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DEVELOPMENT OF A POLYSILICON PROCESS BASED ON CHEMICAL VAPOR DEPOSITION (PHASE 1 & PHASE 2)

Final Report for the Period October 6, 1979—June 25, 1982

By
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A. Arvidson
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August 1982

Work Performed Under Contract No. NAS-7-100-955533

Hemlock Semiconductor Corporation
Hemlock, Michigan

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FINAL REPORT

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on

DEVELOPMENT OF A POLYSILICON PROCESS BASED ON CHEMICAL VAPOR DEPOSITION

(PHASE 1 & PHASE 2)

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August 1982

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ABSTRACT

The goal of this program was to demonstrate that a dichlorosilane based reductive chemical vapor deposition (CVD) process is capable of producing a high-purity, low-cost polycrystalline silicon. Physical form and purity of this material was to be consistent with FSA material requirements for manufacturing high efficiency solar cells.

The feasibility phase (Phase 1) provided information through laboratory experiments relating to the kinetics of trichlorosilane redistribution, catalyst behavior, and decomposition characteristics of dichlorosilane. Of particular importance, Dowex® MWA-1 was shown to be an effective redistribution catalyst at moderate temperatures and very few reactor related operational problems were observed during dichlorosilane decomposition.

The demonstration phase (Phase 2) evaluated technology developed during Phase 1 at a dichlorosilane production and decomposition scale sufficient to allow scale-up for the Experimental Process System Development Unit (EPSDU). Catalyst life, polysilicon deposition rate, and product purity were established as acceptable in addition to defining process limitations.

An economic analysis was completed for a 1000 metric ton per year commercial facility using Hemlock Semiconductor's Polysilicon Process Based On Chemical Vapor Deposition. This analysis indicated that polycrystalline silicon of semiconductor quality could be produced at a price of $20.27 per kilogram. (1980 dollars, 10% ROI).

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1.0 Summary

This final report describes a process for the low-cost production of polycrystalline silicon from dichlorosilane via reductive chemical vapor deposition (CVD). The dichlorosilane is generated from the catalyzed redistribution of trichlorosilane. The by-product silicon tetrachloride, is converted to trichlorosilane via hydrogenation. Objectives of Phase 1 were to demonstrate the feasibility of using dichlorosilane as a CVD reactor feed material and to utilize base catalyzed redistribution of trichlorosilane to produce high-purity dichlorosilane. A review of dichlorosilane chemistry with its relevant advantages over the existing Siemen's polycrystalline silicon process are discussed.

Specific tasks were accomplished during Phase 1 and can be summarized as follows:

Laboratory kinetic evaluation completed of the gas and liquid phase redistribution processes.

Safety related hazards associated with the production and decomposition of dichlorosilane were identified.

DCS decomposition conditions evaluated within operating limits of a small experimental reactor.

Decomposition conditions were optimized via a two-level experimental design and characterized vent product composition.

Designed, constructed and started-up the dichlorosilane Process Development Unit (PDU).

Preliminary design of a 220 metric ton per year Experimental Process System Development Unit (EPSDU) was completed.

Phase 2 project objectives encompassed the evaluation of technology developed during Phase 1 at a reactor scale approaching that anticipated for the EPSDU. Demonstration of this technology occurred on a production scale basis. Performance highlights for dichlorosilane production and decomposition are summarized below:

> The dichlorosilane Process Development Unit was operated at a rate of 500,000 pounds per year.
>
> Evaluation of both a 3" and 5" diameter redistribution reactor was completed.
>
> Dichlorosilane decomposition was evaluated in an intermediate sized CVD reactor.
>
> Evaluation of mixtures of dichlorosilane/trichlorosilane and dichlorosilane/silicon tetrachloride as reactor feedstock was completed.
>
> Polycrystalline silicon was produced that met or exceeded photovoltaic industry requirements.
>
> An economic analysis of the 1000 metric ton per year plant was completed.

Significant progress was made during the 33 months Hemlock Semiconductor was under contract. Work was terminated before process optimization on a production scale reactor system could be accomplished. The economic evaluation indicates that the original JPL price target of \$14/kg in 1980 dollars cannot be achieved using DCS decomposition in quartz reactors.

2.0 Introduction

2.1 Program Objectives

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

The planned overall program covered a 33-month period and consisted of a feasibility phase (Phase 1), an EPSDU design/evaluation phase (Phase 2), and an EPSDU construction/demonstration phase (Phase 3). Phase 2 activity was integrated with Phase 1 activity to provide a continuing comprehensive program. Specific Phase 1 project objectives included:

1. Characterization of dichlorosilane as a feedstock material for an experimental CVD reactor including quantative determination of reaction products.
2. Design and construction of a dichlorosilane CVD reactor to demonstrate dichlorosilane performance in a production size reactor.
3. Design, construction and start-up of a process development unit to characterize the trichlorosilane to dichlorosilane redistribution process, determine product purity, and produce sufficient dichlorosilane to permit operation of a production sized reactor.
4. Preparation of 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.

Phase 2 encompassed the evaluation of technology developed during Phase 1 at a reactor scale approaching that anticipated for the EPSDU. Specific Phase 2 project objectives included:

1. Modification and operation of two intermediate sized production reactors for use with dichlorosilane.
2. Operation of DCS-PDU and decomposition reactor using mixed chlorosilane feed (DCS/TCS/STC).
3. Modification and operation of an advanced reactor for DCS decomposition.
4. Continued updating of the 1000 MT/Y plant design and economic evaluation based on information collected in the experimental program, and detailed engineering design for the EPSDU.

The general approach taken in meeting the overall program objective is discussed in Section 2.2. A brief overall process description is contained in Section 2.3 along with a dicsussion of relevant chemistry. Technical aspects and progress in meeting the objectives in the basic areas are discussed in Section 3.0.

2.2 Program Approach

Chemical vapor deposition (CVD) of high purity polycrystalline silicon from a chlorosilane feedstock forms the basis of the entire semiconductor-grade polycrystalline silicon industry. These processes, utilizing trichlorosilane as an intermediate material (feedstock for CVD), currently produce material of proven quality that meets the demanding needs of the electronics industry as well as the emerging photovoltaic industry. Process improvements coupled with expanding capacity have resulted in a steadily declining polycrystalline silicon price in constant dollars. The industry has established a technology base sufficient to permit rapid commercialization of a chlorosilane based process. The inability of the current polycrystalline silicon process to meet the goals of the DOE/JPL program is a matter of high manufacturing costs: not product quality or raw materials availability.

Considering this shortcoming along with the maturity of the current process and the ability of its product to meet requirements for high efficiency cell manufacture, innovations that could significantly reduce product cost were evaluated. The HSC low cost process for the production of high purity polycrystalline silicon via reductive chemical vapor deposition from dichlorosilane is depicted in Figure 1. This process consists of the hydrogenation of silicon tetrachloride in the presence of metallurgical-grade silicon (Mg-Si) to produce trichlorosilane, synthesis of dichlorosilane via redistribution of trichlorosilane, chemical vapor decomposition of dichlorosilane to produce polycrystalline silicon, and recovery of decomposition by-products. Silicon tetrachloride, a major by-product of trichlorosilane redistribution and minor by-product of dichlorosilane decomposition, is recycled into the hydrogenation process. Also shown in Figure 1 are the distillation processes required for chlorosilane separation/purification.

The only by-product shown as not being recycled in Figure 1 is hydrogen chloride. This material represents a relatively low volume stream and may be sold as a by-product.

The HSC process addresses the shortcomings of the current trichlorosilane process by:

1. Use of dichlorosilane as a feed material for the CVD process. Dichlorosilane decomposes more readily than trichlorosilane, resulting in higher deposition rates.[1,2,3] Increased deposition rates reduce labor and capital costs. Dichlorosilane also produces less vent material, thereby reducing capital associated with the recovery system.
2. Hydrogenation of Mg-Si and $SiCl_4$ to produce trichlorosilane. This process accommodates the largest by-product stream associated with the existing trichlorosilane-based CVD process and the largest by-product stream of a dichlorosilane-based process. Work done at Dow Corning Corporation, and under JPL contracts

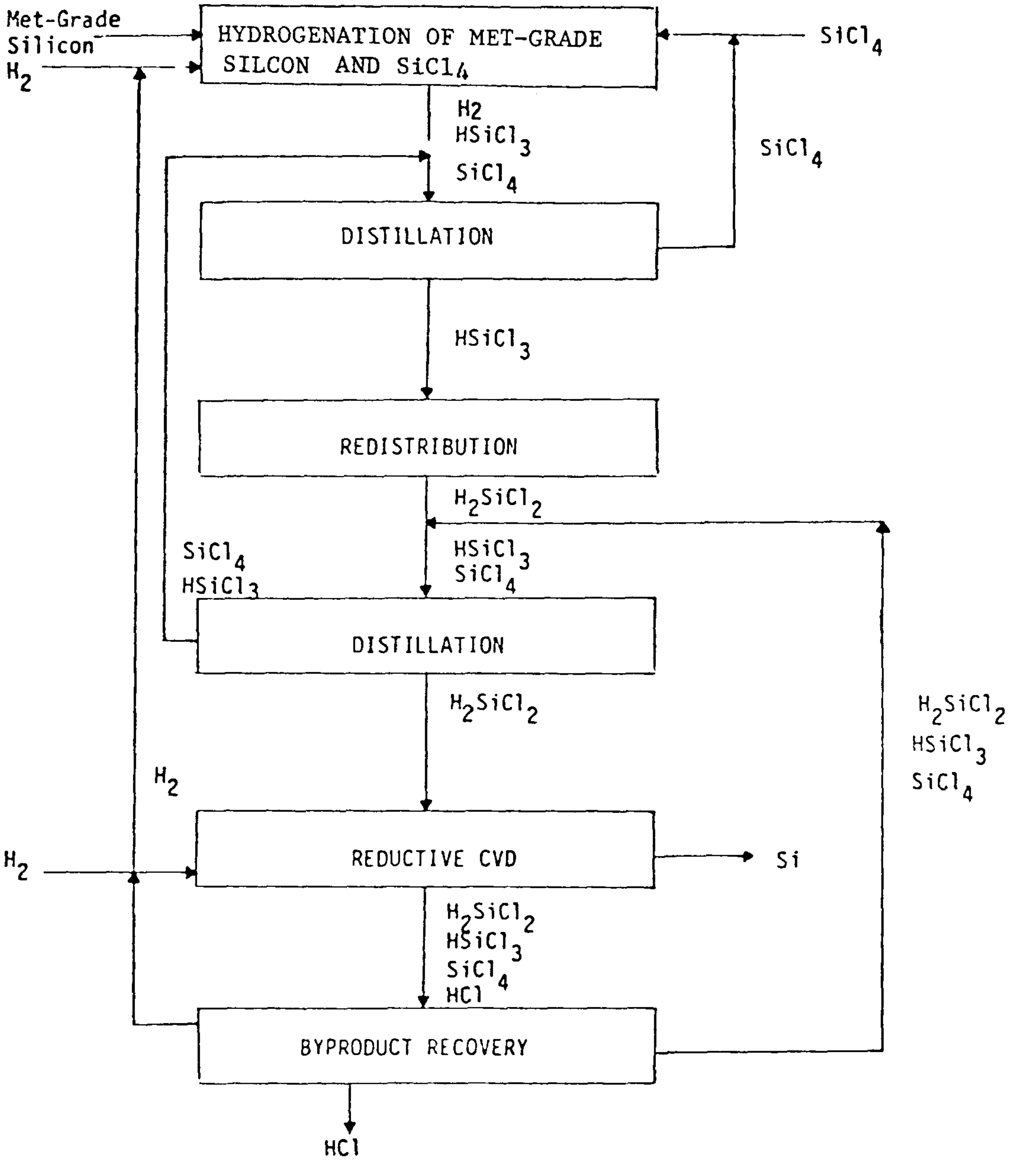


FIGURE 1. SCHEMATIC OF HSC DICHLOROSILANE BASED CVD PROCESS

by Union Carbide Corporation, Massachusetts Institute of Technology, and Solarelectronics, indicates that the hydrogenation process can produce trichlorosilane cost-effectively.[4,5,6,7]

3. Improved CVD reactor design. In addition to changes in CVD reactor feedstock, reactor optimization is required to further increase deposition rate and reduce power consumption. Hemlock Semiconductor, with its years of experience in reductive chemical vapor deposition using trichlorosilane as an intermediate, has developed experimental reactor configurations that should meet deposition requirements for a low cost reductive CVD process.

2.3 Process Description

2.3.1 Relevant Chemistry

The chemistry involved in the low cost dichlorosilane CVD process is relatively well established, as is the supporting technology. Basic processes required for the cost-effective production of polysilicon via the decomposition of dichlorosilane include:

Hydrogenation of Metallurgical-Grade Silicon and Silicon Tetrachloride

$$SiCl_4 + H_2 + Si \rightleftharpoons HSiCl_3 \ (+ H_2 + SiCl_4)$$

Dichlorosilane Synthesis

$$HSiCl_3 \overset{\text{Catalyst}}{\rightleftharpoons} H_2SiCl_2 + SiCl_4$$

Dichlorosilane Decomposition

$$H_2SiCl_2 + H_2 \longrightarrow Si + (H_2 + H_2SiCl_2 + HSiCl_3 + SiCl_4 + HCl)$$

The above equations are written only qualitatively since exact reaction products are temperature and composition dependent. Relevant points regarding the advantages and limitation of these reactions are now discussed.

HYDROGENATION OF METALLURGICAL-GRADE SILICON AND SILICON TETRACHLORIDE

The substantial amount of silicon tetrachloride which is generated in the redistribution and decomposition process requires a means of recycling the material and/or converting it into a more useful material. Such reactions were not explored under this contract; however, Union Carbide Corporation (UCC) has demonstrated the feasibility of producing trichlorosilane from hydrogen/silicon tetrachloride mixtures in a high-pressure silicon fluidized bed reactor operating in the vicinity of 500°C.[5] Further study of the process was conducted by The Massachusetts Institute of Technology[6] and Solarelectronics, Inc.[7] Although the yield of trichlorosilane produced by hydrogenation is expected to be less than 30%, the only by-products are unreacted hydrogen and silicon tetrachloride, which are recycled. UCC, MIT, and Solarelectronics were funded for demonstrating technology readiness of the hydrogenation process. Efforts in the hydrogenation area by Hemlock Semiconductor were not warranted until reactor/reactant feasibility had been established and applicability of the UCC hydrogenation process to this project was established.

DICHLOROSILANE SYNTHESIS

Considerable experience at Dow Corning,[8] UCC[5] and elsewhere has demonstrated the preferred route to dichlorosilane to be the acid or base-catalyzed redistribution of trichlorosilane.

$$SiHCl_3 \overset{\text{Catalyst}}{\rightleftharpoons} SiH_2Cl_2 + SiCl_4$$

This process is superior to a "direct process" reaction of HCl with silicon. A wide variety of species, including ammonium salts, free amines, phosphonium salts, phosphoramides, and aluminum chloride have been shown capable of catalyzing redistribution reactions under mild conditions.

UCC has demonstrated that an amine-functionalized organic polymeric resin will catalyze redistribution of chlorosilane mixtures at temperatures between 50-80°C. A similar basic resin, Dowex® MWA-1, manufactured by The Dow Chemical Company has been chosen as the catalyst for this process. The resin is a methylamine modified organic polymer supplied as spherical beads averaging 0.4 mm in diameter.

Equilibrium relationships among chlorosilanes are known from research conducted at both Dow Corning[8] and Union Carbide.[5] A fully equilibrated system at 80°C with a Cl/H ratio of 3 (pure trichlorosilane as reactant) should consist of ca. 11% dichlorosilane, 12% silicon tetrachloride, <1% monochlorosilane, with the balance being trichlorosilane.

REDUCTIVE CHEMICAL VAPOR DEPOSITION VIA DICHLOROSILANE

The principal advantages of dichlorosilane with respect to trichlorosilane for reductive chemical vapor deposition are two-fold: its relative instability both thermodynamically and kinetically, and its lower chlorine content.

In thermodynamic terms, dichlorosilane is a substantially better source of silicon than is trichlorosilane. For instance, at 1070°C and 7 mole % chlorosilane (in H_2) as a reactant, the theoretical thermodynamic equilibrium conversion of trichlorosilane and dichlorosilane into silicon are, respectively, 40% and 65%.[1]

A perspective on equilibrium relationships between the two chlorosilanes is presented in Figure 2. The figure shows the Cl/H ratio in the reactor feed stream (and vent, since no hydrogen or chlorine is deposited in the reactor) versus the equilibrium determined Si/Cl ratio in the vent products (that is, not including the elemental silicon deposited). The figure can be used to ascertain the mole percent conversion into silicon for a range of feed compositions (Cl/H ratios), since

$$\text{Percent conversion} = \frac{(\mathrm{Si/Cl})_{in} - (\mathrm{Si/Cl})_{out}}{(\mathrm{Si/Cl})_{in}}$$

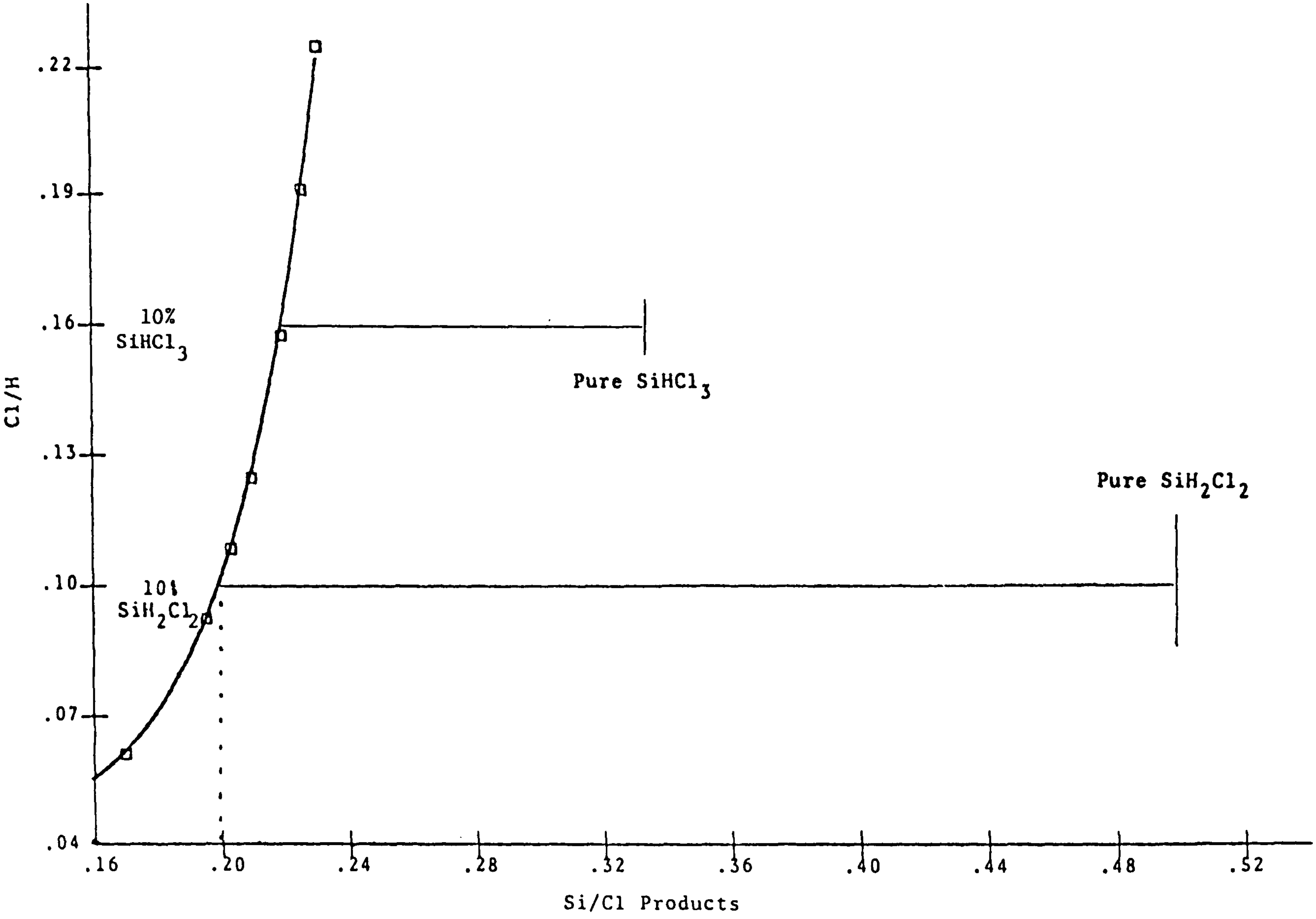


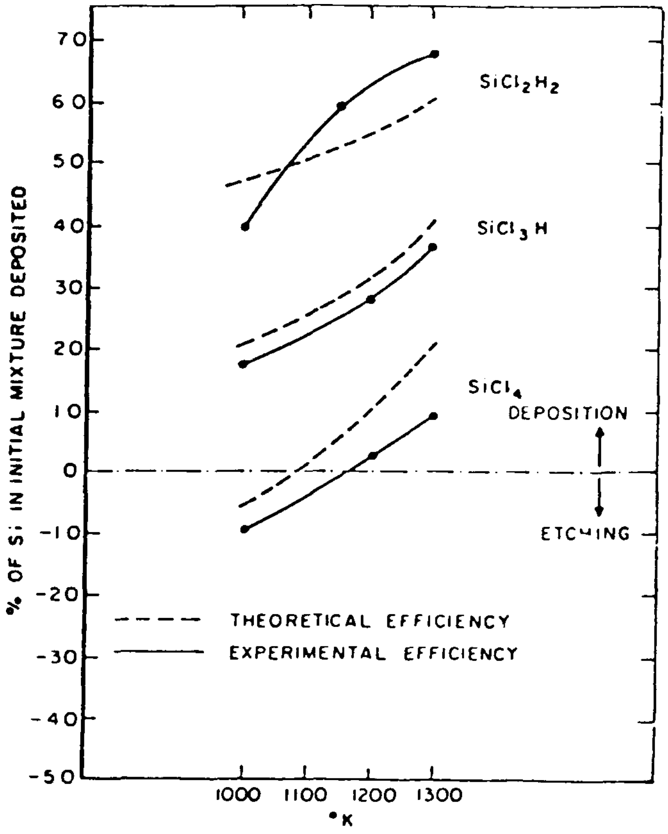
Figure 2. THEORETICAL EQUILIBRIUM RELATIONSHIPS FOR SILICON GENERATION FROM CHLOROSILANES AT 1050°C

At a feed of 10 mole percent dichlorosilane in H_2 and 1050°C, for example, the Cl/H ratio = .10, and:

Conversion = (.50-.20)/.50 = 60 mole percent

A further thermodynamic advantage of dichlorosilane relative to trichlorosilane is its lower sensitivity to increases in reactant concentration. For trichlorosilane, doubling the mole percent of reactant from 7 to 14 percent decreases the percent conversion into silicon from 40 to 31 percent. Dichlorosilane suffers proportionately less from concentration increases; an increase from 7 to 14 percent causes an equilibrium conversion decrease from 65 to only 58 percent.

Since equilibrium conditions do not in fact prevail in CVD processes anticipated for application in this program, the above equilibrium relationships are modified by the kinetic realities. Several investigators have demonstrated that, under conditions used for epitaxial deposition, formation of silicon from dichlorosilane is characterized by a lower activation energy than corresponding formation from trichlorosilane. Typical values are 13 and 22 kcal/mole,[9,10] respectively. Conditions utilized in epitaxial reactors typically involve substantially lower mole percent chlorosilane and flow rates than polysilicon production process reactions. However, recent work by Ban of RCA Laboratories[2] has been conducted at mole fractions and temperatures compatible with the polycrystalline silicon production process. Ban's work is summarized in Figure 3, in which decomposition rates for dichlorosilane, trichlorosilane and silicon tetrachloride are plotted versus temperature. It is evident from the figure that under conditions in which silicon tetrachloride and trichlorosilane are far from equilibrium conditions, dichlorosilane has achieved equilibrium. Yields in excess of equilibrium values may be related to non-equilibration of HCl with the elemental silicon in the system. Ban's work, along with other recent related work indicates that the activation energy for decomposition of dichlorosilane into



Theoretical and experimental efficiencies of deposition of silicon from $SiCl_2H_2$, $SiCl_3H$, and $SiCl_4$ in temperature interval of 1000°-1300°K; $Cl/H = 10^{-1}$ in all cases.

FIGURE 3. SILICON DEPOSITION EFFICIENCIES

V. Ban (Ref. 2)

silicon is considerably less than that for trichlorosilane under a wide variety of conditions.

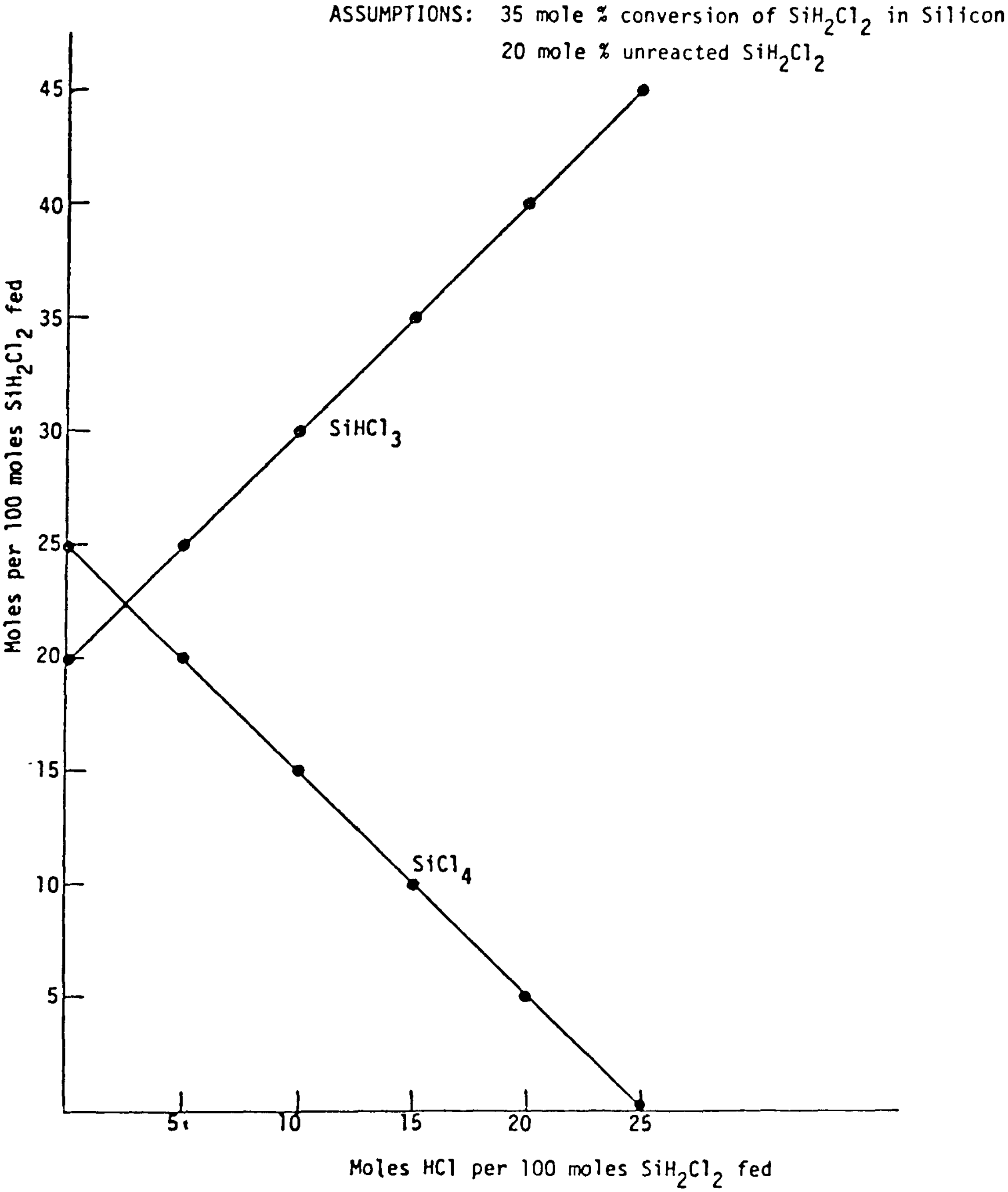
Additional support for approaching equilibrium in dichlorosilane systems comes from Union Carbide patents which claim conversions into silicon of up to 60 percent in a single rod CVD reactor.[3]

The effect of kinetic behavior is to enhance the thermodynamic advantage of dichlorosilane over trichlorosilane for silicon manufacture.

The lower molar chlorine content of dichlorosilane than trichlorosilane has a beneficial effect on the amount of by-product chlorosilane which must be recirculated or otherwise accommodated in a polycrystalline silicon CVD process. Not only will the weight of chlorosilanes in reactor vents be lower when dichlorosilane is utilized, but the distribution of these by-products will be more favorable. The present process based on trichlorosilane as previously discussed generates substantial quantities of silicon tetrachloride; with dichlorosilane as a feed material, the principal by-products should be a mixture of trichlorosilane and unreacted dichlorosilane. This assumption has been borne out in preliminary gas chromatographic analyses of runs on an experimental reactor.

These by-products (trichlorosilane, silicon tetrachloride, HCl and unreacted dichlorosilane) of the reaction which generates silicon from dichlorosilane are an important part of the chemical scheme. The expense of operation of the recovery system, which must separate the components, and the amount of silicon tetrachloride generated, which would have to be sold or recycled in a separate process, are obviously dependent on the specific product distribution.

