phase, capturing the effect of stress will also be very difficult, as there are few, if any, materials that could be used to construct the requisite fixture while at the same time not influencing the results of the experiment. Novel techniques will have to be developed to study stress effects, especially hydrogen embrittlement and stress corrosion cracking.

As noted earlier, component materials play a significant role in the initial investment and upkeep cost of the hydrogen plant. Thus, it is beneficial to investigate approaches that can reduce the overall cost. Techniques such as cladding or alternative corrosion control methodology are all worth looking into. The qualified candidates will dictate the direction in the development phase as different materials require different approaches.

3.4.1. Section 1 – Sulfuric Acid and Hydriodic Acid Generation

The materials testing requirement will be same as those for Sec. 3, see Sec. 3.1.1.

3.4.2. Section 2 – Sulfuric Acid Concentration and Decomposition

3.4.2.1. Materials Selection. The combination of elevated temperatures and pressures with the highly aggressive environment make the application of traditional electrochemical experimentation difficult, if not impossible. As such, immersion coupon tests remain the only truly viable means to assess the performance of materials to these conditions. Capturing the effect of stress will also be very difficult, as there are few, if any, materials that could be used to construct the requisite fixture while at the same time not influencing the results of the experiment.

One of the greatest materials testing challenges will be for sulfuric acid vaporization. Exposing test coupons to the boiling acid environment and evaluating their performance will provide only limited data to guide materials selection. For concepts such as the dry wall boiler, replicating relevant environments for all materials may not be possible in coupon testing. Small-scale systems testing will provide the only reliable method for evaluating the performance of materials in these complex environments.

Coupon tests are proposed for the test conditions identified in Table 3-7. Initial screening tests are to be performed for 500 hours, followed by longer-term (1000 hours, or more if possible) tests on materials that appear promising. If possible, test specimens will be manipulated to evaluate the impact of mechanical stress. Following each test series, the coupons will be evaluated to determine the degree weight loss and the nature of the observed attack. An initial test matrix of materials is proposed in Table 3-8. To accomplish this, pressure vessels which can accommodate the high temperature and high pressure will need to be designed, as there is no readily available alternative on the market.

Table 3-7. Proposed Test Conditions for Section 2.

Environment	Chemistry	Temperature	Pressure	Phase
Concentration-1	15% H ₂ SO ₄	Boiling (~375 K)	1 atm	Liquid
Concentration-2	70% H ₂ SO ₄	Boiling (~450 K)	1 atm	Liquid
Concentration-3	95% H ₂ SO ₄	Boiling (~600 K)	1 atm	Liquid
Vaporization-1	95%+ H ₂ SO ₄	700 K	TBD	Liquid/gas
Vaporization-2	95%+ H ₂ SO ₄	800 K	TBD	Liquid/gas
Decomposition-1	H ₂ SO ₄ + H ₂ O + SO ₂ + SO ₃ + O ₂	900 K	TBD	Gas
Decomposition-2	H ₂ SO ₄ + H ₂ O + SO ₂ + SO ₃ + O ₂	1100 K	TBD	Gas

Table 3-8. Proposed Test Matrix for Section 2.

Materials	Concentration-1	Concentration-2	Concentration-3	Vaporization-1	Vaporization-2	Decomposition-1	Decomposition-2
Incoloy 800HT	X	X	X	X	X	X	X
Hastelloy C-276						X	X
Platinum	X	X	X	X	X	X	X
Gold	X	X	X	X	X	X	X
SiC				X	X	X	X
Si ₃ N ₄				X	X	X	X

3.4.2.2. Materials Development. Upon selecting the candidate(s), the test matrix needs to be expanded to understand the processing and long-term environmental effect on its chemical resistance. Table 3-9 shows a test matrix for immersion tests to investigate the different processing techniques on the possible candidates. At present, it is not possible to specify the degree to which contaminants, such as iodine, may be present in the sulfuric acid stream. Therefore, it is proposed to construct the test program to determine the sensitivity of the materials behavior to the presence of these contaminants. This information can then be used to select materials that are insensitive to the expected contaminant levels, or if necessary, impose a limit on the degree to which these contaminants can be carried over into the concentration system. Initially, it is proposed to repeat the test matrix for the most promising materials with the addition of 5 ppm and 50 ppm iodine to evaluate this sensitivity. Additional contaminant tests will be proposed as the system design work continues. This will require in-house capability to process the materials and possibly additional reactors for testing.

One of the key efforts in the development stage is to investigate the use of qualified candidate as cladding material. For example, both platinum and gold may also be capable of containing the acid and mixture with acid. The materials may be applied in the form of a cladding over a stronger, structural alloy (such as a nickel-based material). Caution must be used where clad materials are concerned – a structural material known to be resistant to hydrogen embrittlement should be selected – materials such as high-silicon steels would not be appropriate (note – these materials gain their electrochemical properties due to the silicon dioxide layer which forms on the surface – in a clad application, this layer would not be present). We will need to either acquire the capability to do the cladding or collaborate with other parties to make the cladding possible.

Table 3-9. Materials Test Matrix for Section 2 Development Phase. Actual Materials Will Be Determined by the Selection Processed.

