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SIXTH QUARTERLY PROGRESS REPORT

1 JANUARY TO 31 MARCH 1981

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(PHASE 1)

prepared by

J. McCormick, A. Arvidson, D. Sawyer and F. Plahutnik

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June 1981

JPL Contract 955533

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HSC HEMLOCK SEMICONDUCTOR CORPORATION
a wholly owned subsidiary of Dow Corning Corporation
12334 Geddes Rd., Hemlock, Michigan 48626

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ABSTRACT

The goal of this program is to demonstrate that a dichlorosilane-based reductive chemical vapor deposition (CVD) process is capable of producing, at low cost, high quality polycrystalline silicon. Physical form and purity of this material will be consistent with LSA material requirements for use in the manufacture of high efficiency solar cells.

Experimental data generated by Hazards Research Corp. indicate that the ease of ignition and explosion severity of dichlorosilane (DCS)/air mixtures is substantially attenuated if the DCS is diluted with hydrogen. DCS/hydrogen mixtures will accordingly be transported in preference to transfer or storage of pure DCS.

Testing of decomposition reactor heat shields to insure that the shield provides adequate personnel protection assuming a worst case explosion was completed. Minor modifications to a production reactor heat shield provided adequate heat shield integrity.

Construction of the redesigned PDU (Process Development Unit) to accommodate all safety related information is proceeding on schedule. Structural steel work is completed as is the piping and instrumentation design work. Major pieces of process equipment have been received and positioned in the support structure and all transfer piping and conduits to the PDU have been installed. Start-up is scheduled for June, 1981.

Construction was completed on a feed system for supplying DCS to an intermediate sized reactor. The feed system was successfully interfaced with a reactor equipped with a modified heat shield. Reactor checkout was completed and testing to establish baseline PDU operating conditions will be completed early in the second quarter of 1982.

Preliminary EPSDU design was completed. Base case assumption was for a 220 ton/yr. unit which would not include a hydrogenation process.

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1.0 Summary

This report describes a process for the low-cost production of polycrystalline silicon from dichlorosilane (DCS) via reductive chemical vapor deposition (CVD) with hydrogen. The DCS is generated from the catalyzed redistribution of trichlorosilane. The by-product silicon tetrachloride may, if desirable, be converted to trichlorosilane via hydrogenation. Objectives of Phase 1 (the current contract) are to demonstrate the feasibility of using DCS as a CVD reactor feed material and to utilize base catalyzed redistribution of trichlorosilane to produce high purity DCS. Phases 2 and 3 of the program will demonstrate the technology readiness of the process at the EPSDU level.

Experimental data generated by Hazards Research Corp. indicate that the ease of ignition and explosion severity of dichlorosilane (DCS)/air mixtures is substantially attenuated if the DCS is diluted with hydrogen. DCS/hydrogen mixtures will be transported accordingly in preference to transfer or storage of pure DCS.

Redesign of the PDU (Process Development Unit) to accommodate this new safety-related information is complete. All major process equipment has been ordered, and construction of the facility is on schedule, with start-up scheduled for June, 1981.

Testing of decomposition reactor heat shields to insure that they provide adequate personnel protection, assuming a worst case explosion, was completed. Two heat shields were tested. Minor modifications to a production reactor heat shield resulted in a structure of adequate structural strength to withstand a DCS/H_2/Air explosion.

Construction of the redesigned PDU (Process Development Unit) to accommodate all safety related information proceeded on schedule. Structural steel work is completed as is piping and instrumentation design work. Major pieces of process

equipment have been received and are positioned in the support structure. Transfer piping and conduits to the PDU have been installed and start-up is anticipated for June 1981.

Preliminary EPSDU design is complete. The base case assumption is for a 220 metric ton/yr plant with no provisions for silicon tetrachloride hydrogenation. High purity trichlorosilane will be purchased as feedstock with high purity polycrystalline silicon, silicon tetrachloride and hydrogen chloride being EPSDU products.

Silicon grown in the experimental reactor from commerically purchased DCS was converted to single crystal material and solar cells fabricated. Cell efficiencies met or exceeded baseline cell efficiencies.

2.0 Introduction

2.1 Program Objectives

The objective of this program is to demonstrate that a chlorosilane based chemical vapor deposition (CVD) process can produce a low cost polycrystalline silicon in high volume. Product quality both in terms of purity and form should be comparable to material produced by the existing trichlorosilane (TCS) CVD process which meets or exceeds requirements for use in the manufacture of high efficiency solar cells.

The overall program covers a 42 month period and consists of a feasibility phase, which is the subject of the current contract, an EPSDU design phase, and an EPSDU construction/demonstration phase. The schedule for the program is shown in Figure 1. Specific Phase 1 project objectives include:

1. Characterization of dichlorosilane (DCS) as a feedstock material for an experimental CVD reactor including quantitative determination of reaction products. (CVD Reactor Feasibility)

2. Design and construction of a DCS CVD reactor which will demonstrate DCS performance in a larger size reactor. (Intermediate Dichlorosilane Reactor Development)

3. Design, construction, and operation of a laboratory scale redistribution reactor and a process development unit (PDU) to characterize the TCS-to-DCS redistribution process, determine product purity, and produce sufficient DCS to permit operation of a production sized reactor. (Dichlorosilane Process/Product Evaluation)

4. Conduct preliminary design of an EPSDU based on information collected in the areas previously described and develop supporting information for an economic evaluation of a 1000 metric ton plant. (EPSDU Design)

The general approach taken in meeting the overall program objective for the 1000 MT/Y plant will consist of: the hydrogenation of silicon tetrachloride (STC) to produce TCS; synthesis of DCS via redistribution of TCS; high temperature decomposition of DCS to produce polycrystalline silicon; and recovery of decomposition by-products. STC, a major by-product of TCS redistribution and minor byproduct of DCS decomposition, is recycled into the hydrogenation process.

The basic chemical nature of the various steps in the DCS-based low-cost silicon process have been described in previous Quarterly Reports.[1,2]

3.0 Technical Status

Phase 1 technical efforts are limited to the four areas discussed in Section 2.1. No effort is being expended in the area of STC hydrogenation due to JPL support of the Union Carbide program. Also, no effort is being devoted to the development of CVD reactor vent product recovery technology. This technology is closely aligned with recovery system technology currently employed in the TCS CVD process at Hemlock Semiconductor Corporation. Phase 1 efforts thus consist of the following:

CVD Reactor Feasibility
Intermediate Dichlorosilane Reactor Development
DCS Process/Product Evaluation
EPSDU Design
1000 Tonne Plant Preliminary Design
1000 Tonne Plant Economic Analysis

A milestone chart detailing work to be accomplished in these four general areas is shown in Figure 2. The four major areas of technical activity are discussed in Sections 3.1 through 3.5.

3.1 CVD Reactor Feasibility

This task has been successfully completed; results are described in detail in previous reports.(1-3)

3.2 Intermediate Reactor Development

3.2.1 Objectives

The safe and efficient production of polycrystalline silicon from commercially purchased dichlorosilane, as well as the dichlorosilane produced by the process demonstration unit (PDU) installed at HSC, is to be demonstrated in an intermediate sized reactor. This task includes the following specific goals:

1. Design and installation of a reactor/feed system for safe handling of DCS from a 250 pound cylinder source.

2. Installation and checkout of a gas chromatographic analytical support system.

3. Integration of the intermediate sized reactor with the dichlorosilane PDU. The reactor/reactor feed system using purchased dichlorosilane contained in 250 lb. cylinders provides data to establish baseline conditions for integrated reactor/PDU operation.

4. Collection and evaluation of operational data on the DCS/hydrogen reactor system.

3.2.2 Reactor and Feed System Design

3.2.2.1 Dichlorosilane-Hydrogen Vaporizer System

The system for feeding a mixture of dichlorosilane and hydrogen was constructed, installed, and operated during this quarter. A system is shown schematically in Figure 3. The vaporizer system consists of a 250 pound dichlorosilane cylinder from which liquid is withdrawn and fed to a packed bed countercurrent contactor for vaporization and mixing with preheated hydrogen. The resulting mixture is then fed to the polysilicon decomposition reactor. Because of the flammability and explosion hazards associated with pure dichlorosilane, the vaporizer system itself is remotely located from the reactor area and equipped with pneumatic control and safety valving. Its operation can be controlled or shut down from the reactor site. Personnel exposure is thus limited and a "safety buffer zone" will exist in the event of fire or explosion at the vaporizer site. As a further precaution this system will only be operated if the ambient temperature is below 40 ^{o}F (the boiling point of dichlorosilane).

3.2.2.2 Reactor System

As reported previously, unmodified reactor heat shields lack adequate structural integrity to contain an explosion of DCS/H_2/Air and insure personnel safety. Based on the use of a reactor feed stream consisting of 90 mole percent hydrogen and 10 mole percent dichlorosilane calculated maximum pressure is generated for a gas mixture within the reactor of:

27% by volume H_2
3% by volume Dichlorosilane
70% by volume Air

Assuming an adiabatic expansion of these gases upon ignition, calculated pressure on the inner heat shield wall reaches a pressure of 77 psig assuming deflagration occurs rather than detonation.

Explosion Test Results

Explosion testing was conducted at the Dow Chemical Systems Research Laboratory (Larkin Laboratory test facility). Two tests of reactor heat shields were conducted.

Explosion testing involved (1) setting up the reactor system as shown schematically in Figure 4, (2) filling the quartz bell jar with the dichlorosilane-hydrogen-air test mixture and (3) initiating the explosion via the spark generation detonator wire which was within the quartz bell jar.

As mentioned previously two heat shields were tested. The first was equipped with heat shield extensions which were retrofitted, i.e., top and bottom heat shield extensions were held in place with sheet metal screws. During the first explosion test both top and bottom extensions were blown off (velocity was calculated at >50 mph), (2) the top clamp device was blown off and the middle clamp device opened, and (3) the bell jar hold down mechanism was blown out the top of the heat shield. The explosion occurred in a span of 0.030 seconds indicating deflagration. The heat shield contained broken quartz fragments but did not maintain mechanical integrity.

This heat shield design was not considered "safe" for use on the dichlorosilane project.

The second explosion test was conducted with a heat shield modified with extensions integrated into the main heat shield, (1) clamp bolts were extended in length and equipped with backing plates and nuts to distribute the force and (2) the bell jar "hold down mechanism" was pinned to the hold down arm. The explosion test was conducted as before except (1) the detonator was placed near the baseplate as opposed to the center of the jar in order to allow a maximum flame front travel distance in hope of propagating a detonation (worst case), (2) steel pads were placed under the reactor table legs to prevent loss of some of the explosive force due to driving the table legs into the soil which occurred during the first explosion test. The explosion again occurred in 0.03 seconds indicating deflagration. The diaphragms in all the Bikini gauges remained intact indicating overpressures of less than 0.5 psig at 10 feet from the reactor. The heat shield was highly stressed during this explosion. However, it maintained its integrity. Some quartz fragments escaped via the top opening in the heat shield but not in amounts that would pose a serious personnel risk. These fragments could easily be stopped via a coarse screen (<0.5 inch openings) placed above the quartz bell jar. This heat shield design was considered "safe" for use on the dichlorosilane project.