Unfortunately, equilibrium calculations cannot provide unambiguous values for vent gas composition: mass balance requirements can be met with a variety of combinations of individual concentrations. For example, Figure 4 shows possible



ASSUMPTIONS: 35 mole % conversion of SiH_2Cl_2 in Silicon
20 mole % unreacted SiH_2Cl_2

FIGURE 4. VENT COMPOSITION RELATIONSHIPS FOR SILICON PRODUCTION FROM SiH_2Cl_2

concentrations for an assumed percent conversion to silicon and mole percent unreacted dichlorosilane.

2.3.2 Process Implementation

The low cost dichlorosilane based CVD process is illustrated schematically in Figure 5. Hydrogenation of metallurgical-grade silicon and silicon tetrachloride occurs in a fluidized bed reactor. The fluidized bed is made up of finely ground metallurgical grade silicon fluidized with a H_2 - $SiCl_4$ gas stream. The hydrogenation product (H_2, $HSiCl_3$ and $SiCl_4$) is first stripped of hydrogen and any highly volatile impurity species. The bottoms material from this first separation feeds a second distillation column where the trichlorosilane-silicon tetrachloride separation is accomplished. Silicon tetrachloride is returned to the fluidized bed reactor while the purified trichlorosilane is fed into a redistribution column for dichlorosilane synthesis. Output of the redistribution column contains approximately 11 percent H_2SiCl_2 along with H_3SiCl, $HSiCl_3$ and $SiCl_4$, with $HSiCl_3$ representing the bulk of the chlorosilanes present in this stream (approximately 80 percent). Dichlorosilane separation is accomplished by a second distillation process and taken off the distillation column as an overhead stream. The bottoms from this distillation column are recycled into the $HSiCl_3$ - $SiCl_4$ distillation column.

Dichlorosilane is introduced with hydrogen into a polycrystalline silicon CVD reactor where it is decomposed on a resistively heated substrate. Reaction by-products are collected and processed through a recovery system which serves to remove and purify the hydrogen for recycle to the CVD reactor and separate chlorosilanes in the vent stream from the HCl. The recovered chlorosilanes are introduced into distillation column 3 where they begin the recycle process either forward to the reactor (H_2SiCl_2) or back to the H_2SiCl_2 synthesis and $SiCl_4$

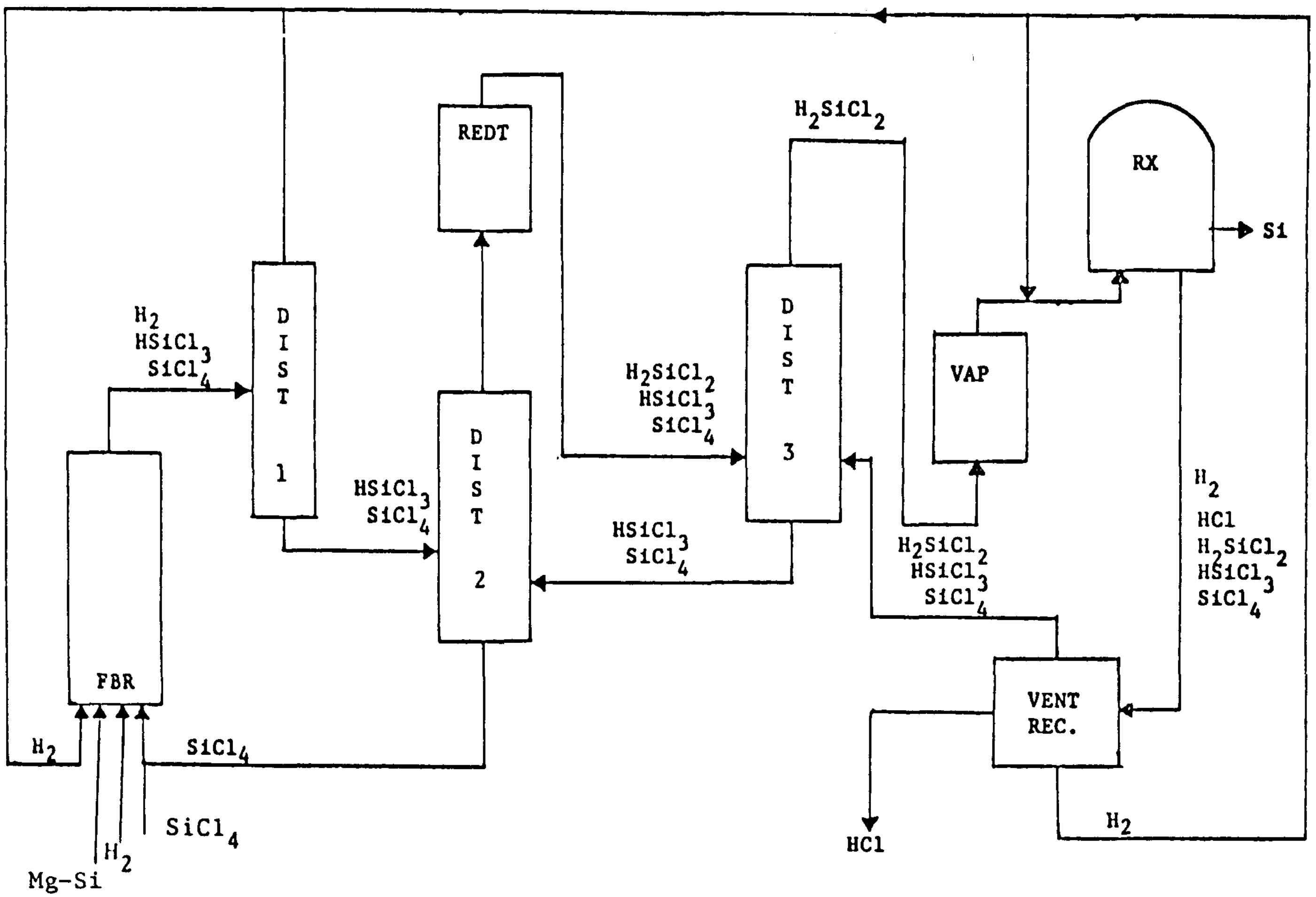


FIGURE 5. SCHEMATIC OF HSC LOW COST DICHLOROSILANE BASED POLYCRYSTALLINE SILICON PROCESS

hydrogenation segments of the process. Basic processes contained in the recovery system are condensation, compression, separation, and purification.[11]

The process is characterized by nearly complete chlorine and hydrogen recycle. Chlorine loss occurring as HCl at the output of the recovery system is made up by the addition of $SiCl_4$ into the fluidized bed reactor.

3.0 Technical Status

Phase 1 and Phase 2 technical efforts were limited to the areas discussed in Section 2.1. No efforts were expended in the area of trichlorosilane production due to JPL support of others for this process. Neither have efforts been devoted to the development of CVD reactor vent product recovery technology. This technology is closely aligned with recovery system technology currently employed in the trichlorosilane CVD process.

Section 3.1 through 3.9 detail technical results achieved during the contract period.

3.1 Reactor Feasibility

A small experimental CVD reactor[12] was modified to decompose dichlorosilane as part of the reactor feasibility task. The objectives of the reactor feasibility task were:

1. Establish feasibility of dichlorosilane as a feed material in a high deposition rate CVD reactor.
2. Optimize reactor operating parameters for dichlorosilane feed.
3. Develop comparative data regarding dichlorosilane and trichlorosilane behavior in a CVD reactor.
4. Provide necessary information for scale-up to an intermediate size or full-scale production reactor.
5. Establish vent product composition to permit EPSDU design, and 1000 metric-ton plant design and costing.
6. If necessary, evaluate the performance of a reactor operating on mixed feed (dichlorosilane and trichlorosilane).

A schematic of the experimental reactor showing the feed manifold and vent line configuration is shown in Figure 6. Rotameters were used to measure flow of various combinations of feed (TCS, DCS, or redistributed material) to the reactor. The reactor is composed of a heat shield, quartz bell jar, baseplate, and power supply. Feed and vent gas compositions were analyzed using a Bendix Model 170 gas chromatograph, a Perkin-Elmer Sigma

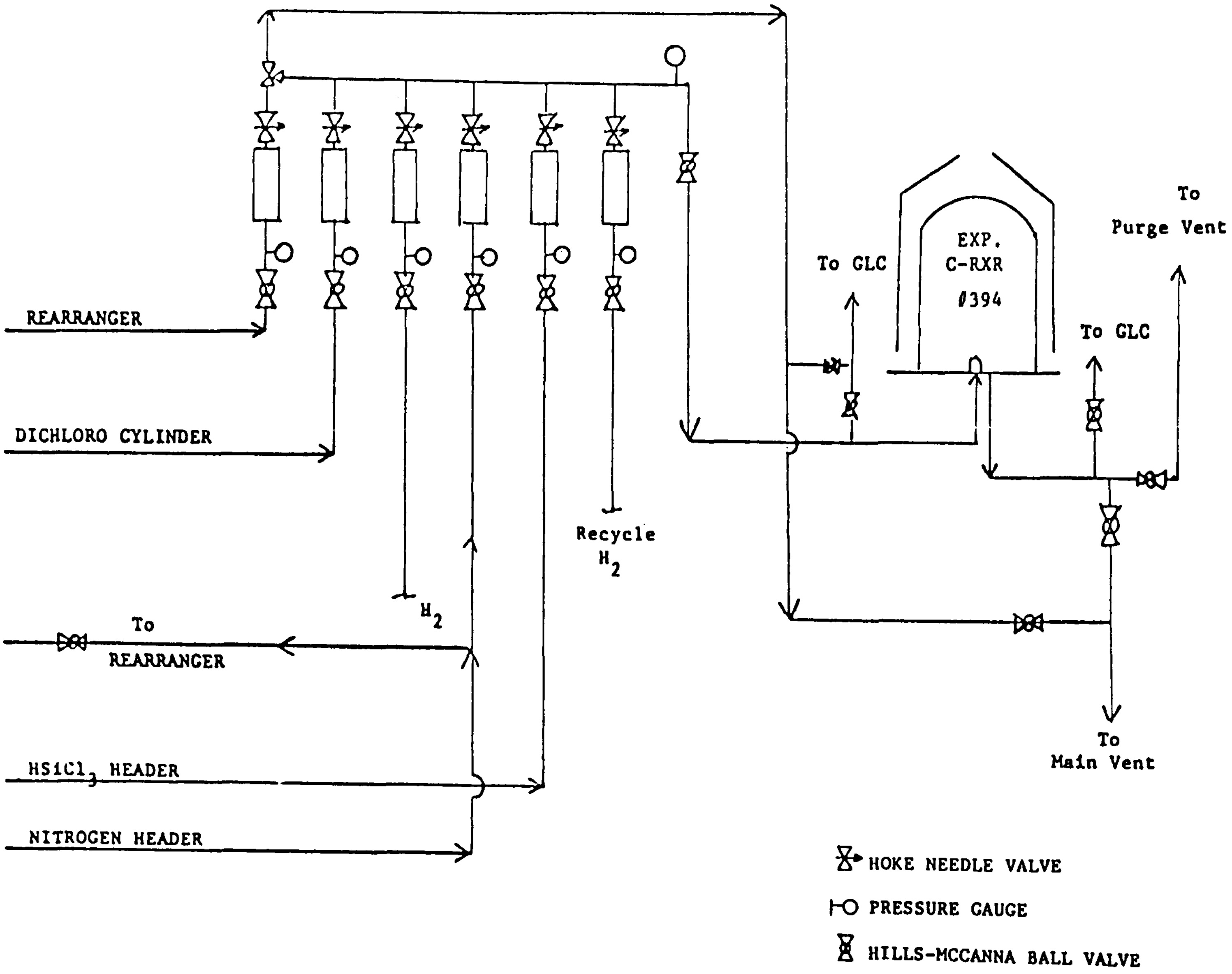


FIGURE 6. SCHEMATIC OF REACTOR FEED AND VENT PIPING

10 data system, and a North Star Horizon micro-computer. Typical dichlorosilane chromatographic results are found in Figure 7.

To conserve time and dichlorosilane, experimental runs were segmented. Segmentation involves introducing trichlorosilane early in an experimental run to produce rods of adequate size, while dichlorosilane was used later in the run where reactor operating conditions were more severe and more representative of production reactor operation.

Optimization experiments utilizing a two-level experimental design[13] were conducted to establish quantitative correlation between reactor operating parameters (total flow rate, mole percent dichlorosilane, and temperature) and measured responses (silicon deposition rate, conversion, and power consumption).

Nine DCS run segments, at conditions illustrated in Figure 8, were made along with replicate runs. Rod diameter ranges were classified as 26-32 mm, 33-39 mm, and 39-45 mm. The replicate experiments were made to confirm the assumption that rod diameter effects were minimal over the 26-45 mm range under these operating conditions. The eight experimental points (1-8) correspond to the corners of a cube in which the edges represent the variables: flow, mole percent DCS, and temperature.

Polynomial expressions describing the relationship between operating parameters and responses were developed using a least squares multiple regression analysis program.

In general, the equations predict that an increase in any independent variable will result in an increase in silicon deposition rate and decrease in power consumption with the stipulation that the reactor is not "feed starved." Dependence of conversion efficiency is more complex in that conversion is enhanced by increasing temperature, but diminished by increasing mole percent DCS and flow rate. A summary of data for the 9 cube locations is shown in Table 1.

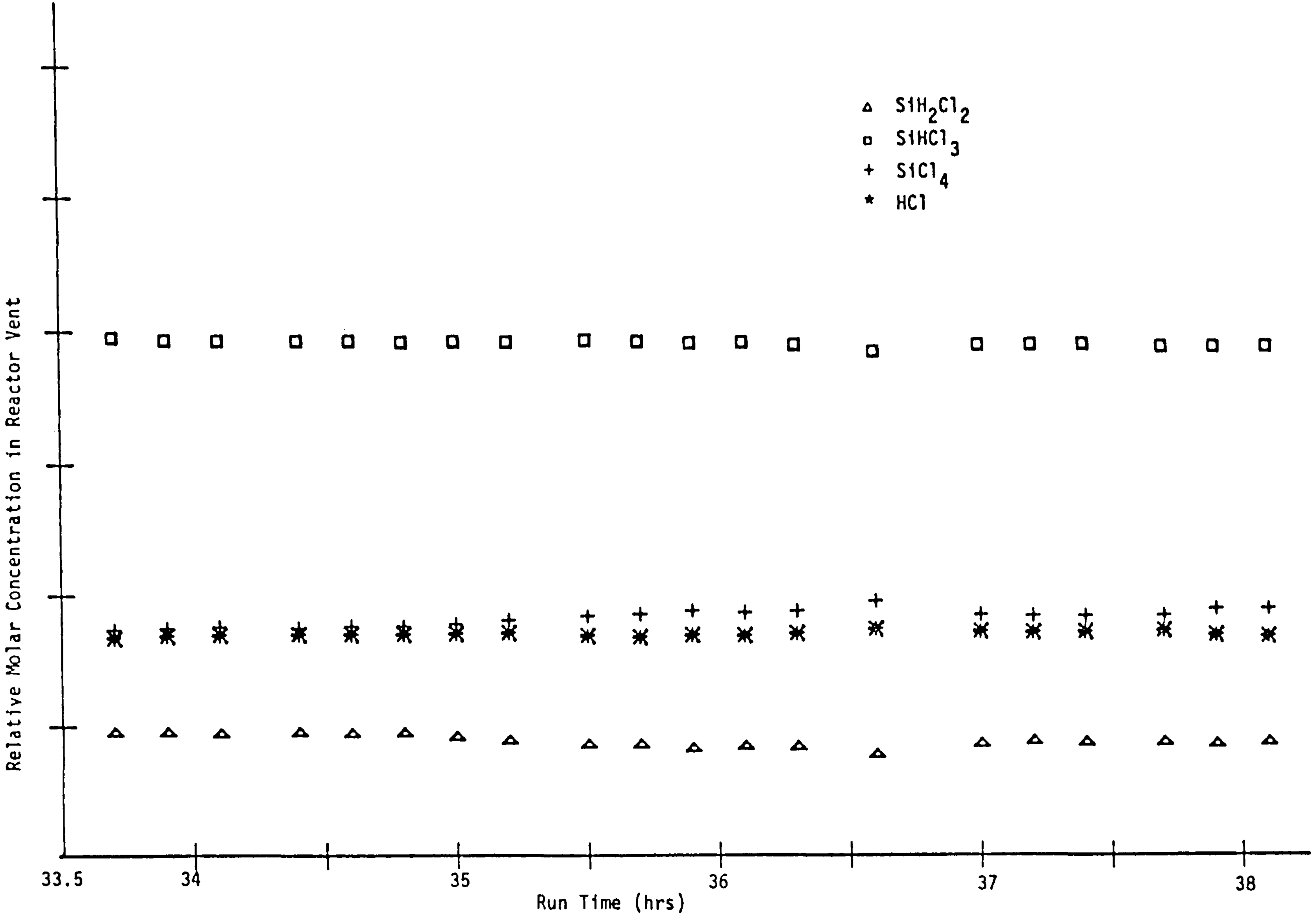
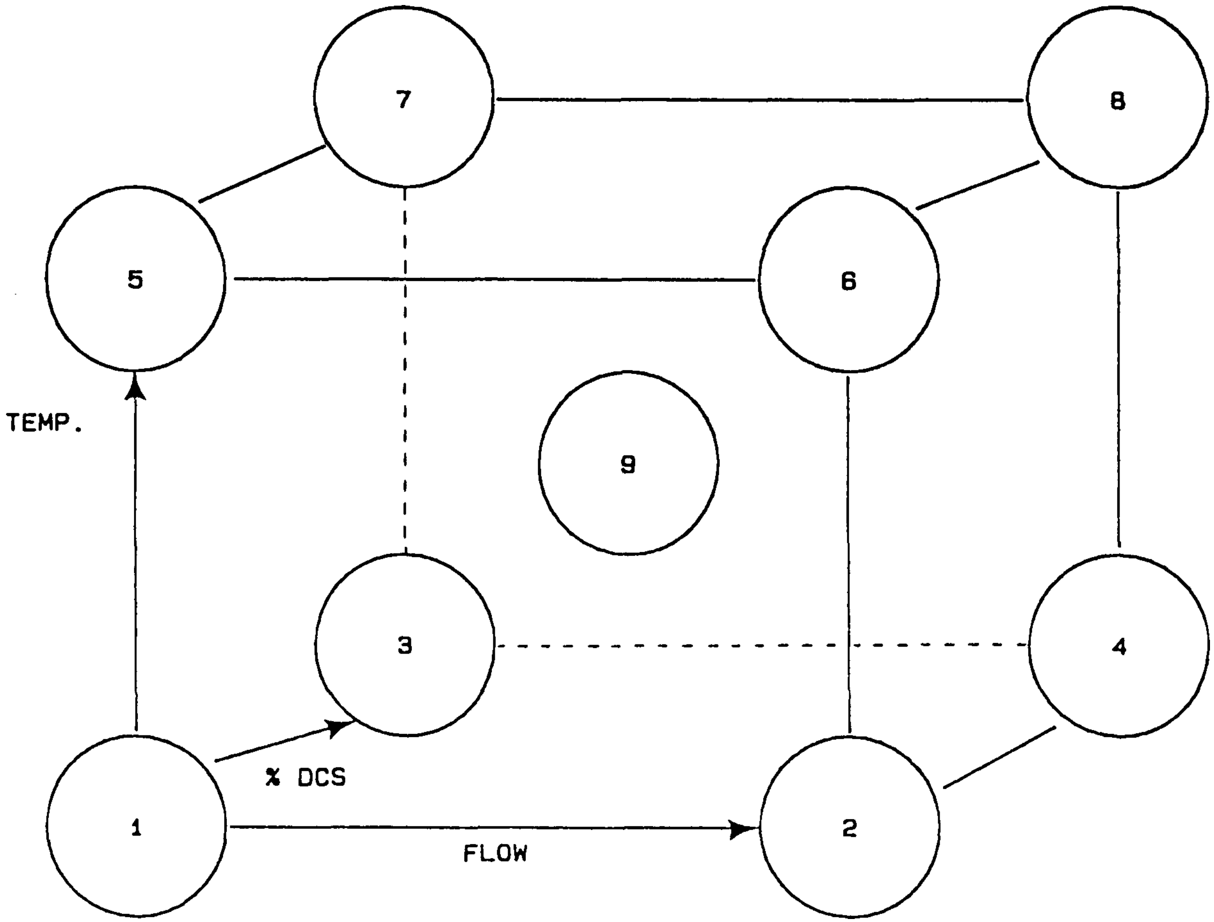


FIGURE 7 . CHROMATOGRAPHIC DATA FROM DICHLOROSILANE-TO-SILICON (Run #394-052-2)

Figure 8. DICHLOROSILANE EXPERIMENTAL DESIGN



RANGE OF VARIABLES: FLOW 90 SCFH - 180 SCFH

TEMP. 1020 DEGREES C - 1120 DEGREES C

% DCS 6 - 12

TABLE 1. SUMMARY OF RESULTS OBTAINED FROM DCS DECOMPOSITION DESIGNED EXPERIMENT

RUN NO.	POINT ON CUBE	SCFH/ MOLE %	TEMP. °C	ROD DIAMETER MM	SILICON DEPOSITION $gh^{-1}cm^{-1}$	CONVERSION MOLE %	POWER CONSUMPTION kWh/Kg
394-063-5	1	92/8.1	1020	31.6-35.8	0.648	40.7	165.8
394-063-4	2	180/6	1020	28.8-31.6	0.774	33.7	138.8
394-067-2	3	90/12	1020	26.4-31.2	0.723	31.7	143.6
394-068-4	replicate	90/12	1020	38.5-43.1	0.763	33.4	168.2
	(Average of previous two runs)				0.743	32.5	155.9
394-067-3	4	180/12	1020	31.2-39.1	1.069	23.5	114.1
394-067-4	5	92/8.1	1120	39.1-44.7	0.859	54.1	177.3
394-069-2	replicate	92/8.1	1120	26.8-32.4	0.809	50.5	164.6
	(Average of previous two runs)				0.834	52.3	171.0
394-068-3	6	180/6	1120	31.5-38.5	1.121	49.2	133.9
394-068-2	7	90/12	1120	26.9-31.5	0.983	43.2	131.7
394-063-6	8	180/12	1120	35.8-40.4	1.603	35.2	96.3
394-069-3	9	135/9	1070	32.4-38.6	1.007	39.2	126.4
Extrapolated Data Points for 90/6							
	1	90/6	1020		0.506	44.4	177
	5	90/6	1120		0.648	56.8	182

The order of importance of each variable and interaction terms are listed below in descending order for each of the three responses:

Silicon Deposition Rate	Conversion Efficiency	Power Consumption
1. Flow	1. % DCS	1. Flow
2. Temp.	2. Temp.	2. % DCS
3. % DCS	3. Flow	3. Int. of Temp. X % DCS
4. Int. of Flow and Temp.	4. Int. of Temp. and % DCS	4. Temp.
5. Int. of Flow and % DCS	5. Int. of Flow and Temp.	5. Int. of Flow and Temp.
6. Int. of Temp. and % DCS	6. Int. of Flow and % DCS	6. Int. of Flow and % DCS

Further analysis of the data for varying rod diameter indicated the rod diameter was less important than any of the variables or interaction terms.

As previously discussed, these runs were normally continuations of prior trichlorosilane runs. Run conditions were selected which were considered demanding. The expectation was that, at high feed rates and/or large rod diameters, operational problems such as vapor nucleation, or silicon deposition on the bell jar, or a significant loss in surface quality of the silicon would be apparent. Vapor nucleation--formation of silicon "dust" particles--was not observed, and jar deposition was slight, and quite comparable to trichlorosilane runs. Moreover, silicon surface quality remained consistently high.

Only one run segment (cube location 4) the high flow, high mole percent, low temperature combination caused operational problems. Material was deposited on the bell jar, baseplate, feed nozzle, and vent pipe. The material deposited in the vent pipe at a high rate, caused back pressure on the reactor which blew the bell jar seal. This behavior has not been observed under other conditions of operation.

Analysis of deposition residues from 394-067-3 were performed using X-ray diffraction techniques.

A Gandolfi camera can examine a single particle of material in the 30-1000 µm size range. This camera was used to examine the brown colored particles from the vent pipe deposit and feed nozzle deposit. Special care was taken to exclude the gray colored, nodular crystals, because the crystals were obviously silicon. The diffraction patterns which resulted from the residue were identified as silicon with a fine crystallite size of 100-1000 µm.

A high resolution Guinia camera was used to examine the baseplate residue and feed nozzle deposit. The samples were ground and run simultaneously using a multi-sample holder. Based on the resultant diffraction patterns, these samples were also identified as fine crystallite size (100-1000 µm) silicon.

In summary, there was almost a complete absence of reactor-related operational problems (broken bell jars, silicon build-up on bell jar walls, seal leaks, etc.) encountered with dichlorosilane decomposition. This may be the result of dichlorosilane decomposition being analogous to trichlorosilane decomposition, or run segmentation not being representative of the over all dichlorosilane decomposition process.

3.2 Trichlorosilane Redistribution

A preferred route to dichlorosilane production has been demonstrated to be the acid or base-catalyzed redistribution of trichlorosilane.

$$SiHCl_3 \underset{\text{Catalyst}}{\rightleftharpoons} SiH_2Cl_2 + SiCl_4$$

Dowex® MWA-1 is a basic resin (methyl-amine organic polymer) that is capable of inducing a redistribution reaction at reasonable rates and at moderate temperatures.

3.2.1 Catalyst Properties

The following properties of Dowex® MWA-1 ion exchange resin have been determined experimentally since the program was initiated:

Moisture Content	50-52 wt% (as received)
Bulk Density	0.54 gms/cc (wet) 0.35 gms/cc (dry)
Deformation (and Particle Bridging)	None @ 189°C and 0 psi load (after 28 hours) None @ 129°C and 32 psi load (after 4 hours)
Bed Swelling (Dry to Wet)	22% in Acetone 12% in Silicon Tetrachloride

Various methods for drying the resin catalyst were evaluated which included: solvent displacement, vacuum drying, oven drying, dessication and inert gas purging. With the exception of dessication, all of these methods were equally effective in removing the moisture.[12]

A partially equilibrated mixture of dichlorosilane, trichlorosilane and silicon tetrachloride was collected from the laboratory scale redistribution reactor unit and stored first at room temperature and then at 60°C. The mixture was reanalyzed after each storage period. Results are shown on the following page:

Sample No	Sample History	Composition (Mole %) MCS	DCS	TCS	STC
85XXa	Fresh from Catalyst Bed	0.2	8.6	81.4	9.8
85XXb	162 hrs a 18-24°C	0.2	8.3	82.2	9.4
85XXc	26 hrs at 60-65°C	0.2	8.1	82.2	9.4

From these results continued catalytic activity in storage does not appear to be a problem.

The catalyst was exposed to approximately 3200 ml of trichlorosilane prior to sample collection. No loss in catalytic activity was observed during experimental runs involving 4000 grams trichlorosilane and 50 grams Dowex® MWA-1 resin.

3.2.2 Laboratory Trichlorosilane Rearranger Unit

A laboratory-scale redistribution unit was designed and constructed and is shown schematically in Figure 9. The unit consists of a manifold which includes two stainless steel sample cylinders and a small rearranger. One of the cylinders is used to feed pure trichlorosilane or mixed feeds of trichlorosilane and silicon tetrachloride to the rearranger. The other cylinder is used to collect effluent from the stainless steel tubing which is immersed in an oil recirculating bath to insure constant temperature operation. Provisions exist for removal of samples for analysis (by gas chromatography), waste removal, and automatic venting to a purge line under upset conditions. The apparatus was designed for manipulation of liquid streams, but can also be adapted for vapor phase operation.

A Varian Model 3400 gas chromatograph equipped with a Valco® automatic gas sampling valve was installed to evaluate gas and liquid redistribution kinetics of trichlorosilane. An OV-101 on chromosorb W.H.P. column was found to quantitatively and reliably separate chlorosilane mixtures.

The most satisfactory method of analyzing liquid process streams was by expansion of ca. 1 cc of liquid into an evacuated

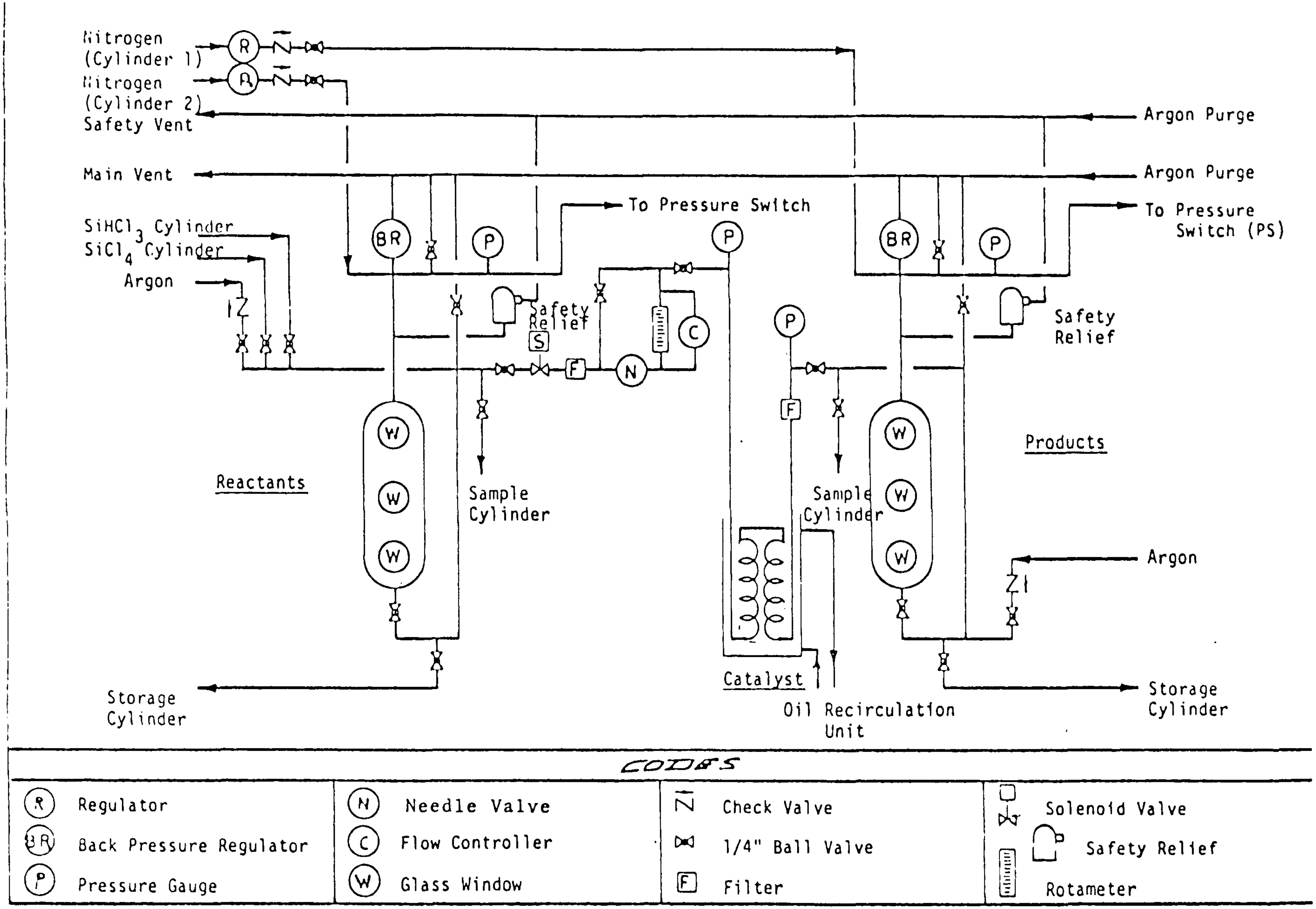


FIGURE 9. SCHEMATIC OF LABORATORY TRICHLOROSILANE REARRANGER UNIT

volume of 4 liters, followed by pressurization to 30 psig with helium and injection of 1 cc samples into the GLC column via the automatic gas sampling valve.