Materials	Laser Machining	TIG and Resistance Welding	Bending	Spinning	Drilling	Rolling
Incoloy 800HT	✓	✓	✓	✓	✓	✓
Hastelloy C-276	✓	✓	✓	✓	✓	✓
SiC (sintered)					✓	
Si ₃ N ₄					✓	

The final issue we will address is alternative corrosion protection to protect the passivation layer. Cathodic and anodic protection is commonly used throughout the chemical process industry (a relevant example being the high-silicon iron piping used in sulfuric acid production) to enable materials which would otherwise be inappropriate (from a corrosion point of view) to be effectively utilized. The two techniques are similar in that they both substantially reduce, or altogether eliminate the oxidation of the protected material. In the case of anodic protection, an externally applied voltage is used to drive oxidation of the metal surface, resulting in the production and maintenance of a protective, passive oxide film on the metal surface. Of the materials described above, it may be possible to protect tantalum and high-silicon iron through this technique. In the case of cathodic protection, an externally applied potential is again utilized. In this case, the applied voltage is used to drive reduction reactions at the metal surface, thereby rendering the metal oxidation reaction thermodynamically unfavorable at the metal surface. This technique would be applicable to most of the materials described above. The primary disadvantage of this technique is that the current required to protect the surface will likely be very high. Alternatively, for materials which exhibit active-passive behavior (such as most of the nickel and iron based materials discussed above), anodic protection may be used. In this technique, the material is polarized anodically (i.e., oxidation is driven on the surface) to the extent that it is driven into the passive regime. Currents required will tend to be significantly lower for anodic protection than for cathodic. This will require a lab-scale set up to test out such ideas.

3.4.3. Section 3 – Hydrogen Iodide Decomposition

3.4.3.1. Materials Selection. In order to duplicate the chamber conditions in the initial materials selection phase; a pressurized vessel heated to temperature is required to perform static immersion corrosion test with material coupons. A schematic of the set up is shown in Fig. 3-4. Specimen is submerged in liquid HI_x for testing within a glass capsule that is closed with a capillary. The capillary helps to equalize the pressure

between the interior of the capsule and the vessel but at the same time minimizes the evaporation of the test liquid. The entire vessel is situated in a tube furnace, which controls the test temperature. In this set up the contact between HI_x liquid and the vessel wall is minimized so that the integrity of the vessel can be assured.

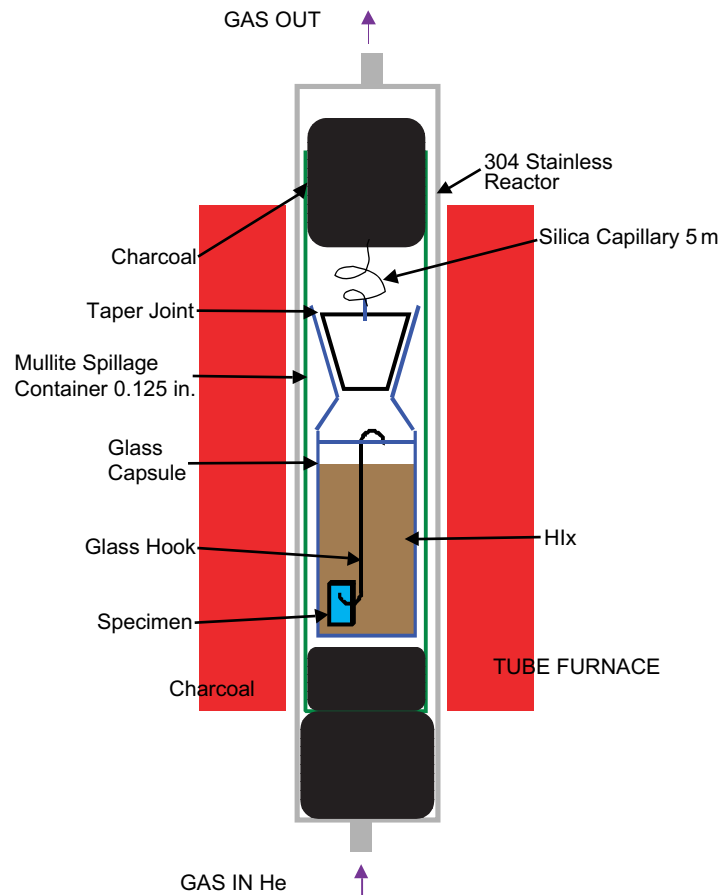


Fig. 3-4. Experimental setup for pressurized high temperature immersion corrosion test.

The test conditions are shown in Table 3-10 and the materials candidates with and a test matrix are listed in Table 3-11. These test conditions represent the most extreme environment that will be encountered in Sec. 3. It is paramount that materials must be able to withstand such setting environment in order for Sec. 3 to work on an industrial scale.

In the initial phase, the immersion test will be run up to a maximum of 100 hrs and during which, specimens will be retrieved from the capsule for analysis at specific time interval to gauge the progression of any corrosion attack. These intervals are 4, 12 and

Table 3-10. Immersion Corrosion Test Conditions for Section 3.

Column Reactants	Test Conditions	Mole Fraction (<i>Weight Fraction</i>)		
		HI	I ₂	H ₂ O
1. Feed HI _x	262°C, 22 bar	0.10 (0.084)	0.38 (0.813)	0.52 (0.079)
2. Column bottom	310°C, 22 bar	0.02 (0.062)	0.89 (0.982)	0.09 (0.007)

Table 3-11. Materials Test Matrix for Section 3 Selection Phase.