3.2.2.3 Gas Chromatographic Support System

A Bendix gas chromatograph has been installed and coupled to the present Sigma data collection system for use with the above polysilicon reactor. A schematic diagram of this system is presented in Figure 5.

3.2.2.4 System Integration

An intermediate sized reactor was equipped with a modified heat shield and valve panel to permit integration with the DCS-H_2 vaporizor and Bendix Gas Chromatograph system. System integration was completed and system check completed. The initial DCS run was completed without difficulty.

Results of the first set of decomposition experiments will be reported in the next quarterly progress report.

3.2.3 Experimental Results

The purpose of this cylinder fed DCS reactor work is to provide baseline data for selecting operational parameters for DCS PDU start-up.

System integration and check out was completed late this quarter. Data collection is very limited and requires further analysis.

3.3 Dichlorosilane Process/Product Evaluation

3.3.1 General

The objectives of this task are:

1. Establish purity of DCS produced via catalyzed redistribution of TCS.

2. Permit characterization and optimization of the redistribution process through design, construction, and operation of a laboratory rearranger unit (PDU support) and a process development unit (PDU), and provide design information for the EPSDU and 1000 metric ton plant.

3. Provide sufficient DCS at a reasonable cost from the PDU to permit regular operation of an intermediate size CVD reactor at high feed rates.

These objectives will be met through dual tasks designed to provide a data base for PDU design and operation, and actual PDU design, construction and optimization. The PDU support effort is discussed in section 3.3.2 while PDU design activities are reviewed in section 3.3.3.

3.3.2 PDU Support

Since the PDU is integrated with operation of the Hemlock Semiconductor plant, it is essential that dichlorosilane processing not contaminate any HSC process streams. Several different sources of trichlorosilane were evaluated to establish material suitability as feed to the redistribution reactor. Purity evaluation of three grades of trichlorosilane using the laboratory rearranger and experimental reactor 394 was completed. Purity data for all three sources is presented in Table 1.

Two of the three sources (B and C) yield silicon with less than 0.3 ppba boron. The third source (A) yields silicon with greater than 0.4 ppba boron. Although this level of boron is well within the requirements of solar grade silicon the PDU-Reactor integration with the overall Hemlock Semiconductor plant dictate use of source B or C. All sources yield silicon with equivalent levels of donor, aluminum and carbon.

3.3.3 PDU Design and Construction

3.3.3.1 PDU Design

Design of a PDU capable of producing DCS in adequate quantity and quality to establish the ability of the redistribution process to meet program objectives and provide sufficient material for decomposition reactor evaluation was completed. The detailed design of the PDU is shown in Figure 6.

Trichlorosilane is received from a plant storage tank and heated in a shell and tube heat exchanger (2504). The hot TCS is passed through the redistribution reactor (2502), which contains Dowex MWA-1® ion exchange resin, in which the TCS is redistributed to DCS, and STC. The effluent from the redistribution reactor is approximately 10% mol DCS, 10% mol STC and 80% mol TCS. This mixture is fed to the distillation column (2501) where the DCS is removed overhead as a vapor and the TCS and STC are removed as liquid from the bottom of the column. The DCS is mixed with hydrogen and is discharged to a feed line supplying the decomposition reactors.

Equipment identified in Figure 6 includes:

1. Feed tank. HSC storage tank is used as the feed supply tank for trichlorosilane.

2. The feed pump is a Chempump, model GB 1 1/2K-751H-1S with a 5 1/2 inch impeller.

3. The feed heater (2504) is a Doyle and Roth Model LLS66U4-HH with 13 square feet of surface area. It is heated with steam on the shell side and the TCS flows through the tubes.

4. The redistribution reactor (2502) is a 3 inch by 14 foot pipe filled with Dowex MWA-1® resin. The catalyst is contained by Mack Iron strainers with 65 mesh screen.

5. The strainer is a Filterite Model G10AW20S with G20AW20S elements and 10520-031 gaskets.

6. The distillation column (2501) is a 10 inch by 30 foot column with Goodloe packing. There are 8.5 feet of packing above the feed tray and 6.5 feet of packing below.

7. The reboiler (2503) is a Doyle and Roth Model VT661-4V shell and tube reboiler, with 20 square feet of surface. The reboiler has steam on the shell side and chlorosilanes in the tubes.

8. The condenser (2505) is a Doyle and Roth Model VS66U4-8H with 25 square feet of area. Service water is in the tubes and chlorosilanes in the shell.

Overall process control is achieved with the following instrumentation and control scheme.

Trichlorosilane is supplied to the feed preheater via the Chempump . If this pump cavitates or is run with the suction side closed, the pump will automatically shut off due to activation of the pressure differential switch low (PDSL-1). Also, if low feed flow is detected by flow switch low (FSL-2), then steam to the trichlorosilane preheater is shut off.

The trichlorosilane feed flow rate is controlled by flow indicator and controller 2 (FIC-2). FIC-2 receives a setpoint from feed forward multiplier FY-2-2 initiated by feed forward multiplier FY-2-1 and fine tuned with feedback trim from the temperature differential indicator and controller 8 (TDIC-8). The objective of this control scheme is to initiate feed flow proportionally to the overhead product use rate. TDIC-8 adjusts the feed to product take off ratio to maintain the desired overhead product purity. FIC-2 adjusts the flow valve (FV-2) until the flow, as transmitted by flow transmitter 2 (FT-2) coincides with the flow required by FY-2-2.

The feed temperature is controlled by temperature indicator and controller 3 (TIC-3). If the temperature transmitted (by TT-3) is different than the set point, TIC-3 will adjust the steam valve (TV-3) to allow more or less steam flow to the preheater.

The pressure in the DCS/H_2 feed line is maintained by pressure indicator and controller 4 (PIC-4). If the pressure transmitted by PT-4 is different than setpoint, PIC-4 will adjust the hydrogen valve, PV-4, allowing more or less hydrogen flow to effect the required pressure in the feed line.

The DCS/H_2 ratio in the DCS/H_2 feed line going to the decomposition reactors is established by use of flow fraction indicator and controller 5, FFIC-5. Flow transmitter 5-1 (FT-5) transmits the flow rate of hydrogen which is established by PIC-4 through operation of PV-4. FFIC-5 activates the DCS flow control valve (FV-5) until the flow of DCS as transmitted by FT-5-2 is the same as required by FFIC-5. During normal modes of operation FFIC-5 has its setpoint positioned to allow 1 mole DCS per 9 moles H_2, resulting in a 10 mole percent DCS in H_2 mixture.

Distillation column pressure is controlled by pressure indicator and controller 6 (PIC-6). If pressure is above the set point, PIC-6 adjusts the pressure control valve PV-6 to allow non-condensables to flow from the system. High pressure is alarmed by pressure alarm high-6 (PAH-6) which receives its input from pressure transmitter 6 (PT-6).

Distillation column bottoms and overhead temperature, vent temperature, and TCS feed temperature are recorded on temperature recorder TJR-7. Items labeled TE-7-1, TE-7-2, TE-7-3, and TE-7-4 are thermocouples.

Differential temperature of the column is used to tune the feed to product ratio as previously described. Temperature differential indicator and controller 8 (TDIC-8) provides feed back control as described above. TDIC-8 receives input from thermocouples TE-8-1 and TE-8-2. Reflux flow to the column is maintained by flow indicator and controller 9 (FIC-9) in conjunction with the reboiler steam flow indicator and controller (FIC-10).

FIC-9 is used to monitor and control DCS vapor going to the condenser. If the vapor rate is not at setpoint FIC-9 adjusts the setpoint of FIC-10. FIC-10 then adjusts the steam flow valve FV-10 until the setpoint established by FIC-9 is attained.

Bottoms level is controlled by a Fischer Leveltrol (LC-11). When the liquid level in the column is too high or too low, LC-11 adjusts the bottoms take off valve LV-11 to increase or decrease bottoms flow. Bottoms level is indicated by LC-11, located at the control panel.

Automatic high pressure shut down is affected by the pressure switch high-12 (PSHH-12). If the pressure is at or above 80 psig PSHH-12 activates and stops all process and steam flows. Manual operation of the shut down circuit occurs by activating hand switch 12, (HS-12).

Steam pressure to the process is controlled by a pressure regulator PCV-13. The steam supply line pressure is kept at 80 psig to insure the control valves for steam will work well.

A nitrogen purge of the system can be initiated remotely by activation of hand switch 14.

Rotameters used to set nitrogen purge rate to the overpressure relief discharge piping are labeled FIVC-15 and FIVC-16.

Blowing the column dry is accomplished by HS-17, which is a hand switch used to remotely open a bypass around the bottoms level control valve.

3.3.3.2 PDU Construction

PDU construction is on schedule. All detailed designs have been completed. All equipment is on site and has been mounted at the site, and transfer piping to the facility completed.

3.3.4 PDU Evaluation

No activity has occurred in this area. PDU start-up is scheduled for early June 1981.

3.4 Preliminary EPSDU Design

3.4.1 General Description and Technical Objectives

The proposed Experimental Process System Demonstration Unit (EPSDU) is designed to produce 220 tonne/yr of polycrystalline silicon in a plant that uses TCS as feedstock and has products of silicon, silicon tetrachloride (STC), and HCl. The plant is to be totally independent of the existing production facilities at Hemlock Semiconductor Corporation (HSC), although it will use plant services such as steam, electrical, water, hydrogen, nitrogen, and air.

Technical objectives of the EPSDU are to demonstrate:

1. 2.5-3.0 Kg/hr/Rx deposition rates
2. 70 KWH/Kg or less electric power consumption at the decomposition reactor.
3. adequacy of the equipment selections for DCS production, purification, and the hydrogen recovery system.
4. adequate silicon purity and surface quality for use as solar grade silicon.

3.4.2 EPSDU Design

This section serves as a preliminary process package for the EPSDU. Process Flow Diagrams (PFD'S) are included as are tables showing flow, storage requirements, and raw materials and services summaries.

3.4.2.1 Safety

DCS was found to have unusually severe combustion characteristics. Results, as reported by Hazards Research Corporation, have been reported in previous monthly and quarterly reports.[4,5] The underlying conclusion is that detonation of DCS/air mixtures is possible, with an approximate TNT equivalent of 1 lb TNT/lb of DCS released as a vapor. Therefore, remote location of equipment containing high concentrations of DCS must be employed. Mixtures of H_2 and DCS

(90% H_2 and 10% H_2) have combustion characteristics similar to hydrogen. Hydrogen will therefore be used to transport the DCS.

3.4.2.2 General Process Description

Figure 7 represents the EPSDU process in block diagram form. TCS will be purchased and polycrystalline silicon, STC, and HCl sold in EPSDU operation.

The redistribution reactor converts the TCS to a mixture of DCS, TCS, and STC. This mixture will be distilled to separate the DCS from the TCS and STC. The DCS will be mixed with H_2 and fed directly to chemical vapor decomposition reactors. The TCS and STC mixture will be fed to another distillation column where separation occurs. TCS will be recycled to the redistribution reactor and the STC by-product will be sold.