3.2.3 Redistribution Kinetics

The procedure used to evaluate redistribution kinetics was to feed trichlorosilane to the Dowex® MWA-1 catalyst bed at a controlled rate (temperature, pressure, and concentration) and measure the composition of the bed output stream by gas chromatography.

3.2.3.1 Vapor Phase Trichlorosilane Kinetics

Results of three runs made using a 65 mole percent trichlorosilane in helium mixture with the laboratory rearranger unit are shown in Table 2. Problems were encountered with the stability of the feed system resulting in trichlorosilane concentration varying ± 15 mole percent. However, the following conclusions were drawn from these experiments:

> Diffusion phenomena which have an effect on the kinetic rate constant in liquid phase systems do not appear as important in the gas phase system; for example, the k_o/a* rate values for 6-inch and 12-inch bed lengths are approximately equal.
>
> Dowex® which was conditioned by air (and inert gas) purge drying exhibits an unusually high k_o/a rate value. It is expected that this high k_o/a rate value or catalytic activity is the result of trimethylamine evolution with vacuum drying and that once the trimethylamine is "baked out", subsequent catalytic activity will be reduced to that of the 100°C vacuum baked Dowex®.

The Micrometer® flow control valve was moved downstream of the trichlorosilane cylinder,[14] which then allowed the trichloro-

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* Defined on page 38

TABLE 2. VAPOR PHASE TRICHLOROSILANE REDISTRIBUTION DATA
(65 Mole % Trichlorosilane in Helium)

	Conditions				Products (Mole %)			
Ref No	Dowex Preparation	Bed Length (Ins)	Linear Flow (Ft/Hr)	Res Time (sec)	MCS	DCS	TCS	STC
18B	100 degC Vac Bake	6	10312	0.17	0.0	1.0	97.8	1.2
16A	" " " "	"	6714	0.29	0.0	1.3	96.9	1.7
16B	" " " "	"	2398	0.75	0.0	2.9	93.7	3.3
16C	" " " "	"	720	2.5	0.0	5.1	88.6	6.2
18A	" " " "	"	120	15	0.5	11.0	76.1	12.4
30B	Air (Inert) Purge	12	10312	0.35	0.0	4.7	90.6	4.6
30C	" " " "	"	6714	0.54	0.1	6.2	87.5	6.2
30D	" " " "	"	2398	1.5	0.2	8.8	81.8	9.2
30A	" " " "	"	720	5.0	0.4	9.7	79.7	10.2
30E	" " " "	"	120	30	0.7	12.9	72.8	13.5
37C	100 degC Vac Bake	12	10312	0.35	0.0	1.1	97.9	1.0
37A	" " " "	"	6714	0.54	0.0	1.3	97.6	1.1
37B	" " " "	"	2398	1.5	0.0	2.7	94.7	2.6
37E	" " " "	"	720	5.0	0.2	7.6	84.2	8.0
37D	" " " "	"	120	30	0.5	10.8	75.8	12.9

Catalyst : Dowex Ion Exchange Resin
Bed Diameter : 0.25 inch (0.036 inch wall) tubing
Bed Temperature: 85 degC
Feed : 65 mole% Trichlorosilane in Helium
Feed Phase : Gas

Note : Linear flow and residence time have been corrected for the void volume of the catalyst, e.g. a=0.50

silane cylinder to be operated under a constant 10 psig pressure. Constant pressure enabled the system to operate much closer to the feed concentration desired.

Three more runs were made in order to evaluate lower concentrations, and the effect of thermal pretreatment of Dowex® resin on its catalytic activity. The data shown in Table 3 were collected using a feed of 40 mole percent (± 3 mole percent) trichlorosilane in helium. Unpublished runs indicate that diluent concentration has no observable effect on redistribution kinetics in the gas phase. The data have been fitted to the second order kinetic rate equation for reversible reactions and are shown in Figure 10.

3.2.3.2 Liquid Phase Trichlorosilane Kinetics

Data were collected to evaluate the kinetics of the trichlorosilane redistribution reaction at liquid flow rates greater than 5 ft/hr. The data are presented in Tables 4 and 5, and Figure 11 and 12. Product composition data were fitted to the kinetic rate expression for reversible second order reactions, i.e.

$$2\mathrm{TCS} \overset{k}{\rightleftharpoons} \mathrm{DCS} + \mathrm{STC}$$

$$(1-x) \qquad (x/2) \quad (x/2)$$

and $$k=x_e/(2t(1-x_e))\ln((x(1-2x_e)+x_e)/(x_e-x)) \qquad \text{(Eq 1)}$$

where k is the kinetic rate constant (min^{-1}), t is the residence time (min), x_e is the equilibrium mole fraction and x is the mole fraction at time t. In the above expression x is twice the observed mole fraction of DCS and x_e is twice the equilibrium mole fraction of DCS calculated according to:

Table 3. Vapor Phase Trichlorosilane Redistrubution Data
(40 Mole % Trichlorosilane in Helium)

	Conditions				Products (Mole %)			
Ref No	Dowex Preparation	Bed Size	Linear Flow (Ft/Hr)	Res Time (sec)	MCS	DCS	TCS	STC
46B	100 degC Vac Bake	C	3592	0.17	0.0	1.7	97.3	1.0
46E	" " "	"	2338	0.26	0.0	1.8	96.8	1.3
46A	" " "	"	834	0.72	0.1	2.9	94.7	2.3
46C	" " "	"	250	2.4	0.1	5.5	89.4	5.0
46D	" " "	"	42	14	1.4	11.0	74.9	12.7
53C	100 degC Argon	C	3592	0.17	0.0	0.6	98.8	0.6
53A	" " "	"	2338	0.26	0.0	0.3	99.4	0.3
53D	" " "	"	834	0.72	0.0	1.8	96.3	1.9
53E	" " "	"	250	2.4	0.0	4.6	90.9	4.5
53B	" " "	"	42	14	0.2	8.5	82.9	8.3
44D	165 degC Vac Bake	C	3592	0.17	0.0	0.5	98.7	0.8
44A	" " " "	"	2338	0.26	0.0	0.8	98.2	0.9
44E	" " " "	"	834	0.72	0.0	0.9	97.8	1.3
44B	" " " "	"	250	2.4	0.0	2.1	95.7	2.2
44C	" " " "	"	42	14	0.0	3.9	91.8	4.3

Catalyst : Dowex Ion Exchange Resin
Bed Sizes : A = 1/4" x 6"
(Tubing Wall = 0.035") B = 1/4" x 12"
C = 3/8" x 2"
Bed Temperature : 85 degC
Feed : 40 mole % Trichlorosilane in Helium

Note : Linear flow and residence time have been corrected for the void volume of the catalyst, e.g., a=0.50

FIGURE 10. KINETIC DATA FROM VAPOR PHASE REDISTRIBUTION OF TRICHLOROSILANE BY DOWEX® MWA-1 RESIN (85°C)

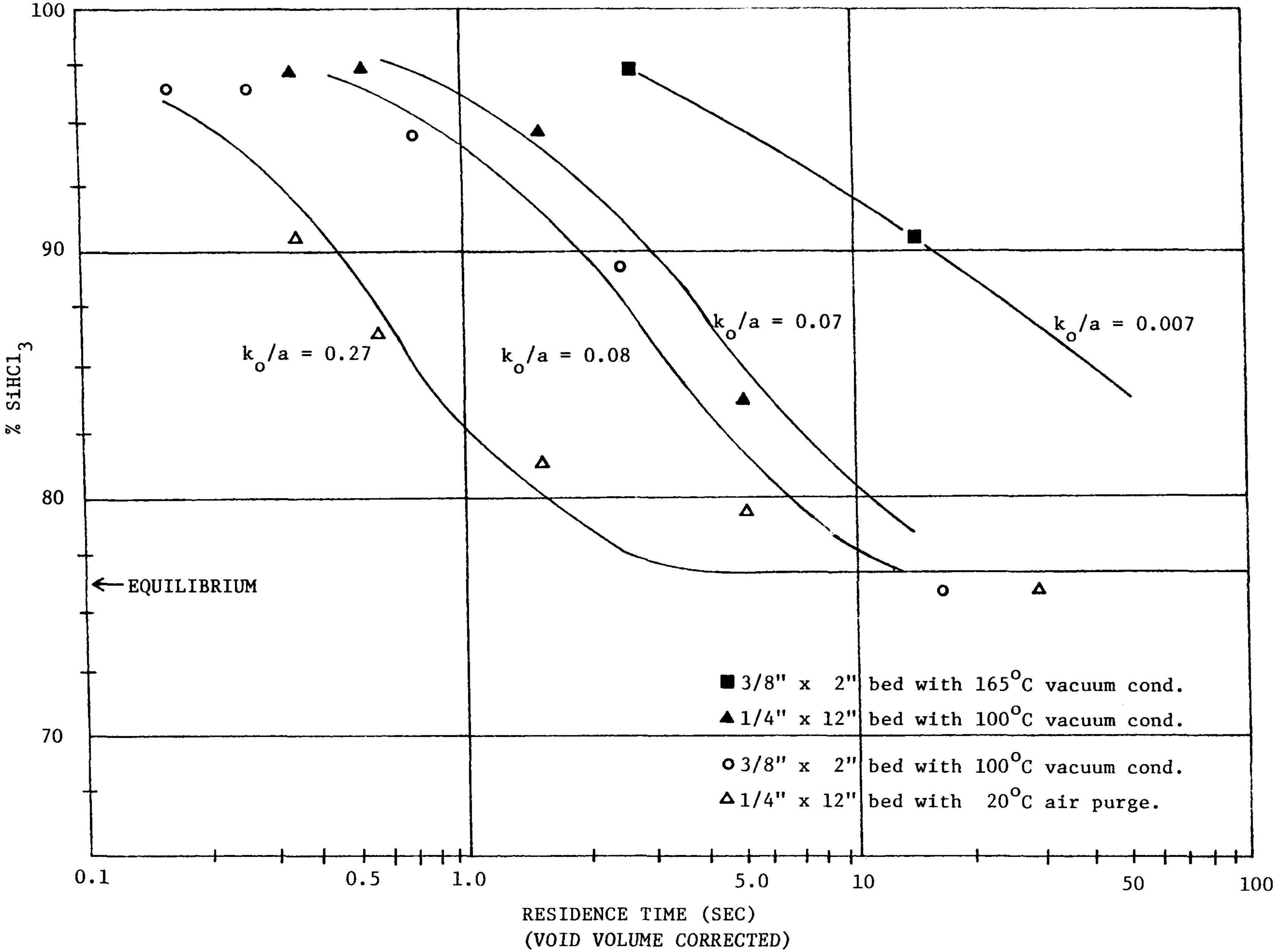


TABLE 4. LIQUID PHASE TRICHLOROSILANE REDISTRIBUTION DATA

	Conditions			Products (Mole %)			
Ref No	Bed Length (Ins)	Linear Flow (Ft/Hr)	Res Time (Mins)	MCS	DCS	TCS	STC
81A	40	95.0	2.1	0.2	10.2	78.9	10.7
80A	"	65.6	3.0	0.3	10.0	79.3	10.4
80C	"	49.2	4.1	0.4	11.3	77.0	11.2
80B	"	29.4	6.8	0.4	11.5	76.1	11.8
81B	"	8.4	23.8	0.4	11.2	76.6	11.8
83A	20	95.0	1.0	0.1	7.4	85.1	7.4
82C	"	65.6	1.6	0.2	8.5	83.3	8.0
82A	"	49.2	2.0	0.4	11.0	77.0	11.6
82B	"	29.4	4.5	0.3	10.7	78.0	10.9
83B	"	8.4	13.2	0.3	11.4	76.8	11.4
85XA	15	95.0	0.79	0.1	5.7	88.4	5.7
84XB	"	65.6	1.1	0.2	8.3	83.5	7.9
84XA	"	49.2	1.5	Rejected Sample			
84XC	"	29.4	2.6	0.4	11.6	76.8	11.0
85XB	"	8.4	8.9	0.3	9.3	80.3	10.0
90A	15	95.0	0.79	0.1	6.6	87.1	6.1
91C	"	65.6	1.1	0.1	9.0	82.5	8.4
91B	"	49.2	1.5	0.2	9.8	81.1	8.9
91A	"	29.4	2.6	0.2	10.6	79.3	9.8
90B	"	8.4	8.9	0.3	10.9	78.4	10.4
87A	10	95.0	0.53	0.2	6.6	86.9	6.3
86C	"	65.6	0.76	0.2	7.4	85.4	7.0
86A	"	49.2	1.0	0.1	5.0	90.3	4.7
86B	"	29.4	1.7	0.3	8.5	89.0	8.2
87B	"	8.4	6.0	0.5	11.6	76.9	11.1
89B	5	95.0	0.26	0.0	3.3	93.6	3.0
88B	"	65.6	0.38	0.0	2.8	94.6	2.5
88C	"	49.2	0.51	0.1	4.2	91.9	3.8
88A	"	29.4	0.85	0.2	6.5	87.3	6.0
89A	"	8.4	3.0	0.2	9.1	82.3	8.5
92A	2	95.0	0.11	0.0	2.4	95.2	2.4
93C	"	65.6	0.15	0.0	2.8	94.7	2.5
93A	"	49.2	0.20	0.0	3.5	93.7	3.0
93B	"	29.4	0.34	0.0	4.4	91.9	3.7
92B	"	8.4	1.2	0.1	5.3	89.6	5.0

Catalyst : Dowex Ion Exchange Resin
Bed Diameter: 0.5 inch (0.035 inch wall) tubing

Bed Temp: 77-79 degC
Feed : TCS Liquid

TABLE 5. LIQUID PHASE TRICHLOROSILANE REDISTRIBUTION KINETIC DATA SUMMARY

Linear Flow (Ft/Hr)	TCS Data Basis k_o/a Rate Value (min-1)		DCS Data Basis k_o/a Rate Value (min-1)	
95.0	0.23	(0.02)	0.22	(0.02)
65.6	0.22	(0.02)	0.20	(0.02)
49.2	0.18	(0.02)	0.19	(0.03)
29.4	0.19	(0.03)	0.20	(0.02)
8.4	0.10	(0.01)	0.10	(0.02)

Catalyst : Dowex Ion Exchange Resin
Bed Diameter : 0.50 inch (0.035 inch wall) tubing
Bed Temperature: 77-79 °C
Feed : Trichlorosilane Liquid

Note: Linear flow has been corrected for the void volume of the catalyst, i.e. a=0.50

FIGURE 11. KINETIC DATA FROM REDISTRIBUTION OF TRICHLOROSILANE BY DOWEX® RESIN (77°C, liquid)

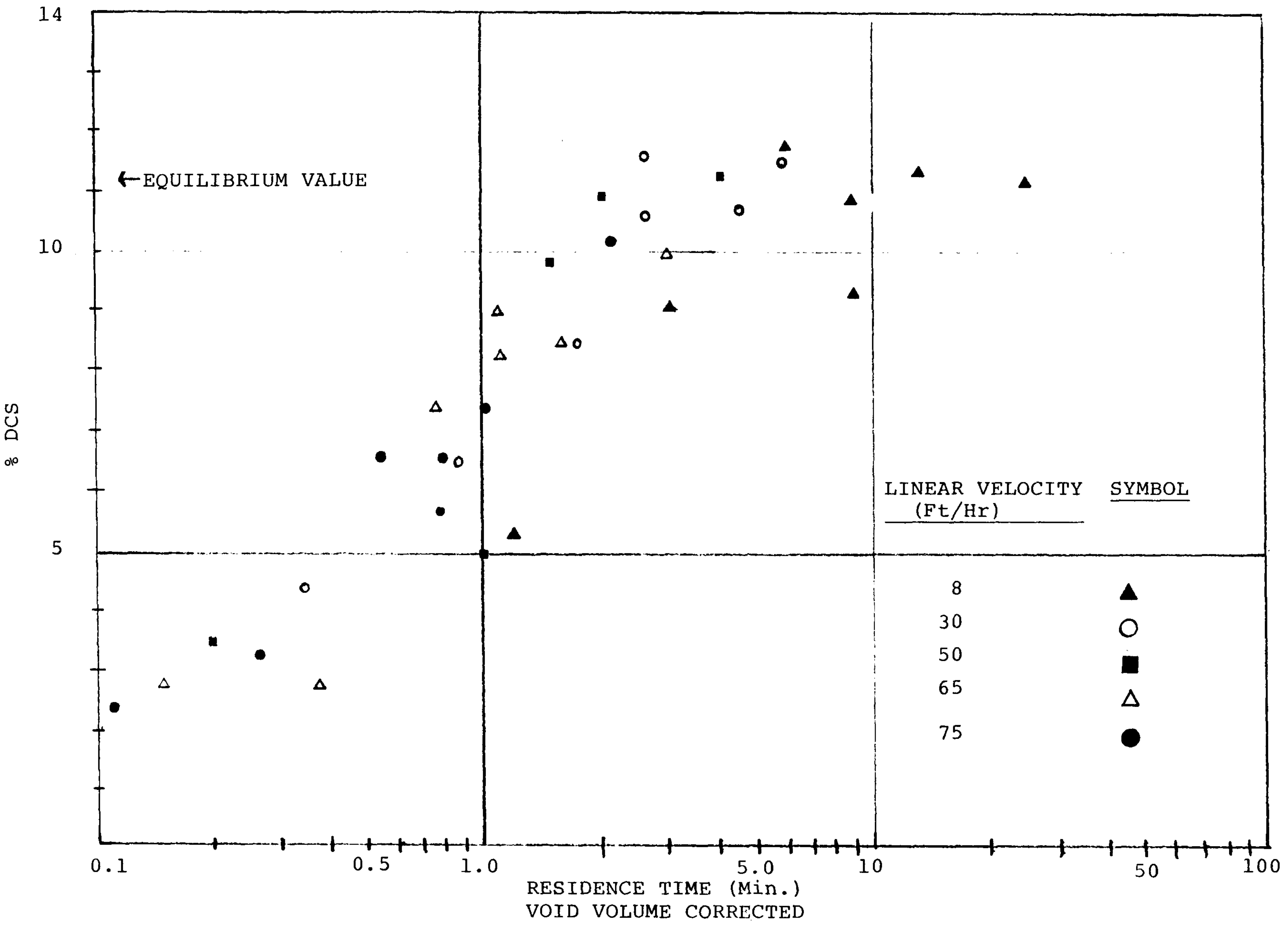
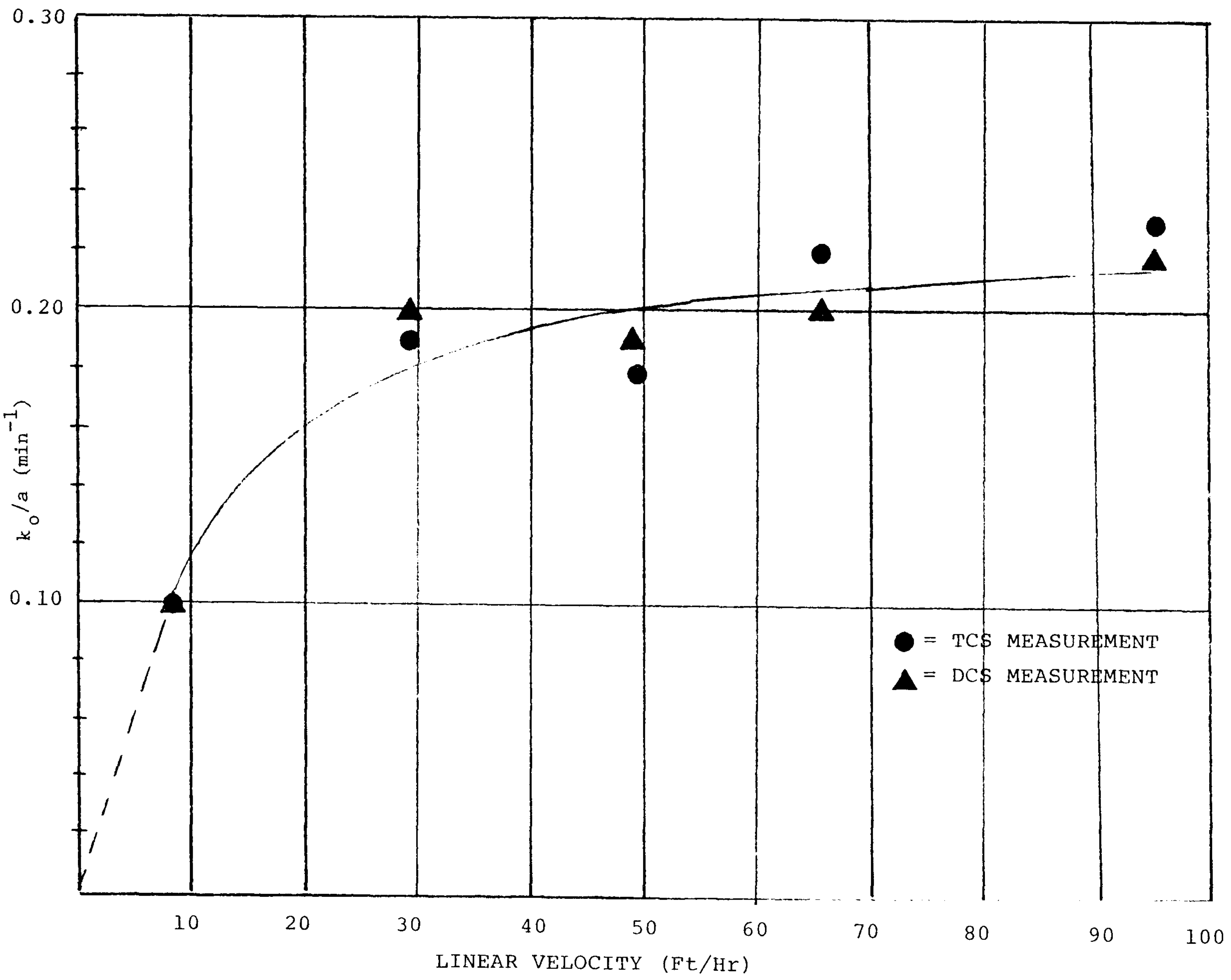


FIGURE 12. RATE CONSTANT VS. LINEAR VELOCITY FOR LIQUID PHASE REDISTRIBUTION OF TRICHLOROSILANE BY DOWEX® RESIN (77°C)



$$x_e=(4K_p-2\ \ K_p)\ /(4K_p-1) \qquad \text{(Eq 2)}$$

and $K_p=\exp((-\ \ H/\ RT)+C_o)$

where $H=1486$ cal/mole and $C_o=-1.7540$ (Eq 3)

If the open tube residence time (t) in Eq 1 is used the rate constant will also be that for the open tube conditions (k_o). In this report open tube rate constants have been corrected for the presence of catalyst by dividing the open tube rate constant by the void volume fraction of the catalyst (a). The values k_o/a used in this report refer to this correction process. A void volume fraction of 0.50, i.e. a=0.50, was used for Dowex® resin. It appears from these data that the k_o/a rate value versus velocity (ft/hr) levels off at ca. 0.20 min-1 at velocities greater than 25-30 ft/hr. This behavior indicates that reasonably good mixing at the solid liquid interface is present and that problems associated with liquid diffusion have been minimized at the higher velocities.

In view of the substantial change in kinetic rate behavior observed between air (and inert gas) purge dried and vacuum dried Dowex® in the gas phase catalytic system (see above), a similar experiment was conducted with the liquid phase system. The data are presented in Table 6 and indicate little if any difference between the two methods of conditioning.

3.2.3.3 Liquid Phase Trichlorosilane-Silicon Tetrachloride Kinetics

According to available thermodynamic data it seemed possible to suppress the formation of unwanted monochlorosilane by feeding a 80% trichlorosilane/20% silicon tetrachloride mixture to the catalyst bed. A screening run was made with a 0.5-inch diameter by 100-inch long Dowex® bed. This bed length was chosen to insure sufficient residence time to achieve

TABLE 6. LIQUID PHASE TRICHLOROSILANE REDISTRIBUTION DATA. CATALYST PREPARATION METHODS

	Conditions				Products (Mole %)			
Ref No	Preparation Method	Bed Length (Ins)	Linear Flow (Ft/Hr)	Res Time (Mins)	MCS	DCS	TCS	STC
85XA	Air (Inert) Purge	15	95.0	0.79	0.1	5.7	88.4	5.7
84XB	" " "	"	65.6	1.1	0.2	8.3	83.5	7.9
84XA	" " "	"	49.2	1.5	Rejected Sample			
84XC	" " "	"	29.4	2.6	0.4	11.6	76.8	11.0
85XB	" " "	"	8.4	8.9	0.3	9.3	80.3	10.0
90A	100 °C Vac Bake	15	95.0	0.79	0.1	6.6	87.1	6.1
91C	" " " "	"	65.6	1.1	0.1	9.0	82.5	8.4
91B	" " " "	"	49.2	1.5	0.2	9.8	81.1	8.9
91A	" " " "	"	29.4	2.6	0.2	10.6	79.3	9.8
90B	" " " "	"	8.4	8.9	0.3	10.9	78.4	10.4

Catalyst : Dowex Ion Exchange Resin
Bed Diameter : 0.50 inch (0.035 inch wall) tubing
Bed Temperature: 77-79 °C
Feed : Trichlorosilane Liquid

Note: Linear flow and residence time have been corrected for the void volume of the catalyst, i.e. a=0.50

equilibrium. The results are presented below:

Feed (Mole %)	MCS	DCS	MCS/DCS Ratio
	Product (Mole %)		
100% TCS	0.37	10.8	0.033
80% TCS/20% STC	0.10	5.0	0.021

Although the reduction in the MCS/DCS ratio with the mixed system is indeed lower than the ratio with 100 mole % trichlorosilane system, the reduction is not as great as expected and, in view of the 54% decrease in DCS production, the mixed feed system is not considered to be a viable alternative.

3.2.4 Purity of Polysilicon from Laboratory Rearranger

The purity of material from the laboratory scale liquid phase rearranger was evaluated by collecting a 6-liter sample of redistributed chlorosilanes for use as feedstock for depositing a silicon rod by chemical vapor deposition. A 100-inch bed of Dowex® MWA-1 resin was used for redistribution. The deposited silicon rod was analyzed for boron, donor (phosphorus) and aluminum by a multipass zone refining technique and for carbon by Fourier transform infrared (FTIR) analysis. Results are shown below.

Ref No	Silicon Rod Feed Source	Boron (ppba)	Donor (ppba)	Aluminum (ppba)	Carbon (ppma)
394-022	77°C Dowex®	Bed Conditioning Run - No Rod Grown			
394-023	Control	0.19	1.1	0.30	0.5
394-024	24°C Dowex®	0.48	1.4	0.09	0.5
394-025	Control	0.15	1.7	0.18	0.3
394-026	77°C Dowex®	0.69	1.2	0.06	0.4

These results indicate a slight degree of boron contamination, with respect to semiconductor grade silicon, which may be caused by redistribution using Dowex®. The boron levels in runs with both heated and room temperature Dowex® were a factor of 3 to 4 higher than the control runs made without the presence of the catalyst. Such boron levels have no impact on the utility of the product for solar grade silicon.

3.3 DICHLOROSILANE SAFETY DATA

DCS was reported in the literature to undergo combustion that is easily initiated and unusually violent. In order to properly design and locate a DCS plant, a more thorough understanding of properties was required. Accordingly, Hazards Research Corporation[*] (HRC) was engaged to conduct a series of tests relating to the flammability and hydrolytic characteristics of DCS.

Specific tests were:

1. Autoignition: determine temperature at which DCS/air mixtures spontaneously ignite.

2. Explosion severity: determine rate of pressure rise in a closed vessel upon ignition of DCS/air.

3. Hydrolytic: determine if ignition occurs when a simulated DCS spill was subjected to a water deluge, or water into DCS.