	Materials	Condition 1	Condition 2
1	Ta	✓	✓
2	Ta-10%W	✓	✓
3	Mo	✓	✓
4	Nb-1%Zr	✓	✓
5	Nb	✓	✓
6	Zircaloy 702	✓	✓
7	SiC (sintered)	✓	✓
8	Vitreous Carbon	✓	✓

100 h respectively. The coupons will be cleaned, weighted and visually recorded before being returned to the capsule for continuing testing. An outline of the data collection procedure can be found in Appendix A. To successfully complete the selection process, the following items are required:

- Pressurized vessel that can perform at the test temperature.
- Detachable specimen capsules with capillary attachment.
- Furnace which can accommodate the vessel (tube).
- Specimen cleaning and weighting capability.
- Computer system with image capturing capability for data base storage.
- Specimen preparation and analysis facilities: metallography, optical and electron microscopy with elemental analysis capability.

3.4.3.2. Materials Development. In the development stage, a more comprehensive approach to look at different aspects of the qualified materials performance and applicability is required. This include studying:

- Long term corrosion effect of the reaction environment on materials.
- Processing effects on the corrosion integrity of the material candidate.
- The capacity to manufacture components form the selected materials.

Furthermore, other established corrosive resistant materials, such as Ti and Ni based alloys should be tested for they may be applicable to some of the less corrosive environment found through out Sec. 3. They have the potential to provide substantial cost benefits in the manufacturing of various components.

From the preliminary results, three candidates will be selected for an expanded set of testing. The conclusion of the development phase shall yield suitable candidate(s) for building various parts of Sec. 3. The primarily gauge for qualification will still be the immersion corrosion test with test time extended up to 1 year. The coupons will be examined at 1, 5, 10, 26 and 52 weeks respectively. Instead of using virgin material, processed features, such welds and drilled holes will be incorporated into the coupons. Table 3-12 shows the test matrix for extended immersion testing with different processed conditions. Another means to probe the long-term durability of the materials is by using accelerated corrosion test conditions. This will be accomplished by raising the test temperature and a set of proposed test conditions are shown in Table 3-13. The coupon examination interval will be 4 h, 12 h, 100 h, 1 wk and 5 wk. Addition reactors and capability to process the materials will be needed.

Table 3-12. Materials Test Matrix for Section 3 Development Phase. Actual Materials Will Be Determined by the Selection Processed.

Materials	Laser Machining	TIG and Resistance Welding	Bending	Spinning	Drilling	Rolling
Ta	✓	✓	✓	✓	✓	✓
Ta-10% W	✓	✓	✓	✓	✓	✓
Mo	✓	✓	✓	✓	✓	✓
Nb-1% Zr	✓	✓	✓	✓	✓	✓
Nb	✓	✓	✓	✓	✓	✓
Zircaloy 702	✓	✓	✓	✓	✓	✓
SiC (sintered)					✓	✓
Vitreous carbon					✓	✓

Table 3-13. Accelerated Immersion Corrosion Test Conditions for Section 3.

Column Reactants	Test Conditions	Mole Fraction (<i>Weight Fraction</i>)		
		HI	I ₂	H ₂ O
1. Feed HI _x	301°C, 22 bar	0.10 (0.084)	0.38 (0.813)	0.52 (0.079)
2. Feed HI _x	340°C, 22 bar	0.10 (0.084)	0.38 (0.813)	0.52 (0.079)
3. Column bottom	356°C, 22 bar	0.02 (0.062)	0.89 (0.982)	0.09 (0.007)
4. Column bottom	403°C, 22 bar	0.02 (0.062)	0.89 (0.982)	0.09 (0.007)

To help confirm the preliminary results, qualified material corrosion coupons will be tested in the Sec. 3 reactive still prototype that is to be constructed at GA. A schematic of the set up is shown in Fig. 3-5. This prototype column is built from glass and is kept within a pressurized vessel. Coupons can be placed at different locations within the column, which bear the corrosion environment of interest. By running such tests, not only is the testing environment more realistic, the effect of a dynamic circulating flow on the corrosion resistance of the materials can also be judged. Another added advantage is the capacity to study the corrosion effect of any impurities, e.g. H₂S and S, which results from side reactions in the column.

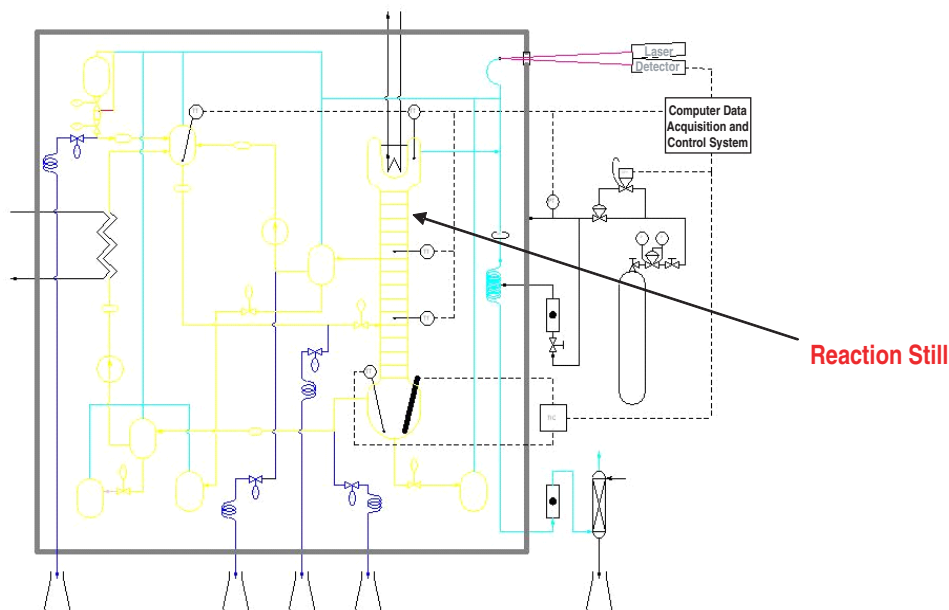


Fig. 3-5. Schematic of the prototype for Section 3.

