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DOE/JPL/955533-79-3

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

Third Quarterly Progress Report, April 1—June 30, 1980

MASTER

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August 1980

Dist-340
PT15-25

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

Hemlock Semiconductor Corporation
Hemlock, Michigan

U.S. Department of Energy

Solar Energy

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DRL No 125
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THIRD QUARTERLY PROGRESS REPORT

1 April TO 30 June 1980

on

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

prepared by

K. Sharp, Principal Investigator

and

A. Arvidson, F. Plahutnik and D. Sawyer

August 1980

JPL Contract 955533

"The JPL Low-Cost Silicon Solar Array Project is sponsored by the U. S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology by agreement between NASA and DOE."

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12334 Geddes Rd., Hemlock, Michigan 48626

ABSTRACT

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

The feasibility of silicon generation from dichlorosilane has been well established in the program to date. A number of runs have been conducted over a broad range of conditions in an experimental CVD reactor. Silicon rods of very good surface quality and up to 53 mm in diameter--the largest ever grown in the reactor--have been generated in predominantly or exclusively dichlorosilane-fed reactor runs. Molar silicon conversion efficiencies as high as 54% have been observed and are also unprecedented for this reactor. Under comparable conditions, deposition rates and conversions for dichlorosilane runs approach or exceed twice those for trichlorosilane runs. Of particular importance is the fact that few reactor-related operational problems were observed during any of the dichlorosilane runs.

Optimization of silicon production reactor behavior has been approached via an experimental design program in which system responses are correlated with reactor operating parameters. The program has been conducted in the experimental reactor by systematically varying the conditions of feed and rod temperature for the various runs.

In support of the Process Development Unit (PDU), a laboratory rearranger unit has been utilized to provide information relating to kinetics of trichlorosilane redistribution, catalyst behavior, and to allow development of reliable analytical techniques. Kinetic parameters have been determined for liquid phase redistribution at 77 °C and are more favorable than originally anticipated. The concept of mixed ($\text{SiHCl}_3/\text{SiCl}_4$) feed to the rearranger as a means for suppression of monochlorosilane has been abandoned, since experimental data indicate insufficient suppression of SiH_3Cl results, and no reactor problems attributable to the molecule have been apparent.

Detailed design and vendor quotations for major equipment for the PDU are complete; however, construction of the PDU has been temporarily suspended pending receipt of safety-related experimental information from Hazards Research Corp. with respect to combustion and hydrolytic behavior of dichlorosilane.

Activities related to the EPSDU have progressed to include an energy balance for the plant, and a material balance revised on the basis of new analytical data from gas chromatographic sampling of reactor vent gases.

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1.0 Summary

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

The feasibility portion of the experimental reactor program has been completed. More than 30 runs with dichlorosilane have been successfully conducted over a wide range of reactor operating conditions. Highlights include a molar conversion of dichlorosilane into silicon in excess of 54%, and power consumption of < 90 kwh/kg silicon. Two runs were conducted exclusively with dichlorosilane (in others, rods were first grown to a desired diameter with trichlorosilane). In one of these runs, silicon rods were grown to a diameter of 53 mm. This is the largest material ever grown in the experimental reactor. No operational problems were encountered in the "pure" dichlorosilane runs, and surface quality of the silicon for almost all runs was judged from good to excellent.

An optimization program in the experimental reactor is nearly completed. The program consists of an experimental design in which independent variables of reactor operation are systematically varied between runs and system responses such as deposition rate are monitored. Detailed correlations between system responses and operating parameters can thus be established and optimization strategies formulated. For instance, per cent conversion of dichlorosilane into silicon was found to increase with increasing rod temperature, but to decrease with increasing flow rate and mole % dichlorosilane in

the reactor feed.

In support of the Process Development Unit (PDU), a laboratory rearranger unit has been utilized to provide information relating to kinetics of trichlorosilane redistribution, catalyst behavior, and to allow development of reliable analytical techniques. Kinetic parameters have been determined for liquid phase redistribution at 77 °C and are more favorable than originally anticipated. The concept of mixed ($\text{SiHCl}_3/\text{SiCl}_4$) feed to the rearranger as a means for suppression of monochlorosilane has been abandoned, since experimental data indicate insufficient suppression of SiH_3Cl results, and no reactor problems attributable to the molecule have been apparent.

An analytical procedure for chlorosilane mixtures based on vapor phase sampling and gas chromatography has been developed, and has proved highly reliable.

Detailed design and vendor quotations for major equipment for the PDU are complete; however, construction of the PDU has been temporarily suspended pending receipt of safety-related experimental information from Hazards Research Corp. with respect to combustion and hydrolytic behavior of dichlorosilane. Such information is deemed necessary before adequate fire and spill can be designed.

Activities related to the EPEDU--a 100- to 200-tonne plant including dichlorosilane generation, purification and feed to production scale reactors-- have progressed to include an energy balance for the plant, and a material balance revised on the basis of new analytical data from gas chromatographic sampling of reactor vent gases.

2.0 Introduction

2.1 Program Objectives

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

The overall program covers a 39 month period and consists of a feasibility phase, which is the subject of the current contract, an EPSDU design phase, and an EPSDU construction/demonstration phase. The schedule for the program is shown in Figure 1. Specific Phase 1 project objectives include:

1. Characterization of dichlorosilane as a feedstock material for an experimental CVD reactor including quantitative determination of reaction products. (CVD Reactor Feasibility)
2. Design and construction of a dichlorosilane CVD reactor which will demonstrate dichlorosilane performance in a production sized reactor. (Intermediate Dichlorosilane Reactor Development)
3. Design, construction and operation of a laboratory scale redistribution reactor and a process development unit (PDU) to characterize the trichlorosilane-to-dichlorosilane redistribution process, determine product purity, and produce sufficient dichlorosilane to permit operation of a production sized reactor. (Dichlorosilane Process/Product Evaluation)

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

The general approach taken in meeting the overall program objective is discussed in Section 2.2. A brief overall process description is contained in Section 2.3. Technical aspects and progress in meeting the objectives in the four basic areas are discussed in Section 3.0.