The DCS will be reduced to polycrystalline silicon in the decomposition reactors. Gaseous effluent from the reactors contains HCL, DCS, TCS, STC, and H_2. The recovery system will separate the H_2 from the rest of the mixture for recycle to the decomposition reactors. HCl will be sold. All recovered chlorosilanes will be sent to the EPSDU distillation area for separation.

3.4.2.3 EPSDU Design

Figures 8 and 9 are process flow diagrams of the EPSDU. Table 2 contains flow rate and composition data corresponding to operation at 220 tonne/yr silicon production and 85% on-line time. Line designation is by numbers placed near the lines. Numbers that are at line beginnings or ends represent the line number continuation on another figure. Controls are not shown since they will essentially encompass existing designs or standard practice. Equipment has been labeled with letters.

3.4.2.3.1 Redistribution - Distillation Process Description

Purchased TCS will be placed in feed tank AC via line 104. Recovered chlorosilanes will be placed in storage tank AA via line 103. On a demand basis, chlorosilanes will be fed to distillation column, AH, through the preheater, AG, and the redistribution reactor, AF, to produce DCS in near equilibrium concentrations. AE represents a filter to remove any fine catalyst particles that may be carried over from the redistribution reactor.

The DCS distillation column, AH, will separate DCS from the TCS and STC. The DCS will be removed as a vapor from the distillation column top (line 110) and immediately mixed with H_2 (line 109). The mixture will be sent to the decomposition area via line 113. The TCS and STC will flow from the bottom of distillation column AH to distillation column AK via line 115.

Distillation column AK will separate the TCS from the STC. The TCS will be sent to storage tank AC. The STC will be sent to tank AN for storage prior to sale.

Line 120 will supply STC for dilution of recovered chlorosilanes to less than 10% DCS.

Sizing and location of the redistribution reactor will not be specified until after PDU operation. Table 3 shows feed rates, anticipated feed compositions, and specifications of overheads and bottoms products for the distillation system.

The TCS distillation column will be located at the recovery area, while the DCS distillation column will be remotely located.

Location of the DCS distillation column will be based on DCS accumulation. Its location must be remote from other equipment and personnel areas in accordance with the equation:

$$X = 100(\text{lbs DCS hold-up}/60)^{0.33}$$

where X = distance in feet from non-expendable facilities, and represents the distance at which a 1 psig over pressure would occur due to detonation of a vapor cloud caused by the maximum credible leak from the column. Minimization of the DCS hold-up in the column is important to minimize the remote distance required. This equation also requires that the dichlorosilane distillation column be operated at 60 psig. If operating conditions are other than 60 psig, the remote distance should be calculated by the equation :

$$X = 100((\text{lb of DCS vented})/(14.3))^{0.33}$$

where lbs vented is the maximum credible spill.

Table 4 shows the anticipated flows in and out of the various tanks (TCS feed, recovered mixture, and STC) required to allow this facility to operate independently of the HSC production facility. Included in the table is the desired days buffer provided by the tank and the nominal tank size required to provide the buffer.

The recovered material will be blended (with STC from line 120) to obtain a mixture with about 10 mole % DCS. This provides acceptable safety for operation of the plant. Vapor pressure calculations show that the composition in the vapor space of a nitrogen blanketed tank at 30° C and 30 psig with recovered material will be 7.9% DCS, 9.0% TCS, 7.4% STC, and 75.8% N_2. If a rapid leak of vapor occurs there would be no composition at which detonation of the vapor would occur. If a liquid spill occurred the vapor above the spill would be approximately 23.6% DCS, 27.5% TCS, 22.5% STC, and 26.4% air. At 70% air there would be 9.6% DCS, 11.2% TCS, and 9.2% STC. These compositions fall outside the detonable region. There is, however, a significant fire hazard in either a vapor or liquid spill. Spill protection and relief system discharge will be designed to minimize the possibility of fire.

3.4.2.3.2 EPSDU Decomposition-Recovery System

The DCS/H_2 mixture from the DCS distillation column will be fed to the decomposition reactors via line 201. The reactor effluents (line 202) pass to the recovery unit. Streams out of the recovery unit are, line 210 - miscellaneous vents, line 207 -recovered chlorosilanes, line 208 - recovered hydrogen, and line 209 - HCl.

Twelve decomposition reactors will be required. A schematic representation of a reactor is provided in Figure 9.

Use of a computer and associated hardware will provide a control system similar to designs currently in use at HSC.

The heat shield must provide explosion containment with a system that does not become dismembered if a bell jar filled with DCS/H_2 and air is ignited within the heat shield. Experience with smaller reactor assemblies indicates that a design based on adiabatic combustion, where static pressure would reach approximately 80 psig, provides sufficient containment and prevents dismemberment of the heat shield. Calculation of the pressure resulting in the heat shield due to adiabatic combustion of a stoichiometric H_2/air mixture within the jar, with the assumption that no gas exits the heat shield will be done as part of the final shield design. This pressure will be used in place of the 80 psig static pressure stated above.

The recovery system will receive vent gases from the decomposition reactors. The vent gases are H_2, HCl, DCS, TCS, and STC. The recovery system separates the vent gases into H_2 (for recycle to the reactor), HCl, and chlorosilanes. The HCl will be sold. The chlorosilanes will be sent to the distillation section of the EPSDU.

Figure 9 shows the recovery system as presented by Carl Yaws in JPL publication 79-110[6]. The recovery scheme selected by HSC will be similar to the one described by Yaws but will be modified to meet specific safety and operating criteria developed by HSC.

Location of the vent recovery system will be based on site preparation cost and building separation requirements.

Table 5 summarizes inputs and outputs of raw materials, services, products, and by-products. This project has been based on the assumption that all services will be available from existing HSC facilities; slim rods, TCS, and H_2 are to be supplied at the required rates; STC will be disposed of at an adequate rate.

3.4.4 Future Work

After PDU operation, flow schedules must be updated, redistribution reactor design must be specified, and a recommendation concerning H_2/DCS/TCS mixed feeds must be made.

3.6 1000 Tonne/Yr. Plant Design

Due to hazards associated with DCS, the 1000 tonne/yr. plant design has been modified to eliminate DCS storage and the DCS vaporizer. Figures 10, 11, and 12 represent the new design. Flows, shown in Table 6, are all the same as previously itemized except that stream 220 has been eliminated and stream 222, hydrogen formerly line 302 has been added. Stream 221 (301) is now a hydrogen/DCS mixture instead of pure DCS.

No significant cost difference should exist between the modified design and the original. Less equipment costs in the modified design will probably be offset by increased instrumentation costs.

Reliability of the system should be essentially the same as the previous system. Both systems would have comparable on-line times.

4.0 Conclusions and Recommendations

Construction of a dichlorosilane feed system for an intermediate size reactor has been completed. This system using 250 pound cylinders of dichlorosilane as reactor feed will permit decomposition reactor checkout prior to PDU start-up.

Decomposition reactor heat shield explosion testing has been successfully concluded for the intermediate reactor.

Modification of the heat shield for the first intermediate size reactor has been completed and the heat shield installed at reactor site 324. Modifications of the feed control system for reactor 324 has been completed to accept dichlorosilane-hydrogen feed from both the temporary DCS feed system and the PDU when it becomes operational.

Evaluation of DCS feed in the intermediate size reactor was initiated and will be carried out early in the second quarter of 1981.

PDU construction is proceeding on schedule. All major pieces of equipment have been received and installation is in progress.

Preliminary design of a 220 ton/year EPSDU has been completed. The design meets all safety requirements. It is recommended that this effort move forward to the detailed design phase.

5.0 Program Schedule/Plans

The program is proceeding according to plan. Efforts planned in the various task areas in accordance with the Program Schedule shown in Figure 2 are summarized below:

1. Experimental Reactor Feasibility/Optimization (3.1)
   Task completed - Mixed feed and reactor cooling will be investigated with the intermediate size reactor.

2. Intermediate Dichlorosilane Reactor Development (3.2)
   Characterization of reactor with DCS from cylinders will be completed during the next reporting period.

3. Dichlorosilane Process/Product Evaluation (3.3)
   PDU construction is on schedule and will be completed as will PDU start-up during the next reporting period.

4. Preliminary EPSDU Design (3.4)
   Preliminary design complete. No further effort in this task area prior to start of detailed design.

6.0 New Technology

No new technology was developed during this quarter.

7.0 References

1. Hemlock Semiconductor Corp., "First Quarterly Report", Low-Cost Silicon Solar Array Project, DOE/JPL Contract No. 955533, January, 1980.

2. Hemlock Semiconductor Corp., "Second Quarterly Report", Low-Cost Silicon Solar Array Project, DOE/JPL Contract No. 955533, May, 1980.

3. Hemlock Semiconductor Corp., "Third Quarterly Report", Low-Cost Silicon Solar Array Project, DOE/JPL Contract No. 955533, August, 1980.

4. Hemlock Semiconductor Corp., "Fourth Quarterly Report", Low-Cost Silicon Solar Array Project, DOE/JPL Contract No. 955533, December, 1980.

5. Hemlock Semiconductor Corp., "Fifth Quarterly Report", Low-Cost Silicon Solar Array Project, DOE/JPL Contract No. 955533, March, 1981.

6. Silicon Materials Outlook Study for 1980-85 Calendar Years DOE/JPL 1012-33, November 1, 1979.

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FIGURE 1. SCHEDULE OF EFFORT BY PHASES