One of the key long-term performance issues deals with the effect of hydrogen. Hydrogen embrittlement has been shown to cause accelerated crack growth and can lead to catastrophic failure. It is essential to study if the reaction environment will cause the

materials to become brittle. Since it is difficult to do any kind of corrosion crack growth with the present system, we thus propose to test the mechanical properties of tensile test coupons which have been treated/submerged in the corrosion medium at the reaction conditions time scale of 1, 10, 20 and 50 wk. The current reactor design in principle should be able to achieve this. Hence no additional capability is needed.

Another key aspect of the development work is to identify alternative materials that are able to contain HI_x solutions in less corrosive environments and component manufacturing techniques that can reduce the capital investment. The material candidates are the Ti and Ni based corrosion resistant alloys. We shall perform immersion tests with these coupons. Because of the lower temperature requirement, we should also investigate the possibility of using cladding or coated parts for such application in order to reduce the cost. The medium composition will be similar to those listed in Table 3-18. The test temperature will be significantly lower at around 120°C which corresponds to components in parts of the HI decomposition cycle.

Table 3-14. Materials Test Matrix for Section 3 Development Phase. Actual Materials Will Be Determined by the Selection Processed.

Materials	Laser Machining	TIG and Resistance Welding	Bending	Spinning	Drilling	Rolling
Tantalum	✓	✓	✓	✓	✓	✓
Niobium	✓	✓	✓	✓	✓	✓
FeCrMo	✓	✓	✓	✓	✓	✓
304 stainless	✓	✓	✓	✓	✓	✓
Multimet	✓	✓	✓	✓	✓	✓
Hastelloy B	✓	✓	✓	✓	✓	✓
SiC (sintered)					✓	
Graphite					✓	

To accomplish these goals, a much more comprehensive set of testing capabilities is needed. These include:

- Multiple furnaces with pressurized chambers as shown in Fig. 3-5.
- Incorporation of agitation/aeration capability into the apparatus.
- High temperature autoclave lined with perspective candidate material lining for large scale materials testing and to probe the corrosion performance of the coating.
- Material processing capabilities: machining, cold working, welding etc.

- Materials processing capability to deposit the materials as protective coating: plasma spraying, CVD etc.
- Test equipment to determine materials mechanical properties, fatigue performance under environmental conditions, hydrogen embrittlement effect and stress corrosion cracking: Instron or MTS with autoclave.
- Slow strain rate stress corrosion cracking (SCC) testing machine.
- Galvanic corrosion test set up.
- Computer system to collect and store the data generated.
- D/A electronics interfaces to control and monitor large scale and long term testing.

One of the key issues to keep in mind is to understand the overall impact of the selected material on the overall system design. It is not known at this point how this will be addressed as it rest upon the material of choice.

3.4.3.3. Materials Qualification. For the final qualification phase, the key is to monitor the performance of the prototypes in a true working environment. This feedback can be used to improve the manufacturing techniques developed for the various components. One will need non-destructive equipment and techniques to track and analyze the test specimen. They include:

- Ultrasound, eddy current testing, and analytical capability.
- Fluid based test set up to search for crack.
- Automated data collection and analytical system which can be expanded to industrial application.
- Materials analysis in the event of component failure.

3.4.3.4. Regulatory and Codification Requirements. In the course of materials testing detailed in the previous sections, one will encounter hazardous conditions resulting from:

- High temperature and pressure testing vessel.
- Corrosive HI_x liquid within the testing vessel.
- Corrosive HI and I_2 (liquid and gas).
- High pressure inert gas supply to pressurize the vessel.
- Materials processing hazards: plasma spraying, welding etc.
- High power equipment for materials testing.

To have the laboratory function in a safe and sound manner, the safety regulation and design code must be strictly followed for these operations:

- Building and testing the vessel.
- Maintenance and monitoring the performance of the vessel.
- Mixing the HI_x for testing.
- Disposing the HI_x solution after testing.
- Capturing leaked HI_x vapor.

Standard, code and guidelines which are applicable:

- ASME BOILER AND PRESSURE VESSEL CODE Section VIII Div 1 and 2 “Rules for construction of Pressure Vessel,” 1998.
- ANSI B31.1 Power Piping Code.
- ANSI B16.5 Pressure-Temperature Rating for Pipe Flanges and Flanged Fittings.
- EPA: Acute Exposure Guide Line.
- GA IH-Accident Prevention Program Manual for chemical handling and disposal.
- Fusion Safety Manual.

3.5. Industrial Base and Infrastructure Requirements

The size of the components in the hydrogen production plants can measure up to 30 m in length and 8 m in diameter. It is essential to conduct a survey of the process readily available for component manufacturing. Otherwise, techniques will have to be developed to fabricate the parts. Table 3-15 shows the form in which the preliminary selected materials are available and how they can be further processed. For the refractory metal and alloy candidates, there is in general no issue in machining and joining them to form the component size and shape as required. In contrast, SiC and glassy carbon cannot be joint which leads to a requirement in the size of the processing chamber to fabricate the necessary components. Manufacturing of these parts is best to be out-sourced.