2.2 Program Approach

The low cost process for the production of high quality polycrystalline silicon via reductive chemical vapor deposition from dichlorosilane is depicted in Figure 2. This process consists of the hydrogenation of silicon tetrachloride to produce trichlorosilane, synthesis of dichlorosilane via redistribution of trichlorosilane, high temperature decomposition of dichlorosilane to produce poly-crystalline silicon, and recovery of decomposition byproducts. Silicon tetrachloride, a major by-product of trichlorosilane redistribution and minor byproduct of dichlorosilane decomposition is recycled into the hydrogenation process. Also shown in Figure 2 are the distillation processes required for chlorosilane separation/ purification

The only byproduct shown as not being recycled in Figure 2 is hydrogen chloride. This material represents a relatively low volume stream and may be sold as a by-product, although it could also be used in a hydrochlorination process to produce additional trichlorosilane.

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 polycrystalline silicon via the decomposition of dichlorosilane include:

Hydrogenation of Silicon Tetrachloride

Dichlorosilane Synthesis

Catalyst

Dichlorosilane Decomposition

2.3.2 Process Implementation

Implementation of the low cost chlorosilane based CVD process is illustrated schematically in Figure 2. Hydrogenation of silicon tetrachloride occurs in a fluidized bed reactor. The bed is made up of finely ground metallurgical grade silicon fluidized with a H_2/SiCl_4 gas stream. The hydrogenation products (H_2 , HSiCl_3 and SiCl_4) are 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 chlorosilane present in this stream (approximately 80 percent). Dichlorosilane separation is

effected by a second distillation process and dichlorosilane 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 vaporized and, along with hydrogen, is introduced into a polycrystalline silicon CVD reactor where it is decomposed on a resistively heated substrate. Reaction 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 hydrogenation segments of the process.

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. If HCl generation becomes excessive, the material can be recycled by conversion into trichlorosilane.

3.0 Technical Status

Phase 1 technical efforts are limited to the four areas discussed in Section 2.1. No efforts are being expended in the area of silicon tetrachloride hydrogenation due to JPL support of the Union Carbide program. Neither are efforts being devoted to the development of CVD reactor vent product recovery technology. This technology is closely aligned with recovery system technology currently employed in the trichlorosilane CVD process. Phase 1 efforts thus consist of the following:

- CVD Reactor Feasibility
- Intermediate Dichlorosilane Reactor Development
- Dichlorosilane Process/Product Evaluation
- EPSDU Design

A milestone chart detailing work to be accomplished in these four general areas is shown in Figure 3. The four major areas of technical activity are discussed in Sections 3.1 through 3.4.

3.1 CVD Reactor Feasibility

3.1.1 Objectives

The objectives of the reactor feasibility task are to:

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 an experimental CVD reactor.
4. Provide necessary information for scale-up to an intermediate size or full-scale production reactor.
5. Establish vent product composition necessary for 1000 metric-ton plant design and costing.

6. If necessary, evaluate the performance of a reactor operating on mixed feed (dichlorosilane and trichlorosilane).

The reactor and support systems employed in this experimental program are described in Section 3.1.2, while experimental results are presented in Section 3.1.3.

3.1.2 Experimental CVD Reactor and Feed System

The dichlorosilane vaporization system for experimental reactor 394 has been modified to prevent the cylinder from overheating. Two changes were made to the existing heat tracing. A major portion of the heat tape (70%) was concentrated at the bottom of the cylinder and two thermostats were installed on the outside of the cylinder. A control thermostat was placed on the bottom of the cylinder and set at 65°C. The other thermostat was placed at the top of the cylinder and set at 60°C. The control thermostat maintains a constant vaporization temperature while the top thermostat functions as a safety cut-off device. The vaporization system now contains safety cut-off devices for pressure and temperature.

Two other modifications have been made to this system. The valve just down stream from the regulator has been changed from a needle valve to a ball valve, and the flow meter for dichlorosilane has been heat traced and insulated. Since these two modifications have been made, there has been no condensation of dichlorosilane in the rotameter, as reported in the previous Quarterly Report.¹

3.1.3 Experimental Results

General

"Segmented" runs² are being used for experimental purposes. Optimization experiments for dichlorosilane using a two-level experimental design have been undertaken in reactor 394.

The feed vaporization system has been performing very well. The accuracy of the flow meters has been verified by weighing the 250 lb. dichlorosilane cylinders before and after a series of experiments. Weight loss calculated from feed flow measurements agreed with directly measured values to within 1.5%, well within the specified accuracy of the flow meters.

Trichlorosilane Reactor Behavior.

Table 1 is a summary of reactor performance using trichlorosilane as feed. Trichlorosilane segments in runs 394-059 through 394-069 have been completed this quarter and can be compared with trichlorosilane segments previously reported.¹ Where possible, conditions were deliberately chosen to replicate those of earlier dichlorosilane runs.

High rates of throughput, as in those runs listed in Table 1, have the general effect of decreasing conversion but increasing deposition rates.