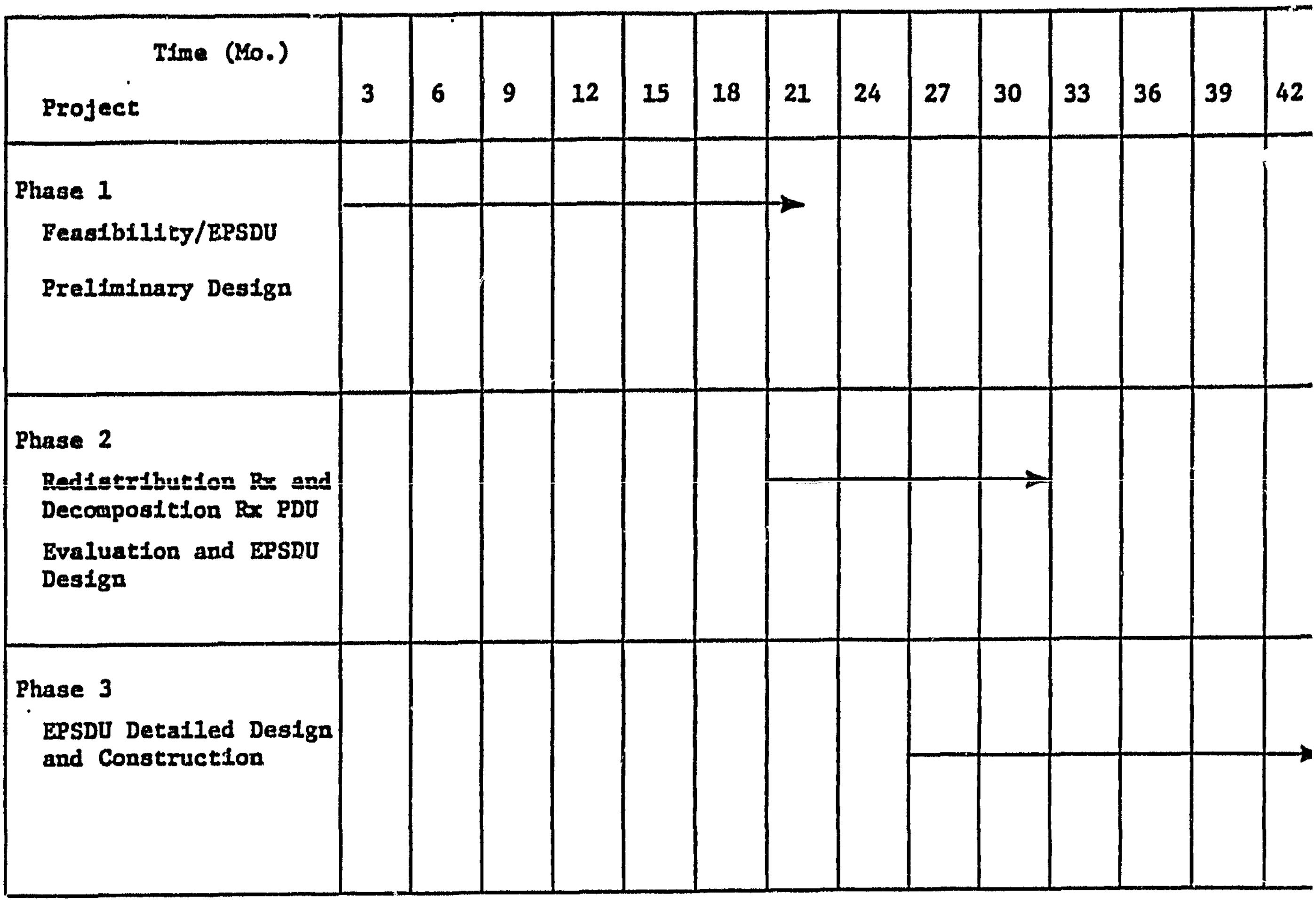

FIGURE 2. PROGRAM PLAN/MILESTONE SCHEDULE

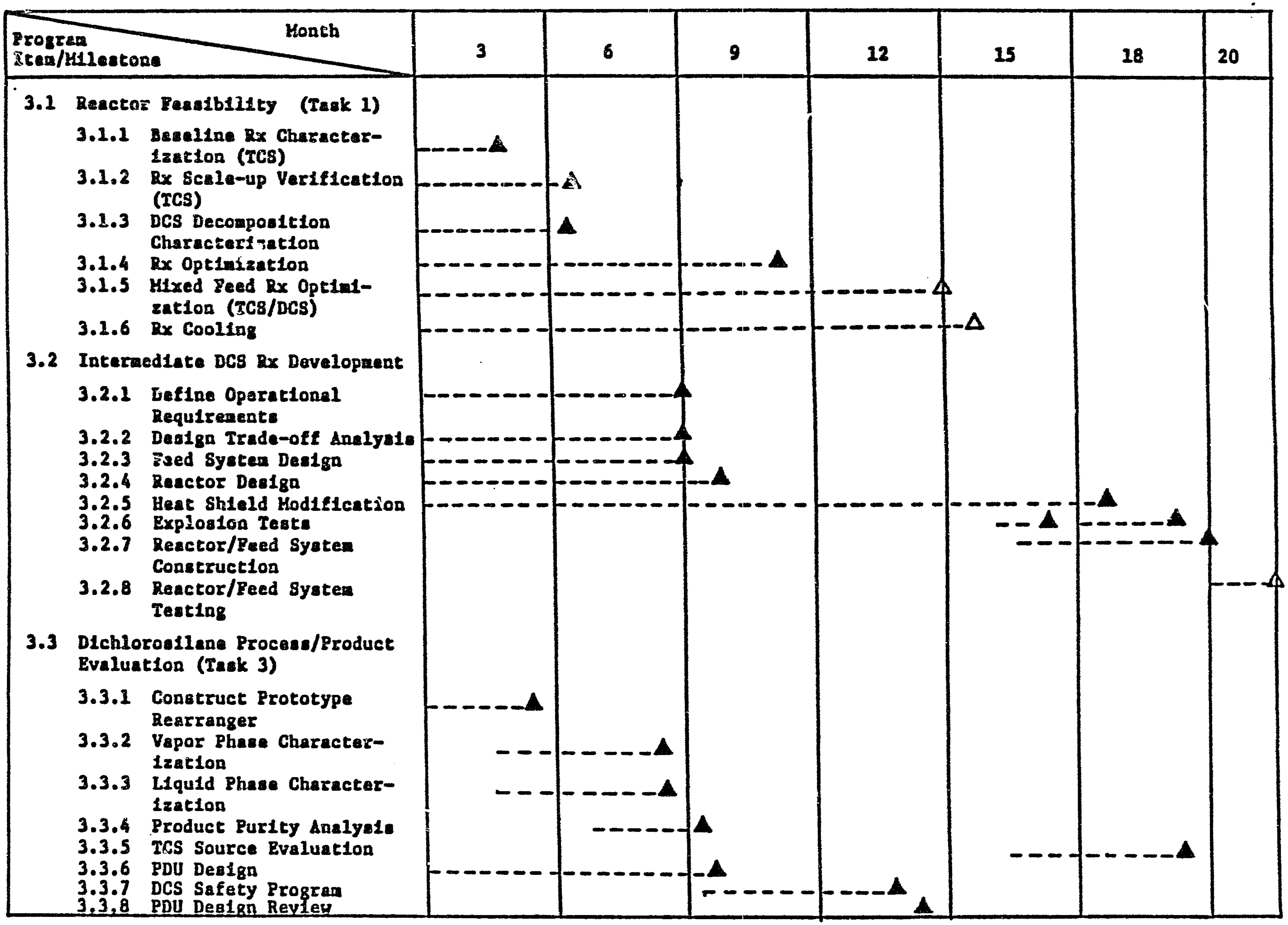

FIGURE 2. PROGRAM PLAN/MILESTONE SCHEDULE (Continued)