For construction of components using the refractory metals, the internal processing equipment need includes:

- e-beam, gas tungsten-arc arc, resistance welding capability.
- Machining capabilities such as: grinding, milling drilling etc.

Table 3-15. Survey of Materials Candidate in Available Form Method of Processing

Materials	Available Form	Processing
Ta	Rod, tube, sheet, plate, wire, strips, billet	Milling, drilling turn, grinding, boring, welding
Ta-10%W	Plate, tube, bar wire	Spinning, bending, drawing, welding, turning, boring, drilling, milling
Mo	Plate, sheet, bar, wire	Grinding, sawing, turning, boring, drilling, milling welding,
Nb-1%Zr	Plate, sheet, billet, bar, wire, rod	Spinning, drawing, grinding, sawing, turning, boring, drilling, milling welding, forging
Nb	Plate, sheet, billet, bar, wire, rod	Spinning, drawing, grinding, sawing, turning, boring, drilling, milling welding, forging
Zircaloy	Ingot, billet, block, bar, plate, sheet, wire, pipe, tubing, castings, fittings, forging	Spinning, drawing, grinding, sawing, turning, boring, drilling, milling welding, forging
SiC (sintered)	As sintered shapes	Grinding, drill, turning, milling
Vitreous Carbon	Tubes, plate	Grinding, sawing, drill, turning, milling

3.6. S-I Backup Cycle — Phosphoric Acid Cycle

HI_x decomposition can be accomplished by another more elaborate means instead of reactive distillation, as discussed earlier. In this scheme, concentrated phosphoric acid is first added to HI_x to separate the majority of HI into a second phase. The chemical potential of water is lowered correspondingly through binding with phosphoric acid. As a result, HI can be separate from the mixture by fractional distillation. The resulting HI is then “cracked” to form the $\text{H}_2 + \text{I}_2$ mixture.

3.6.1. Status — Current Materials Understanding

A review of the literature found no reported corrosion testing results concerning a HI_x and phosphoric acid mixture. On the other hand, there is ample information on materials

used in phosphoric acid related processes. The choice of applicable materials depends mainly on acid concentration and operation temperature. For temperature up to 150°C with low acid concentrations, the 300 series, Ni-Cr and Ni-Mo stainless steel have shown good corrosion resistance. For higher temperature applications with stronger acids, Ni based and Ti-based corrosion resistance alloys have performed well. The corrosion rate for some commercial alloys in phosphoric acid is listed in Table 3-16 and the boiling point for phosphoric acid is plotted in Fig. 3-6. In addition, ceramics and ceramic-coated parts have also been used to contain phosphoric acid. For heat exchanger applications, graphite and tantalum have been used.

Table 3-16. Corrosion Rate of Commercially Available Alloy in Phosphoric Acid

Materials	Conc. (wt%)	Temp. (°C)	Corrosion Rate (mm/yr)
304 stainless	25	Boiling	0.025
Hastelloy B	50	Boiling	0.076
Hastelloy C	85	Boiling	0.71
Fe-Cr29-4Mo	54	Boiling	0.03
Multimet	50	Boiling	0.08
Hastelloy C	85	Boiling	1.14
Hastelloy G	85	Boiling	0.66
Tantalum	85	100	0
Inconel 617	85	Boiling	0.66

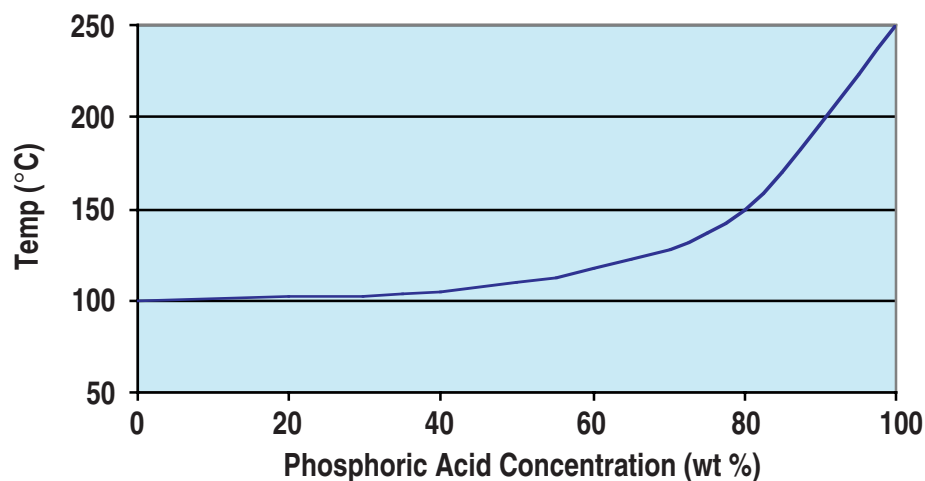


Fig. 3-6. Boiling point of phosphoric acid with respect to concentration.

3.6.2. Materials Selection, Development, and Qualification

The procedures and criteria for materials selection and development are similar to those used in the baseline cycle. The primary effort is to search out materials that have the right corrosion properties. Candidates will then be put through the development process to determine if their long-term corrosion performance and other properties will be suitable for the phosphoric acid HI decomposition cycle.