Reactor segments 394-061-1 through 394-061-3 were used to grow rods to a diameter of 29 mm. In a subsequent run, the single segment 394-062-1 was conducted to slightly smaller rod diameters, under the same feed conditions. The time averaged deposition rate for the 394-061 segments is $.568 \text{ ghr}^{-1}\text{cm}^{-1}$; that of the 394-062-1 run was $.531 \text{ ghr}^{-1}\text{cm}^{-1}$. (the smaller diameter should result in a somewhat lower deposition rate). The close correspondence in deposition rates (and conversions) in the two sets of runs indicates the insensitivity of reactor behavior to segmentation.

Segments 394-062-2 and 394-062-3 resulted in the highest trichlorosilane conversion observed in reactor 394 at these feed rates. The larger diameters provide more reactive silicon sites, which results in higher conversions and deposition rates. These diameters are the largest grown with trichlorosilane under this contract. No operational problems were encountered during these runs. The bell jar has been coated with a silicon deposit, but it has been less than 1 millimeter in thickness.

Experimental reproducibility has been very good as evidenced by segments 394-067-1, 394-068-1, and 394-069-1. The deposition rate for these three segments was calculated to be $0.458 \pm 0.011 \text{ ghr}^{-1}\text{cm}^{-1}$.

Dichlorosilane Reactor Feasibility.

Run 394-059-1 (See Table 2 for a summary of run data) was aborted due to a faulty frangible on the 250 lb. dichlorosilane cylinder.

Run 394-063-3 was aborted because of a plugged valve on the gas chromatograph.

A special run (394-065-1) was conducted exclusively with dichlorosilane feed at JPL's request, in order to grow silicon for subsequent solar cell fabrication. The rods grown attained a diameter of 52.8 mm --the largest material ever grown in the experimental reactor.

A run (394-066-1) was made to examine the purity of silicon grown from dichlorosilane and to determine possible complications from producing very large diameter silicon from the previous run.

Dichlorosilane Reactor Optimization.

A set of two-level experimental design runs was formulated and begun during the quarter. Nine dichlorosilane run segments were made at various large rod diameters. Rod diameter ranges have been classified as 26-32 mm, 33-39 mm, and 39-45 mm. Two replicate experiments were made to check the assumption that rod diameter effects are minimal in this overall size range (26-45 mm) under the run conditions.

The objective of the experimental design is to establish quantitative correlations between reactor operating parameters and responses which will permit optimization of reactor behavior. In the experimental design, the independent variables are the reactor operating parameters of total flow rate, mole % dichlorosilane, and temperature. The eight experimental points (1-8) correspond to the corners of a cube in which the edges

(coordinate axes) represent the three variables cited above (See Figure 4). The cube and its interior represent the overall range in which experiments are run. An additional run corresponding to the cube center (centroid) will also be made. Measured responses are the dependent variables of silicon deposition rate, conversion, and power consumption.

Table 3 is an excerpt of Table 2 which includes only the experimental design data. Data from the runs have included a power consumption of <100 kWh/kg at 1120°C (394-063-6), and a conversion in excess of 54% (394-067-4). The latter is the highest conversion observed in the program to date.

A least squares multiple regression analysis program was used to calculate the silicon deposition rate, conversion, and power consumption from these data. Polynomial expressions describing the relationship between operating parameters and responses are provided in Table 4. Any response can be satisfactorily predicted if the operating conditions are within the limits set on the experimental design. In general, these equations predict that an increase in any independent variable will result in an increase in silicon deposition rate and a decrease in power consumption if the reactor is not "feed starved". Dependence of conversion efficiency on reactor parameters is more complex: conversion is enhanced by increasing temperature but diminished by increasing mole % DCS and flow rate.

The relative magnitudes of the correlation of responses with independent variables can be determined from the "coded" coefficients provided in Table 4. These coefficients are arrived at by normalizing the variable ranges to from -1 to +1. Regression analysis of responses using these coded data provides comparative data for both the sign and magnitudes of correlations.

It is interesting to note that power consumption for low flow, low mole% dichlorosilane conditions (points 1 and 5) is lower at 1020°C than at 1120°C. All other power consumption values at comparable feed conditions are lower for the higher

temperature. At these low flow conditions, there is no advantage in operating at higher temperatures because the reactor is already "feed starved".

From the absolute values of the coded coefficients, conversion efficiency was found to be most strongly correlated with mole % dichlorosilane (negatively), followed by temperature (positively), and flow rate (negatively). Of the second order (interaction) terms examined, the interaction of mole % dichlorosilane and temperature had the greatest effect on conversion efficiency. Conversion values for each run are represented in Figure 4.

The order of importance of the variables on each response can be found in Table 5. The analysis has shown that diameter (that is, in the range 26-45mm) is less important than any of the interaction terms in the specified range of operating parameters. Therefore the assumption made prior to the experimental design runs that diameter would not have a substantial impact on the results is valid.

Due to an unfortunate error in reading an isobar chart for the dichlorosilane Matheson flow meter, the low flow, low mole % experiments (points 1 and 5 on the cube) were conducted at somewhat higher feed levels than intended. To facilitate data reduction, it was necessary to extrapolate power consumption and conversion values at 90 SCFH at 6 mole % dichlorosilane from the polynomials generated from the actual run data. Silicon deposition rate was calculated from the extrapolated conversions and is included in Table 3.

A good indication of the predictive powers of the equations for this system can be observed by examining the extrapolated power consumption values. As mentioned previously, the "feed starved" situation causes power consumption to be higher than anticipated both for the low and high temperature segments at low flow, low mole % dichlorosilane. The polynomial for power consumption did, in fact, predict this behavior.