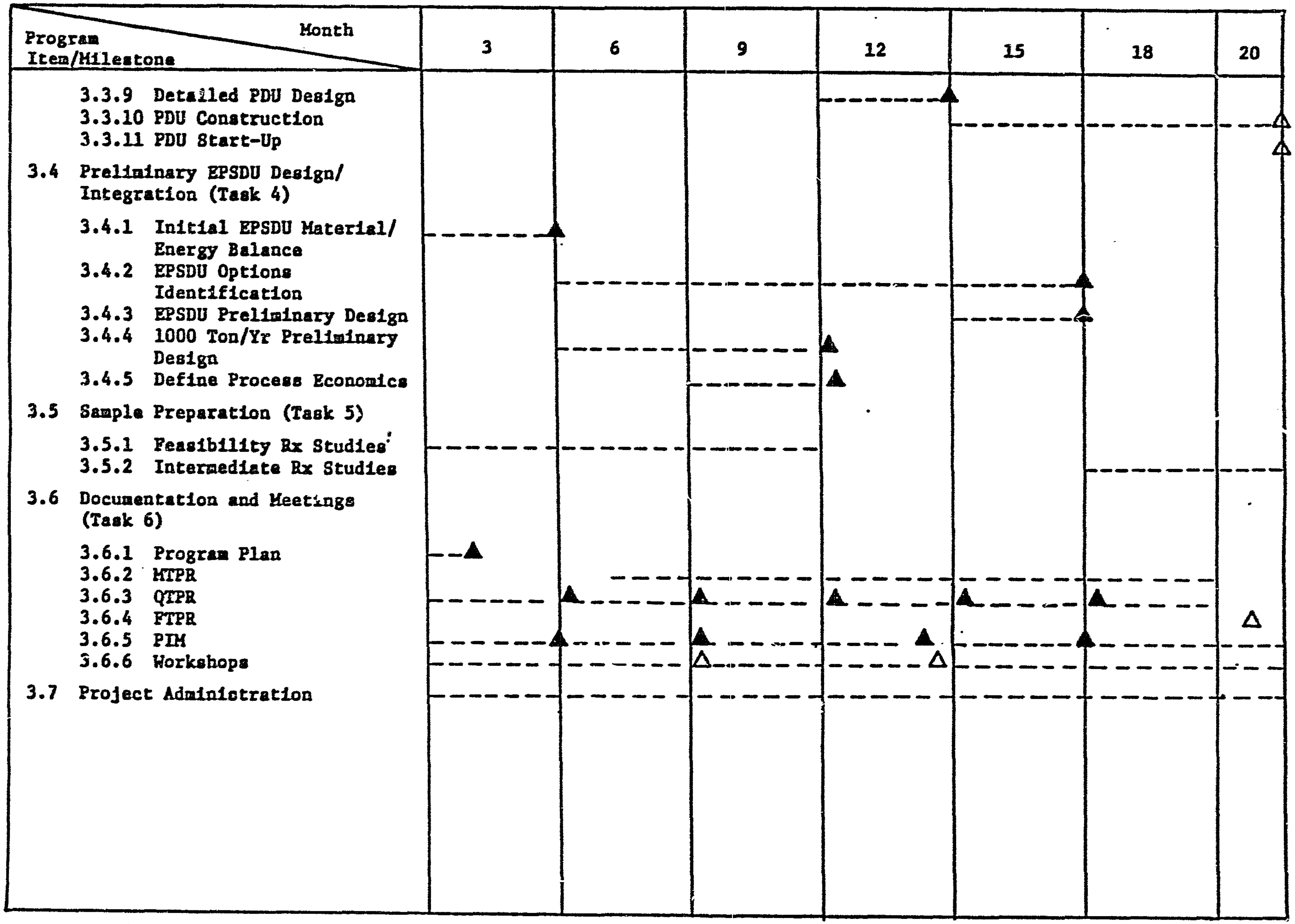

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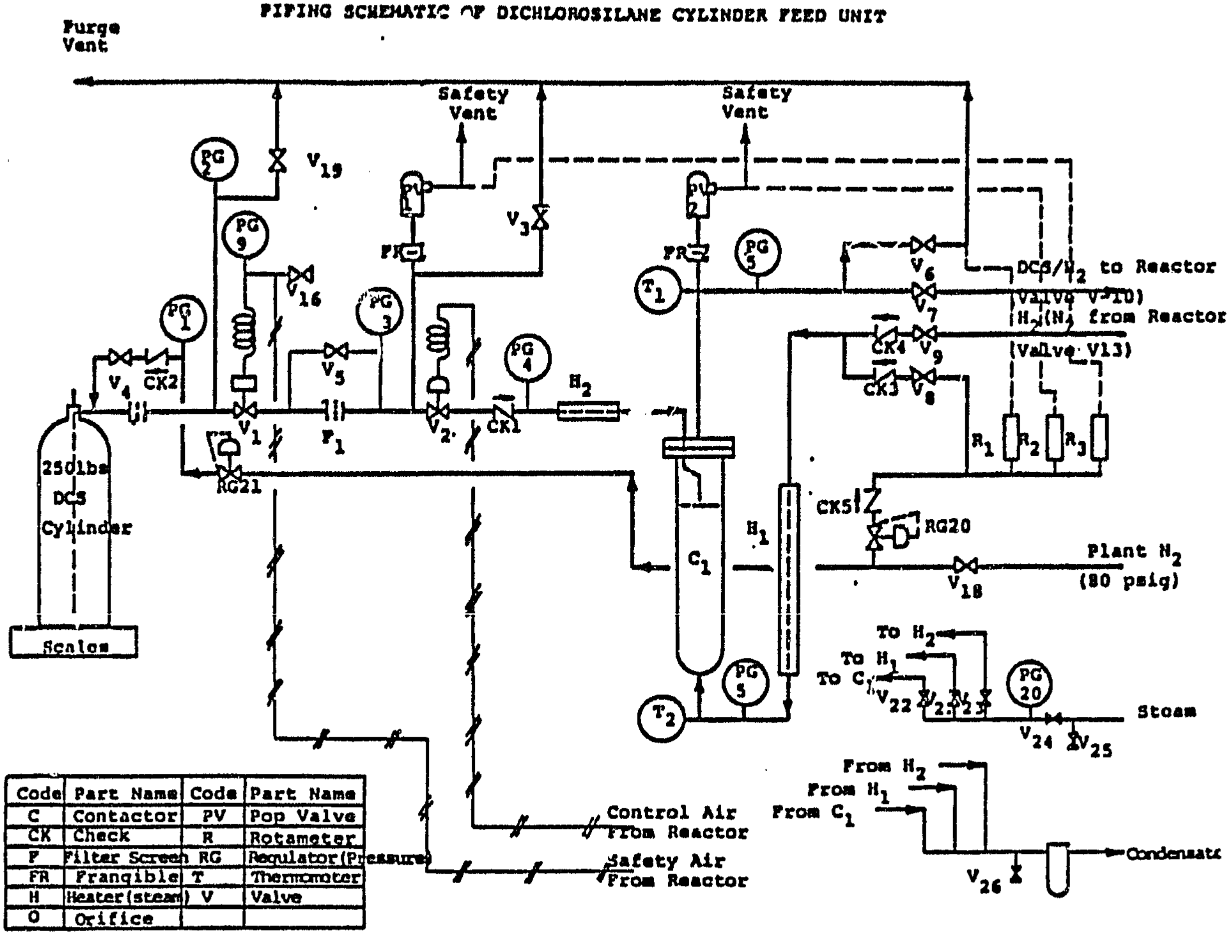
FIGURE 3.
PIPING SCHEMATIC OF DICHLOROSILANE CYLINDER FEED UNIT



Code	Part Name	Code	Part Name
C	Contactor	PV	Pop Valve
CK	Check	R	Rotameter
F	Filter Screen	RG	Regulator(Pressure)
FR	Frangible	T	Thermometer
H	Heater(steam)	V	Valve
O	Orifice		

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FIGURE 4 - Explosion Test Set Up

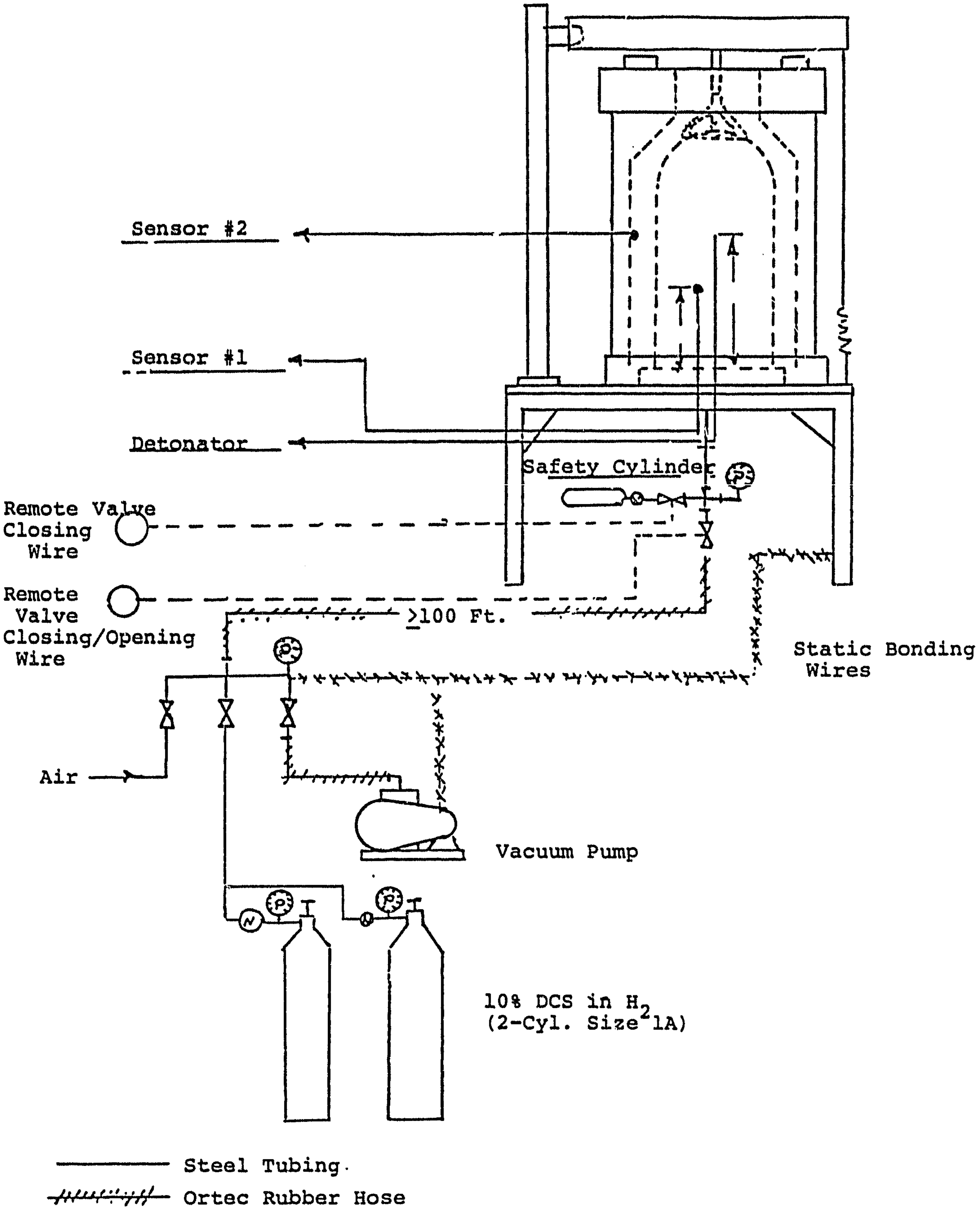
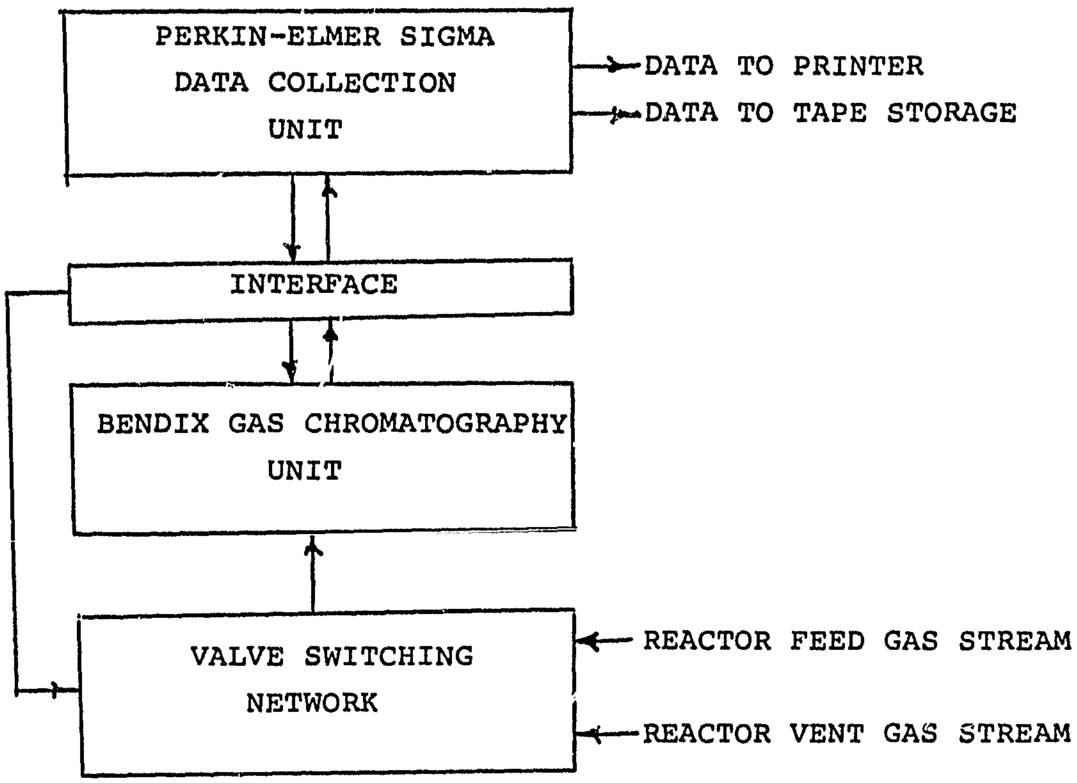


FIGURE 5.- Schematic Diagram of Perkin-Elmer Sigma Data Collection and Bendix Gas Chromatography Units