3.6.2.1. Material Selection. The preliminary material selection criteria will be based on the immersion corrosion performance of the candidates under chemical composition conditions through out the cycle. Qualified candidate(s) should satisfy the following requirements:

- General corrosion rate TBD ($\sim <0.02$ mm/yr).
- Absence of pitting corrosion.
- Absence of crevice corrosion.
- Absence of intergranular corrosion cracking.

The immersion test will be carried out under elevated temperature and pressure in the vessel described earlier.

3.6.2.2. Materials Development. Once the suitable materials candidates are determined, we need to investigate their performance under more critical working environment and probe their long-term corrosion resistance and the effect of corrosion on their other properties. Their performance will be gauged based on:

- Dynamic corrosion rate TBD ($\sim <0.03$ mm/yr) i.e. testing with agitation or aeration.
- Minimal hydrogen embrittlement effect.
- Minimal stress corrosion cracking.
- Corrosion integrity of processed materials .e.g. weld joints, machined surface etc.
- Minimal thermal fatigue effects.

In addition to the requirements cited above, the applicability of the chosen materials to component manufacturing will also need to be addressed. These include:

- Ability and cost for the materials to be formed or machined into different forms and shapes such as pipe, shell heat exchanger, connectors etc.
- Capability to develop techniques to manufacture components from the materials candidate.
- Ease and reliability of processing materials into large sections of different geometry.

- Ease of materials to be joined and processed e.g. welding, machining etc.
- Material compatibility with environmental regulation for disposal.
- Galvanic and general compatibility with other parts of the system.
- Ease of monitoring long term performance of the components.
- Possibility in applying the material candidate as a corrosion resistive coating.

3.6.2.3. Materials Qualification. To qualify the selected material candidate(s), prototype(s) of the intended components need to be built and tested under normal and accelerated corrosion conditions. In addition to demonstrating the corrosion integrity and a capacity to be readily manufactured, the prototype also needs to show:

- Acceptable serviceability.
- Ease of long term performance monitoring.
- Environmentally compatible.

3.6.3. Materials Testing and Data Base Requirements

3.6.3.1. Material Selection. The temperature and pressure requirement for phosphoric acid version of the HI decomposition cycle is lower. On the other hand, phosphoric acid is also present in many parts of the flow sheet. Some of the more severe conditions through out the cycle have been identified and they are listed in Table 3-17 and they will serve as conditions for the corrosion coupon tests. These conditions can be divided into the ones with phosphoric acid only and those that contain HI_x . The materials that will be used for testing will be different between them. Table 3-18 shows a test matrix for the phosphoric acid S-I cycle.

Table 3-17. Phosphoric Acid HI_x Decomposition Column: Physical Conditions and Chemical Content

Column Reactants	Chamber Conditions	Mole Fraction			
		HP_3O_4	HI	I_2	H_2O
1. Conc. HP_3O_4	211°C, 1 bar	0.815	0	0	0.185
2. Column feed	120°-241°C, 3-9 bar	0.514	0.057	0.011	0.418
3. Column off gas	30°C, 9 bar	0	0.998	494 ppmv	990 ppmv
4. Dil. HP_3O_4	250°C, 9.5 bar	0.551	0	0	0.449
5. Reactor feed*	166°C, 51 bar	0	0.499	0.499	996 ppmv

*With an additional mole fraction of 0.00144 H_2 .

Table 3-18. Materials Test Matrix for Phosphoric Acid HI_x Decomposition
(See also Table 3-17)

Materials	Conditions				
	1	2	3	4	5
SiC	✓	✓	✓		✓
Tantalum	✓	✓	✓		✓
Niobium		✓	✓		✓
304 Stainless	✓	✓	✓	✓	✓
Hastelloy B	✓	✓		✓	✓
FeCrMo	✓	✓		✓	✓
Multimet	✓	✓		✓	✓
Graphite	✓	✓	✓	✓	✓

Similar to version 1, the immersion test will be run up to a maximum of 100 h and during which, specimens will be retrieved from the capsule for analysis at specific time interval to gauge the progression of any corrosion attack. These intervals are 4, 12 and 100 h respectively. The coupons will be cleaned, weighted and visually recorded before being returned to the capsule for continuing testing. An outline of the data collection procedure can be found in Appendix A. To successfully complete the selection process, the following items are required:

- Pressurized vessel that can perform at the test temperature.
- Detachable specimen capsules with capillary attachment.
- Furnace which can accommodate the vessel (tube).
- Specimen cleaning and weighting capability.
- Computer system with image capturing capability for data base storage.
- Specimen preparation and analysis facilities: metallography, optical and electron microscopy with elemental analysis capability.

3.6.3.2. Material Development. In the development stage, a more comprehensive approach to look at different aspects of the qualified materials performance and applicability is required. This includes studying:

- Long term corrosion effect of the reaction environment on materials.
- Processing effects on the corrosion integrity of the material candidate.
- The capacity to manufacture components from the selected materials.

From the preliminary results, three candidates will be selected for an expanded set of testing. The conclusion of the development phase shall yield suitable candidate(s) for building various parts of Sec. 3. The primary gauge for qualification will still be the immersion corrosion test with test time extended up to 1 year. The coupons will be examined at 1, 5, 10, 26 and 52 weeks respectively. Instead of using virgin material, processed features, such as welds and drilled holes will be incorporated into the coupons. Table 3-12 shows the test matrix for extended immersion testing with different processed conditions. Another means to probe the long-term durability of the materials is by using accelerated corrosion test conditions. This will be accomplished by raising the test temperature and a set of proposed test conditions are shown in Table 3-13. The coupon examination interval will be 4 h, 12 h, 100 h, 1 wk and 5 wk. Additional reactors and capability to process the materials will be needed.

