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PROCESS FEASIBILITY STUDY IN SUPPORT OF SILICON MATERIAL
TASK I

Quarterly Technical Progress Report (XII), June—August 1978

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C. S. Fang, Keith C. Hansen,
and Carl L. Yaws

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Approval Signature

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ABSTRACT

Major activities during this reporting period were devoted to process system properties, chemical engineering and economic analyses.

On analyses of process system properties, major activities centered on properties of silicon tetrachloride, the source material for several alternate processes under consideration for solar cell grade silicon. The following property data are reported for silicon tetrachloride: critical constants, vapor pressure, heat of vaporization, gas heat capacity, liquid heat capacity, density, surface tension, gas viscosity, liquid viscosity, gas thermal conductivity, liquid thermal conductivity, heat of formation and free energy of formation.

In the viscosity investigation, a constant volume glass viscometer was fabricated and assembled for the measurement of gas viscosity values of silicon source materials from 30°C to 350°C. A description of the apparatus and the experimental procedure, and a discussion of the calculation of the viscosity values from the data is presented. In addition, calibration and evaluation of the gas viscometer previously assembled was initiated. Experimental work with gases of known viscosity, such as argon and nitrogen, was conducted between 40°C and 200°C in order to evaluate the accuracy of data obtained on this viscometer. Using argon as a reference, experimentally determined viscosity values for nitrogen deviate from literature values by less than 2%.

Major activities were continued on the Union Carbide Silane Process (Case C-Revised Process) involving an improved arrangement of major process equipment and operating conditions. The preliminary process design was completed including raw material useage, utility requirements, major process equipment list and production labor for a plant to produce 1000 MT/yr of solar cell grade silicon. The silicon product is produced by pyrolysis of silane in the process.

Cost analysis was initiated for the completed preliminary process design for the Union Carbide Silane Process (Case C-Revised Process). In current activities, estimates are being prepared for plant investment (\$million for 1000 MT/yr) and product cost (\$/KG Si) for the process to produce silicon by pyrolysis of silane.

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I. PROCESS SYSTEM PROPERTIES ANALYSES (TASK 1)

A. SILICON TETRACHLORIDE PROPERTIES

Analysis of process system properties was continued during this reporting period for silicon source materials under consideration for solar cell grade silicon production. Primary activities focused on property data for silicon tetrachloride which is the source material for silicon in several processes.

Critical Properties (Table IA-1)

Experimental results for the critical temperature, pressure and volume of silicon tetrachloride are available (B5, B8, B9, B11, B32, B33, B35, B36, B44, B50, B56, B59, B82, B83). The results among the several investigators are in general agreement. Deviations from the selected values are 1.71%, 0.5%, and 10.8% respectively for critical temperature, pressure and volume.

The critical compressibility factor, Z_c , was calculated using the following equation:

$$Z_c = P_c V_c / RT_c \quad (\text{IA-1})$$

Also given in the table are values for the acentric factor, ω which is defined by:

$$\omega = -\log P_r - 1.000 \quad (\text{at } T_r = 0.70) \quad (\text{IA-2})$$

The acentric factor is an important parameter in generalized thermodynamic correlations involving virial coefficients, compressibility factor, enthalpy and fugacity.

Vapor Pressure (Figure IA-1)

Experimental vapor pressure data for silicon tetrachloride are available (B7, B22, B24, B27, B30, B32, B43, B53, B78, B103) from slightly above the melting point (mp) to boiling point (bp) and at the critical point (cp). Available data were extrapolated using the YSSP vapor pressure correlation (B102):

$$\log P_v = A + \frac{B}{T} + C \log T + DT + ET^2 \quad (\text{IA-3})$$

where

P_v = vapor pressure of saturated liquid, mm of Hg

A, B, C, D, E = correlation constants for chemical compound

T = temperature, °K

The correlation constants (A, B, C, D and E) were determined using a generalized least squares computer program for minimizing deviation of

calculated and experimental data values screened from the literature. Average absolute deviation was about 0.7% for the fifty-eight data points.

Heat of Vaporization (Figure IA-2)

Heat of vaporization data for silicon tetrachloride are available only at the boiling point (B5, B11, B22, B30, B36, B65, B82, B86). Watson's correlation was used to extend the heat of vaporization over the entire liquid phase:

$$\Delta H_v = \Delta H_{v_1} \left[\frac{T_c - T}{T_c - T_1} \right]^n \quad (\text{IA-4})$$

where ΔH_{v_1} is the heat of vaporization at the boiling point (T_1) and $n = 0.38$.