4. Explosive output: determine output of an unconfined vapor cloud of DCS/air mixture.

3.3.1 Test Methods

AUTOIGNITION TEMPERATURE DETERMINATIONS

Autoignition temperature determination was made using a steel autoclave with a volume of 300 milliliters. A Wood's metal bath was used to provide controlled temperature. A small amount of sample vapor from a reservoir was injected into the thermally equilibrated vessel at a preselected temperature and the result observed for up to 10 minutes. Temperature of the internal vapor space was monitored using a thermocouple-recorder system. If the result was combustion, a successive trial was performed at a

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[*] Hazards Research Corp., 200 East Main Street, Rockaway, New Jersey

lower temperature; if no combustion was obtained, a higher temperature was used. The procedure was continued until the lowest temperature for combustion and the highest temperature for non-combustion were separated by less than 10°C. The sample charge was then increased and decreased in subsequent trials to assure that the lowest autoignition temperature as a function of composition had been determined.

EXPLOSION SEVERITY DETERMINATION

The explosion severity experiments were conducted in a ten liter spherical vessel equipped with pressure and temperature monitoring systems. The sphere also contained a rupture disc, a gas injection system and a nichrome coil ignition system. The injection and ignition systems were centrally located.

DCS vapor was admitted to the evacuated sphere to a desired partial pressure, followed by admission of dry air to one atmosphere total pressure. The vessel was allowed to stand to permit mixing for 5 minutes, then the nichrome coil was fused. The pressure history of the reaction was recorded by a fast acting transducer in combination with an oscillograph or, for unusually high velocities, an oscilloscope. Experiments were conducted at ambient temperature.

HYDROLYTIC

Two tests were conducted to determine the effect of water on DCS. One test consisted of spraying water into a pool of DCS; in the other, DCS was sprayed into a pool of water. Both tests used a pan approximately 12 inches in diameter by 2 inches deep to contain liquid. Five pounds of DCS were placed in a cylinder and released by remote control. Water flow was controlled by remotely located manual valves. Provisions were made to ignite vapor clouds resulting from hydrolysis with a "squib" pyrotechnic igniter.

EXPLOSIVE OUTPUT

In an attempt to simulate an unconfined vapor cloud explosion, a cube 5 feet on a side was constructed from wood and covered with a transparent polyethylene film. A small fan within the enclosure provided mixing of the contents and a squib was located within the cube to act as an ignition source. "Bikini" gauges were placed at varying distances from the cube to measure overpressure waves caused by the explosion. High speed photographic equipment was positioned approximately 80 feet away and real-time photography was placed above the area at approximately a 45° angle to provide visual documentation.

The enclosure started with air inside. DCS was introduced into the cube as either vapor or liquid from a cylinder at a remote site to the cube. Cylinder weight change was used to establish when the predetermined amount of DCS had been admitted to the cube. DCS concentration was adjusted to that corresponding to the maximum pressure rise in the explosion severity scans. The process of filling the cube required about 45 minutes.

3.3.2 Results and Discussion

AUTOIGNITION TEMPERATURE (AIT) TEST RESULTS

Material (In Air)	AIT	
DCS	58 ± 5°C	
DCS/H_2	255 ± 5°C	10 m %/DCS/90 m % H_2
Redistributed TCS	130 ± 5°C	~ 10 m % DCS, 80 m % TCS, 10 m % STC

Irrespective of the precise value of the AIT of DCS in dry air, it is clear that the thermal ignition requirements of such mixtures are very small.

EXPLOSION SEVERITY TEST RESULTS

Material	Expt.	$(dP/dt)_{max}$ psi/sec	P(static) psig	P(dynamic) psig
DCS	1	1.1×10^6	112	280
	2	1.1×10^6	125	280
	3	0.8×10^6	125	225
DCS/H_2 10/90		5.4×10^4	90	
H_2		2.4×10^4		
Redistributed TCS		1.2×10^3	84	

Figure 13 is a plot of maximum pressure rise (psi/sec) versus concentration of DCS in air. (Note that the peak value is less than from the above table where higher resolution of the pressure time curve was obtained.)

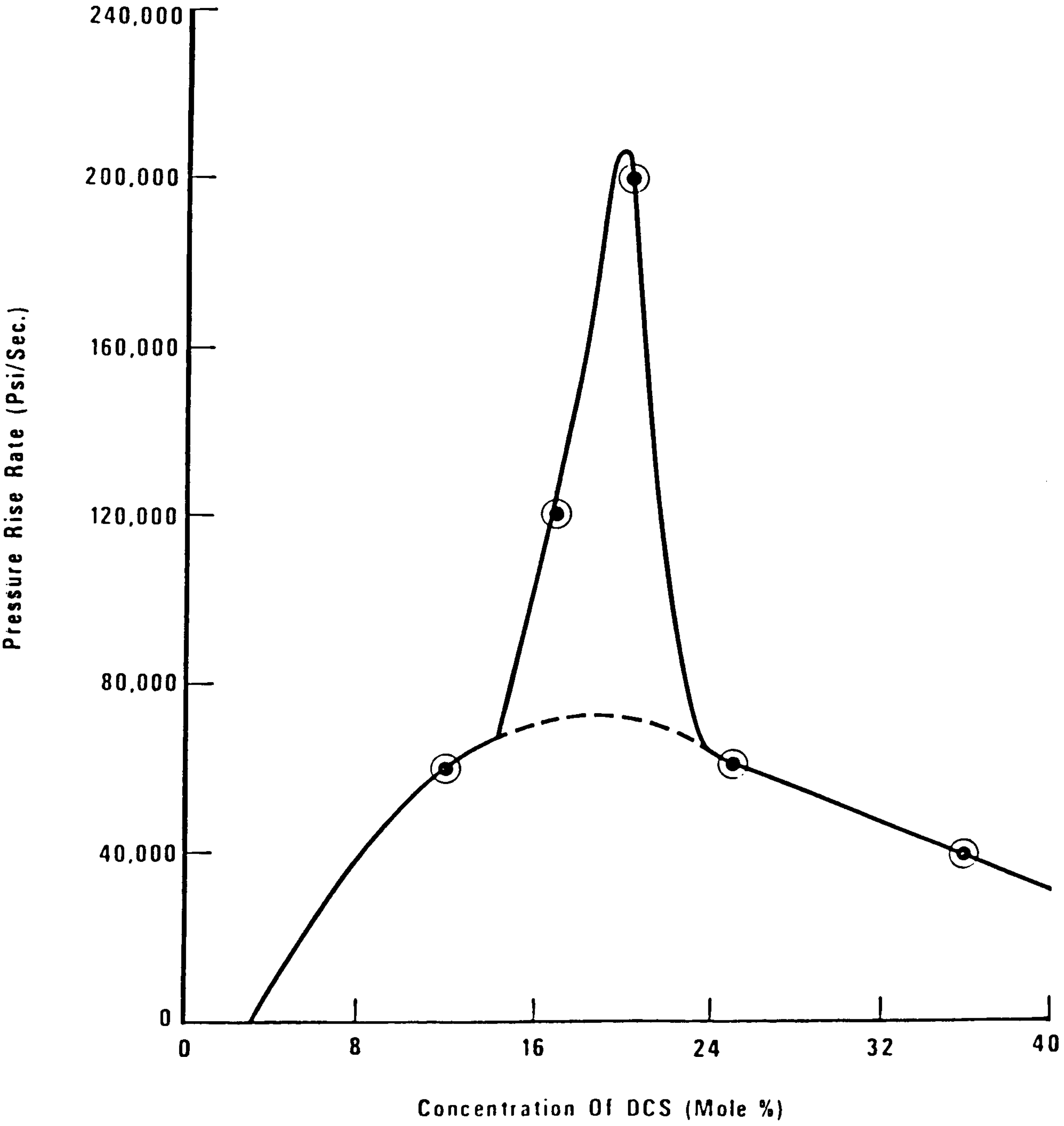
From this test it was established that a detonation can occur with DCS in a confined system. These results were obtained from equipment that confines the combustion products. It is possible that the high peak rate of pressure rise is affected by confinement; however, it must be assumed that partially confined or unconfined vapor clouds of DCS could detonate under certain conditions.

HYDROLYTIC TESTS RESULTS

Hydrolytic tests showed no ignition when water was added to DCS, or when DCS was added to water. The hydrolytic reactions were accompanied by copious fuming and left white powdered, or rubbery flammable residues. In neither test was spontaneous ignition of the vapor cloud observed.

In the trial in which DCS was discharged into a pool of water, the resultant vapor cloud was successfully ignited with the squib. A flame was also sustained in the pan, at this point even when a water spray was turned on the pan. Reaction both before and after the deliberate ignition was not considered violent.

FIGURE 13. PRESSURE RISE RATE FOR DCS EXPLOSIONS IN 10 LITER SPHERE



These results do not conclusively demonstrate that ignition cannot be initiated by addition of water, however. Based on experience one would conclude that nearly any thermal, mechanical, or chemical reaction energy could be sufficient to ignite a mixture of DCS and air.

Cleanup procedures for the flammable hydrolyzate should prohibit storage in closed containers such as trash cans or bags. If incineration is available as a disposal technique, it would be the best method as it would convert the material into silica.

EXPLOSIVE OUTPUT TEST RESULTS

Two trials of the explosive output experiment were conducted. The first test, in which DCS was admitted as a gas, proceeded by plan only until the required amount of DCS had been added to the cube. When the valve on the (remote) DCS cylinder was closed, ignition occurred. Unfortunately this unplanned ignition occurred without any photographic or visual documentation. The report was barely audible from the observation stations, and the Bikini overpressure gauges were unaffected.

The second test was run with DCS being admitted as a liquid spray to promote mixing and shorten loading time. Subsequent to loading, the fan was started and run for one minute. Ignition occurred--as scheduled--when the squib was fired. A slight report was heard, but the Bikini gauges did not indicate blast wave overpressures. Both trials produced a rapid deflagration with no detonation.

Based on volume of the report and damage incurred by the cube structure it was estimated that the explosive output was 4-5 times that of the propylene test run as a standard.

This series of tests indicates that DCS is unpredictable in behavior with respect to combustion. Ignition may be induced by something as minor as turning off flow through a line. Although detonation did not occur in this test it is not possible to say that detonation could not occur in a larger vapor cloud. Given sufficient distance the rapid deflagration observed could transform into a supersonic flame front, or detonation. Factors such as initial temperature, partial confinement, and efficiency of mixing seem to affect the combustion process significantly.

3.3.3 CVD Reactor Explosion Test Results

Because of the extreme fire and explosion hazard associated with pure dichlorosilane, an explosion test of the reactor system planned for use in the "Intermediate Reactor Development" phase of this program was considered necessary to insure that the system would maintain sufficient integrity in the event of explosion within the reactor to prevent personnel injury and minimize equipment damage.

Two tests[15] of reactor heat shields were performed at the Dow Chemical Company (Larkin Test Laboratory). The first heat shield test used an older model heat shield that did not maintain its mechanical integrity. The second explosion test was conducted with a modified heat shield reinforced with three bands which maintained its integrity.

3.3.4 Summary of DCS Combustion Hazards

The HRC experimental program confirmed the suspicions that DCS/air mixtures are both very easily and sometimes unpredictably ignited, and that the explosive potential from such ignitions is unusually high. In summary, the low boiling point, broad flammability range, low autoignition temperature, and rapid rate of combustion combine to make dichlorosilane a much more hazardous material than trichlorosilane, silicon tetrachloride, or hydrogen. Alternative designs and procedures for the PDU and intermediate and advanced reactors have accordingly been formulated and are discussed in their respective sections.

Information as well as experience indicates that DCS can be handled safely. Safety features such as equipment location or explosion confinement must be carefully considered and implemented as required for each system containing DCS, to assure personnel safety.

3.4 Process Development Unit (PDU) Evaluation

3.4.1 Objectives

The dichlorosilane PDU objectives were to design, construct, operate, and evaluate a DCS production/purification system that would provide DCS in adequate quantity and quality to evaluate the decomposition process and provide scale-up information necessary for EPSDU and commercial designs.

The specific objectives were:

1. Provide 35 lb/hr of DCS.
2. Provide DCS of a quality equal to or better than required for production of solar grade silicon.
3. Evaluate kinetics of the PDU scale redistribution reactor.
4. Determine pressure drop versus mass flow gpm/ft^2 for Dowex® MWA-1 ion exchange resin.
5. Determine distillation limitations in terms of through put and DCS purity.

3.4.2 PDU Process Description

The detailed piping and instrument diagram for the PDU[15] is shown in Figure 14. 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% mole DCS, 10% mole STC and 80% mole 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.*

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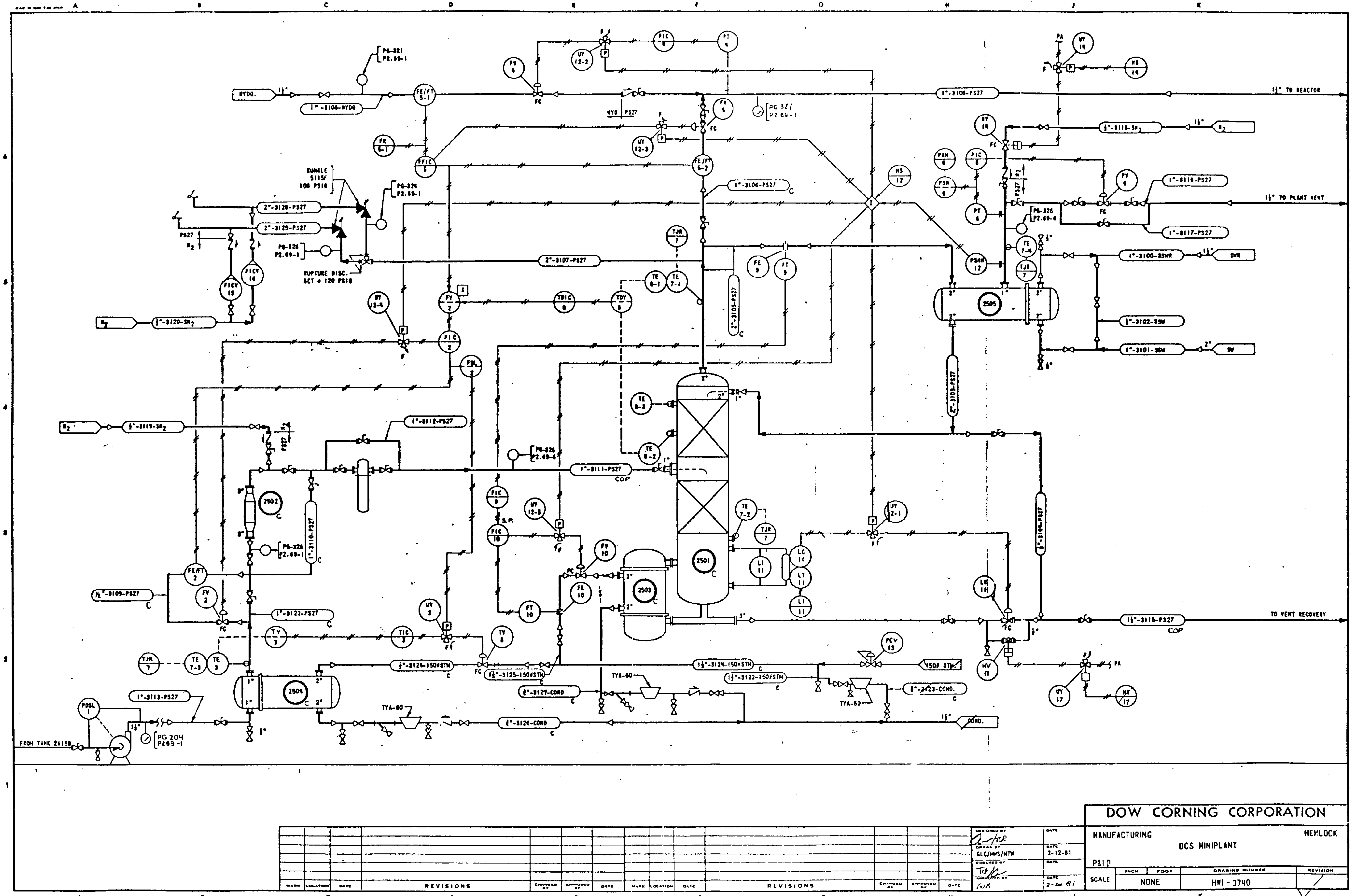
* A detailed description of the PDU operation is contained in the Sixth Quarterly Progress Report on Contract 955533.

Equipment identified in Figure 14 includes:

1. Feed tank. HSC storage tank is used as the feed supply tank for trichlorosilane.
2. The feed pump is a Chempump, model GB1 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.

FIGURE 14. DETAILED DESIGN OF PDU



3.4.3 Three-Inch-Diameter Redistribution Reactor

Catalyst pressure drop and catalyst kinetic performance were evaluated. Data collection was accomplished using pressure gauges located immediately before and after the redistribution reactor. Pressure drop through both containment screens was measured.

Empirical relationships were developed to allow scale-up of the redistribution system. For an 11 ft. deep bed of Dowex® MWA-1 ion exchange resin with TCS (80-90°C) as the flowing fluid, pressure drop versus flow (Figure 15) can be expressed by the empirical relationship.

$$Y = 0.0611\ (X) + 0.0387$$

where

Y = pressure drop per foot of catalyst bed, in psig, excluding liquid head contribution, and

X = flow of liquid, in gal/min/ft^2, area open tube cross sectional area of reactor.

This correlation should not be used beyond 20 gal/min/ft^2 because pressure drop versus flow is not normally a straight line function as expressed above. However the expression is adequate for design purposes within the specified operating range, because the operating range approximates linearity.

During normal operation some fouling of the 65-mesh containment screens occurred. A simple reverse-flow nitrogen purge proved to be successful in dislodging the foreign material. Pressure drop returned to normal after using the reverse-flow nitrogen purge method.

Kinetic performance of the 3" diameter redistribution reactor is presented in Figure 16. Figure 16 is a plot of percent of thermodynamic equilibrium versus temperature for trichlorosilane flows of 400 and 650 lb/hr. Besides flow rate and feed temperature data, composition data for still feed, overheads, and bottoms were obtained by GC analysis. Data were manipulated to form a mass balance of the system to determine

FIGURE 15.

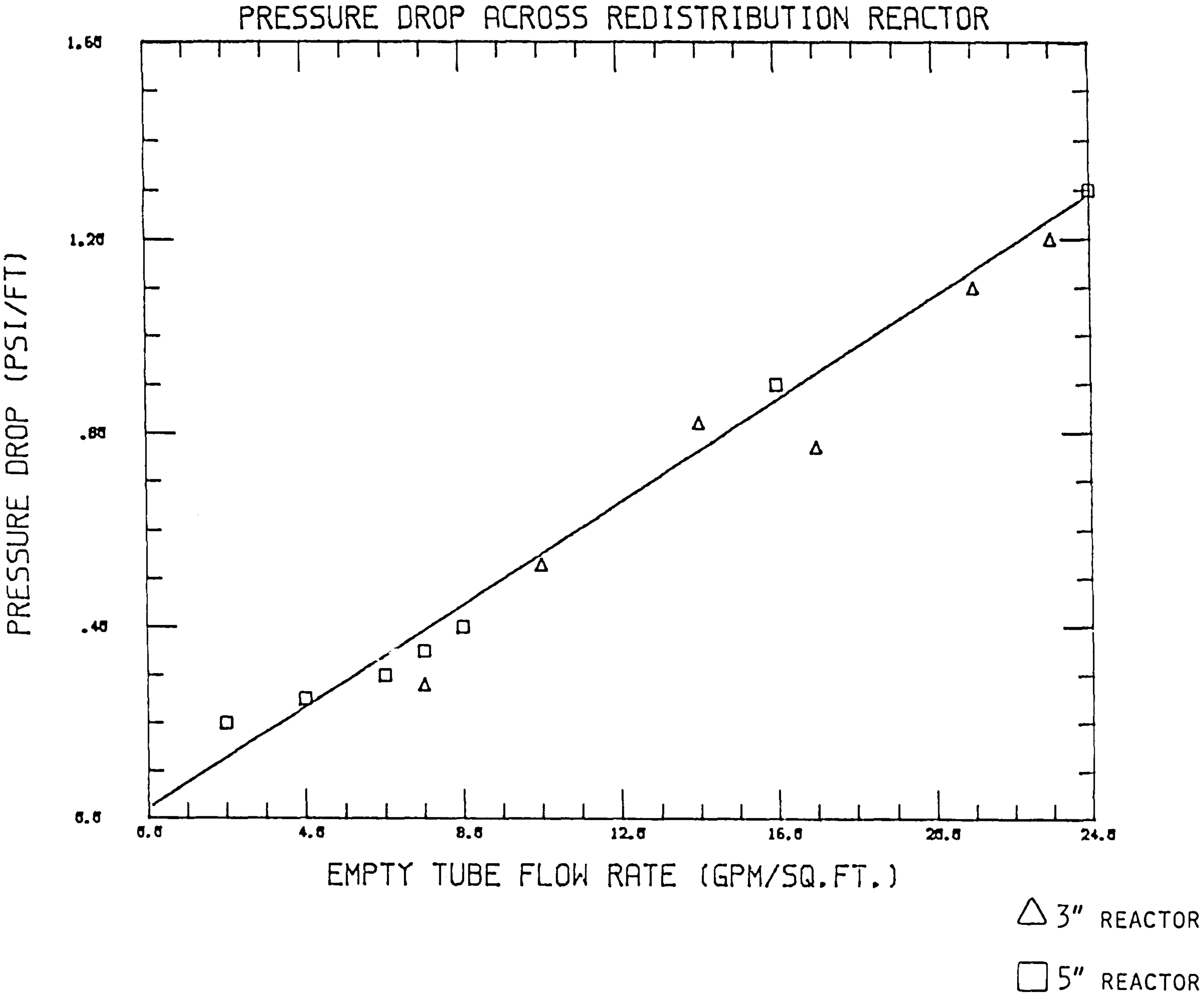
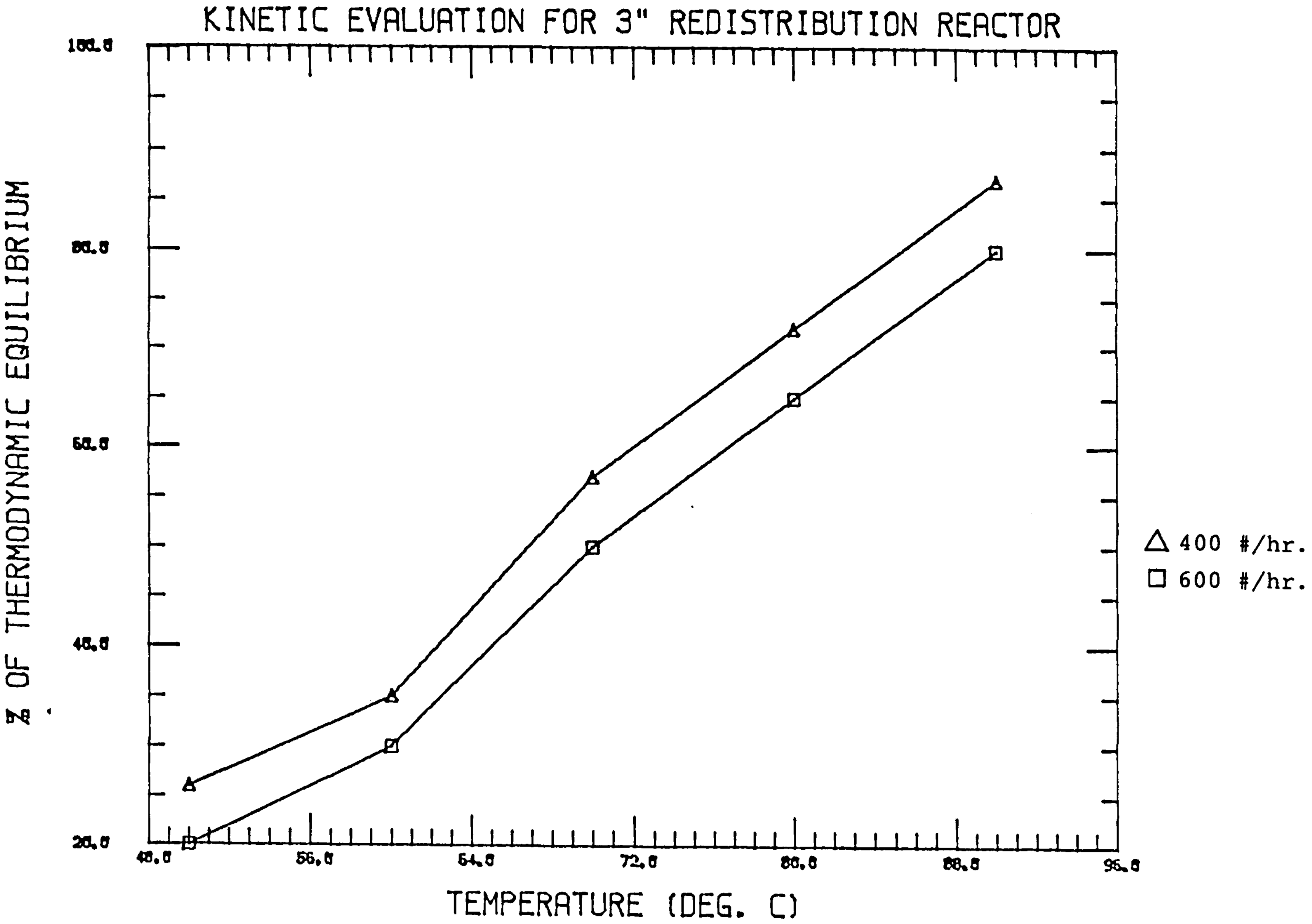

PRESSURE DROP ACROSS REDISTRIBUTION REACTOR

FIGURE 16.


KINETIC EVALUATION FOR 3" REDISTRIBUTION REACTOR
100.0
80.0
60.0
40.0
20.0
% OF THERMODYNAMIC EQUILIBRIUM
48.0
56.0
64.0
72.0
80.0
88.0
96.0
TEMPERATURE (DEG. C)
△ 400 #/hr.
□ 600 #/hr.

STC/TCS observed, for comparison to STC/TCS theoretical, based on feed composition.

3.4.4 Five-Inch-Diameter Redistribution Reactor

Pressure drop versus flow rate shown in Figure 15 indicated that the empirical relationship developed for the 3" diameter redistribution reactor be used for the 5" diameter (11 ft. packed bed) redistribution reactor up to 24 gal/min. ft^2.

Kinetic performance of the 5" diameter redistribution is shown in Figure 17. Data indicate that for identical flow rates, the slightly larger residence time increases the percent of thermodynamic equilibrium achieved from TCS to DCS for the same length columns.

3.4.5 Distillation Performance

Distillation performance was investigated relative to feed rate and reflux rate. The raw data are presented in Table 7. Tests 1 through 6 were completed using the 3" diameter redistribution reactor, while test 7 was completed using the 5" diameter redistribution reactor. Test 7 is detailed in Figure 18.

From the compositional data there are no reflux conditions which yield low percent TCS in the still overheads and low percent DCS in the still bottoms for the 650 lb/hr, or 1000 lb/hr feed condition.

The 400 lb/hr feed condition operated successfully up to 750 pounds per hour reflux.

An empirical scaling design for DCS distillation systems configured and operated as the current column follows:

$$D = 10\sqrt{\frac{\text{DCS Rate}}{31.5}}$$

where

D = diameter of new column, inches

DCS Rate = desired DCS capacity, lb/hr.

FIGURE 17.