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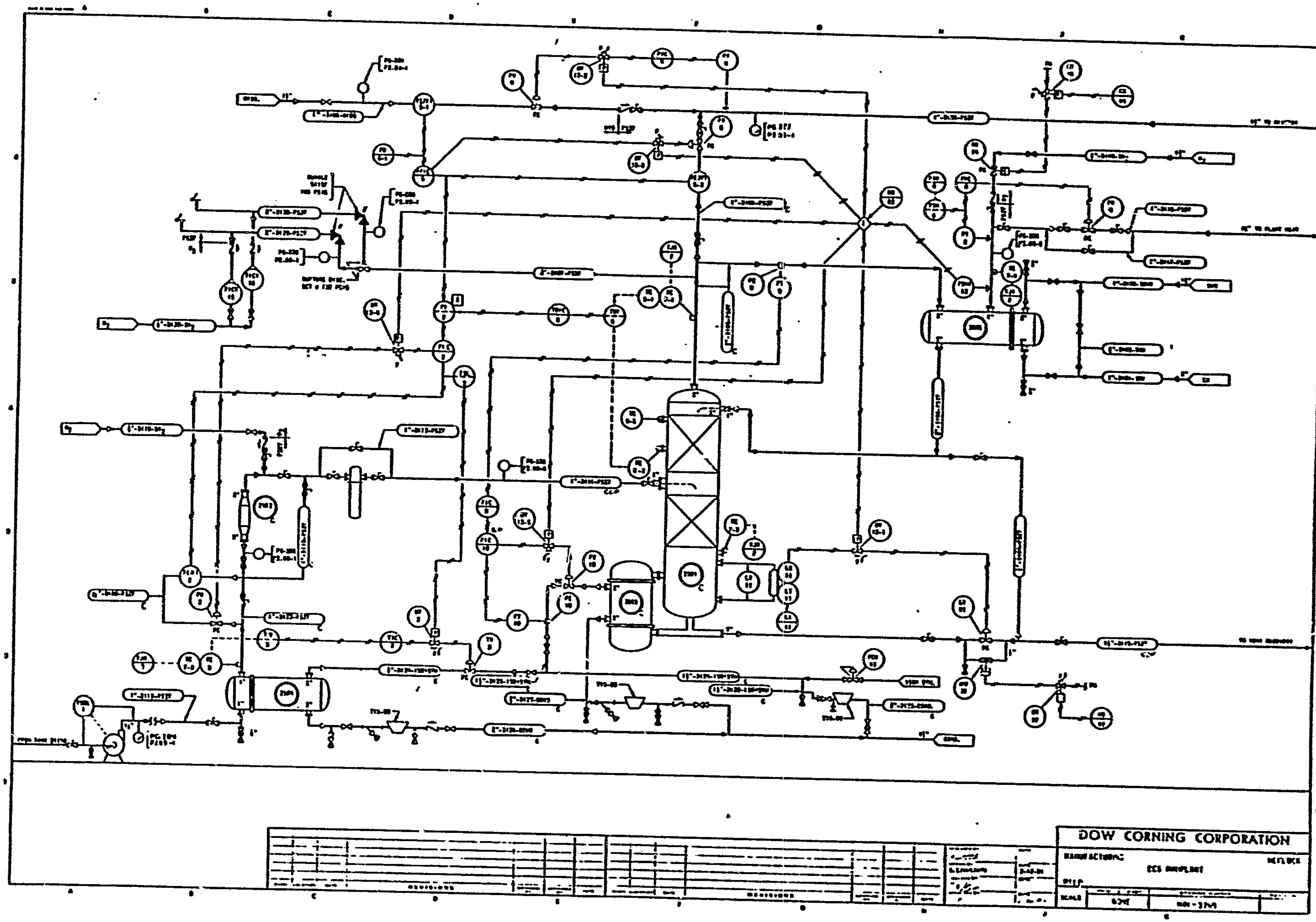