Experimental Problems.

The high flow, high mole %, low temperature combination caused operational problems for segment 394-067-3 during the run. Material was deposited on the bell jar, baseplate, feed nozzle, and vent pipe. The material deposited in the vent pipe at a high rate, causing 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.

3.2 Intermediate Reactor Development

3.2.1 General

Much of the scheduled activity in this task involved design modification of existing (trichlorosilane) production reactors to accommodate dichlorosilane feed. However, the nearly complete absence of reactor-related operational problems encountered with dichlorosilane in the experimental reactor to date has made activity in this area unnecessary. Indeed, plans are to feed a standard production reactor with commercially purchased dichlorosilane. A preliminary design of a feed system to support production reactor feed from a 250 lb. dichlorosilane cylinder has been completed. However, finalization of the design and construction must await results of the safety-related experimental work at Hazards Research Corp. (see Table 11).

3.3 Dichlorosilane Process/Product Evaluation

3.3.1 General

The objectives of this task are:

1. Establish purity of dichlorosilane produced via catalyzed redistribution of trichlorosilane.
2. Permit characterization and optimization of the redistribution process through design, construction and operation of a laboratory rearranger unit (PDU support) and a process development unit (PDU), and provide design information for the EPSDU and 1000 metric ton plant.
3. Provide sufficient dichlorosilane at a reasonable cost from the PDU to permit regular operation of an intermediate size CVD reactor at high feed rates.

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

3.3.2 PDU Support

General. The overall objective of the PDU Support laboratory program is to provide data to support the design and safe and efficient operation of the dichlorosilane mini-plant. The chemical reactions and principles of operation of this plant are described elsewhere. Information is needed in the following general areas:

- Process Stream Analysis
- Catalyst Stability
- Redistribution Kinetics
- Product and Process Stream Safety

A discussion of the objectives and approach in each of these areas follows:

Process Stream Analysis. In order to monitor and control the mini-plant process some form of liquid product stream

analysis is desirable. The simplest method is gas chromatography (GLC). Besides the basic GLC equipment, information on the detector response factors for the various chlorosilanes, in particular, dichlorosilane and monochlorosilane, and a method of sampling the pressurized liquid process chlorosilane streams are required.

The approach to instrument calibration has been to prepare calibrated gas mixtures of the chlorosilanes via conventional vacuum line techniques, inject these into the gas chromatograph and compare peak areas relative to trichlorosilane to obtain the necessary detector response factors.

The approach to process stream sampling is to determine the feasibility of the following techniques and select the most favorable.

- 1) Direct syringe injection of the liquid chlorosilanes into the GLC.
- (2) Injection of the liquid chlorosilanes into the GLC via an automatic liquid sampling valve.
- (3) Flash evaporation of the liquid chlorosilanes with subsequent gas injection into the GLC.

Catalyst Stability. Since the solid catalyst used to effect the redistribution of trichlorosilane, Dowex MWA-1 Ion Exchange Resin, is an organic aminofunctional material, there is some question as to its thermal stability. Of particular concern is the extent to which the material loses nitrogen and whether this nitrogen is in a reactive form, such as an amine, which might cause unwanted redistribution during the distillation and storage of dichlorosilane.

Two experimental approaches have been used. The first is to subject the Dowex resin to temperatures in excess to those practical for the redistribution section of the mini-plant, e.g., 150-200 °C, and determine what and how much material is liberated. The second approach has consisted of passing trichlorosilane through the catalyst so as to cause partial redistribution equilibration, then storing the sample and checking for subsequent reaction due to catalyst transport.

Conventional vacuum line techniques in combination with infrared analysis are employed for characterization.

Redistribution Kinetics. Because of the possible hazard of monochlorosilane, and to simplify the PDU design principles previously described, it was felt desirable to use a reactant feed mixture composed of 80% trichlorosilane and 20% silicon tetrachloride in order to suppress the formation of monochlorosilane and silane. A laboratory scale redistribution unit was designed and constructed to obtain this information and extend the available kinetic information on a pure trichlorosilane feed system to higher liquid flow rates. It will also be possible to assess product purity by depositing a silicon evaluation rod from the material produced by this laboratory unit.

Laboratory Rearranger Unit.

The laboratory scale redistribution unit has been described in the previous quarterly report.¹ 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 will be 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 has also been adapted for vapor phase operation.

RESULTS OF EXPERIMENTAL WORK

A. Process Stream Analysis

The Varian Model 3400 gas chromatograph, equipped with a Valco automatic gas sampling valve,³ which was set up and checked out during the previous quarter has performed without

difficulty in extensive daily service during this quarter.

The most satisfactory method of analyzing liquid process streams is by expansion of ca. 1 cc of liquid into an evacuated volume of 4 liters, followed by pressurization to 30 psig with helium and injection of 1 cc samples onto the GLC column via the automatic gas sampling valve.

B. Catalyst Stability

Work previously reported^{1,4} indicated that Dowex resin upon heating can liberate trimethylamine. It also appeared from the work that this is a transient phenomenon in that after suitable "bake out" conditioning further evolution of trimethylamine does not occur, or becomes undetectable by simple weight loss measurements. The liberation of catalytically active species would be of concern in a production operation if sufficient material passed through the distillation system and into the dichlorosilane storage to cause unwanted redistribution of dichlorosilane into monochlorosilane and silane.

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 indicated below:

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

The catalyst bed had been exposed to approximately 3200 ml of trichlorosilane prior to sample collection.