Heat Capacity (Figures IA-3 and IA-4)

Heat capacity data for silicon tetrachloride as ideal gas at low pressure are available (E3, B10, B17, B20, B28, B32, B34, B43, B45, B52, B67, B73, B76, B82, B84, B86, B91). The values, which are primarily based on structural and spectral measurements, are in close agreement.

The heat capacity data for the gas phase were correlated by a series expansion in temperature

$$C_p = A + BT + CT^2 + DT^3 \quad (\text{IA-5})$$

where C_p = heat capacity of ideal gas at low pressure, cal/(g-mol)(°K); A, B, C and D = characteristic constants for the chemical compounds; and T = temperature, °K. Average absolute deviation is about 0.6%.

Liquid heat capacity data are available (B5, B22, B28, B30, B26, B43, B52, B60, B65, B76, B77, B82, B104) in the mp-bp temperature interval. The data were extended to cover the entire liquid phase with the relation:

$$\text{liquid heat capacity} \times \text{density} = \text{constant} \quad (\text{IA-6})$$

The constant value was 0.3054. Testing of the relationship with the available data produced average deviation of 4%.

Density (Figure IA-5)

Liquid density data are available (B1, B49, B50, B59, B65, B77, B79, B81, B82) from near the melting point to the critical point. The Yaws-Shah equation (B100, B107) for density of the saturated liquid was used to extend the data to the critical point:

$$\rho = AB^{-(1-T_r)^{2/7}} \quad (\text{IA-7})$$

The agreement of calculated and experimental values was very good with average absolute deviation of only 0.44%.

Surface Tension (Figure IA-6)

Data for surface tension (B5, B22, B27, B49, B82) are available in the melting point to boiling point temperature range. The data were extended using the Othmer relation:

$$\sigma = \sigma_1 \left[\frac{T_c - T}{T_c - T_1} \right]^n \quad (\text{IA-8})$$

where σ_1 = surface tension at T_1 , dynes/cm

T_c = critical temperature, °K

T = temperature, °K

and n = the correlation parameter, 1.14. Testing of the relationship with the available data produced average deviation of less than 1%.

Viscosity (Figure IA-7 and IA-8)

The modified Yoon and Thodos correlation (B105, B106) was used to augment limited data (B36, B51) on gas viscosity at low pressure:

$$\eta\xi = 4.610 T_r^{0.618} - 2.04 e^{-0.449 T_r} + 1.94 e^{-4.058 T_r} + 0.1 \quad (\text{IA-9})$$

where $\xi = T_c^{1/6} M^{-1/2} P_c^{-2/3}$

The deviation between data and correlation was 2%.

Liquid viscosity data are available (B5, B8, B32, B36, B49, B51, B107) in both mp-bp and bp-cp temperature ranges. The data were extended to cover the entire liquid range with the following correlation (B107) for viscosity of the saturated liquid as a function of temperature.

$$\log \mu_L = A + B/T + CT + DT^2 \quad (\text{IA-10})$$

Average deviation between correlation and data was less than 3%.

Thermal Conductivity (Figure IA-9 and IA-10)

Gas-phase thermal conductivity data are available (B75, B109) in the temperature range of 70 to 300°C. The data were correlated by a series expansion in temperature (B107):

$$\lambda_G = A + BT + CT^2 + DT^3 \quad (\text{IA-11})$$

where λ_G = gas thermal conductivity, cal/cm²sec°C; A, B, C and D = characteristic constants for the chemical compounds and T = temperature, °K. The estimates of Svehla (B73) agree with the above correlation. The deviation between data and correlation values was 1.10%.

Thermal conductivity for liquid phase is available (B25) at only one temperature (32°C). The modified Stiel and Thodos equation (B107) was used to cover the entire saturated-liquid phase.

Heat and Free Energy of Formation (Figures IA-11 and IA-12)

Values for the heat of formation (ΔH_f) and Gibbs' free energy of formation (ΔG_f) for the ideal gas are available from American (B72) and Russian (B17, B64) sources. American values were selected.