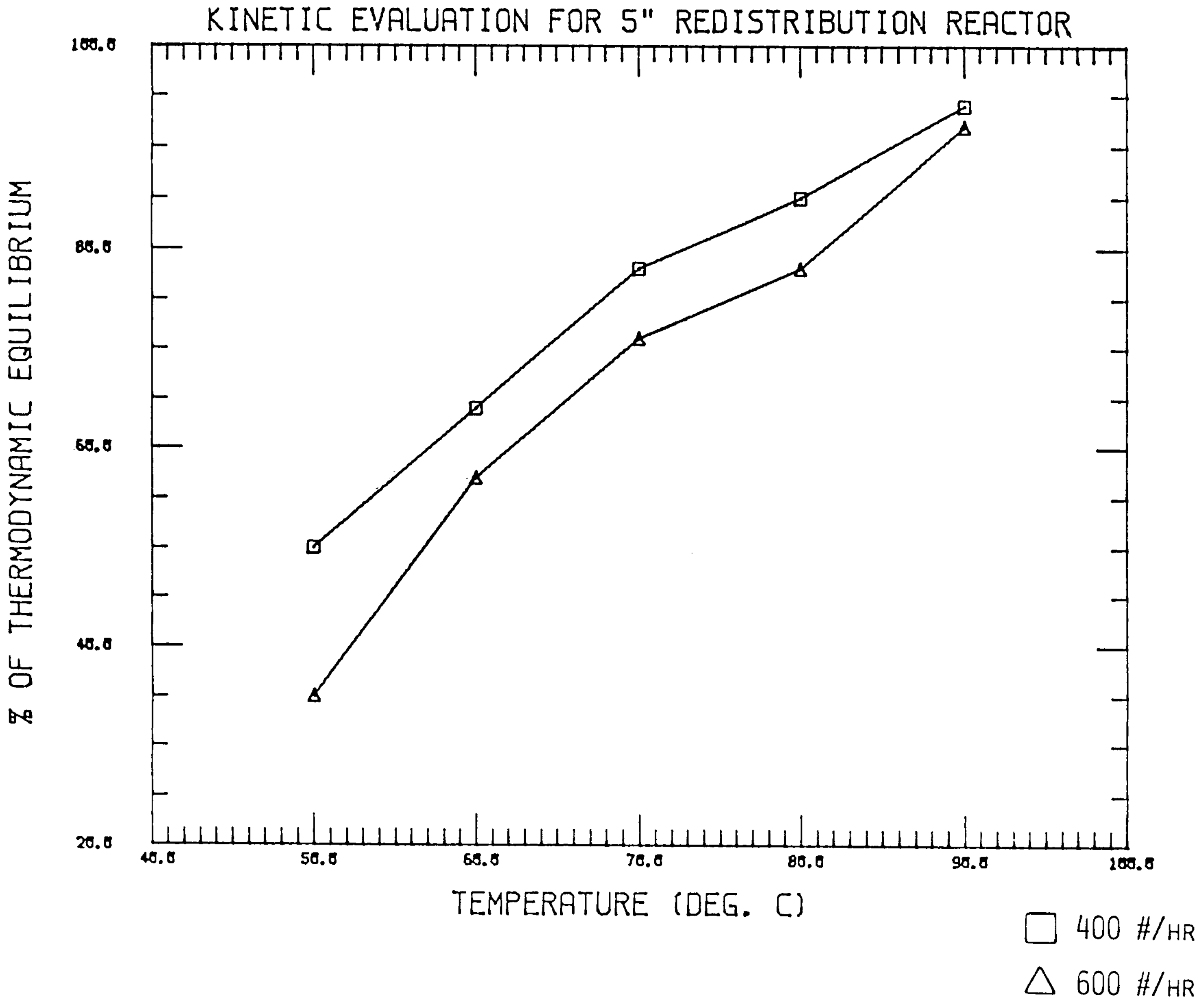

KINETIC EVALUATION FOR 5" REDISTRIBUTION REACTOR
% OF THERMODYNAMIC EQUILIBRIUM
100.0
80.0
60.0
40.0
20.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
TEMPERATURE (DEG. C)
400 #/HR
600 #/HR

TABLE 7. DISTILLATION PERFORMANCE DATA

Test	1	2	3	4	5	6	7
Feed Rate lb/hr.	400	400	400	650	650	650	1000
Feed Temp. °C	90	87	88	89	92	82	
Overhead Take Off lb/hr.	31.5	30.1	32.9	39.9	40.6	39.9	82
Reflux lb/hr.	550	750	970	500	750	950	700
Column Pressure, psig	60	60	60	60	60	60	60
Overhead Composition							
Mole % MCS	3.8	3.1	3.1	3.4	3.4	3.5	4.0
DCS	96.2	94.8	90.7	95.9	91.2	87.8	83.0
TCS	0.04	2.1	6.2	0.7	5.4	8.7	13.0
STC	0	0	0	0	0	0	0
Bottoms Composition							
Mole % DCS	0.2	0.2	0.8	3.0	3.0	2.6	6.0
TCS	88.0	88.0	87.8	87.1	87.1	87.1	82.0
STC	11.8	11.8	11.3	9.9	9.9	10.4	12.0

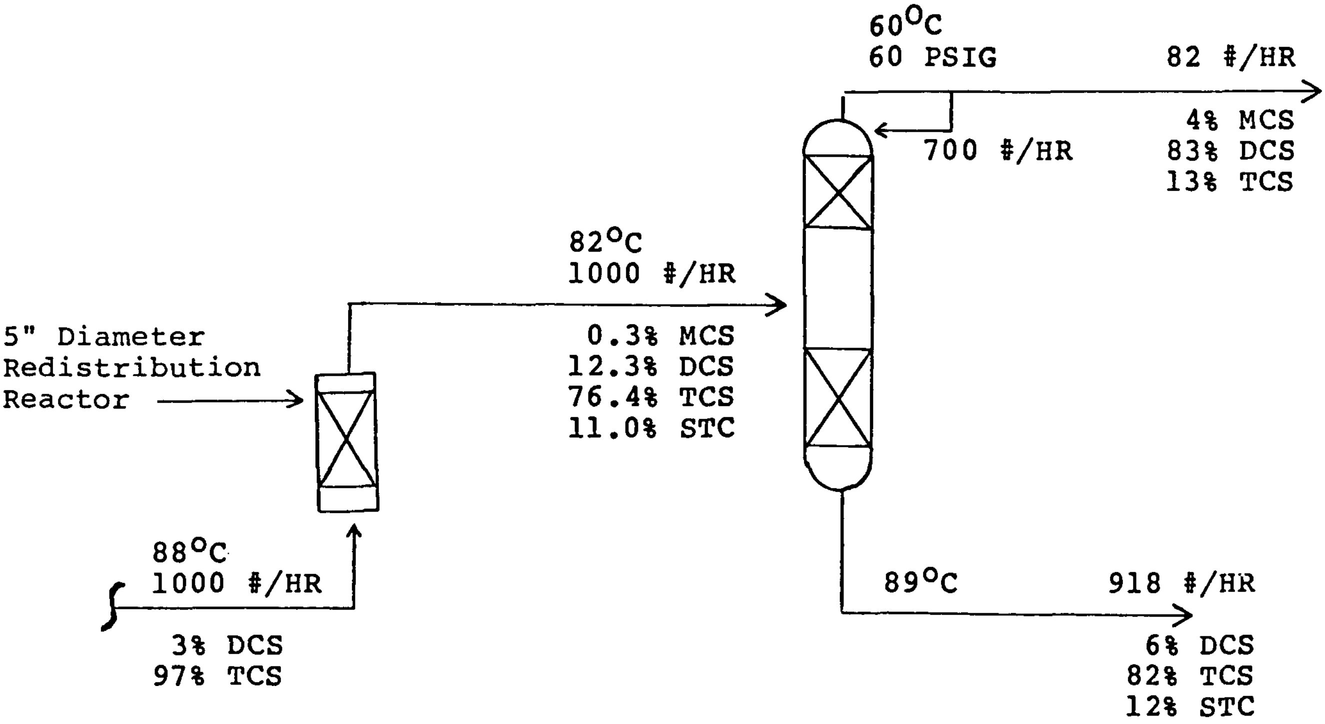
Approximate Feed Composition For All Cases

Mole %	MCS	0.3
	DCS	11.3
	TCS	78.1
	STC	10.2

FIGURE 18.

5" DIAMETER REDISTRIBUTION REACTOR

PDU CONDITIONS AT CAPACITY



Feed and reflux rate are as related to a constant term (K)

$$\text{Feed} = 400 \cdot K, \text{ lb/hr.}$$

$$K = \frac{\text{DCS Rate}}{31.5}$$

$$\text{Reflux} = 550 \cdot K, \text{ lb/hr.}$$

Using this empirical relationship provided a design that yielded DCS at desired rates while allowing negligible (0.04 mole percent TCS) TCS in the still overheads and only 0.2 mole percent loss of DCS in the still bottoms. Scaling up a 1000 MT/yr plant using these empirical relationships resulted in a column 94 inches in diameter. One should evaluate alternate distillation column designs to determine economic optimization prior to selecting a column designed by this empirical relationship.

3.4.6 Discussion

Throughout the program to manufacture DCS, the process development unit had periodic maintenance (minor and major) safely performed on it. On line times greater than 95% were demonstrated during periods of the contract.

3.5 Intermediate Reactor Development

3.5.1 Objectives

The safe and efficient production of polycrystalline silicon from commercially purchased dichlorosilane, as well as the dichlorosilane produced by the process development unit (PDU) installed at HSC, was demonstrated in an intermediate sized reactor. This task included 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 pound cylinders provided data to establish baseline conditions for integrated reactor/PDU operation.
4. Collection and evaluation of operational data on the DCS/hydrogen reactor system.

3.5.2 Intermediate Reactor Operation

Two HSC production reactors normally used for the production of silicon rods for use in the float zone crystal growing process were used in evaluating dichlorosilane decomposition characteristics. Reactor modifications were minimal. They consisted of heat shield reinforcement to assure containment of potential DCS/H_2/air explosions, and feed distribution systems which permitted DCS and TCS to be fed to the reactor.

Prior to integrating reactor operation with the DCS-PDU, four deposition runs[16] were conducted using DCS packaged in 250 lb. cylinders that were provided by an outside vendor. Data collected on these four relatively short deposition experiments were coupled with the results of the previously described designed experiment conducted in a small reactor to establish initial operating conditions for the integrated system. Following completion of the four experimental runs using cylinder supplied DCS, the DCS-PDU was put into operation. DCS was put into the reactor feed lines and the total system safety tested.

The major reactor performance characteristics of interest were: silicon deposition rate, silicon conversion efficiency, and power consumption. Based on the preliminary design of the 1000 T/Y plant and the resulting economic analysis of the process at the 1000 T/Y production rate, target values for these parameters were:

Silicon deposition rate	2 $gh^{-1}cm^{-1}$
Conversion efficiency	40 mole %
Power consumption (at reactor)	60 kWh/kg

where the deposition rate is expressed in terms of weight per unit length of deposition substrate in the reactor, conversion efficiency is defined as the ratio of silicon produced by the silicon fed, and power consumption is measured at the decomposition reactor. All reactor run data and evaluations have been reported as run averages unless otherwise stated. In addition to reactor performance evaluation, mass balance information was collected by gas chromatography during operation of the intermediate sized reactor.

3.5.3 Intermediate Reactor Performance

Initial baseline operating conditions were established using material (DCS) supplied from 250 lb. cylinders. Once the DCS-PDU was integrated with the reactor system, routine operation was achieved. In one year of operation more than 100 reactor runs were completed in each reactor.

Reactor performance was evaluated for four basic operating conditions at constant rod temperature (approximately 1050°C). Operating conditions are identified as A, B, C, & D for abbreviation and correspond to the following parameters:

Condition	Mole % DCS Fed
A	6
B	6
C	6
D	4

Performance data on deposition runs varying in time from 4 to 87 hours in length and producing silicon rods of 12 to 96 mm diameter are presented in Tables 8 through 11 for each feed rate.

3.5.3.1 Results

Reactor performance data have been evaluated and normalized for 50 mm and 80 mm rod diameters and are shown in Table 12 as run average results.

Examination of this table indicates that lower deposition rate, conversion, and higher power consumption occur at the smaller rod diameter. Also the trade off between silicon deposition rate (and power consumption) and conversion can be seen by examination of the values for Conditions C and D.

Silicon deposition versus run time is presented in Figure 19 for the four reactor operating conditions. Silicon deposition in this plot is the "run average" silicon deposition rate. Figure 20 and 21 illustrate run average conversion and power consumption respectively.

The results are sufficient to determine parametric tradeoffs between deposition rate, conversion and power consumption for intermediate reactor operation. The deposition rate goal of 2.0 $gh^{-1}cm^{-1}$ was achieved with Condition C at the expense of the conversion goal (40 mole percent), while the conversion goal was exceeded with Condition D at the expense of the deposition goal. The 60 kWh/kg target value for power consumption was not achieved in the intermediate reactor. However, power consumption of 85-95 kWh/kg was routinely achieved.

TABLE 8. DICHLOROSILANE INTERMEDIATE-SIZE REACTOR PERFORMANCE DATA; CONDITION A

Run No.	Feed Type/ Mole %	Run Time (hours)	Rod Diameter (mm)	Silicon Fed (gh^{-1}cm^{-1})	Silicon Deposition (gh^{-1}cm^{-1})	Conversion (mole %)	Power Consumption (kWh/kg)
324-419	DCS/6	59	72-75	4.2	1.5	37.4	N.A.
324-420	DCS/6	53	65-68	4.1	1.5	35.0	N.A.
324-421	DCS/6	79	85-90	4.3	1.6	38.7	90
324-423	DCS/6	40	55-58	4.1	1.4	33.5	89
324-424	DCS/6	10	23-24	3.3	0.8	25.2	132
324-442	DCS/6	61	74-75	4.2	1.6	38.7	96
324-443	DCS/6	71	80-86	4.2	1.6	38.3	85
324-444	DCS/6	35	56-58	4.1	1.3	32.7	102
325-451	DCS/6	20	38-39	3.9	1.3	32.6	N.A.
325-452	DCS/6	30	47-50	4.0	1.3	33.8	92
325-453	DCS/6	4	12.7	1.8	0.4	23.9	142

TABLE 9. DICHLOROSILANE INTERMEDIATE-SIZE REACTOR PERFORMANCE DATA; CONDITION B

Run No.	Feed Type/ Mole %	Run Time (hours)	Rod Diameter (mm)	Silicon Fed ($gh^{-1}cm^{-1}$)	Silicon Deposition ($gh^{-1}cm^{-1}$)	Conversion (mole %)	Power Consumption (kWh/kg)
324-425	DCS/6	25	43-45	4.7	1.4	29.9	91
324-426	DCS/6	25	42-45	4.6	1.3	27.1	99
324-427	DCS/6	35	55-59	4.8	1.6	32.9	97
325-450	DCS/6	46	69-72	4.9	1.7	34.8	92
325-454	DCS/6	47	68-72	4.9	1.7	33.7	85
325-455	DCS/6	18	37-39	4.4	1.4	32.0	88

TABLE 10. DICHLOROSILANE INTERMEDIATE-SIZE REACTOR PERFORMANCE DATA; CONDITION C

Run No.	Feed Type/ Mole %	Run Time (hours)	Rod Diameter (mm)	Silicon Fed ($gh^{-1}cm^{-1}$)	Silicon Deposition ($gh^{-1}cm^{-1}$)	Conversion (mole %)	Power Consumption (kWh/kg)
324-422	DCS/6	30	51-54	5.4	1.6	29.4	87
324-430	DCS/6	10	25	4.3	1.0	23.3	76
324-431	DCS/6	30	52-54	5.4	1.5	26.8	91
325-435	DCS/6	20	41-42	5.1	1.5	30.1	83
325-457	DCS/6	60	81-83	5.7	2.1	36.3	81

TABLE 11. DICHLOROSILANE INTERMEDIATE-SIZE REACTOR PERFORMANCE DATA; CONDITION D

Run No.	Feed Type/ Mole %	Run Time (hours)	Rod Diameter (mm)	Silicon Fed (gh^{-1}cm^{-1})	Silicon Deposition (gh^{-1}cm^{-1})	Conversion (mole %)	Power Consumption (kWh/kg)
325-465	DCS/4	17	32-33	3.5	1.1	30.8	82
325-466	DCS/4	7	18	2.7	0.8	30.1	122
325-467	DCS/8	60	70-73	3.8	1.5	37.9	107
325-470	DCS/8	87	91-96	3.9	1.7	43.6	89
325-471	DCS/6	78	83-89	3.9	1.6	41.6	96
325-472	DCS/6	26	45-48	3.6	1.4	39.1	88

TABLE 12. SUMMARY OF DICHLOROSILANE PERFORMANCE FOR INTERMEDIATE REACTOR

ROD DIAMETER	50 MM ROD DIAMETER		
PARAMETER / CONDITION	SILICON DEPOSITION RATE ($gh^{-1}cm^{-1}$)	CONVERSION (Mole %)	POWER CONSUMPTION (kWh/kg)
A	1.40	34.4	92.8
B	1.51	32.0	91.8
C	1.65	30.8	84.3
D	1.44	38.8	95.7

ROD DIAMETER	80 MM ROD DIAMETER		
PARAMETER / CONDITION	SILICON DEPOSITION RATE ($gh^{-1}cm^{-1}$)	CONVERSION (Mole %)	POWER CONSUMPTION (kWh/kg)
A	1.59	37.5	89.6
B	1.74	35.0	88.8
C	2.00	35.1	82.0
D	1.61	41.6	93.9

FIGURE 19.

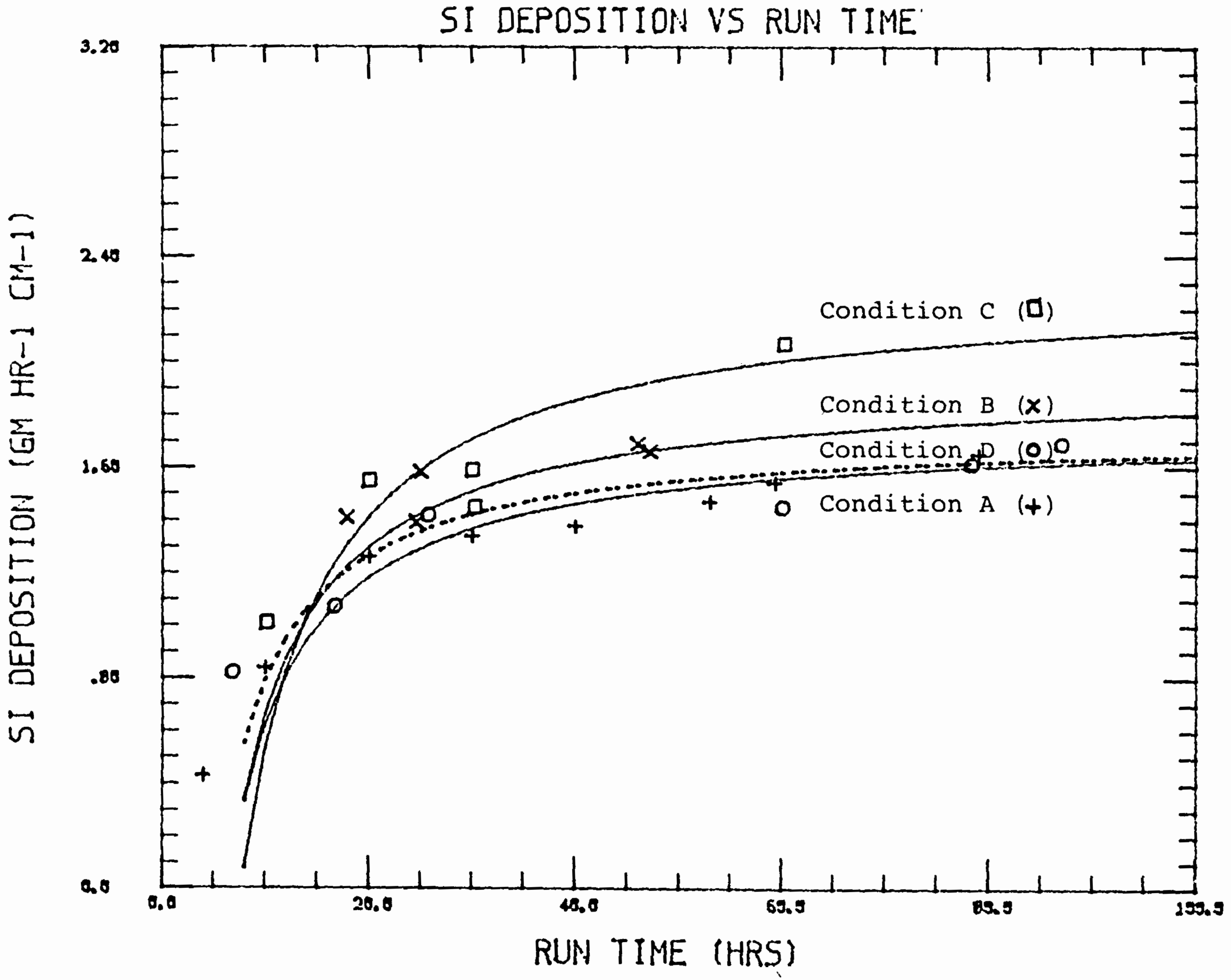

SI DEPOSITION VS RUN TIME
SI DEPOSITION (GM HR-1 CM-1)
3.20
2.40
1.60
.80
0.0
RUN TIME (HRS)
0.0
20.0
40.0
60.5
80.5
100.5
Condition C (□)
Condition B (×)
Condition D (○)
Condition A (+)

FIGURE 20.

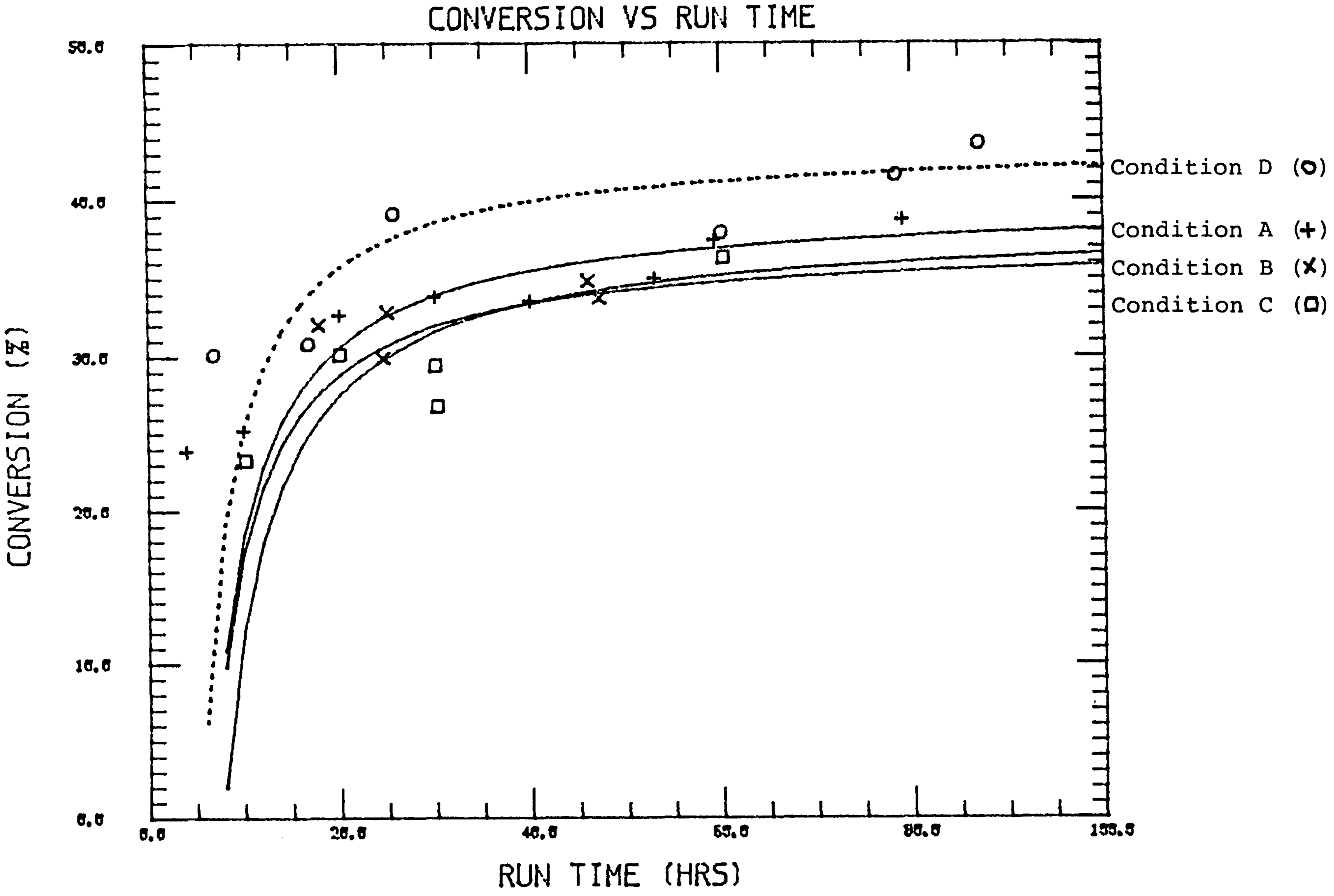
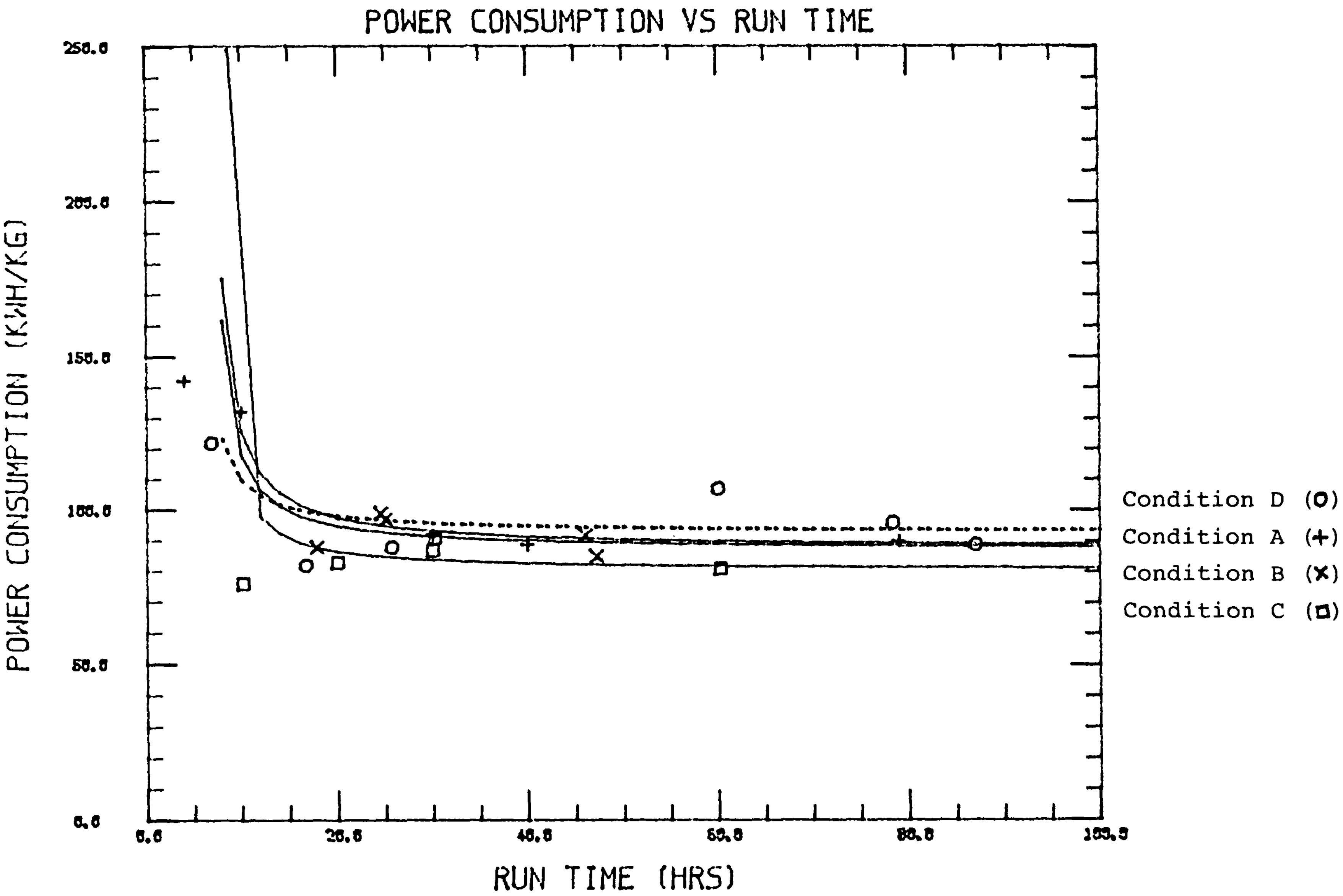

CONVERSION VS RUN TIME
CONVERSION (%)
50.0
40.0
30.0
20.0
10.0
0.0
0.0
20.0
40.0
60.0
80.0
100.0
RUN TIME (HRS)
Condition D (○)
Condition A (+)
Condition B (×)
Condition C (□)

FIGURE 21.


POWER CONSUMPTION VS RUN TIME
POWER CONSUMPTION (KWH/KG)
RUN TIME (HRS)
250.0
200.0
150.0
100.0
50.0
0.0
0.0
20.0
40.0
60.0
80.0
100.0
Condition D (O)
Condition A (+)
Condition B (X)
Condition C (□)

During operation of the intermediate reactors, data for determining mass balance were collected by gas chromatographic analysis of the gaseous feed and vent streams of the reactors. Data for reactor conditions A through D are presented in Tables 13 through 16 and Figures 22 and 23 respectively. This data is "instantaneous" in the fact that it is a measure of the product distribution at a particular time in a deposition run. The data were manipulated to force both silicon and chlorine balances. This data analysis technique produced consistent results compared to balancing only the silicon or chlorine independently.

It should be noted that conversion efficiencies for Conditions A through C are very similar (Figure 20). Not surprisingly, vent products are very similar at the same rod diameter. Therefore, Figure 22 is typical of Conditions A, B, C and Figure 23 is typical of Condition D.

For comparison purposes reactor vent products at 50 and 80 mm rod diameters are shown in Table 17. Silicon deposited is increased and unreacted dichlorosilane greatly reduced at the larger rod diameter.

3.5.3.2 Intermediate Reactor Operational Problem

The only problem of any consequence that occurred during reactor operation was silicon deposition on the bell jar wall. This detrimental effect resulted in reduced bell jar lifetime. To quantify the magnitude of this problem data were collected by actually weighing the bell jar before and after each reactor run. The data indicated that silicon deposition on the bell jar increases with the number of runs made from 1.0% silicon deposited per kilogram of silicon produced, when the bell jar is new, to 7.7% silicon deposited per kilogram silicon produced as bell jar life time increases. Typical silicon deposit after several runs is depicted in Figure 24.

The data indicate that the most serious deposition occurred in the bell jar dome area with progressively less deposition from top to bottom on the side walls. The weight of silicon

TABLE 13.

DCS REACTOR PROCESS EVALUATION

MASS BALANCE DATA

Run Number	Reactor Conditions	Run Time (Hrs)	Rod Diameter (mm)	Products (Moles per 100 Moles Si Fed)					
				Si	HCl	MCS	DCS	TCS	STC
325-453	A	3	12	25	13	1	44	28	2
324-424	A	9	23	29	6	2	26	38	5
325-451	A	15	38	33	4	2	17	37	11
325-452	A	21	47	39	10	1	10	35	15
324-423	A	39	55	40	7	1	7	35	17
324-420	A	51	65	42	9	0	6	34	19
324-419	A	54	72	42	12	0	4	34	20
324-421	A	74	85	44	13	0	4	32	20

TABLE 14.