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

The maximum lifetime of Dowex resin cannot be determined from the experimental work performed to date. However, no loss in catalytic activity has been observed during experimental runs involving 4000 gms trichlorosilane and 50 gms Dowex resin.

C. Redistribution Kinetics

1. Vapor Phase Trichlorosilane Kinetics

A small reactor unit was constructed from existing equipment to evaluate vapor phase trichlorosilane redistribution kinetics. In this unit, the catalyst bed is fed at a controlled rate of flow by a 65 mole% mixture of trichlorosilane in helium and the composition of the bed output stream is analyzed by gas chromatography.

The results of three runs made during this quarter are shown in Fig. 6 and Table 6. The data in Fig. 6 have been fitted to the second order kinetic rate equation for reversible reactions. These results indicate the following:

- 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_0/a rate values for 6 inch and 12 inch bed lengths are approximately equal.
- Dowex which has been conditioned by only air (and inert gas) purge drying exhibits an unusually high k_0/a rate value. It is expected that this high k_0/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.

2. Liquid Phase Trichlorosilane Kinetics

The laboratory scale liquid phase redistribution reactor unit constructed during the previous quarter was successfully placed into operation during this quarter. Data

were collected to evaluate the the kinetics of the the trichlorosilane redistribution reaction at liquid flow rates greater than 5 ft/hr. The data are presented in Figures 7-8 and Table 7. Product composition data were fitted to the kinetic rate expression for reversible second order reactions, i.e.

$$\frac{k}{2TCS} = \frac{DCS}{(1-x)} + \frac{STC}{(x/2)(x/2)}$$

and $k = x_e / (2t(1-x_e)) \ln((x(1-2x_e) + x_e) / (x_e - x))$ (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:

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

and $K_p = \exp((- \Delta H / RT) + C_0)$ where $\Delta H = 1486$ cal/mole and $C_0 = -1.7540$ (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_0/a rate value vs ft/hr flow 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 the effects of gross 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 given in Table 9 and indicate little if any difference between the two methods of conditioning.

3. Liquid Phase Trichlorosilane-Silicon Tetrachloride Kinetics

According to available thermochemical 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 equilibrium. The results are presented below:

Feed (Mole %)	Product Mole %		MCS/DCS Ratio
	MCS	DCS	
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 feed system is indeed lower than the ratio with the 100 mole% trichlorosilane system, the reduction is not as great as expected and, in view of the 54% decrease on DCS production, the mixed feed system is not considered worthwhile.

D. Future Activities

An equilibrium mixture from the laboratory scale liquid phase rearranger unit is to be collected, vaporized and fed to an evaluation silicon deposition reactor. The deposited polysilicon rods will then be evaluated for donor, base boron, aluminum and carbon. Sample collection is currently in progress and evaluation will be completed during the next quarter.

E. Product and Product Stream Safety

Safety-related data are discussed in section 3.3.4.

3.3.3 Process Development Unit Design

Design and proposed operating characteristics of the PDU was discussed in the previous Quarterly Report.¹ Briefly, the design features a redistribution reactor, feed and product storage vessels, and a single distillation column. The still will be used to purify dichlorosilane and, as the last stage in a production cycle, to distill a trichlorosilane/silicon tetrachloride mixture to provide feed of appropriate composition for the next run. Proposed operating sequences for the unit were provided in the first Quarterly Report.⁴

The initial design included a feed composition of 80% trichlorosilane and 20% silicon tetrachloride to the redistribution reactor, with the expectation of suppressing formation of monochlorosilane. However, laboratory data (discussed in section 3.3.2) indicate that the extent of SiH_3Cl suppression is insufficient to justify the factor of two loss in conversion of trichlorosilane into dichlorosilane, and it is now anticipated that the PDU will utilize pure trichlorosilane feed. It is noteworthy that no reactor operational problems attributable to the presence of monochlorosilane have been experienced.

Design of major equipment for the unit is complete, and quotations from vendors received. However, actual construction of the unit has been suspended until key safety-related data are obtained from Hazards Research Corp. (discussed in the next

section).

PDU sizing was based on a 35 lb/hr production rate of dichlorosilane for feed whose composition is 80% trichlorosilane and 20% silicon tetrachloride; with a pure trichlorosilane feed to the redistribution unit, the production rate of the PDU could be a factor of two higher due to the higher equilibrium yield of dichlorosilane.

3.3.4 SAFETY-RELATED DATA ON DICHLOROSILANE

As discussed in the previous Quarterly Report¹, a review of the literature relating to combustion and hydrolytic behavior of dichlorosilane indicated that under some conditions, dichlorosilane/air mixtures spontaneously and violently explode at room temperature. Other accounts have described dichlorosilane/air ignition events as unusually forceful, and to some extent unpredictable. These reports are difficult to reconcile with the literature value for autoignition temperature of 100 °C. Our own recent laboratory experience with ignition of dichlorosilane has confirmed the ease of its ignition. Moreover, little has been reported on interaction of dichlorosilane and water; there are indications that dichlorosilane can ignite when the material contacts a small amount of water, and that unstable, shock-sensitive polymers of approximate composition $(\text{SiH}_2\text{O})_x$ can be formed from hydrolysis of dichlorosilane.

To assure adequate design of fire and spill protection, a decision on required data was made with the help of Dow Corning Corporation's Safety and Loss Prevention department. We have engaged Hazards Research Corp., of Rockaway, N. J., to conduct the series of tests itemized in Table 11 relating to dichlorosilane combustion and hydrolysis. Their findings will be accompanied by recommendations for equipment separation, fire protection, spill protection, and emergency vent discharge requirements.