FIGURE 6. DETAILED DESIGN OF PDU

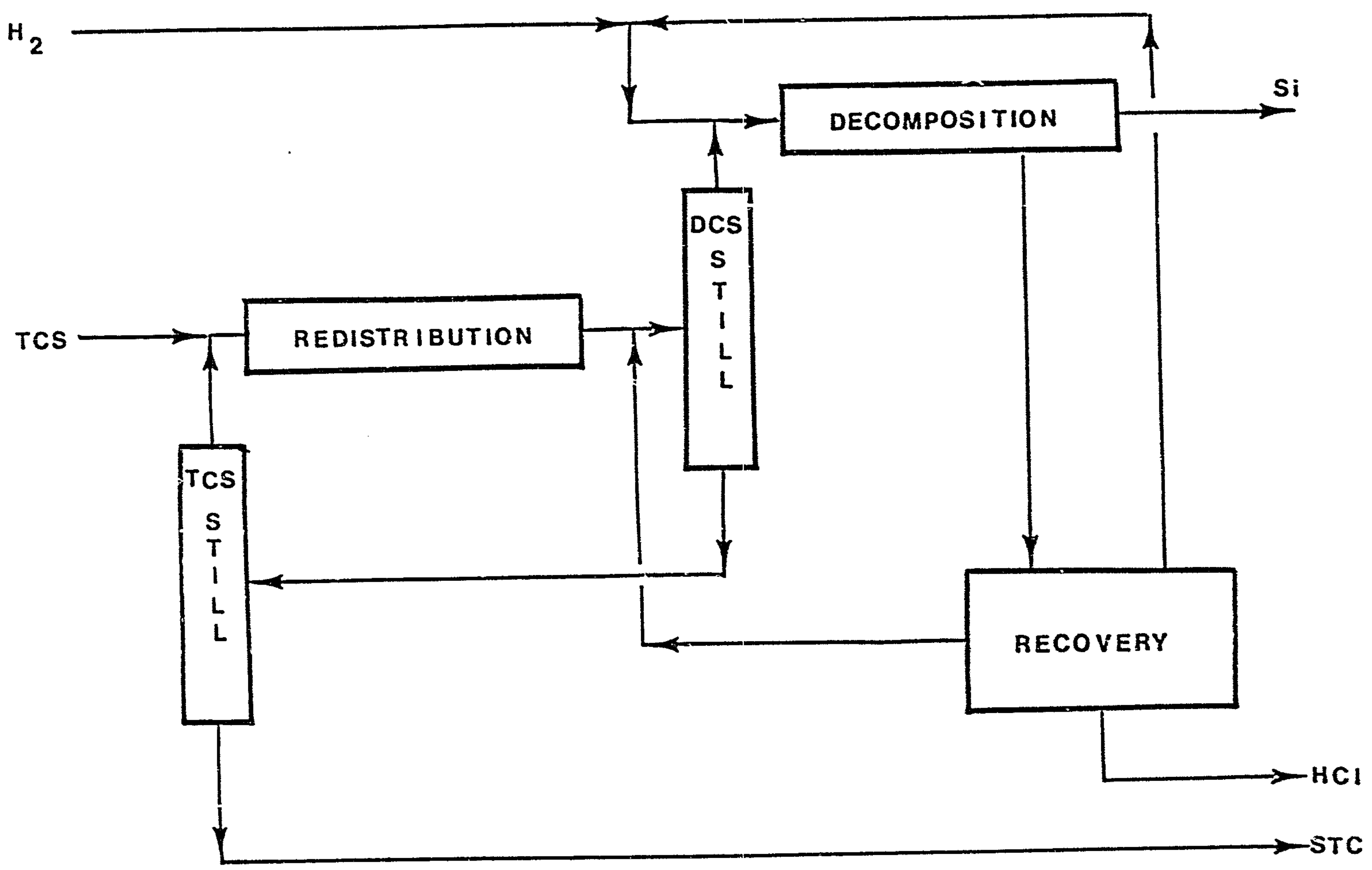

FIGURE 7. EPSDU - BLOCK DIAGRAM

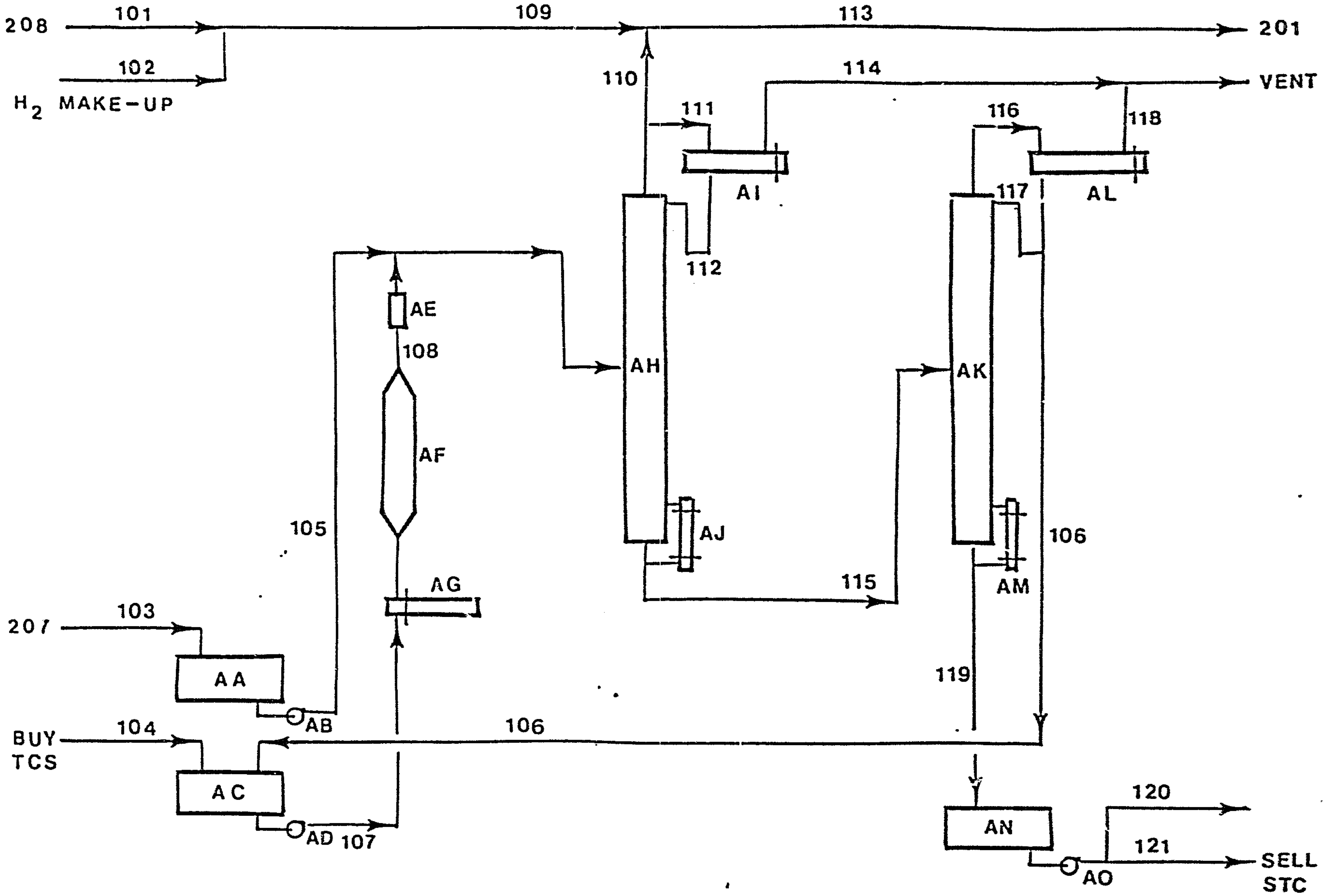

FIGURE 8. PROCESS FLOW DIAGRAM OF EPSDU STORAGE, REDISTRIBUTION, AND DISTILLATION SYSTEM

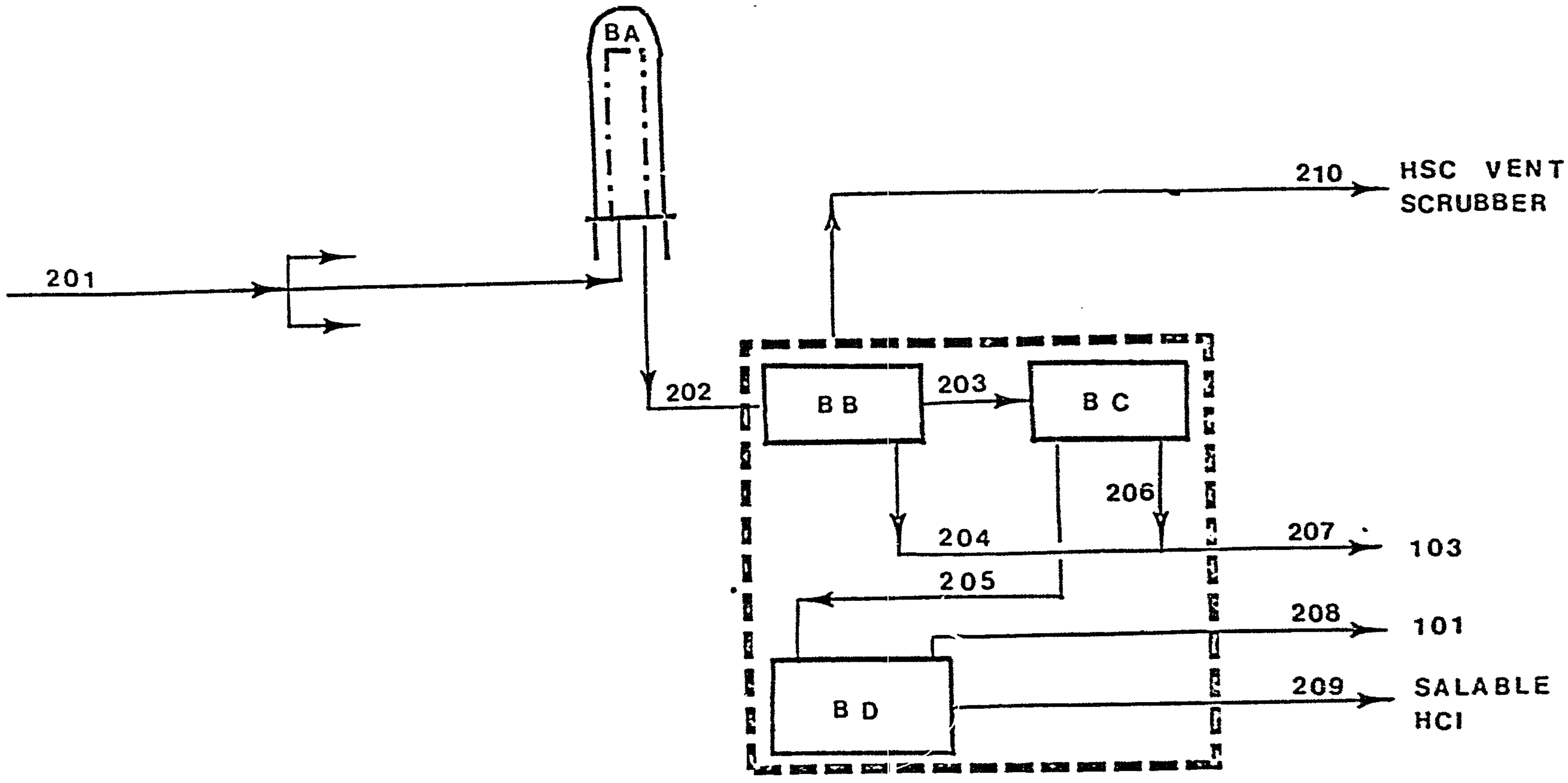

FIGURE 9. PROCESS FLOW DIAGRAM OF EPSDU DECOMPOSITION REACTOR - RECOVERY SYSTEM

FIGURE 10.

HSC PROCESS

SILICON TETRACHLORIDE
HYDROGENATION SYSTEM

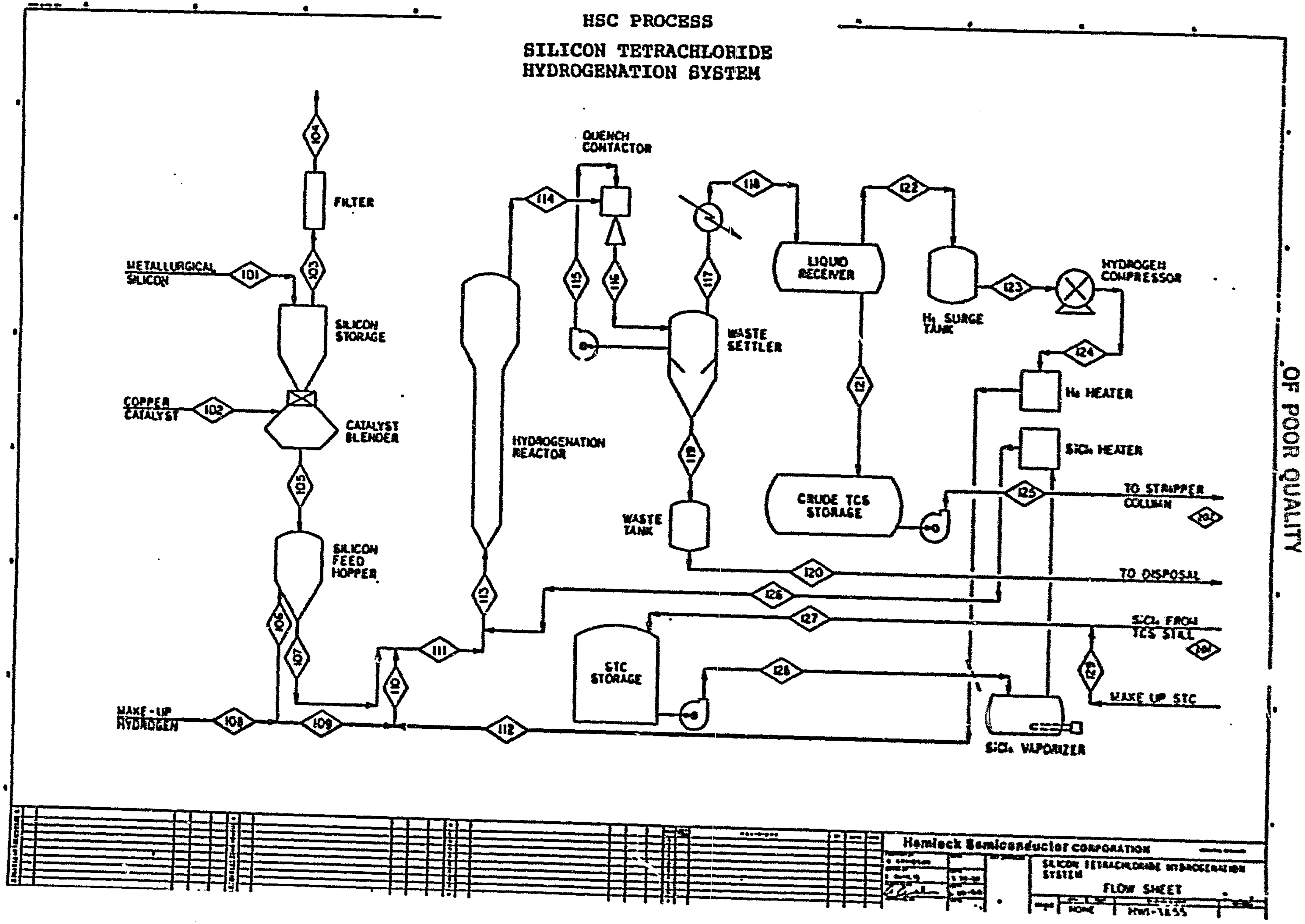

FIGURE 11.

DICHLOROSILANE PRODUCTION AND PURIFICATION

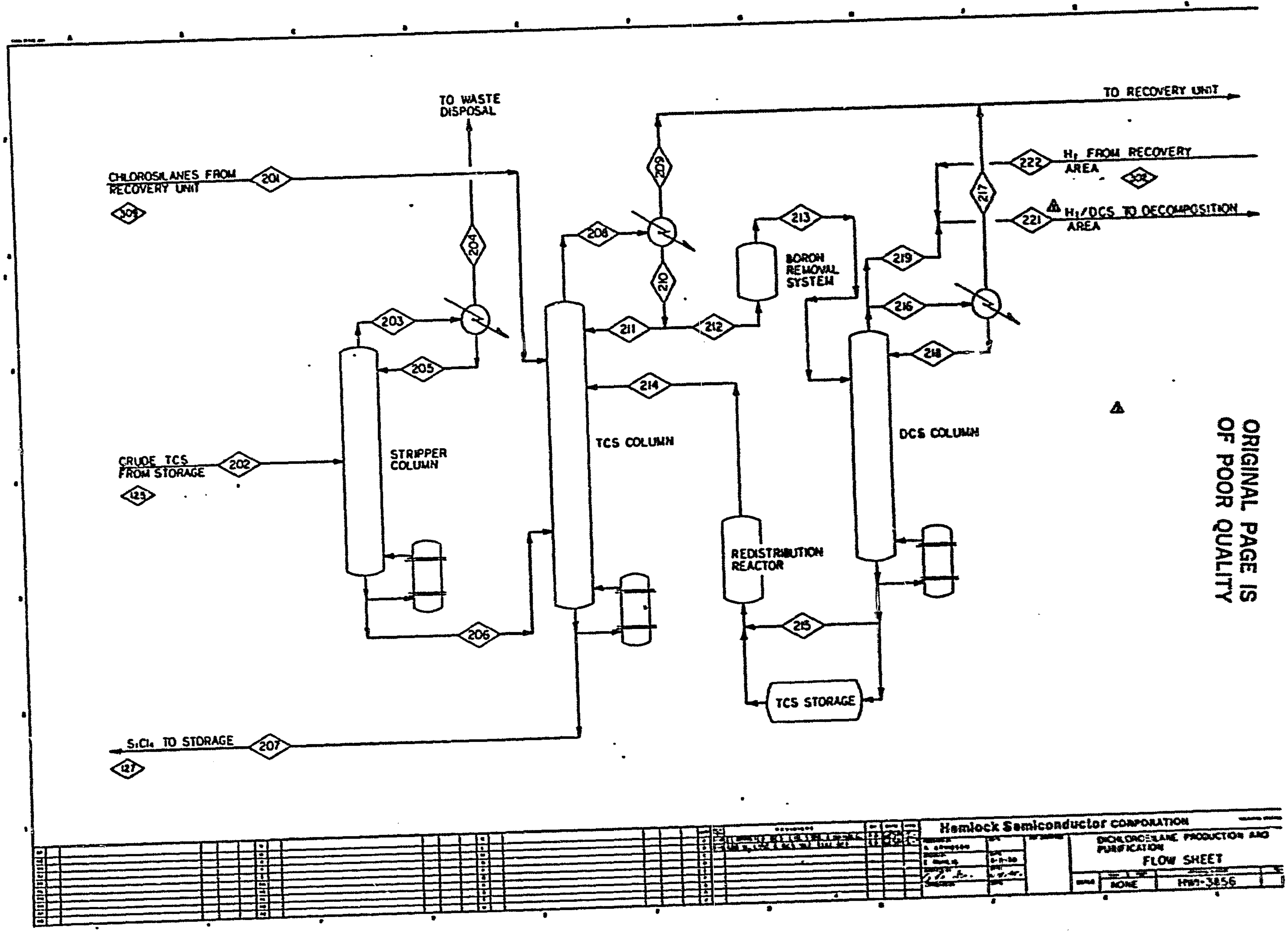

FIGURE 12.