To accomplish these goals, a much more comprehensive set of testing capabilities is needed. These include:

- Multiple furnaces with pressurized chambers as shown in Fig. 3.5.
- Incorporation of agitation/aeration capability into the set up.
- High temperature autoclave lined with perspective candidate material lining for large scale materials testing and to probe the corrosion performance of the coating.
- Material processing capabilities: machining, cold working, welding, etc.
- Materials processing capability to deposit the materials as protective coating: plasma spraying, CVD, etc.
- Test equipment to determine materials mechanical properties, fatigue performance under environmental conditions, hydrogen embrittlement effect and stress corrosion cracking: Instron or MTS with autoclave.
- Slow strain rate stress corrosion cracking (SCC) testing machine.
- Galvanic corrosion test set up.
- Computer system to collect and store the data generated.
- D/A electronics interfaces to control and monitor large scale and long term testing.

One of the key issues to keep in mind is to understand the overall impact of the selected material on the overall system design. It is not known at this point how this will be addressed as it rests upon the material of choice.

3.6.3.3. Materials Qualification. For the final qualification phase, the key is to monitor the performance of the prototypes in a true working environment. This feedback can be

used to improve the manufacturing techniques developed for the various components. One will need non-destructive equipment and technique to track and analyze the test specimen. They include:

- Ultrasound and eddy current testing and analytical capability.
- Fluid based test set up to search for crack.
- Automated data collection and analytical system which can be expanded into industrial application.
- Materials analysis in the event of component failure.

4. Development Tasks, Costs, and Schedules for S-I Materials

4.1. Materials Selection

Task	Cost	Completion
Corrosion laboratory (Phase 1)	TBD	12/2004
High temperature and pressure immersion corrosion test set up	TBD	6/2004
Materials data base initiation	TBD	6/2004

4.2. Materials Development

Task	Cost	Completion
Corrosion laboratory (Phase 2)	TBD	TBD
Long term corrosion testing	TBD	TBD
Processing effects on corrosion resistance	TBD	TBD
Corrosion resistive coatings	TBD	TBD
Version manufacturing guide	TBD	TBD

4.3. Materials Qualification

Task	Cost	Completion
Prototyping	TBD	TBD
Final report and recommendation	TBD	TBD

5. Summary

The materials containment candidates for the three chemical sections within the SI thermochemical hydrogen production cycle have been selected. The sections are: (i) *Sulfuric Acid and HI Generation (Bunsen Reaction)*, (ii) *Sulfuric Acid Concentration and Decomposition* and (iii) *HI Decomposition* respectively. Two different HI decomposition processes, Reactive distillation and extractive distillation are considered in this report. A plan to develop and qualify these candidates for component fabrication has also been laid out.

The flowsheet of each individual section has been reviewed to identify the critical corrosive environment(s) within the reaction loops. These are the conditions in which the construction materials will be subjected to. Based on these, a literature review was conducted and the information was used to help select suitable materials candidate(s) for the different sections. For the sulfuric acid concentration and decomposition reactions, Fe, Ni, Co based super alloys along with certain ceramics materials were chosen for further testing. For the HI decomposition process, refractive metals such as Ta, Nb and Mo and their alloys were identified as leading candidates for their demonstrated stability in an iodine environment. In addition, Zr alloys and ceramics are also included on the list. The candidates chosen for HI decomposition will be applicable to the Bunsen reaction as the chemicals and reaction conditions involved are very similar. In addition, it was concluded that priority should be placed on the effort to develop materials used in the HI reactive distillation and sulfuric acid decomposition processes as these reaction environment poses the greatest obstacles to moving the SI cycle from the laboratory to the industrial floor.

The materials development and qualification plan can be broken down to three stages. First, corrosion immersion coupon tests will be conducted at the critical reaction conditions to narrow the list of containment material candidates. The second stage probes the effect of materials processing steps such as welding and mechanical deformation on the corrosion resistant of the materials. The first two stages will require custom design autoclaves that can accommodate the specimens and provide the required temperature and pressure. Finally, prototype components will be fabricated from the qualified material to gauge its performance within the actual reaction loop. This will provide knowledge useful in scaling the components up to an industrial scale.

The initial materials selection process is expected to be completed by June 2004 based on early test results of the immersion corrosion coupon tests. The second stage will begin in the fall of 2004 on at least one candidate albeit the immersion corrosion coupons will continue. The first metal section prototype is scheduled be fabricated in early 2006.