3.4.0 Preliminary EPSDU Design

3.4.1 General

The EPSDU will consist of the following processes:

- dichlorosilane synthesis and purification
- polycrystalline silicon CVD using dichlorosilane
- vent product recovery

The production scale of the plant is anticipated to lie between 100 and 200 metric tonne of silicon.

Trichlorosilane available from existing HSC process streams will be used as feedstock for dichlorosilane synthesis and silicon tetrachloride will be disposed of in the manner currently employed by HSC. Some integration of the vent product recovery system with the existing HSC recovery system may be possible.

Demonstration of the hydrogenation process is being undertaken by Union Carbide Corporation under a separate JPL contract.

3.4.2 EPSDU Status

Material flow schemes and operating characteristics of the EPSDU were presented in the last Quarterly Report.¹ During this quarter, a preliminary energy balance for the facility was completed. Table 10 and Figure 9 indicate projected energy requirements in tabular and schematic form. A completely independent recovery system for the EPSDU was assumed.

3.4.3 1000 Tonne Plant Design

During the past quarter a preliminary design of a 1000 metric tonne plant has been undertaken. This facility includes dichlorosilane generation, purification and decomposition into silicon on a scale of 1000 metric tonne of silicon per year. Also included are chlorosilane recovery and recycle, and generation of trichlorosilane from the hydrogenation of the byproduct silicon tetrachloride. Process flow sheets and descriptions of unit operations will be presented in the next report for two different design options.

The two schemes differ in the extent to which boron removal is accommodated. The first option mixes the trichlorosilane streams from reactor recovery and hydrogenation; the second segregates trichlorosilane from the hydrogenation for distillation and boron removal, and requires an additional still. The quantity of chlorosilanes which pass through the boron removal device per kg silicon generated is approximately five times greater in the first (single trichlorosilane still) option. Some general considerations relating to boron removal requirements and strategies and presented in the next section.

Boron Removal Considerations.

Uncertainties exist as to the molecular nature and concentration of boron-containing impurities in the system. In particular, the amount of boron in the effluent from the silicon tetrachloride hydrogenation reactor is unknown. Since boron trichloride has a boiling point very close to that of dichlorosilane, it is important that the boron level is acceptably low in the trichlorosilane fed to the redistribution reactor, and that the reactor itself does not serve as a boron contamination source.

Our preliminary design for a boron removal device includes a fixed bed packed with an adsorptive, basic material which will form a stronger complex with volatile boron compounds than with chlorosilanes. When chlorosilane streams are passed through such a bed, the boron will be selectively adsorbed. There exist indications of the feasibility of such an approach in the literature.⁵⁻⁶ We also plan to examine its feasibility directly by exposing BCl_3 /trichlorosilane mixtures to Dowex MWA-1 resin (our redistribution catalyst) at temperatures below those at which redistribution is rapid.

4.0 Conclusions and Recommendations

The feasibility of generating high quality silicon from dichlorosilane via CVD is now well established. Over a range of reactor operating conditions conducive to high silicon deposition rates and/or high conversion efficiencies, dichlorosilane-fed systems generate high quality silicon smoothly and reliably. Only in a single run were operational problems encountered. Both deposition rates and conversions are approximately twice those of comparable trichlorosilane runs.

Correlations between system behavior and reactor operating parameters are now available through a set of experimental design runs conducted with the experimental reactor.

Laboratory results with the chosen redistribution catalyst, Dowex MWA-1, indicate favorable reaction kinetics for liquid phase redistribution at 77 °C. Pure trichlorosilane rather than trichlorosilane/silicon tetrachloride mixtures will be fed to the redistribution reactor. No loss in activity of properly conditioned catalyst has yet been observed.

PDU design has been somewhat simplified because of the choice of a single component feed to the redistribution reactor. Construction of the PDU, however, must await resolution of safety-related experiments currently underway at Hazards Research Corp.

An energy balance and a revised material balance have been constructed for the preliminary EPSDU design.

Except for the safety-related delay in PDU construction, the program is proceeding on plan. Because of the highly encouraging results to date in the experimental reactor, it may be possible to accelerate Task 2 (intermediate reactor development), and feed commercially purchased dichlorosilane to a slightly modified production reactor.

5.0 Program Schedule/Plans

Except as noted above (PDU construction), the program is proceeding according to or exceeding plan. Efforts planned in the various task areas in accordance with the Program Schedule shown in figure 1 are summarized below.

1. Reactor Feasibility/Optimization (3.1)

Determine validity of scale-up parameters for use in extrapolation from reactor 394 to a production scale reactor.

2. Intermediate Dichlorosilane Reactor Development (3.2)

Identify operational parameters required to demonstrate a high deposition rate consistent with EPSDU requirements.

Ascertain feasibility of utilizing unmodified (HSC) production reactor for this task.

3. Dichlorosilane Process/Product Evaluation (3.3)

Characterize operating limits, lifetime of catalyst
Analyze purity of redistributed chlorosilanes via silicon CVD.

Investigate possibility of boron removal from chlorosilanes by Dowex resin.

Acquire safety-related information on dichlorosilane necessary to complete fire/spill protection PDU design.

Order PDU major equipment items.

Initiate PDU construction.

4. Preliminary EPSDU Design (3.4)

Complete Process Flow Diagrams.

Identify plant, reactor locations.

Preliminary design of 1000 metric ton plant

Economic analysis of 1000 metric ton plant

6.0 New Technology

No new technology was developed during this quarter.