DCS REACTOR PROCESS EVALUATION

MASS BALANCE DATA

Run Number	Reactor Conditions	Run Time (Hrs)	Rod Diameter (mm)	Products (Moles per 100 Moles Si Fed)					
				Si	HCl	MCS	DCS	TCS	STC
325-455	B	17	38	33	3	2	16	38	12
324-425	B	24	43	36	4	1	12	37	13
324-427	B	32	55	39	8	1	8	36	17
325-470	B	43	69	41	11	1	9	33	17

TABLE 15.

DCS REACTOR PROCESS EVALUATION

MASS BALANCE DATA

Run Number	Reactor Conditions	Run Time (Hrs)	Rod Diameter (mm)	Products (Moles per 100 Moles Si Fed)					
				Si	HCl	MCS	DCS	TCS	STC
325-456	C	15	41	30	3	3	20	38	10
324-422	C	24	51	36	4	1	12	37	13
324-431	C	29	52	37	5	1	10	37	15
325-457	C	55	81	42	11	0	7	30	20

TABLE 16.

DCS REACTOR PROCESS EVALUATION

MASS BALANCE DATA

Run Number	Reactor Conditions	Run Time (Hrs)	Rod Diameter (mm)	Products (Moles per 100 Moles Si Fed)					
				Si	HCl	MCS	DCS	TCS	STC
325-476	D	10	21	29	2	3	20	40	9
325-478	D	10	22	30	2	3	20	39	8
325-479	D	11	23	29	2	2	21	43	6
325-479	D	20	38	36	6	1	13	39	12
325-479	D	30	49	42	15	0	7	38	14
325-477	D	31	49	39	10	0	8	38	14
325-477	D	38	57	41	13	0	7	38	14
325-467	D	56	70	42	19	1	9	33	16
325-471	D	74	83	46	19	0	5	31	18

FIGURE 22.

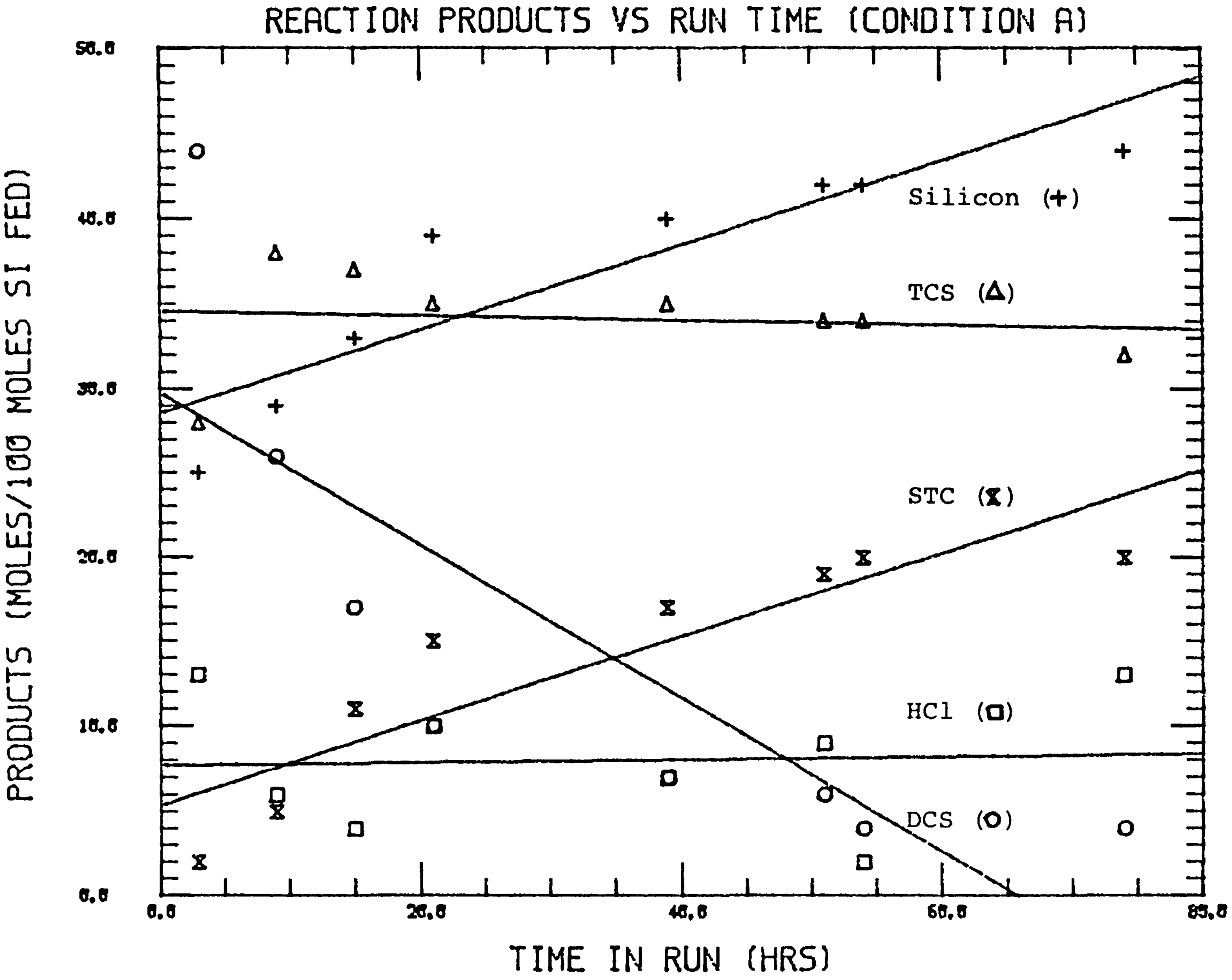

REACTION PRODUCTS VS RUN TIME (CONDITION A)
PRODUCTS (MOLES/100 MOLES SI FED)
TIME IN RUN (HRS)
50.0
40.0
30.0
20.0
10.0
0.0
0.0
20.0
40.0
60.0
80.0
Silicon (+)
TCS (Δ)
STC (X)
HCl (□)
DCS (O)

FIGURE 23.

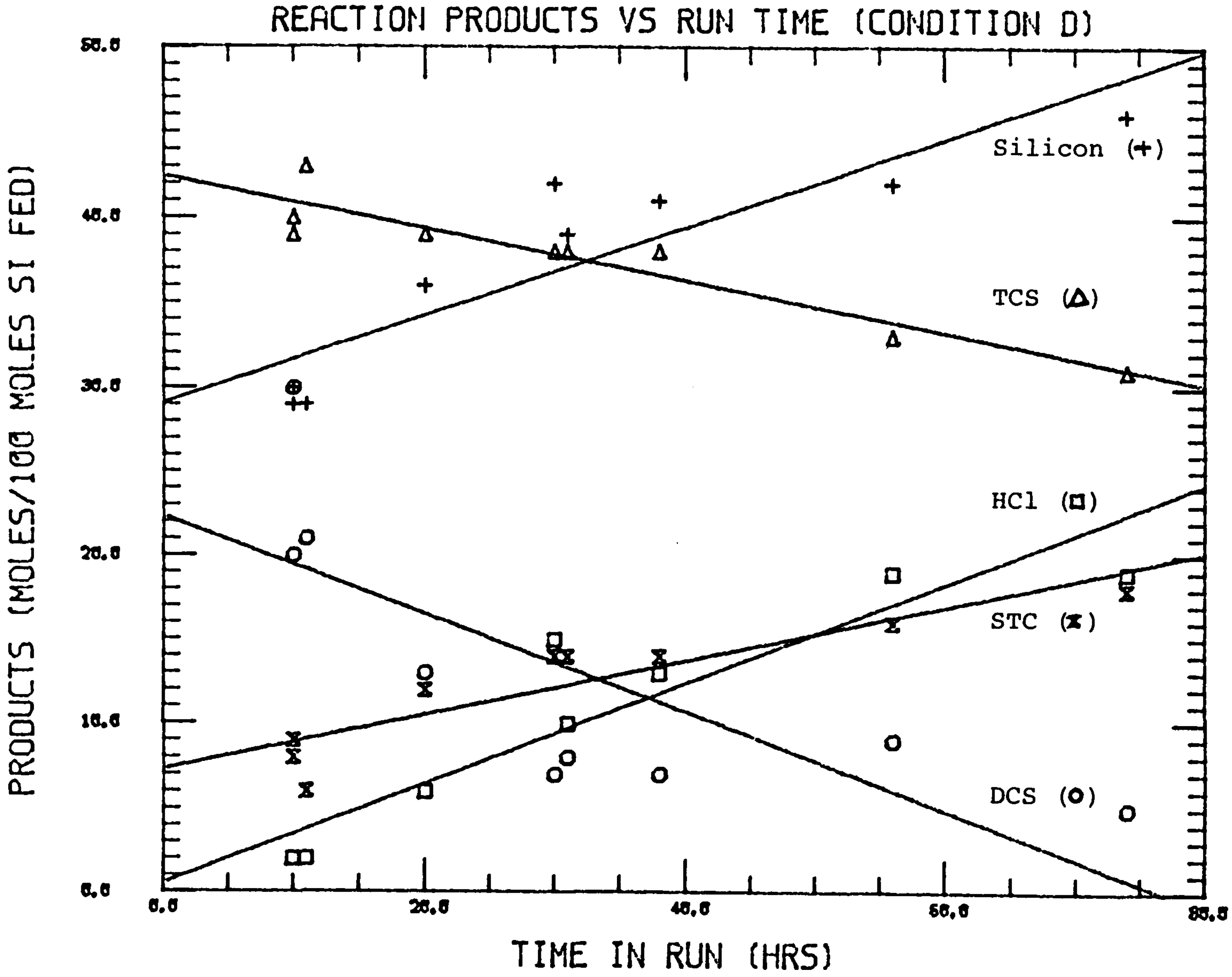
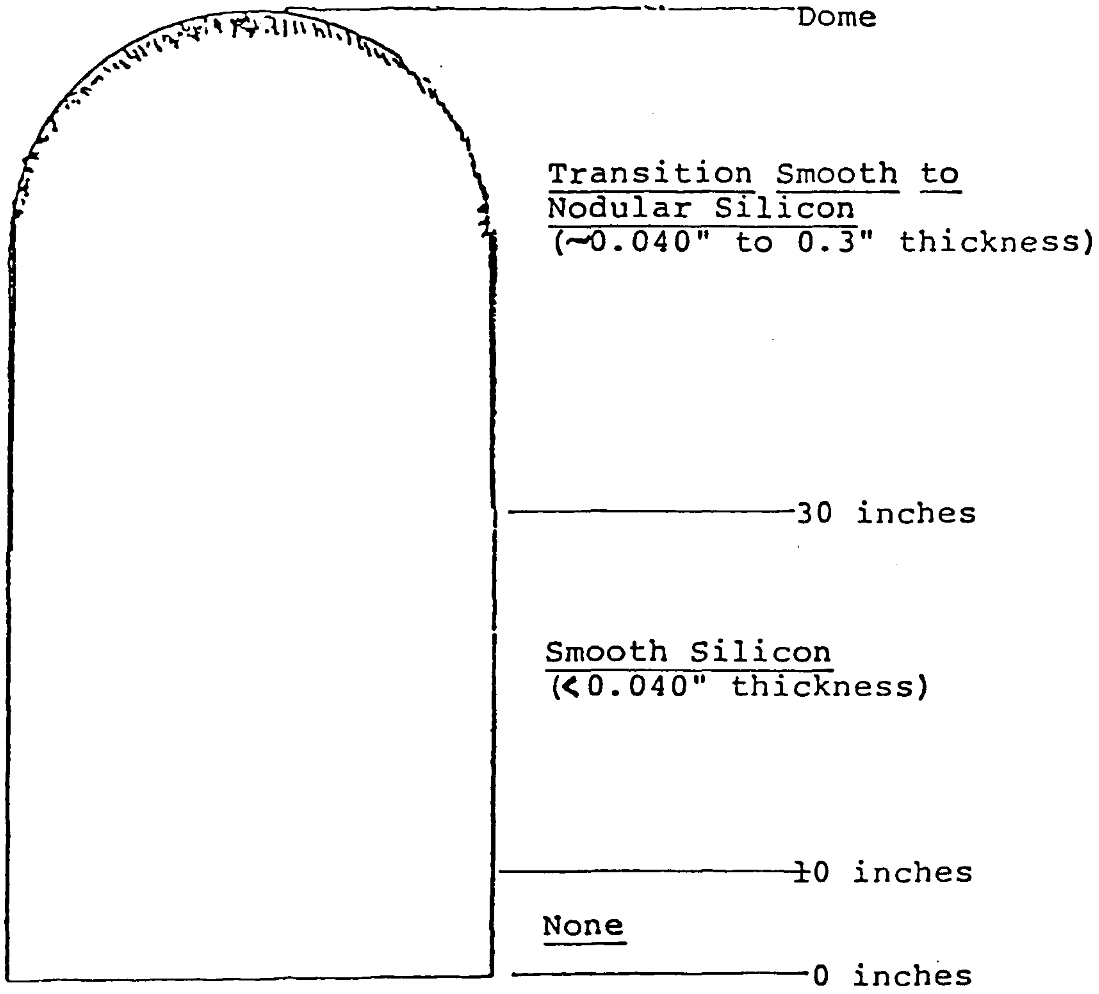

REACTION PRODUCTS VS RUN TIME (CONDITION D)
PRODUCTS (MOLES/100 MOLES SI FED)
TIME IN RUN (HRS)
0.0
10.0
20.0
30.0
40.0
50.0
0.0
20.0
40.0
60.0
80.0
Silicon (+)
TCS (Δ)
HCl (□)
STC (⧗)
DCS (○)

TABLE 17. SUMMARY OF INSTANTANEOUS MASS BALANCE FOR INTERMEDIATE REACTOR

ROD DIAMETER	50 MM ROD DIAMETER				
PARAMETER / CONDITION	SILICON DEPOSITED	HCL PRODUCED	DCS PRODUCED	TCS PRODUCED	STC PRODUCED
	(MOLES/100 MOLES SI FED)				
A, B, C	36.6	6.6	12.6	35.8	13.9
D	38.1	11.2	11.2	41.4	13.0

ROD DIAMETER	80 MM ROD DIAMETER				
PARAMETER / CONDITION	SILICON DEPOSITED	HCL PRODUCED	DCS PRODUCED	TCS PRODUCED	STC PRODUCED
	(MOLES/100 MOLES SI FED)				
A, B, C	43.8	11.4	3.6	31.9	20.6
D	45.8	20.0	4.2	40.9	17.9

Figure 24. Bell Jar Silicon Deposition (Model 8D Reactor)



deposition on the quartz bell jar increased with each succeeding run until the deposit was so thick that the coefficient of expansion was great enough to break the bell jar.

The following conclusions were drawn from observed DCS decomposition:

- Rod diameters greater than 75 mm result in silicon deposition on the bell jar and may contribute to bell jar breakage.
- Silicon deposition on the bell jar is cumulative.
- Lower DCS feed concentration does not have a significant effect on silicon deposition on the bell jar for large diameter rods.

3.5.3.3 Reactor Operation Modifications

In order to alleviate the problem of silicon deposition on the bell jar, two methods of removing silicon were evaluated using post-run HCl etch and mixed feed (dichlorosilane/trichlorosilane).

Silicon was removed from the bell jar by feeding HCl and hydrogen to the reactor after the run was complete. Thermodynamically, silicon preferentially etches from the bell jar rather than the silicon rod. A 5 hour HCl etch was used after runs were completed. Table 18 and 19 show several runs made with the post-run HCl etch. Results for silicon fed, silicon deposition, and conversion are run averages.

Once silicon has been deposited on the inside of a bell jar, the outside bell jar color becomes gray-white when first observed after a run. The bell jar was checked on an hourly basis upon HCl introduction. The post-run HCl etch gradually took the silicon deposit from the walls of the bell jar. Successive observations indicated this because bell jar color was changing until it was glowing bright red. Bell jar life time increased by a factor of 2 to 3 times (500 to 700 hours) during the course of the post-run HCl etch experiments. Experiments were still in progress at the conclusion of the contract.

TABLE 18. DICHLOROSILANE PROCESS EVALUATION INTERMEDIATE-SIZE, REACTOR 324 DATA

Run No.	Feed Type/ Mole %	Run Time (hours)	Rod Diameter (mm)	Silicon Fed ($gh^{-1}cm^{-1}$) Run Average	Silicon Deposition ($gh^{-1}cm^{-1}$) Run Average	Conversion (%) Run Average
324-481	DCS/4	40.7	48-51	2.9	1.07	36.3
324-482	*DCS/4	75.1	60-65	2.9	0.96	32.5
324-483	*DCS/4	67.5	63-68	2.9	1.12	38.1
324-483	*DCS/4	66.3	70-74	2.9	1.31	44.9
324-485	DCS/4	36.4	49-52	2.9	1.24	42.6
324-486	DCS/5	50.6	62-69	3.7	1.52	41.1
324-487	*DCS/4	75.0	70-75	2.9	1.20	41.2
324-488	*DCS/4	70.0	66-70	2.9	1.15	39.7
324-489	*DCS/5	73.6	70-75	3.7	1.22	33.0
324-490	*DCS/4	75.0	72-78	2.9	1.35	46.5
324-491	DCS/4	46.4	53-56	2.9	1.13	38.7
324-492	DCS/4	66.1	63-70	2.9	1.16	39.8
324-493	DCS/4	66.1	65-68	2.9	1.19	40.7
324-494	*DCS/4	49.1	48-50	2.9	0.88	30.0
324-495	*DCS/4	70.1	59-63	2.9	0.96	33.0
324-496	DCS/3:TCS/1	69.2	57-62	2.9	0.94	32.4
324-497	*DCS/4	34.9	50-53	2.9	1.34	45.9
324-498	DCS/3:TCS/1	75.0	65-70	2.9	1.07	36.8
324-499	DCS/3:TCS/1	75.0	59-64	2.9	0.92	31.6
324-500	DCS/2:TCS/2	56.3	55-58	2.9	1.03	35.3
324-501	DCS/1:TCS/3	75.0	38-42	2.9	0.43	14.7

* 5 Hour etch after run completed

TABLE 19. DICHLOROSILANE PROCESS EVALUATION INTERMEDIATE-SIZE, REACTOR 325 DATA

Run No.	Feed Type/ Mole %	Run Time (hours)	Rod Diameter (mm)	Silicon Fed (gh^{-1}cm^{-1}) Run Average	Silicon Deposition (gh^{-1}cm^{-1}) Run Average	Conversion (%) Run Average
325-514	*DCS/5	78.0	84-89	3.7	1.70	28.8
325-515	DCS/5	31.7	44-46	3.7	1.19	32.4
325-516	*DCS/5	68.4	74-83	3.7	1.54	41.6
325-517	DCS/5	15.2	37-40	3.7	1.60	43.3
325-518	DCS/5	60.5	73-77	3.7	1.61	43.3
325-519	DCS/5	46.0	58-62	3.7	1.42	38.5
325-520	*DCS/5	67.0	79-85	3.7	1.80	48.4
325-521	*DCS/5	66.3	70-73	3.7	1.36	36.7
325-522	*DCS/5	75.0	78-83	3.7	1.55	41.8
325-523	DCS/5	11.5	26	3.7	1.14	31.4
325-524	*DCS/4	70.0	70-76	2.9	1.34	45.8
325-525	*DCS/4	70.0	70-76	2.9	1.34	45.8
325-526	DCS/4	40.3	44-45	2.9	0.88	30.2
325-527	*DCS/4	85.0	71-76	2.9	1.12	38.5
325-528	DCS/2:TCS/2	75.0	51-54	2.9	0.70	23.9
325-529	TCS/4	75.0	41-43	2.9	0.45	15.4
325-530	DCS/1:TCS/3	74.5	40-42	2.9	0.43	14.6
325-531	TCS/4	80.0	38-39	2.9	0.37	12.8
325-532	DCS/3:TCS/1	75.0	51-53	2.9	0.65	22.4

* 5 Hour HCl etch after run completed

The impact of trichlorosilane replacement of dichlorosilane in the CVD reactor feedstock was investigated in the intermediate reactor. This method introduced trichlorosilane into the dichlorosilane feed mixture to produce more HCl. The HCl etched silicon from the bell jar during the course of a deposition run. Nine runs were completed using this technique and can be found in Tables 18 and 19, runs 324-498 through 324-501 and runs 325-528 through 325-532 respectively. All reactor parameters (feed rate, total chlorosilane feed concentration, run time, reactor configuration, etc.) were held constant while the mole ratios of dichlorosilane and trichlorosilane were varied.

Observation of the bell jar took place at the end of runs. The mixed feed was not as effective at removing silicon from the bell jar as originally postulated since the bell jar color was gray-white at the end of runs. Consequently, post-run HCl etch was used to complete the removal of silicon from the bell jar.

The HCl and TCS vent products observed during these experiments are shown below:

Instantaneous Data at 50 mm Rod Diameter

DCS % of Chloro-silanes	% Conversion To Silicon	Moles in Vent/100 Moles Si Fed HCl	MCS	DCS	TCS	STC
0	24.4	55.2	0.0	3.3	50.8	21.5
25	27.8	37.3	0.3	3.5	43.8	23.0
50	31.0	26.0	0.4	4.0	40.8	23.0
75	34.8	17.7	0.5	4.6	37.0	23.0
100	40.4	12.4	0.2	7.6	37.8	14.1

In general, the higher DCS concentration data fit more closely to thermodynamic predictions than the TCS data. This may be a combination of non-isothermal reactor effects as well as the formation of intermediate species during the decomposition of TCS.

3.6 Advanced Reactor Development

An advanced production reactor was also integrated with the Process Development Unit. It was modified so that dichlorosilane could be fed in a safe manner. The reactor was capable of using mixed feeds. The advanced reactor objectives were the same as the intermediate reactor, but specifically concentating on getting power consumption reduced to 60 kWh/kg. Plans were to increase the reactor silicon throughput, thereby reducing power consumption.

3.6.1 Reactor Performance

As previously discussed reactor performance was measured in terms of deposition rate, conversion efficiency, and power consumption.

3.6.1.1 Dichlorosilane Decomposition

The advanced reactor made only nine dichlorosilane runs, which are presented in Table 20 as run averages. One run (382-279) produced a 2.00 $gh^{-1}cm^{-1}$ deposition rate and a conversion efficiency (38.7%) slightly less than the 40 mole percent goal. Power consumption was 90 kWh/kg.

Silicon deposition on the bell jar was typically in the same range as mentioned previously for the intermediate-sized reactor.

The following summary is an average of all runs which were longer than 40 hours in length.

Advanced Reactor Performance Results (Run Averages)

Silicon Fed $gh^{-1}cm^{-1}$	Deposition Rate $gh^{-1}cm^{-1}$	Conversion Efficiency %	Power Consumption kWh/kg
4.2	1.6	38.1	97.4

Unfortunately efforts were terminated before any optimized performance could be achieved.

Typical vent products for these runs normalized to 80 mm rod diameters are:

TABLE 20. ADVANCED REACTOR PERFORMANCE DATA

Run No.	Feed Type/ Mole %	Run Time (hours)	Rod Diameter (mm)	Silicon Fed ($gh^{-1}cm^{-1}$) Run Average	Silicon Deposition ($gh^{-1}cm^{-1}$) Run Average	Conversion (%) Run Average	Power Consumption (kWh/kg) Run Average
+382-264	DCS/4	84.1	75-81	2.9	1.28	43.3	117
	DCS/4						
382-265	DCS/4	17.0	32-33	3.7	1.14	31.0	69
382-266	DCS/4	89.0	85-92	4.0	1.65	40.8	96
	STC/5						
382-267	DCS/5	40.7	59-62	3.7	1.57	42.6	N.A.
382-268	DCS/5	77.3	78-84	4.3	1.58	36.8	108
	STC/5						
382-269	DCS/5	90.0	89-93	4.9	1.66	33.9	104
	STC/5						
382-270	DCS/5	32.9	43-46	3.7	1.53	41.5	63
	STC/5						
382-271	DCS/5	26.6	42-43	3.7	1.20	32.6	93
382-272	DCS/5	90.0	86-92	5.5	1.59	28.7	111
	STC/5						
382-273	DCS/5	96.5	92-100	3.7	1.68	45.8	101
382-274	DCS/5	41.7	54-56	4.7	1.29	27.5	N.A.
382-275	DCS/5	60.3	65-69	5.5	1.38	24.9	103
	STC/5						
382-276	DCS/5	68.4	69-75	3.7	1.42	38.6	102
*382-277	DCS/5	100.0	98-105	7.7	1.82	23.5	102
	STC/5						
382-278	DCS/5	17.6	36-36	5.2	1.42	27.5	81
*382-279	DCS/5	52.0	74-78	5.2	2.00	38.7	90
382-280	DCS/5	90.0	95-101	3.7	1.17	31.8	101
	STC/5						
382-281	DCS/5	34.6	50-53	3.7	1.4	38.0	105

+ 76.6 Hours DCS, 7.5 hours STC at end of run.

Gas Chromatographic Data

Run Number	Si	HCl	MCS	DCS	TCS	STC
	Vent Products (# Mole)/(100 # Mole Si Fed)					
382-273	48.5	11.1	0.0	2.7	17.0	31.9

3.6.1.2 Mixed Feed (Dichlorosilane/Silicon Tetrachloride)

Dichlorosilane was normally used as a feedstock during the first 50 hours of run time, then the feed mixture was changed to a 50/50 mole percent dichlorosilane-silicon tetrachloride feedstock. This was done in an attempt to generate HCl which would then selectively eliminate silicon deposition from the bell jar wall. Nine DCS-STC runs were completed. Results of these runs are found in Table 20. The following summary is an average of all runs which were longer than 60 hours in length.

Silicon Fed $gh^{-1}cm^{-1}$	Deposition Rate $gh^{-1}cm^{-1}$	Conversion Efficiency %	Power Consumption kWh/kg
4.8	1.5	31.2	105

The addition of silicon tetrachloride depressed deposition rate and conversion. Power consumption was much higher than the program goal. In light of program goals of 2.0 $gh^{-1}cm^{-1}$ with a 40 percent conversion, feedstock runs using dichlorosilane-silicon tetrachloride mixtures were not explored further.

Silicon deposition on the bell jar for these runs was moderate to heavy and similar to observations made in the intermediate reactor before the implementation of post-run HCl etch. The silicon tetrachloride etch technique was not successful in removing silicon from the bell jar.

Vent product data for these runs were normalized to 80 mm rod diameters:

Gas Chromatographic Data

Run Number	Si	HCl	MCS	DCS	TCS	STC
	Vent Products (# Mole)/(100 # Mole Si Fed)					
282-277	14.8	10.2	0.2	3.0	41.2	39.6

3.6.1.3 DCS and DCS/STC Decomposition Temperature Measurements

A small laboratory Lindberg tube furnace was utilized to measure decomposition temperatures of dichlorosilane/hydrogen mixtures and dichlorosilane-silicon tetrachloride/hydrogen mixtures as part of the overall effort to understand silicon deposition in quartz systems.

A quartz tube was placed inside the Lindberg tube furnace and DCS mixtures were passed through the tube at residence times comparable to reactor operation. The furnace temperature was increased until silicon deposition was observed on the inner wall of the quartz tube. The deposition results are summarized below:

Feed Type	Relative Concentration	Chloride in Carrier Gas (Mole %)	Minimum Deposition Temperature ºC)
DCS	100	5	760
DCS/STC	50/50	3-6	780-835

The DCS/STC results indicate that the addition of STC increases the minimum deposition temperature above that of pure DCS, but that reactor temperatures are higher than any DCS/STC feed condition that could effectively be fed to retard silicon deposition on the bell jar.

3.6.2 Reactor Comparisons

Results from the reactor program indicated that scale-up can be accomplished to meet deposition goals. The measured responses of deposition rate, conversion, and power consumption for all reactor types are compared in Table 21 with original program goals.

Power consumption remained higher than desirable. Optimization efforts on the advanced reactor were terminated due

TABLE 21. GOALS VERSUS REACTOR DEPOSITION RESULTS

	Deposition Rate $gh^{-1}cm^{-1}$	Conversion Efficiency %	Power Consumption kWh/kg
JPL Goal	2.0	40.0	60
Experimental Reactor	1.6	35.2	96
Intermediate Reactor	2.0	35.1	82
Advanced Reactor	2.0	38.7	90

to budget constraints before higher throughputs reduced power consumption to the 60 kWh/kg range.

3.7 Dichlorosilane/Product Purity Evaluation

3.7.1 Objectives.

The DCS-CVD approach taken by Hemlock Semiconductor is designed to produce polycrystalline silicon that is of semiconductor purity in all respects i.e. impurity levels, surface quality, and product form. In this way material with the same specification can be supplied to all customers to produce solar cells of the highest efficiency.