HSC PROCESS

DICHLOROSILANE DECOMPOSITION
REACTORS AND RECOVERY UNIT

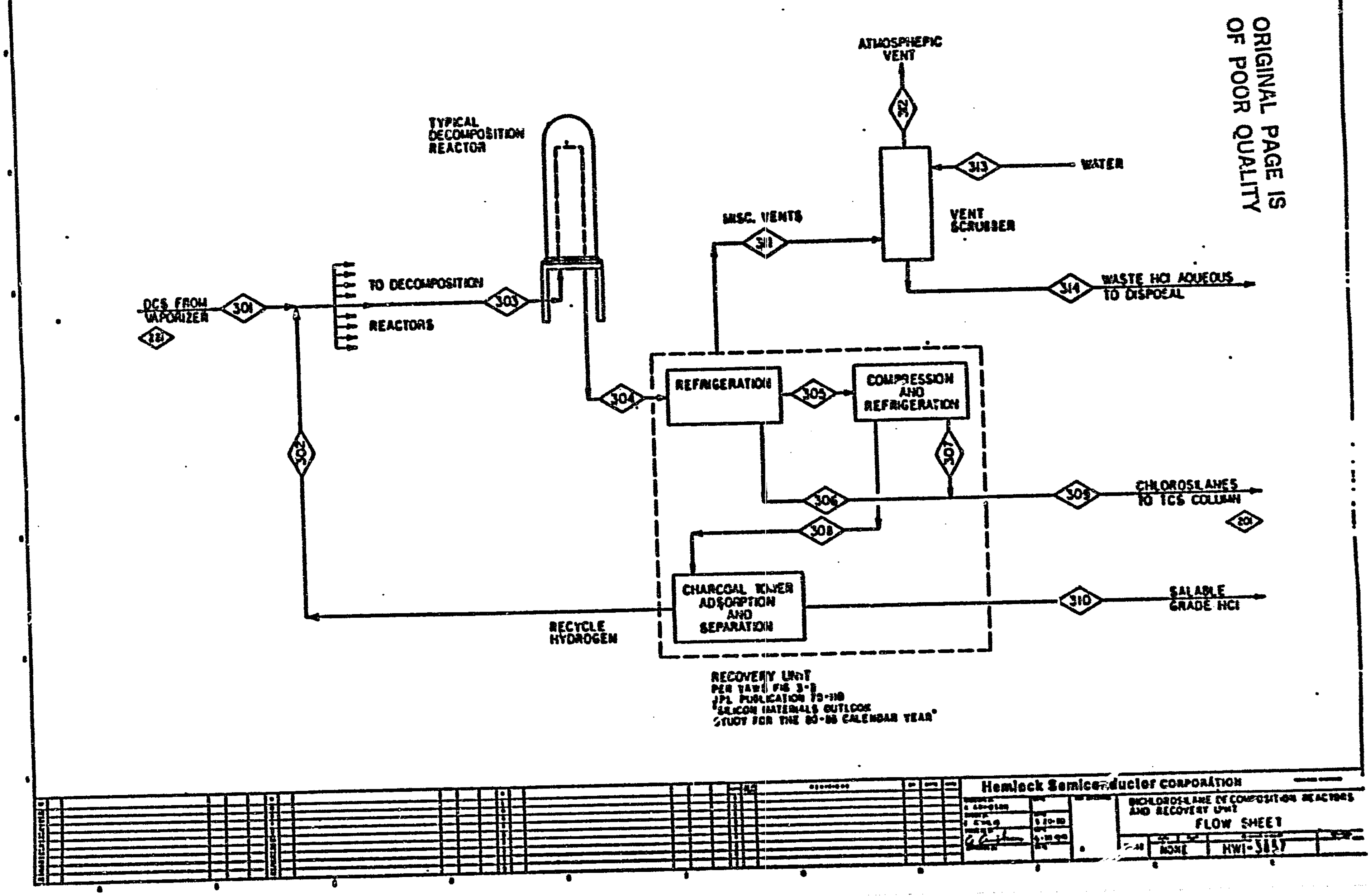

TABLE 1. - LAB REARRANGER PURITY EVALUATION OF TRICHLOROSILANE SOURCES FOR PDU OPERATION

Trichlorosilane Source	Boron (ppba)	Donor (ppba)	Alumminum (ppba)	Carbon (ppma)
Source A (1)	0.53	1.4	0.22	0.4
Source B (2)	0.24	1.0	0.17	0.3
Source C (2)	0.19	0.29	0.08	0.2
Controls (3)	0.15	0.99	0.23	0.4

---

(1) Average of three runs
(2) One run only
(3) Average of four runs

Table 2. Flow Schedule

Line	Mat'l	Total lb/hr CFH		Material			
			DCS lb/hr	TCS "	STC "	H_2 CFH	HCl lb/hr
101	H_2	22780				22780	
102	H_2						
103	V.R.	1470	108	384	977		
104	TCS	1128		1128			
105	V.R.	1470	108	384	977		
106	TCS	6859		6859			
107	TCS	8087		8087			
108	EQ.	8087	597	6474	1015		
109	H_2	22777				22777	
110	DCS	705	705				
111	DCS	7050	7050				
112	DCS	7050	7050				
113	H_2/DCS	22777/705	705			22777	
114	vent						
115	TCS/STC	8851		6859	1992		
116	TCS	15980		15980			
117	TCS	9121		9121			
118	vent						
119	STC	1992			1992		
120	STC	847			847		
121	STC	batch			1145	avg.	
201	H_2/DCS	22777/705	705			22777	
202		24292/647	108	385	130	24292	24.7
203							
204							
205							
206							
207	Chlorosilanes	1470	108	384	977		
208*	H_2	22777				22777	
209							24.7*
210							

* HCl Basis

Table 3. EPSDU Distillation Requirements

Distillation Column	DCS	TCS
Feed rate lb/hr	9310	8605
Feed Composition estimate, Mole %		
DCS	10	0.5
TCS	80	88
STC	10	11.5
Overhead Specification, Mole %		
DCS	99	-
TCS	1.0	-
STC	-	1.0
Bottoms Specification, Mole %		
DCS	0.5	-
TCS	-	0.05
STC	-	-

Table 4. EPSDU Tankage Requirements

Tank	AA	AN	AC
Flow In, lb/hr	6859	1992	1487
Flow Out, lb/hr	8087	847	1487
Daily Rate. lb/day			
In	164620	47800	35688
Out	194100	20328	35688
Buy	29472	0	0
Sell	0	27492	0
Days Surge	7	7	2
Nominal Size, Gal	20000	20000	10000

Table 5. Material and Services Summary

Item	In units/hr	units/kg	Out units/hr	units/kg
TCS	1228 lb.	41.6 lb.		
Slim Rod		0.506 in.		
Hydrogen	1475 ft_3	50. ft_3		
Steam	2950 lb.	100 lb.		
Service Water	18,000 gal	610		
Electric at Decomp	2520 KWH	85.4 KWH		
Refrigeration	30 Ton	1.0 Ton		
Si			29.5 Kg	1.0 Kg
HCl (HCl Basis)			24.5 lb	0.8 lb.
STC			1145 lbs	38.8 lb.

Table 6. EPSDU Equipment List

Item	# of	Description
AA	1	Recovered chlorosilane storage
AB	1	Recovered chlorosilane pump
AC	1	TCS storage tank
AD	1	TCS pump
AE	1	Filter
AF	1	Redistribution reactor
AG	1	Preheater
AH	1	DCS separation column
AI	1	Condenser
AJ	1	Reboiler
AK	1	TCS separation column
AL	1	Condenser
AM	1	Reboiler
AN	1	STC storage tank
AO	1	STC pump
BA	12	Decomposition reactor assembly
BB		Refrigeration
BC		Compression and refrigeration
BD		Charcoal tower adsorption and separation

TABLE 7. 1000 T/Y POLYSILICON PLANT FLOW RATES

FLOW AND MOLE % FOR SYSTEM SHOWN ON (Fig. 8 & 10)

Line Number	lb/hr Flow	Weight %							Comment
		H2	HCl	MCS	DCS	TCS	STC	Si	
101	321							100	Metallurgical Grade
102	6.8								Copper
103	-								
104	-								
105	327.8							99	1% Copper
106	-								
107	327.8							99	1% Copper
108	35.5	100							
109	-								
110	-								
111	327.8							99	1% Copper H_2 not shown
112	180	100							
113	18500	1.16					98.8		Si not shown
114	18710	1.				25	74		
115	67512				0.6	25.1	74.3		
116	86222	1.			0.6	25	73.4		
117	18530	1.			0.6	25	73.4		
118	18530	1.			0.6	25	73.4		
119	182					25.5	74.5		Si not shown in composition
120	182					25.5	74.4		
121	18350				0.6	25.1	74.3		
122	180	100							
123	180	100							
124	180	100							
125	18350				0.6	25.1	74.3		
126	18284						100		
127	17907						100		
128	18284						100		
129	326.4						100		

TABLE 7. 1000 T/Y POLYSILICON PLANT FLOW RATES (Cont.)

FLOW AND MOLE % FOR SYSTEM SHOWN ON (FIG. 9 & 11)

Line Number	lb/hr Flow	Weight %							
		H_2	HCL	MCS	DCS	TCS	STC	SI	Comments
201	2070				12.1	55.2	32.7		
202	18350				0.6	25.1	74.3		
203	-								
204	-								
205	-								
206	18350				0.6	25.1	74.3		
207	17907						100		
208	-								
209	-								
210	-								
211	-								
212	28666				10.8	89.2			
213	28666				8.7	91.3			
214	26153			0.2	7.5	78.5	13.8		
215	26153					100			
216	-								
217	-								
218	-								
219	2508			2.8	91.5	5.7			
220	2508								No Line 220
221	2508	*		2.8	91.5	5.7			No H_2 in Wt. % Basis
222		100							

TABLE 7. 1000 T/Y POLYSILICON PLANT FLOW RATES (Cont.)

FLOW AND MOLE % FOR SYSTEM SHOWN ON (FIG. 12)

Line Number	lb/hr Flow	Weight %							
		H_2	HCL	MCS	DCS	TCS	STC	SI	Comments
301	2508			2.8	91.5	5.7			
302	-	100							
303	2508			2.8	91.5	5.7			No H_2 in wt. %
304	2197		5.8		11.4	52.1	30.77		
305	-								
306	-								Recovery Flows Proprietary
307	-								
308	-								
309	2070				12.1	55.2	32.7		
310	127		100						
311	-								
312	32.8								Produced in Decomposition Reactor
313									Water
314									Aqueous HCl Waste
	279								Silicon Produced