7.0 References

1. Hemlock Semiconductor Corporation, "Second Quarterly Report", Low-Cost Silicon Solar Array Project, DOE/JPL Contract No. 955533, May 1980.
2. As described in Section 3.1.3 of Reference 2.
3. Model No. AH-4-V-6-4, available from Valco Instruments Co., Houston, Texas.
4. Hemlock Semiconductor Corporation, "First Quarterly Report", Low-Cost Silicon Solar Array Project, DOE/JPL Contract No. 955533, January 1980.
5. U.S. Patent No. 2,877,097, issued to Guenter A. Wolff, March 10, 1959.
6. U.S. Patent No. 3,071,444, issued to Bell Telephone Laboratories, January 1, 1963.

8.0 Acknowledgements

We are grateful to D. Goffnet, L. Jones and H. Smith of Hemlock Semiconductor Corp. for their able assistance in the experimental aspects of this projects, and to D. Mueller for the data reduction of the experimental design program. We further wish to acknowledge contributions in the area of project safety by R. Siegel, R. Salinger, T. Elvey and D. Parsels of Dow Corning Corp.

TABLE 1. SUMMARY OF EXPERIMENTAL REACTOR PERFORMANCE
USING TRICHLOROSILANE FEED

RUN NO.	RUN TIME HRS.	ROD DIAMETER MM	SILICON FED $\text{gh}^{-1}\text{cm}^{-1}$	SILICON DEPOSITION $\text{gh}^{-1}\text{cm}^{-1}$	CONVERSION Mole %
394-061-1	7.0	3.5-11.8	5.094	0.333	6.5
394-061-2	10.0	11.8-21.3	5.094	0.573	11.2
394-061-3	10.0	21.3-29.1	5.094	0.730	14.3
394-062-1	27.0	4.0-28.2	5.094	0.529	10.4
394-062-2	8.0	28.2-34.0	5.094	0.826	16.2
394-062-3	8.0	34.0-39.1	5.094	0.853	16.7
394-063-1	24.0	3.8-24.3	3.722	0.444	11.9
394-063-2	5.5	24.3-27.7	3.722	0.588	15.8
394-064-1	12.0	3.5-10.0	2.281	0.134	5.9
394-067-1	28.0	3.5-26.4	3.722	0.447	12.0
394-068-1	28.0	3.5-26.9	3.722	0.465	12.5
394-069-1	28.0	3.5-26.8	3.722	0.461	12.4

TABLE 2. SUMMARY OF EXPERIMENTAL REACTOR PERFORMANCE USING DICHLOROSILANE FEED

RUN NO.	RUN TIME HRS.	ROD DIAMETER MM	SILICON FED $\text{gh}^{-1}\text{cm}^{-1}$	SILICON DEPOSITION $\text{gh}^{-1}\text{cm}^{-1}$	CONVERSION MOLE %	POWER CONSUMPTION kWh/Kg
394-059-1	3.5	4.0-8.8	3.722	0.502	12.5	100.6
394-063-3	1.5	27.7-28.8	2.281	0.758	33.2	135.7
394-063-4	4.0	28.8-31.6	2.281	0.774	33.7	138.8
394-063-5	8.0	31.6-35.8	1.574	0.648	40.7	165.8
394-063-6	4.0	35.8-40.4	4.562	1.603	35.2	96.3
394-065-1	60.0	7.0-52.8	1.922	0.836	43.6	146.0
394-066-1	7.0	3.5-12.0	2.281	0.358	15.7	107.6
394-067-2	7.0	26.4-31.2	2.281	0.723	31.7	143.6
394-067-3	9.5	31.2-39.1	4.562	1.069	23.5	114.1
394-067-4	10.0	39.1-44.7	1.574	0.859	54.1	177.3
394-068-2	5.0	26.9-31.5	2.281	0.983	43.2	131.7
394-068-3	8.0	31.5-38.5	2.281	1.121	49.2	133.9
394-068-4	9.0	38.5-43.1	2.281	0.763	33.4	168.2
394-069-2	7.5	26.8-32.4	1.574	0.809	50.5	164.6
394-069-3	8.0	32.4-38.6	2.566	1.007	39.2	126.4

TABLE 3. SUMMARY OF EXPERIMENTAL DESIGN RUNS USING DICHLOROSILANE FEED

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

TABLE 4. RELATIVE IMPORTANCE OF VARIABLES AND INTERACTIONS
BETWEEN VARIABLES ON SYSTEM RESPONSES FOR
EXPERIMENTAL DESIGN

ORDER OF IMPORTANCE

CONVERSION
EFFICIENCY:

% DCS> TEMP> FLOW> Interaction of,
% DCS x Temp

Interaction of,
Flow x Temp Interaction of
Flow x % DCS

POWER
CONSUMPTION:

Flow> % DCS> Interaction of,
% DCS x Temp Temp>

Interaction of,
Flow x Temp Interaction of
Flow x % DCS

SILICON
DEPOSITION:

Flow> Temp> % DCS> Interaction of,
Flow x Temp

Interaction of,
Flow x % DCS Interaction of
% DCS x Temp

TABLE 5. CORRELATION OF SYSTEM RESPONSE WITH VARIABLES
IN EXPERIMENTAL DESIGN

$$\begin{aligned} \text{Power Consumption} &= -98.15 + 0.1237A + 33.31B + 0.3402C \\ &+ 0.0097D - 0.0006E - 0.0376F \\ (\text{kWh/kg}) \end{aligned}$$

$$\begin{aligned} \text{Conversion Efficiency} &= -76.45 - 0.3513A + 2.854B + 0.1428C \\ &+ 0.0027D + 0.0002E - 0.0050F \\ (\text{mole \%}) \end{aligned}$$

$$\begin{aligned} \text{Silicon Deposition} &= 3.815 - 0.0300A - 0.2870B - 0.0032C \\ &+ 0.0004D + 0.00003E + 0.0003F \\ (\text{g hr}^{-1} \text{cm}^{-1}) \end{aligned}$$

where

- A = Flow (SCFH)
- B = % DCS (Mole)
- C = Temperature ($^{\circ}\text{C}$)
- D = Flow x % DCS
- E = Flow x Temperature
- F = % DCS x Temperature