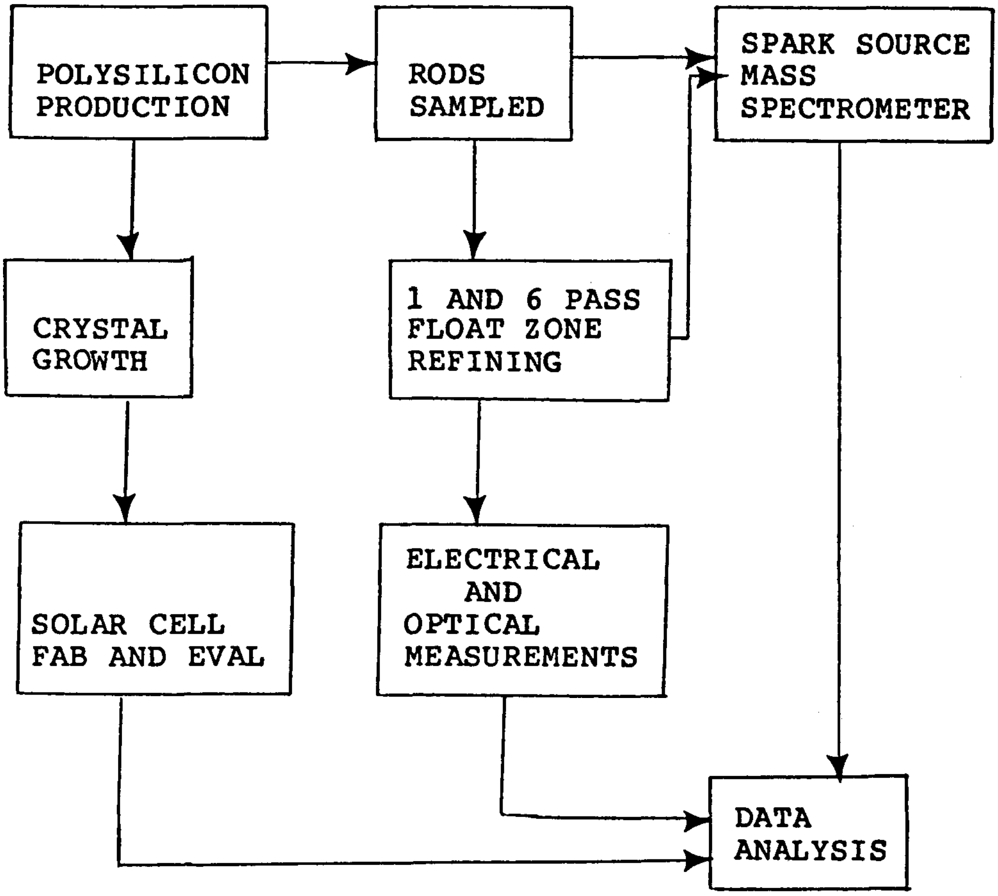
3.7.2 Evaluation Techniques

Figure 25 presents the analysis method for evaluating DCS polycrystalline silicon. The polycrystalline silicon was grown to a specific diameter. An ingot was pulled using Czochralski crystal growth techniques, and solar cells were fabricated and evaluated. This method was a gross technique for determining solar cell output as a percent efficiency at air mass one. It did not define specific impurities in the silicon necessary for the final data analysis.

Specific impurity levels were determined using an electrical resistivity technique that measures boron and phosphorus at the parts per billion atomic (ppba) level. First, a 12-millimeter cylindrical core 75 milimeters in length was taken from the polycrystalline rod. Second, the core was float zone refined one pass in gas into single-crystal silicon to determine the amount of phosphorus in the sample. Third, boron was determined by weekly plant audits and used as the value for all lots produced during the specific time frame. However, approximately 20 percent of the dichlorosilane polysilicon runs were float zone refined 6 passes in vacuum to determine actual boron content. Once float zone refining was accomplished, electrical resistivity measurements were taken to determine magnitude and type (N or P) which were then correlated to the amount of impurity in the sample.

FIGURE 25.

ANALYSIS METHOD FOR EVALUATING DCS POLYSILICON



Optical measurements were taken from the same core location. The slice was lapped and polished. The sample was placed in a Fourier Transform Infrared Spectrometer (FTIR) to determine carbon content in parts per million atomic (ppma).

A small sample of the zoned rod was cleaned and placed in a spark source mass spectrometer (SSMS) to measure parts per billion atomic trace impurities. These results were compared to semiconductor samples grown in the conventional trichlorosilane CVD process.

3.7.3 Electrical Resistivity and Optical Results

Table 22 shows dichlorosilane decomposition purity evaluations for reactors 324, 325 and 382. Runs that had operational problems were not evaluated and were deleted from the data set. All runs shown in this table were analyzed one-pass float zone in gas for donor concentration. FTIR measurements to determine carbon levels were done on a random sample basis.

Actual boron measurements were done on a random sample basis. The data are shown in Table 23, and they are actually a sub-set of the data in Table 22. A total of 32 runs were measured for actual boron content. Of these 32 runs, 24 were sampled and tested for carbon levels. It is interesting to note that the averages as well as the minimum and maximum for all runs was statistically well within the sample sub-set range for boron, donor and carbon levels.

3.7.4 Spark Source Mass Spectrometer Results

Three samples and one standard were prepared for spark source mass spectrographic analysis.

This was done to analyze any trace level elements quantitatively, and to have a direct comparison of trichlorosilane and dichlorosilane polycrystalline silicon.

Two freeze outs on the 5-pass DCS float zone rod and one DCS poly rod were evaluated against a standard that was picked at random from trichlorosilane runs from reactor 325.

TABLE 22. DCS PURITY SUMMARY BY REACTOR (324, 325, 382)

Reactor 324 (Dichlorosilane Purity Data)

Statistics Table

Statistic	Boron (ppba)	Donor (ppba)	Carbon (ppma)
No. of Values	69	69	49
Average	0.059	0.534	0.259
Std. Dev.	0.020	0.390	0.192
Variance	0.000	0.150	0.036

Reactor 325 (Dichlorosilane Purity Data)

Statistics Table

Statistic	Boron (ppba)	Donor (ppba)	Carbon (ppma)
No. of Values	62	62	48
Average	0.065	0.463	0.254
Std. Dev.	0.031	0.263	0.190
Variance	0.001	0.068	0.035

Reactor 382 (Dichlorosilane Purity Data)

Statistics Table

Statistic	Boron (ppba)	Donor (ppba)	Carbon (ppma)
No. of Values	16	16	18
Average	0.043	0.351	0.183
Std. Dev.	0.017	0.159	0.153
Variance	0.000	0.024	0.021

TABLE 23. DICHLOROSILANE POLYSILICON PURITY SUMMARY

All Runs with Actual Boron, Donor, and Carbon Measurements

Runs Evaluated	32 Boron (ppba)	32 Donor (ppba)	24 Carbon (ppma)
Average	0.06	0.50	0.29
Maximum	0.19	1.24	0.70
Minimum	0.03	0.15	0.10
Std. Dev.	0.02	0.16	0.15
Variance	0.000	0.07	0.02

All runs with Actual Donor and Carbon Measurements - Boron Determined by Plant Audit

Runs Evaluated	145 Boron (ppba)	145 Donor (ppba)	110 Carbon (ppma)
Average	0.06	0.47	0.24 (110)
Maximum	0.19	1.60	0.90
Minimum	0.03	0.09	0.10
Std. Dev.	0.03	0.32	0.19
Variance	0.00	0.10	0.04

NOTE: 35 runs removed as obvious upsets.

The spark source mass spectrographic results are summarized below in quantitative terms (ppma) for the DCS poly rod and TCS poly standard.

Element	DCS Poly (324-0429)	TCS Poly Standard (325-0481)
Na	0.03	0.003
Mg	0.004	0.004
Ti	0.005	0.005
Cr	-	0.044
Mn	-	0.003
Cu	0.016	0.016
Zn	0.007	-
Ta	0.003	-

The TCS poly standard represented any impurities possibly present in the material as well as the background of the mass spectrometer. The background contamination can only be eliminated through repeated processing of ultra pure material in the instrument.

The DCS results were typical for poly supplied to the U.S. market. It should be mentioned that sodium was found in varying degrees because of sample handling.

Two 6-pass DCS freeze out sections were analyzed to determine if trace elements not detected on the poly samples due to spark source mass spectrographic limitations would be observed after being concentrated. It was impossible to volume calculate the total amount of trace element detected due to the non-homogeneity of the freeze out material. The following evaluations (ppma) were typical of other polysilicon freeze out samples:

Element	DCS Freeze-Out (324-0429)	DCS Freeze-Out (325-0459)
Na	0.011	>0.011
Mg	>0.014	>0.014
Ti	0.015	>0.015
Cr	>0.013	>0.013
Mn	>0.011	>0.011
Cu	>0.016	>0.016
Ta	>0.011	>0.011
Ag	-	>0.021

It must be emphasized that this was a qualitative method only. The numerical value for each element indicated that the element exists in trace quantities. The value itself had no significance.

3.7.5 Solar Cell Data

A polycrystalline silicon ingot was sent to Westinghouse Electric for processing into solar cells. A single-crystal Czochralski ingot was produced which was doped to a nominal ingot resistivity of 1.5 ohm-cm. Twenty-five wafers were fabricated into solar cells, along with five 4 ohm-cm baseline[17] wafers (refer to Table 24). The individual uncoated cell efficiencies ranged from a low of 8.3 percent (11.6% coated) to a high of 10.1 percent (14.2 percent coated). The majority of the cell efficiencies were in the 9 percent range. Overall efficiency of the solar cells was 102.3 percent of baseline solar cells.

In addition, deep-level transient spectroscopy measurements were taken on representative wafers. No deep levels were found in the DCS material, which was expected since any metals present in the starting material would be segregated during crystal growth.

TABLE 24. SOLAR CELL ELECTRICAL DATA

No SiO Anti-Reflective Coating

No.	V_{OC} mV	J_{SC} mA/cm^2	CFF %	η %	AREA cm^2
1	559	21.3	71	9.52	4.29
2	547	21.0	68	8.27	2.34
3	549	21.2	67	8.30	2.34
4	555	21.1	73	9.05	3.64
5	550	21.1	71	8.75	2.34
6	579	20.9	75	9.53	3.00
7	568	21.1	68	8.66	1.82
8	576	21.4	74	9.64	3.00
9	569	21.0	68	8.56	1.82
10	565	21.1	69	8.65	1.56
11	574	21.2	73	9.32	2.34
12	573	21.1	72	9.17	2.34
13	574	21.3	73	9.42	2.60
14	576	21.3	75	9.68	3.00
15	577	20.8	74	9.36	2.34
16	582	21.2	78	10.11	3.90
17	579	21.3	76	9.88	2.86
18	578	21.2	76	9.83	3.00
19	574	20.7	71	8.89	1.95
20	570	21.0	70	8.87	1.82
21	583	21.1	76	9.87	3.64
22	571	21.1	69	8.79	1.82
23	578	21.1	74	9.58	3.00
24	581	21.2	77	10.01	3.64
25	568	21.2	69	8.83	1.69
Averages	571	21.1	71	9.11	2.30
		Control Cells			
Averages	553	21.2	72	8.90	3.15

A portion of the same lot of polycrystalline silicon sent to Westinghouse, also was sent to the Jet Propulsion Laboratory for solar cell evaluation.* Results are shown in Table 25. A total of thirteen wafers were fabricated into SiO anti-reflectively coated solar cells, along with three control cells. Solar cell efficiencies averaged 12.8 percent with a high of 13.2 percent to a low of 12.6 percent. Overall efficiency of the solar cells was 103.5 percent of control solar cells.

Both evaluations produced good quality solar cells greater than baseline cells in terms of efficiency. Solar cells with anti-reflective coatings had an average efficiency of 12.8 percent while solar cells with no anti-reflective coating had an average efficiency of 8.9 percent.

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* Cells processed by Applied Solar Energy Corporation.

TABLE 25. SOLAR CELL ELECTRICAL DATA

SiO Anti-Reflective Coating

No.	V_{OC} mV	J_{SC} mA/cm^2	CFF %	η %	AREA cm^2
1		Broken			
2	590	29.4	76	13.2	4
3	588	28.9	75	12.7	4
4	592	29.0	77	13.2	3.98
5	588	29.0	74	12.6	4
6	590	29.3	75	12.9	4
7	590	29.3	74	12.9	4
8	590	29.5	75	13.1	4
9	588	29.4	75	12.9	4
10	592	28.0	78	12.9	3.98
11	588	29.3	74	12.7	4
12	588	28.5	75	12.6	4
13		Broken			
14	588	28.8	74	12.5	4
15	590	29.0	74	12.7	3.98
Average	590	29.0	75	12.8	4
		Control Cells			
Average	583	28.2	75	12.4	3.98

3.8 Experimental Process System Development Unit (EPSDU)

A design for an Experimental Process System Development Unit (EPSDU) to produce 220 tonne/yr of polycrystalline silicon that uses TCS as feedstock and has products of silicon, silicon tetrachloride (STC), and HCl was prepared. The plant was to be totally independent of the existing production facilities at Hemlock Semiconductor Corporation (HSC), although use of plant services such as steam, electrical, water, hydrogen, nitrogen, and air was planned. It should be noted that pure trichlorosilane feed was available for redistribution in the EPSDU design.

Although the EPSDU was never built, the objectives, design, process description, and other considerations are reviewed in this section for thoroughness of this report.

3.8.1 Objectives

Technical objectives of the EPSDU were to demonstrate:

1. 2.5-3.0 kg/hr/rx deposition rates.
2. 60 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.

3.8.2 General Process Description

Figure 26 represents the EPSDU process in block diagram form. TCS would be purchased and polycrystalline silicon, STC, and HCl produced in EPSDU operation.

The redistribution reactor converts the TCS to a mixture of DCS, TCS, and STC. This mixture would be distilled to separate the DCS from the TCS and STC. Placement of this reactor prior to the DCS distillation column is warranted since no DCS is present

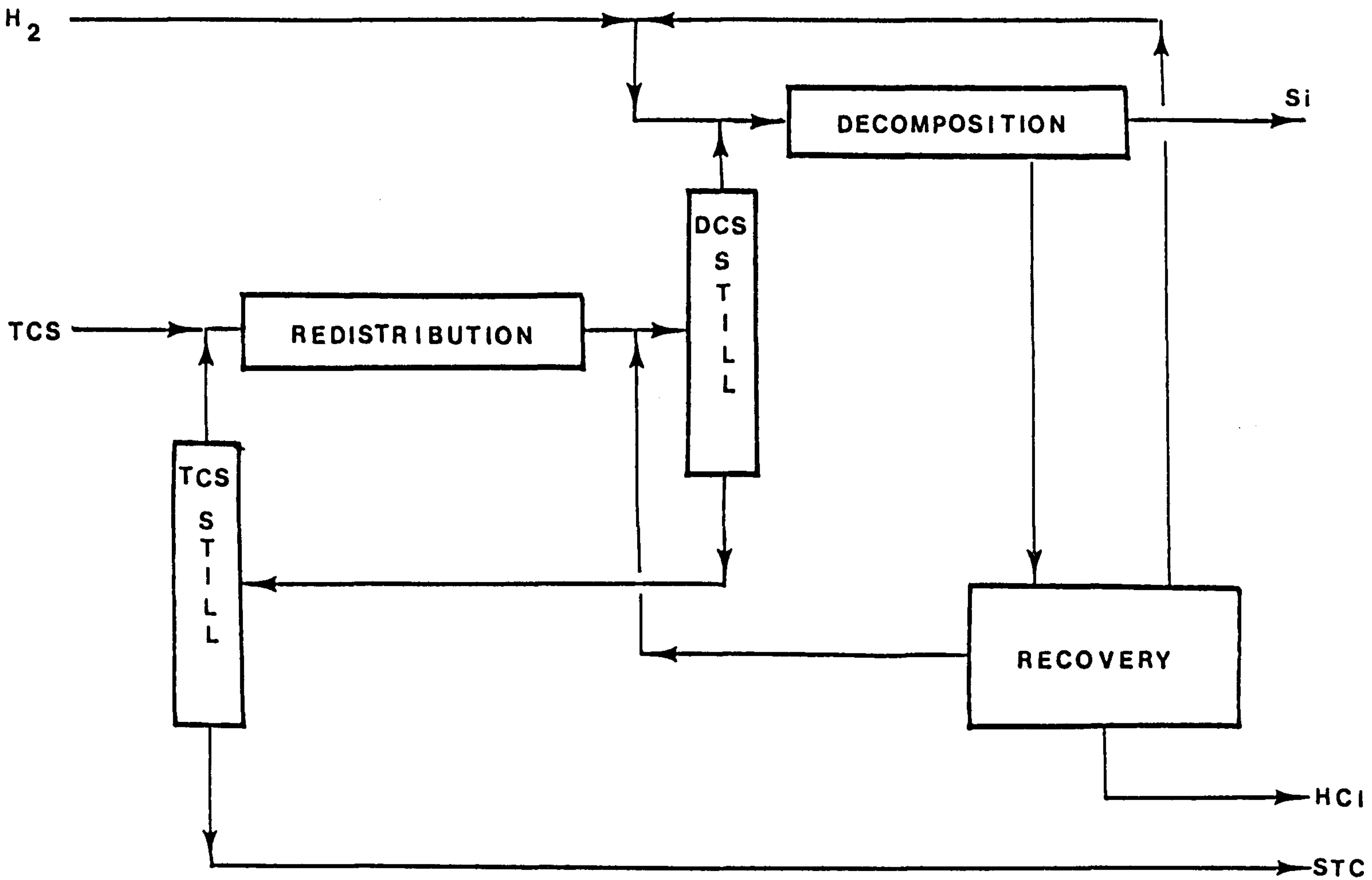

FIGURE 26. EPSDU - BLOCK DIAGRAM

in the TCS feed. The DCS would be mixed with H_2 and fed directly to chemical vapor decomposition reactors. The TCS and STC mixture would be fed to another distillation column where separation occurs. TCS would be recycled to the redistribution reactor and the STC by-product would be sold.

The DCS would 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 would separate the H_2 from the rest of the mixture for recycle to the decomposition reactors. HCl would be sold. All recovered chlorosilanes would be sent to the EPSDU distillation area for separation.

The recovery system would 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 would be sold. The chlorosilanes would be sent to the distillation section of the EPSDU. The recovery scheme selected by Hemlock Semiconductor would be similar to the one described by Yaws but would be modified to meet specific safety and operating criteria developed by HSC. Preliminary mass and energy balances as well as equipment sizing have been reviewed in previous reports.[15]

Detailed mass and energy balances for the EPSDU were halted early due to funding limitations. Therefore, the EPSDU unit was never built.

3.9 1000 Metric Ton Per Year Plant Design

A preliminary design of a 1000 metric ton polycrystalline silicon production facility was completed. This entailed the development of process flow diagrams (Figures 27 through 29), mass balances (Table 26) and energy balances (Table 27), base conditions (Table 28) and capital equipment estimates (Table 29).

3.9.1 Design Basis

The design basis for the 1000 metric ton silicon plant assumed 90% on line time (OLT) for the hydrogenation system, 95% for the stills and recovery unit, and 85% OLT for the decomposition reactors. The decomposition reactor OLT represented 89% OLT for reactors, compounded by 95% building OLT.

Anticipated product yields for the various unit operations were as follows:

1. Hydrogenation

   $3\ SiCl_4 + 2\ H_2 + Si\ (m.g.) \rightleftharpoons 4\ HSiCl_3$

   exit concentrations on a non-hydrogen basis are:

a.	H_2SiCl_2	1% (mole %)
b.	$HSiCl_3$	29.5%
c.	$SiCl_4$	69.5%

2. Redistribution

   $2\ HSiCl_3 \rightleftharpoons H_2SiCl_2 + SiCl_4$

   exit concentrations are

a.	H_3SiCl	0.5% (mole %)
b.	H_2SiCl_2	10%
c.	$HSiCl_3$	78%
d.	$SiCl_4$	11%

FIGURE 27.
HSC PROCESS
SILICON TETRACHLORIDE
HYDROGENATION SYSTEM

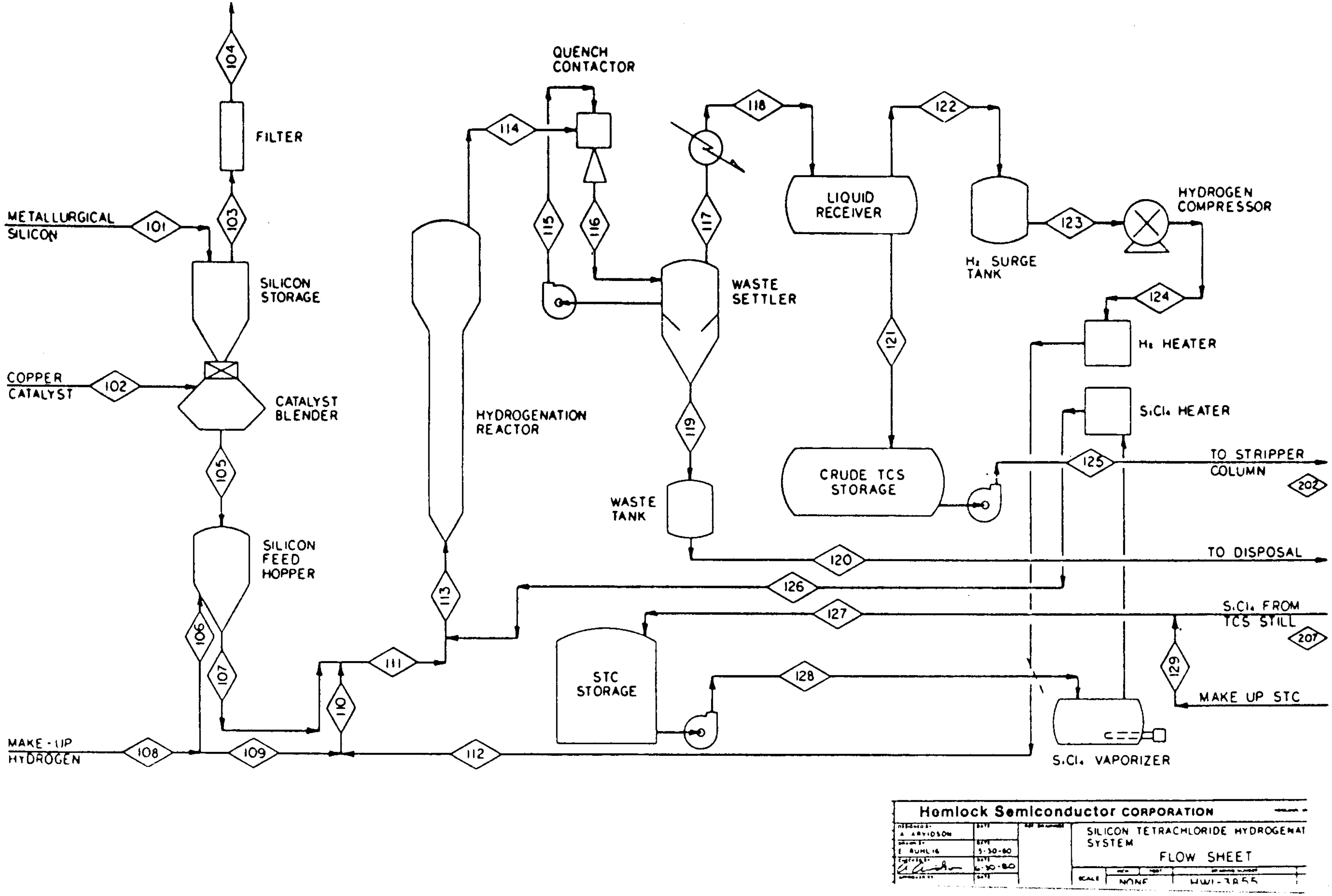

FIGURE 28.

DICHLOROSILANE PRODUCTION AND PURIFICATION

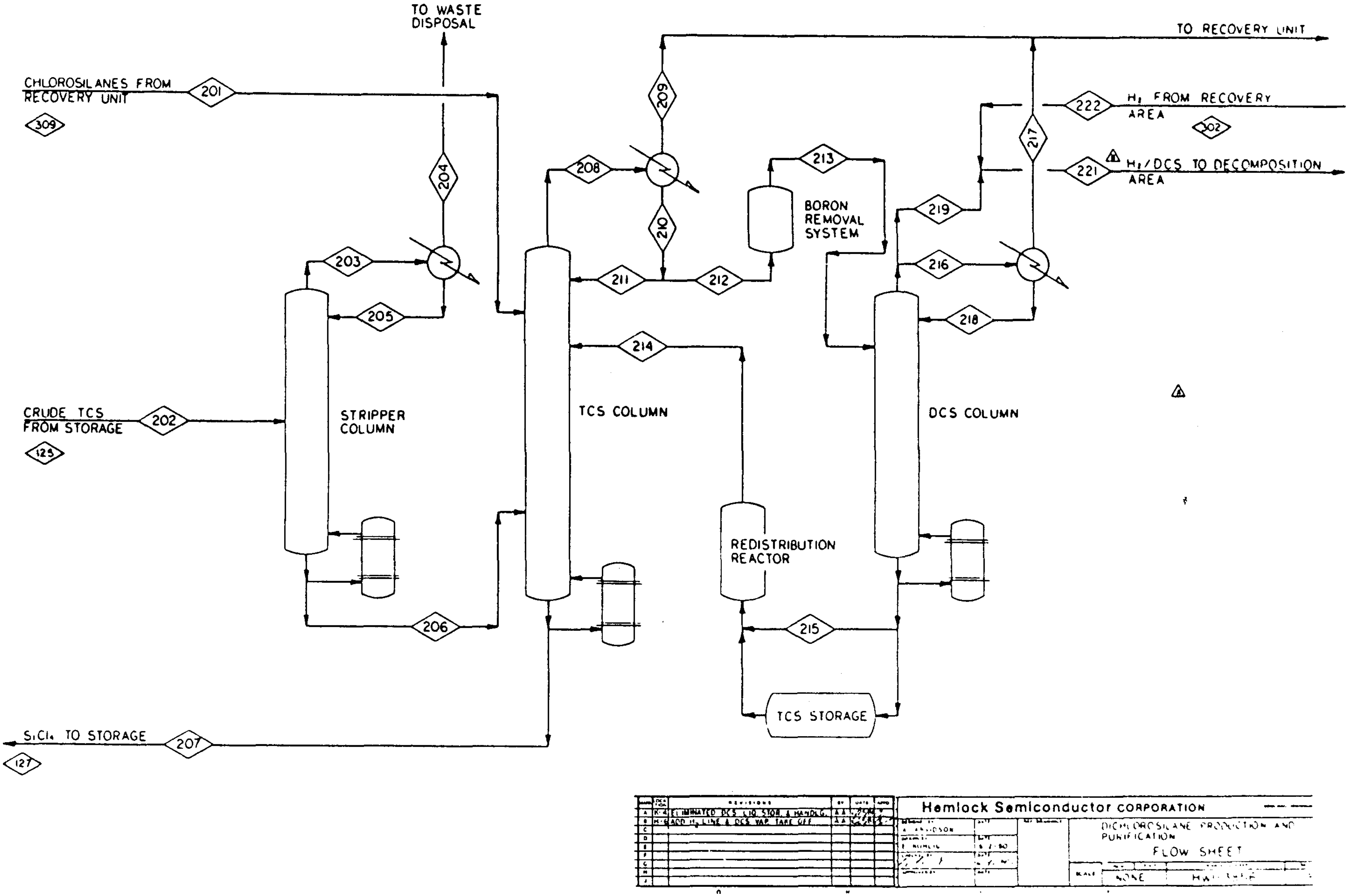

FIGURE 29.

HSC PROCESS DICHLOROSILANE DECOMPOSITION REACTORS AND RECOVERY UNIT

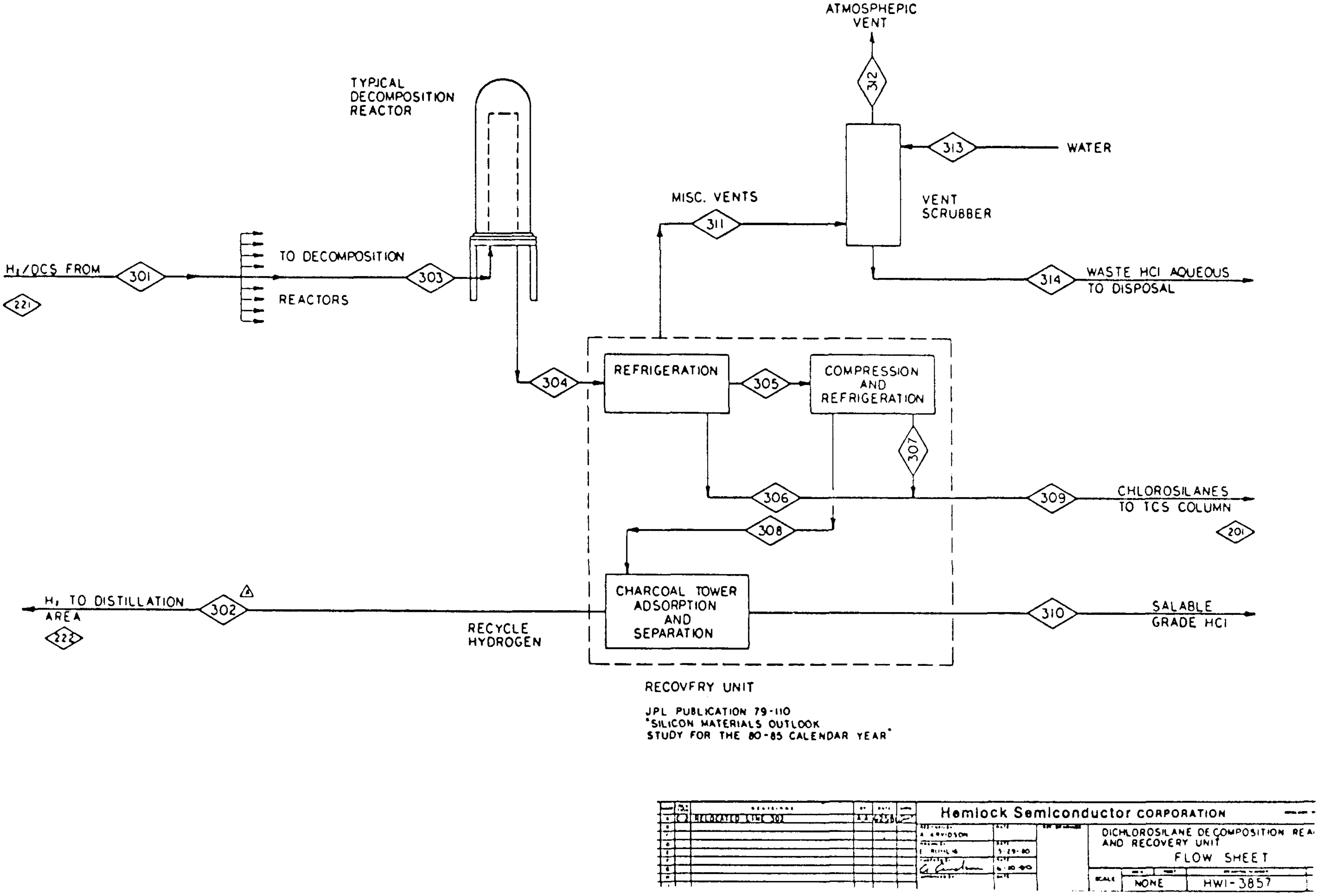

TABLE 26. 1000 MT/Y POLYSILICON PLANT FLOW RATES

FLOW AND WEIGHT % FOR SYSTEM SHOWN ON (FIG. 27)

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.			0.6	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	18284						100		
128	18284						100		
129	326.4						100		

TABLE 26. 1000 MT/Y POLYSILICON PLANT FLOW RATES (Cont.)