Appendix A: GA Results (1977–1981) Summary from Trester and Staley [1]

Materials Tested									
Test	HI	I ₂	H ₂ O	Temp	Pres.	Time	Excellent	Fair	Poor
1	20% ¹ (4%) ²	20% (2%)	60% (93%)	295 K	atm	8760 h	Mo, Nb-1%Zr, Ta, Ta-10%W, Ti (as cast), Ti-0.5%Pd, Zr, Zircaloy 2 TFE, FEP, Kalrez 1050, Kel-F 3700, fluorel 2174, viton A, Parker V-834-70	Chlorimet 2 & 3, Hastelloy B2 and C276 PVC, polycarbonate, vespel Sp.1, CPE, FETFE	Inconel 600, monel, Haynes, Hastelloy G, 304 stainless Nylon, mylar, silicone
2	30% (15%)	50% (13%)	20% (72%)	573- 723 K	13.1 — 17.2 MPa	5—10 h	Mo, Ta	Ti	Inconel 600
3	11% (11%)	82% (40%)	7% (49%)	370 K	atm	3170 h	Mo, Nb-1%Zr, Ta, Zr TFE, FEP, PFA, Tefzel (Teflon) SiC, alumina, boronsilicate glass	Ti—0.2%Pd(annodized), Hastelloy B2, Durichlor 51, Zircaloy 2, Zr702 Kynar 450 Zirconia	Duriron D, Chlorimet 2, Hastelloy B2 and C276, Ti- 0.5%Pd, gold, platinum CPVC, polypropylene
4	11% (11%)	82% (40%)	7% (49%)	398 K	atm	500 h	Mo, Nb, Nb-1%Zr, Ta Alumina, vitreous carbon	TFE, FEP, PFA	Lead Viton VTX 5362, viton B, carbonrundum
5 ³	24% (12%)	55% (14%)	21% (74%)	407 K	atm	178 h	Mo, Nb, Nb-1%Zr, Ta, Zircaloy 2, Ta-10%W, Zr	Ti—0.5%Pd	Ti-0.2%Fe-0.25%O (annodize Ti)

¹ wt%, ² molar%, ³ circulating HI_x.

Ni based alloys: Hastelloy, Chlorimet, Inconel and Monel; Iron based alloys: Duriron, Durichlor; Cobalt based alloys: Haynes Summary.

Appendix B: Specimen Cleaning Procedure for Data Collection (wrt ASTM G31)

- Remove specimen from container with TFE coated tongs.
- Rinse specimen with potassium iodine solution.
- Soak (30 s) and rinse the specimen in acetone.
- Soak (30 s) and rinse the specimen in alcohol.
- Dry with hot air.
- Take picture and collect weight.
- Clean with alcohol ultrasound bath for 3 min.
- Rinse specimen in alcohol for 30 s.
- Take picture and collect weight.
- Collect residue if any.
- Return specimen to HI_x test liquid.

Appendix C: Applicable Standards and Reports

Standard test and guidelines used in corrosion testing and materials development.

C.1. NACE

TM0169-2000 Laboratory Corrosion Testing of Metals

TM0499-99 Immersion Corrosion Testing of Ceramic Materials

TM0177-96 Laboratory Testing of Metals for Resistance to Sulfide Stress Cracking and Stress Corrosion Cracking in H₂S Environments

TM0299-99 Corrosion Control and Monitoring in Seawater Injection Systems

A577/A577M-90(2001) Standard Specification for Ultrasonic Angle-Beam Examination of Steel Plates

RP0296-2000 Guidelines for Detection, Repair, and Mitigation of Cracking of Existing Petroleum Refinery Pressure Vessels in Wet H₂S Environments.

RP0192-98 Monitoring Corrosion in Oil and Gas Production with Iron Counts

RP0300-2003 Pilot Scale Evaluation of Corrosion and Fouling Control Additives for Open Recirculating Cooling Water Systems

RP0497-97 Field Corrosion Evaluation Using Metallic Test Specimens

C.2. ASTM

G31-72 Laboratory Immersion Corrosion Testing of Metals

G111-97 Standard Guide for Corrosion Tests in High Temperature or High Pressure Environment, or Both

G96-90(2001)e1 Standard Guide for On-Line Monitoring of Corrosion in Plant Equipment (Electrical and Electrochemical Methods)

G30 Practice for Making and Using U-Bend Stress-Corrosion Test Specimens

G38 Practice for Making and Using C-Ring Stress-Corrosion Test Specimens

G39 Practice for Preparation and Use of Bent-Beam Stress-Corrosion Specimens

G58-85(1999) Standard Practice for Preparation of Stress-Corrosion Test Specimens for Weldments

G36-94(2000) Standard Practice for Evaluating Stress-Corrosion-Cracking Resistance of Metals and Alloys in a Boiling Magnesium Chloride Solution

G1 Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens

- G3 Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing
- G5 Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements
- G15 Terminology Relating to Corrosion and Corrosion Testing
- G30 Practice for Making and Using U-Bend Stress-Corrosion Test Specimens
- G31 Practice for Laboratory Immersion Corrosion Testing of Metals
- G34 Test Method for Exfoliation Corrosion Susceptibility in 2XXX and 7XXX Series Aluminum Alloys (EXCO Test)
- G38 Practice for Making and Using C-Ring Stress-Corrosion Test Specimens
- G39 Practice for Preparation and Use of Bent-Beam Stress-Corrosion Specimens
- G46 Guide for Examination and Evaluation of Pitting Corrosion
- G48 Test Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by Use of Ferric Chloride Solution
- G49 Practice for Preparation and Use of Direct Tension Stress-Corrosion Test Specimens
- G59 Practice for Conducting Potentiodynamic Polarization Resistance Measurements
- G78 Guide for Crevice Corrosion Testing of Iron-Base and Nickel-Base Stainless Alloys in Seawater and Other Chloride-Containing Aqueous Environments
- G106 Practice for Verification of Algorithm and Equipment for Electrochemical Impedance Measurements
- G58-85(1999) Standard Practice for Preparation of Stress-Corrosion Test Specimens for Weldments
- G111-97 Standard Guide for Corrosion Tests in High Temperature or High Pressure Environment, or Both