TABLE 6
VAPOR PHASE TRICHLOROSILANE REDISTRIBUTION DATA

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. $a=0.50$

TABLE 7
LIQUID PHASE TRICHLOROSILANE REDISTRIBUTION DATA

Ref No	Conditions			Products (Mole %)			
	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 Temp: 77-79 degC
Bed Diameter: 0.5 inch (0.035 inch wall) tubing Feed : TCS Liquid

TABLE 8
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. $a=0.50$

TABLE 9
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. $a=0.50$

TABLE 10. FLOW SCHEDULE FOR EPSDU (FIGURE 10)

<u>Stream</u>	<u>Flow*</u> <u>lb/hr</u>	<u>Mole Fraction</u> <u>H₂</u>	<u>MCS</u>	<u>DCS</u>	<u>TCS</u>	<u>STC</u>	<u>HCl</u>	<u>Si</u>
AA	509.3	0	0	0	1.0	0	0	0
AB	2990.7	0	0	0	1.0	0	0	0
AC	2990.7	0	0	0	1.0	0	0	0
AD	2990.7	0	0.005	0.105	0.780	0.11	0	0
AE	247.2	0	0	0.23	0.606	0.164	0	0
AF	3238.0	0	0.0046	0.110	0.77	0.114	0	0
AG	288.5	0	0.039	0.922	0.039	0	0	0
AH	2949.5	0	0	0.87	0.13	0	0	0
AI	2481.4	0	0	0	1.0	0	0	0
AJ	468.0	0	0	0	0.01	0.99	0	0
AK	288.5	0	0.039	0.922	0.039	0	0	0
AL		1.0	0	0	0	0	0	0
AM	247.2	X	0	0.202	0.530	0.143	0.126	0 Non Hydrogen Basis
AN		1.0	0	0	0	0	0	0
AO	9.75	0	0	0	0	0	1.0	0
AP		1.0	0	0	0	0	0	0
AQ		1.0	0	0	0	0	0	0
AR	28.08	0	0	0	0	0	0	1.0

* Hydrogen produced in the decomposition reactors is not accounted for in the material balance. The difference of pounds in and out, as shown, is hydrogen.

TABLE 11
SAFETY-RELATED RESEARCH PROGRAM FOR DICHLOROSILANE (DCS)
CONDUCTED BY HAZARDS RESEARCH CORPORATION
ROCKAWAY, NEW JERSEY

1. Autoignition temperatures of DCS/air mixtures.
2. Explosion severity scans of DCS/air mixtures (this experiment involves determining pressure rise rates in a closed vessel subsequent to ignition).
3. Hydrolytic tests. A simulated DCS spill will be subjected to a water deluge. In a separate test, DCS will be spilled into a vessel containing a small amount of water.
4. Explosive Output Determination. A DCS/air mixture which exhibited the most powerful explosion in experiment 2. will be placed in a wooden cube whose faces are covered with thin plastic sheet. The mixture will then be ignited with a "squib" inside the cube, and the explosion monitored with high speed photography and remote pressure gauges.

Time (Mo.) Project	3	6	9	12	15	18	21	24	27	30	33	36	39
Phase 1 DCS Reactor Feasibility TCS-DCS Redistri- bution Feasibility EPSDU Plant Design Intermediate Rx Design and Construction					→								
Phase 2 EPSDU Design Production Rx. Eval- uation				→			→						
Phase 3 EPSDU Constnution /Demonstration							Construction				Operation	→	→

FIGURE 1. SCHEDULE OF EFFORTS BY PHASES

FIGURE 2. SCHEMATIC OF HSC LOW COST DICHLOROSILANE BASED POLYCRYSTALLINE SILICON PROCESS

FIGURE 3. PROGRAM PLAN MILESTONE SCHEDULE

FIGURE 3. PROGRAM PLAN MILESTONE SCHEDULE (cont.)

FIGURE 4

DICHLOROSILANE EXPERIMENTAL DESIGN

A. CONDITIONS AND RUN NUMBERS

B. CONVERSION VALUES (MOLE %)

A.

FLOW
TEMP.
% DCS

LOW VALUE	HIGH VALUE
90 SCFH	180 SCFH
1020°C	1120°C
6	12

B.

* Extrapolated

FIGURE 5. SCHEMATIC OF LABORATORY TRICHLOROSILANE REARRANGER UNIT

FIGURE 6.

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

FIGURE 7.
KINETIC DATA FROM REDISTRIBUTION OF TRICHLOROSILANE
BY DOWEX RESIN (77°C, liquid)
(Bed length in inches next to data points)

FIGURE 8.
RATE CONSTANT VS. LINEAR VELOCITY FOR LIQUID PHASE
REDISTRIBUTION OF TRICHLOROSILANE BY DOWEX RESIN
(77°C)

FIGURE 9.

ENERGY BALANCE FOR EPSDU

S = Steam Top BTU/Hr.
Bot. BTU/Kg

W = Water Top BTU/Hr.
Bot. BTU/Kg

E = Electric Top KW
Bot. kWh/Kg