FLOW AND WEIGHT % FOR SYSTEM SHOWN ON (Fig. 28)

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 26. 1000 MT/Y POLYSILICON PLANT FLOW RATES (Cont.)

FLOW AND WEIGHT % FOR SYSTEM SHOWN ON (Fig. 29)

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
307	-								Proprietary
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

TABLE 27. 1000 METRIC TONNE PLANT ENERGY REQUIREMENTS

	Steam/Hot Oil		Water		Electric	
Item	BTU/Hr.	BTU/Kg.	BTU/Hr.	BTU/Kg.	kWh/Hr.	kWh/Kg
Quench Cond.			4981M*	38.77M		
STC Cooler			394M	3.1M		
H_2 Heater	9441M (gas)	74.4M				
STC Heater	1836M (gas)	14.5M				
STC Vaporizer	2226M	17.5M				
Stripper Cond.			14 Ton (-40°)	0.11 Ton		
Stripper Reboiler	815M	6.42M				
TCS Cond.			4312M	34M		
TCS Reboiler	4085M					
TCS Cooler			1242M	9.8M		
DCS Cond.			1751M	13.8M		
DCS Reboiler	2988M	23.5M				
Pumps						0.6
Recovery		22.34M		33.6M		7.0
TOTAL Non Decomp		126.66M + 32M/gas		133.07M + 0.11 Ton at -40°F		7.6
Decomp						60
TOTAL		126.66M +32M gas		133.07M +0.11 Ton at -40°F	8574.	67.6

* M = 1000

TABLE 28. BASE CONDITIONS FOR ECONOMIC ANALYSIS OF HSC DICHLOROSILANE-TO-SILICON PROCESS

1. General

Plant size:	1000 metric tonne of silicon
Product:	High purity silicon
Process:	Production of DCS (SiH_2Cl_2); generation of silicon from reductive chemical vapor deposition (CVD) of DCS

2. Production of TCS ($SiHCl_3$)

From hydrogenation of metallurgical-grade silicon and STC ($SiCl_4$)
Fluidized bed reactor, containing metallurgical grade silicon
Reactor operates at 500°C and 500 psig
Equimolar feed of STC and H_2
Product composition approximately

STC	70%
TCS	29%
DCS	1%

3. Removal/recycle of STC

Distillation (TCS still)
Separation of TCS + DCS from STC
Overhead stream to DCS still
Bottoms stream to hydrogenation reactor

4. Boron Removal

Removal of BCl_3 via complexation with nitrogen or oxygen based on non-volatile support
Fixed bed reactor
Feed from TCS still
Effluent to DCS still
No chlorosilane material loss

5. DCS Production

Redistribution of TCS with Dowex® ion exchange resin
Pure TCS feed
Liquid phase operation @ 70°C, 80 psig
Products to TCS still
Product composition as follows

DCS	10.5% (includes <1% SiH_3Cl (MCS))
TCS	78.5%
STC	11.0%

6. DCS purification

Distillation (DCS still)
Feed from TCS still

TABLE 26. BASE CONDITIONS FOR ECONOMIC ANALYSIS OF HSC DICHLOROSILANE-TO-SILICON PROCESS (Cont.)

6. (Continued)
   Separate DCS (+MCS) from TCS
   Overhead stream to CVD reactors
   Bottoms steam to redistribution reactor

7. Silicon production

   45 Siemens CVD reactors (modified as appropriate)
   DCS/H_2 feed
   Molar conversion to silicon of 40%
   Deposition rate of 3000 g/hr/reactor
   Vent composition (per mole of DCS fed)

HCl	.14
DCS	.10
TCS	.34
STC	.16

8. Operating ratio

   85% utilization (on line time) of CVD reactors
   7445 production hours/yr

9. Waste treatment

   Waste gas streams to water scrubber. Resultant HCl neutralized with $Ca(OH)_2$.

   Waste liquid streams process with current Dow Corning technology. Chlorosilanes neutralized with $Ca(OH_2$; silica generate sold or disposed of depending on quality.

10. Storage requirements

TCS	3 days
STC	3 weeks
Silicon	14 days
$Ca(OH)_2$	14 days

11. Recycle streams

    Hydrogen from CVD reactors returned to same reactors
    Chlorosilanes, HCl from CVD reactor vent to recovery system
    Recovery system condenses, separates HCl, chlorosilanes; HCl sold for credit ($.12/lb), chlorosilanes returned to TCS still
    Recovery system modified Siemens technology

12. Slim rod pullers

    Pull rate average of 470 cm/hr (for each of five machines)
    Thin rod diameter of 6 mm

TABLE 29.

MAJOR EQUIPMENT FOR 1000 METRIC TON/YEAR POLYSILICON PLANT

HYDROGENATION RELATED VESSELS [5]

Equipment No.	Equipment Name	No. Req'd.	Type	Capacity	Material Of Construction	Cost (1st Q,'79)
411-02	M.G. Silicon Storage Bin	1	Bin	1750 cu.ft.	Steel	22,500
411-04	Hydrogen Supply Package	1	Tank	18,000 gal.	Steel	Rental*
421-02	M.G. Silicon Lock Hopper	1	Vert.Tank	450 gal.	Steel	13,400
421-04	Waste Settler Tank	1	Vert.Tank	1,700 gal.	304L Stainless	95,000
421-06	Waste Chlorides Tank	1	Vert.Tank	400 gal.	Steel	7,100
421-08	Quench Condenser Receiver	1	Horiz.Tank	3,000 gal.	Steel	17,900
421-10	Crude TCS Storage tank	1	Horiz.Tank	20,000 gal.	Steel	26,300
421-12	STC Storage Tank	1	API Tank	25,000 gal.	Steel	10,000
421-14	Recycle Hydrogen Receiver	1	Vert.Tank	750 gal.	Steel	7,600
431-02	Stripper Condenser Receiver	1	Vert.Tank	70 gal.	304L Stainless	3,500

HYDROGENATION RELATED REACTORS[5]

Equipment No.	Equipment Name	No. Req'd.	Type	Diameter	Height	Material Of Construction	Cost (1st Q,'79)
425-02	Hydrogenation Reactor	1	Fluid.Bed	2.5 ft.	21 ft.	Incoloy 800	142,500

TABLE 29. (Cont.)

HYDROGENATION RELATED COLUMNS[5]

Equipment No.	Equipment Name	No. Req'd.	Type	Diameter	Number Of Trays	Material Of Construction	Cost
432-02	Stripper Column	1	Trayed	2.5 ft.	25	Steel	21,300
432-04	TCS Column	1	Trayed	6 ft.	30	Steel	56,700

HYDROGENATION RELATED HEAT EXCHANGERS[5]

Equipment No.	Equipment Name	No. Req'd.	Type	Design Duty (BTU/Hr)	Material Of Construction	Cost (1st Q,'79)
424-02	Quench Condenser	1	Fixed Tbsht	9,840,000	Steel/Cupronickel	77,500
424-04	Recycle STC Vaporizer	1	Kettle	4,450,000	Steel/304 SS	8,400
434-02	Stripper Condenser	1	Fixed Tbsht	350,000	Nickel Steel	4,200
434-04	Stripper Reboiler	1	Kettle	1,630,000	Steel	5,000
434-06	TCS Column Reboiler	1	Kettle	8,180,000	Steel	9,700
434-08	TCS Column Condenser	1	Fixed Tbsht	8,630,000	Steel/Cupronickel	15,600
434-24	STC Cooler	1	Hairpin	790,000	Steel	800

TABLE 29. (Cont.)

HYDROGENATION RELATED PUMPS[5]

Equipment No.	Equipment Name	No. Req'd.	Type	Design Flow	Design Head	Material Of Construction	Cost
426-02	Quench Contactor Pump	1	Centrigual	500 GPM	100 PSI	Cast Iron/304 SS	7,500
426-04	Quench Condenser Wash Pump	1	Diaphragm	6.7 GPM	70 PSI	Steel	7,000
426-06	Recycle STC Pump	1	Diaphragm	60 GPM	550 PSI	Steel	18,000
436-02	TCS Distillate Pump	2	Diaphragm	180 GPM	300 PSI	Steel	33,000 ea.

HYDROGENATION RELATED FILTERS[5]

Equipment No.	Equipment Name	No. Req'd.	Type	Design Capacity	Particle Size	Material Of Construction	Cost
417-02	M.G. Silicon Unloading Filter	1	Bag	500 GPM	1	Steel/Polyeth.	600
427-02	Crude TCS Filter	1	Edge	65 GPM	35	Steel	500

HYDROGENATION RELATED SOLIDS HANDLING[5]

Equipment No.	Equipment Name	No. Req'd.	Type	Capacity	Material Of Construction	Cost (1st Q,'79)
428-02	Hydrogenation Catalyst Blender	1	Twin Shell	50 cu.ft.	Steel	19,100

TABLE 29. (Cont.)

HYDROGENATION RELATED COMPRESSORS[5]

Equipment No.	Equipment Name	No. Req'd.	Design Flow	Design Head	Material Of Construction	Cost (1st Q,'79)
423-02	Recycle Hydrogen Compressor	1	55 ACFM	90 PSI	Steel	150,000

MISCELLANEOUS[5]

Equipment No.	Equipment Name	No. Req'd.	Design Specifications	Material Of Construcion	Cost (1st Q,'79)
429-02	Quench & Solids Removal Contractor	1	210 ACFM gas at suction	304 Stainless	15,000
429-04	Gas Superheater Furnace	1	5.57 MM BTU/hr. fired output	Steel/Firebrick	44,000
429-06	Recycle STC Superheater	1	3,680,000 BTU/hr. duty	304 Stainless	429-04*
429-08	Recycle Hydrogen Superheater	1	1,890,000 BTU/hr duty	304 Stainless	429-04*
	UCC Plant Total				$872,700
	HSC = $\left(\frac{\text{HSC throughput}}{\text{UCC throughput}}\right)^{0.6} = (0.6)^{0.6} = 0.736$				$642,300
	Total HSC Plant ($1980) for Hydrogenation				$693,700

TABLE 29. (Cont.)

DICHLOROSILANE PRODUCTION SYSTEM

Equipment No.	Equipment Name	Req'd.	Description	Material	1979 $
	Boron removal system	2	12"x20 ft. packed		10,000/e
	Redistribution Reactor	1	58"x24 ft.		89,300
	DCS Column	1	18 theoretical trays x 52" dia.		56,000
	DCS Reboiler	1	595 FT^2		5,000
	DCS Condenser	1	997 Ft^2		5,000
	Special DCS Safety Features				26,000
	TCS Storage		60 M gallon		93,000
	Total HSC Plant for DCS Production ($1980)				$317,800

* Cost includes packing

TABLE 29. (Cont.)

Recovery System

Recovery Area	
1980 Cost of Equipment =	$1,031,100
Waste Disposal & Control	
1980 Cost of Equipment =	$110,000
Services	
1980 Cost	
Hot Oil Furnace & Pumps	99,400
Hot Oil Surge Tank	16,200
Cooling Water Tower & Pumps	84,900
Total =	$200,500
Filament Pullers (6)	
1980 Cost =	$300,000
HSC Total Direct Plant Investment	$2,653,100

3. Decomposition reactors

$H_2SiCl_2 + H_2 \longrightarrow Si + HSiCl_3 + SiCl_4 + HCl + H_2$

exit concentrations on a non-hydrogen basis per mole of $H_2 SiCl_2$ feed were:

a.	Si	0.40 in reactor
b.	H_2SiCl_2	0.10 in vent
c.	$HSiCl_3$	0.34 in vent
d.	$SiCl_4$	0.16 in vent
e.	HCl	0.14 in vent

Material flows and compositions utilized assumed ideal separations. This approach, although not exact, greatly simplified sizing of equipment.

Redistribution reactor placement was located at the bottom of the DCS distillation column since ideal separation was assumed. Preliminary data produced by Mui[6] from the hydrochlorination of silicon tetrachloride indicated that only a small amount of dichlorosilane is present from the fluid bed reactor stream which could change the placement of the redistribution reactor. Therefore, it is possible to place the redistribution reactor at the top of the TCS distillation column. In either place, equipment cost and operating cost will not change the economics of the 1000 tonne plant. However, if relocated, it will change the plant detailed engineering design.

The overhead of the DCS column will be controlled to provide equal amounts of monochlorosilane and TCS in the DCS, thus maintaining a Cl:Si ratio of 2:1 in the decomposition reactor feed stream.

3.9.2 Unit Operation Description for 1000 Tonne Plant

HYDROGENATION UNIT

The unit shown in Figure 27 represents the same unit as presented by Union Carbide Corporation in JPL FSA Contract 954334.[5] The new drawing includes line designation and flows corresponding to HSC requirements.

The exit composition from the reactor was selected from work of Mui and Seyferth.[18] (See Table 26.)

Detailed design of this unit may differ somewhat from the unit shown, in order to satisfy Hemlock Semiconductor Corporation design and safety criteria.

OPERATION

Metallurgical grade silicon is received in ground form and placed in the silicon storage bin (line 101). The silicon is mixed with copper catalyst (line 102) in the catalyst blender. This mixture is placed in the silicon feed hopper (line 105) where it is purged free from air. Hydrogen is used to pressurize the hopper and force the catalyst and silicon into the hydrogenation reactor (line 107). Hydrogen (line 112) and STC (line 126), in equimolar quantities at just over 500°C enter the bottom of the hydrogenation reactor, which is operated in a fluidized state. Thermodynamic limitations of the reaction restrict the practical conversion to 29.5 mole percent TCS in the effluent.

The products leaving the hydrogenation reactor line (114) enter the quench contactor. A large quantity of cool liquid is pumped from the waste settler to the quench contactor (line 115) to condense some of the chlorosilanes and wash out metallic salts and silicon metal fines in the reactor product. The salts and metal settle in the waste settler and are removed (line 119).

The cooled product gas then passes to the product condenser (line 117), then to the liquid receiver (line 118). Gravity separation of the liquid and vapor occurs in the receiver. Liquid exits to the crude TCS storage tank (line 121) and hydrogen exits to the hydrogen surge tank (line 122). The liquid product is later sent to distillation.

The hydrogen is compressed and sent to the hydrogen heater (line 124). In the same heater housing, STC from the STC vaporizer is heated to greater than 500°C. Both streams then feed the hydrogenation reactor.

STC is received as make up material (line 129) as well as recycle from the TCS still (line 207). Make up material is required to replenish the HCl lost in the waste settler effluent and HCl produced in the decomposition reactor (and subsequently sold).

DISTILLATION

A three-still system was selected, as shown in Figure 28. The first still, the stripper column, removes all materials with boiling points lower than DCS from the hydrogenation reactor product (line 204). DCS, TCS, and STC pass from the bottom of the column (line 206) and enter the TCS column.

The TCS column receives feeds from the bottom of the stripper column (line 206), from the recovery unit (line 201), and from the redistribution reactor (line 214). STC is removed from the bottom (line 207) and is sent to the STC storage tank in the hydrogenation area. The overhead product (line 212) is a mixture of DCS and TCS, which goes through the boron removal system and then is fed to the DCS still (line 213).

The DCS still removes DCS overhead (line 2190 with controls used to maintain equal monochlorosilane and TCS concentration in the overhead stream. The bottoms stream from the still (line 215) is TCS. The TCS goes directly to the redistribution reactor, or into TCS storage.

Storage in the still area will allow 3 days of operation of the decomposition area with the hydrogenation unit shut down. This storage is required to maintain high decomposition reactors OLT, thus avoiding unfavorable utility consumption caused by insufficient feed. System capacitance will be supplied as TCS storage located in the line between the bottom of the DCS still and the redistribution reactor.

DCS/HYDROGENATION MIXING

To avoid storage of DCS, a vapor product will be transported to the CVD reactors. The DCS will be taken from the DCS column (line 219) and mixed with recovered hydrogen. A ratio controller will be fixed to maintain the proper balance of H_2 (from line 222). The DCS/H_2 mixture will be transported to the decomposition area (line 221).

DECOMPOSITION REACTORS

Decomposition reactors (shown with recovery in Figure 29) will receive DCS and hydrogen as feed (line 301). Each reactor will produce 3000 grams per hour of silicon while in operation. Reactor vent gas will exit to the recovery unit (line 304).

RECOVERY UNIT

The recovery unit receives a mixture of hydrogen, HCl, DCS, TCS, and STC from the decomposition reactors (line 304). The unit separates and purifies the hydrogen for recycle (line 302), recovers HCl for sale (line 310), and recovers chlorosilanes for recycle to the TCS still (line 309).

The recovery unit design shown in Figure 29 is extracted from Reference 11.

Vent gases from the decomposition reactors (line 304) are cooled to remove some of the chlorosilanes. After the initial refrigeration step, gases are sent to compression and refrigeration (line 305) where most of the remaining chlorosilanes are condensed. Condensed chlorosilanes are removed (Line 306 + 307) and sent to the distillation area (line 309). The H_2 and HCl, along with traces of chlorosilanes are sent to a charcoal adsorption tower (line 308) for final cleanup of the hydrogen. Purified H_2 is recycled to the decomposition reactors (line 302). Additional equipment is used to recover the HCl as salable grade (line 310).

WASTE CONTROL

Waste streams requiring treatment are those from the waste settler (line 120) and the stripper column (line 204), and the hydrogen generated in the decomposition reactors (line 311). All other streams are recovered by use of the recovery system.

The vapor streams are washed with water (line 313) in a simple scrubber. The resultant aqueous waste (line 314) will be neutralized with calcium hydroxide and the clean gas will be vented to the atmosphere (line 312).

Liquid waste (line 120) are disposed of via Dow Corning technology[19]. The chlorine from this process is neutralized with calcium hydroxide. The silica is collected and appropriate disposition made.

PURITY CONSIDERATIONS

Boron is expected as boron trichloride, generated in the hydrogenation unit. BCl_3 will emerge from the bottom of the stripper column (line 206) and overhead at the TCS still (line 212). From there it will enter the boron removal system. The removal system is a packed column, with selective adsorption of boron trichloride from TCS. This technique has been used to purify STC, with the use of Dowex® 3[20] and other adsorptive media.

Phosphorus is expected to accumulate in the STC stream (line 127) until it reaches steady-state concentration and is eliminated with the waste settler effluent (line 119). No phosphorus is expected in the DCS still overhead. If necessary, a small column could be added to separate phosphorus compounds from STC prior to feeding the hydrogenation unit, (line 127).

THIN ROD PULLERS

Thin rods or silicon substrates are needed to form the initial circuit for electric current and initial surface area for deposition. The slim rods are produced by heating a larger diameter silicon rod with radio frequency energy, RF, until the silicon melts. A seed is then positioned in the molten silicon and pulled away from the melt. The larger rod is continually pushed into the RF field. Dissimilar rates of pull and feed cause a product that is smaller in diameter and suitable for use as a substrate.

3.9.3 Economic Evaluation

An economic analysis of the HSC DCS-based low cost silicon process has been undertaken. The base conditions for the analysis are those corresponding to the 1000 metric ton plant design and description as outlined in the previous two sections. Assumptions about process parameters with economic implications are specified in Table 28.

The following section is devoted to a brief discussion of the calculation procedure used for the analysis.

3.9.3.1 Procedure used for Economic Analysis-General

Where possible, the procedure followed has paralleled that developed by C. Yaws and co-workers at Lamar University[21] for evaluating various low-cost solar silicon processes. Capital categories were estimated as percentages of major process equipment cost and direct plant investment costs.

When such factors have been used, they have been averages of the corresponding values used by Yaws in his analysis of the standard Siemens[22] and Union Carbide[23] low-cost silicon technologies.

3.9.3.2 Manufacturing Capital Requirements

DIRECT PLANT INVESTMENTS

Purchased cost was used for all equipment except for CVD reactors. For these, we utilized installed reactor cost as a portion of the reactor building cost, since it can be estimated quite accurately. Appropriate factors were used to convert purchased into installed cost for other equipment. All figures have been converted into 1980 dollars.

The cost figures for hydrogenation, distillation, and redistribution-related equipment have been derived from the cost analysis of Union Carbide Corp., as presented in their FSA Quarterly Reports.[5] Table 29 is an equipment list for the process as depicted in Figures 27 through 29. Equipment is identified by name only when compared to the figures. Equipment numbers, where listed, correspond to those used by Union Carbide Corporation in their Final FSA Report.[5] The total cost for those items was scaled as suggested by Peters and Timmerhaus[24] as;

$$\text{Cost A} = \left(\frac{\text{capacity A}}{\text{capacity B}}\right)^{0.6} \cdot (\text{cost B})$$

This procedure was used by HSC because design and costing of hydrogenation was not funded by JPL during the course of this contract.

OTHER DIRECT PLANT INVESTMENT COSTS

Installed utilities were treated as a separate category. An estimate was made for installation of a substation capable of supplying 80 MM kWh* of electrical power per year.

INDIRECT PLANT INVESTMENT COSTS

Indirect plant investment costs were made on the basis of factors used by Yaws.

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* MM = 1,000,000

SUMMARY OF FIXED CAPITAL PLANT INVESTMENT

Table 30 is a summary of the fixed capital plant investment required ($21.92 MM)* for building a 1000 MT/yr polycrystalline silicon plant. All figures are in 1980 dollars.

The costs of the DCS production/purification equipment, boron removal system, TCS storage, and plant services were estimated by scaling to similar equipment from the Union Carbide Corporation Final Report.[5]

Recovery area, waste disposal and control, filament pullers, decomposition reactors, and decomposition reactor building were scaled for size, and known costs of past HSC projects were used to calculate the total direct plant investment.

3.9.3.3 Manufacturing Cost Estimate

UTILITIES

Table 31 is an itemization of process utilities for steam, cooling water, and electric power for the various unit operations as units per hour and units per kilogram.

RAW MATERIALS

Raw material requirements and by-product (HCl) production are shown in Table 32. Unit prices for all items and cost (credit) per kg are also shown in the summary.

LABOR

Table 33 is an itemization of the operations (direct labor) for the various unit operations on a per shift basis. Direct labor cost per kilogram is also shown.

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* MM = 1,000,000

TABLE 30. HEMLOCK SEMICONDUCTOR CORPORATION LOW-COST SILICON PROCESS MANUFACTURING CAPITAL

		1980 Dollars
1.	Direct Plant Investment (battery limit)	
	a. Major Process Equipment (except CVD rxs)	$2653.1 M
	b. Installation/Instrumentation/Buildings (not including the reactor building) (100% of 1a.)	2653.1
	Subtotal	5306.2
	c. CVD Reactors (installed)/Reactor Building	5401.0
	d. Total Battery Limit Investment	10707.2
2.	Other Direct Plant Investment Costs	
	a. Utilities, installed	2300.0
	b. Other direct (general offices, shops etc.) (55% of 1a.)	1266.0
3.	Total of Direct Plant Investment	14273.2
4.	Indirect Plant Investment Costs	
	a. Engineering overhead (10% of 3.)	1427.3
	b. Normal contingency (18% of 3.)	2569.2
	Total of Indirect Plant Investment	3996.5
5.	Total Direct & Indirect Investment	18269.7
6.	Overall Contingency (20% of 5.)	3653.9
7.	Fixed Capital Plant Investment (5 + 6)	21923.6

TABLE 31. 1000 MT/Y UTILITIES SUMMARY

		kwh/kg (BTU/kg)	$/unit /kwh	$/kg
1.	Electricity		.036	
	CVD rxs	60.0		
	Recovery system	7.0		
	Pumps	0.6		
	Refrigeration	0.4		
		68.0		2.45
			/MM BTU*	
2.	Steam/hot oil	126.7 M	1.89	.24
3.	Cooling water	133.1 M	1.51	.20
			/M gal	
4.	Process water	2.4 gal.	.567	.001
			/M BTU	
5.	Natural gas	32.3 BTU	1.96	.06
6.	Refrigerant	1.32 M BTU	0.1047	.02
		Total Utilities		2.97

* M = 1,000
MM = 1,000,000

TABLE 32. MANUFACTURING COST ESTIMATE FOR HSC 1000T PLANT (Manufacturing capital = $21.92 MM)

RAW MATERIALS SUMMARY

		lb/kg poly	$/lb	$/kg poly
1.	MG silicon	2.53	.636	1.62
2.	Copper	.053	1.29	.068
3.	STC	2.57	.189	.49
4.	H_2 (ft^3/kg)	50.2	.0075	.37
5.	Lime	1.50	.021	.032
6.	HCl (credit)	1.00	.140	(.14)
7.	N_2 (ft^3/kg)	1.00	0.0034	0.34
		Total Raw Materials		2.78

MM = 1,000,000

TABLE 33. 1000 MT/Y LABOR SUMMARY

Skilled labor @ $9.66/hr

Semiskilled labor @ $6.86/hr

114 kg/hr; 913 kg/shift

Unit Operation	Operators/Shift	$/kg Silicon
DCS production (includes hydrog., rearr., distillation)	1.5	.127
Silicon production	4	.339
Recovery System	1	.085
Thin rod production	1	.085
Waste treatment	1	.085
Total Labor	8.5	.721

MANUFACTURING COST SUMMARY

The product cost without profit was determined to be \$15.60 per kilogram (Table 34). The product cost represents all costs associated with producing 1 kilogram of polycrystalline silicon. Added to this cost is an acceptable rate of return on investment. A complete cost and profitability summary is shown in Table 35. A product price of \$20.27 provides a 10% after tax return on investment for this process.

TABLE 34. HEMLOCK SEMICONDUCTOR CORPORATION LOW-COST SILICON PROCESS MANUFACTURING COST (1980 Dollars)

		$/kg Silicon
1.	Direct Manufacturing Cost	
1.1	Raw Materials	2.78
1.2	Direct Operating Labor	.72
1.3	Utilities	2.97
1.4	Supervision/Clerical	.18
1.5	Maintenance and Repair	2.00
1.6	Operating Supplies	.40
1.7	Laboratory Charge	.18
2.	Indirect Manufacturing Cost	
2.1	Depreciation (10% of manf. cap.)	2.19
2.2	Local Taxes (2% of manf. cap.)	.44
2.3	Insurance (1% of manf. cap.)	.22
3.	Plant Overhead (12.3% of 1 + 2)	1.49
4.	Total Manufacturing Cost	13.57
5.	General Expenses	
5.1	Administration (6% of 4)	.81
5.2	Distribution and Sales (6% of 4)	.81
5.3	R&D (3% of 4)	.41
6.	Product Cost without Profit	15.60

TABLE 35. COST AND PROFITABILITY SUMMARY FOR DCS PROCESS (1980 Dollars)

1.	Process Type	CVD Reactors
2.	Plant Size	1000 Metric Tonnes
3.	Plant Product	Solid Silicon
4.	Product Form	Czochralski or chunk
5.	Plant Investment	$\$25.21 \times 10^6$

Fixed Capital	$\$21.92 \times 10^6$
Working Capital (15%)	$\$3.29 \times 10^6$
Total	$\$25.21 \times 10^6$

6. Return on Original Investment (% ROI after Tax)

	Sales Price of Polycrystalline Silicon ($/kg)
0% ROI	15.60
5% ROI	17.93
10% ROI	20.27
15% ROI	22.60
20% ROI	24.94

7. Federal tax rate 46%

4.0 Conclusions and Recommendations

Phase 1 and Phase 2 of the Development of a Polysilicon Process Based on Chemical Vapor Deposition have made considerable progress toward demonstrating the full potential of dichlorosilane as a feedstock for a low-cost route to high-purity polycrystalline silicon.

The base catalyzed redistribution of trichlorosilane at moderate temperatures using Dowex® MWA-1 has proven to be a cost effective method of manufacturing dichlorosilane. Hazards associated with the production and processing of dichlorosilane were identified, and process design criteria were critically evaluated. Safe operation was demonstrated for a dichlorosilane process demonstration unit with a capacity of 500,000 pounds per year.

High-purity polycrystalline silicon was produced in an experimental, intermediate and advanced CVD reactor. Data from the intermediate and advanced reactors confirmed earlier results obtained in the experimental reactor. Solar cells were fabricated by Westinghouse Electric and Applied Solar Research Corporation which met or exceeded baseline cell efficiencies.

Feedstocks containing trichlorosilane or silicon tetrachloride are not viable as etch promoters to reduce silicon deposition on bell jars. Neither are they capable of meeting program goals for the 1000 MT/yr plant. Post-run HCl etch was found to be a reasonably effective method of reducing silicon deposition on bell jars.

Using dichlorosilane as feedstock met the low-cost solar array deposition goal (2.0 gh^{-1}-cm^{-1}), however, conversion efficiency was approximately 10% lower than the targeted value of 40 mole percent (32-36% achieved), and power consumption was approximately 20 kWh/kg over target at the reactor.

If all program goals are met, economic analysis indicates that high-purity polycrystalline silicon will have an estimated product price of $20.27 per kilogram based on a 10 percent return on investment after tax.

We recommend to JPL that further efforts in the areas of reactor design and optimization be established to achieve all program goals while assuring safe, reliable reactor operation.

5.0 New Technology

Throughout the duration of Phase 1 and Phase 2 of Contract 955533 no new technology has been reported. Prior to the contract, work was completed on dichlorosilane decomposition in a small experimental reactor at Hemlock Semiconductor.

6.0 References

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