TABLE IA-1 CRITICAL CONSTANTS AND PHYSICAL PROPERTIES OF SILICON TETRACHLORIDE

Identification	Silicon Tetrachloride
Formula	SiCl_4
State (Std. Cond.)	Liquid
Molecular Weight, M	169.90
Boiling Point, T_b , °C	57.3
Melting Point, T_m , °C	-69.4
Critical Temp., T_c , °C	234.0
Critical Pressure, P_c , atm	37.0
Critical Volume, V_c , cm^3/gmol	326.3
Critical Compressibility Factor, Z_c	0.290
Critical Density, ρ_c , gr/cm^3	0.5207
Acentric Factor, ω	0.2556

Figure IA-1 Vapor Pressure vs Temperature for Silicon Tetrachloride

Figure IA-2 Heat of Vaporization vs Temperature for Silicon Tetrachloride

Figure IA-3 Gas Heat Capacity vs Temperature for Silicon Tetrachloride

Figure IA-4 Liquid Heat Capacity vs Temperature for Silicon Tetrachloride

Figure IA-5--Liquid Density vs Temperature for Silicon Tetrachloride

Figure IA-6--Surface Tension vs Temperature for Silicon Tetrachloride

Figure IA-7--Gas Viscosity vs Temperature for Silicon Tetrachloride

Figure IA-8---Liquid Viscosity vs Temperature for Silicon Tetrachloride

Figure IA-9--Gas Thermal Conductivity vs Temperature for Silicon Tetrachloride

Figure IA-10--Liquid Thermal Conductivity vs Temperature for Silicon Tetrachloride

Figure IA-11--Heat of Formation vs Temperature for Silicon Tetrachloride

Figure IA-12--Free Energy of Formation vs Temperature for Silicon Tetrachloride

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B. VISCOSITY INVESTIGATION

During this reporting period, preparations were begun to measure gas viscosity values of silicon source materials in the temperature range 30°C to 350°C. The necessary apparatus has been fabricated and assembled, and calibration studies have been initiated.

The viscosity values will be determined by a transpiration method which is based on the rate of flow of the gas through a capillary. In order to determine these gas flow rates, a constant volume, glass viscometer (Figure IB-15) has been fabricated and assembled. The apparatus consists of 1 liter glass bulb which is connected through a glass manifold to a mercury manometer and to a thermostated capillary with a preheater coil. The capillary is 20 cm. in length and has an internal diameter of 0.02 cm. The exit side of the capillary can be continuously evacuated by a two stage mechanical pump.

In order to make a measurement, the viscometer is thoroughly evacuated and then the gas sample is introduced into the bulb up to a pressure of about 18 cm. Hg. The gas sample is then evacuated through the capillary and the resulting rate of flow is monitored by recording the pressure decrease in the bulb with time. The pressure is measured with a standard U-tube mercury manometer to ± 0.5 mm Hg. The rate of flow was determined while the sample was evacuated from 18 cm. Hg. to 12 cm. Hg. This generally requires 60 to 90 minutes. During this period the bulb is maintained at a constant temperature to $\pm 1^\circ\text{C}$ and the capillary is thermostated in an oil bath to $\pm 0.5^\circ\text{C}$.

The rate of flow of a gas through a capillary is dependent upon the coefficient of viscosity (η) of the gas. By combining Poiseuille's equation for laminar flow of a gas through a tube and the ideal gas law equation; the relationship between pressure, time, and viscosity of a gas can be derived. Poiseuille's equation (44) for laminar gas flow is:

$$\frac{dV}{dt} = \frac{\pi(P_1^2 - P_2^2)r^4}{16L\eta P_0} \quad (\text{IB-1})$$

where dV/dt is the volume rate of gas flowing through the capillary, P_1 is the pressure at the capillary inlet, P_2 is the pressure at the capillary outlet, r is the radius of the capillary, L is the length of the capillary, and P_0 is the pressure at which the gas volume is measured. In this method where the gas is continuously evacuated with a pump, P_2 is negligible compared to P_1 and equation IB-1 reduces to :

$$\frac{dV}{dt} = \frac{\pi P_1^2 r^4}{16L\eta P_0} \quad (\text{IB-2})$$

From the ideal gas law, dV , the volume of gas at P_0 , passing through the capillary in unit time can be expressed in terms of dN , the number of moles of gas flowing through the capillary in unit time (equation IB-3).

Figure IB-15. Constant Volume Gas Viscometer

$$dV = dN(RT/P_0) \quad (\text{IB-3})$$

Substituting equation IB-3 into equation IB-2 gives equation IB-4:

$$\frac{dN}{dt} = \frac{\pi P_1^2 r^4}{16L\eta RT} \quad (\text{IB-4})$$

As the gas is evacuated in a constant volume viscometer, the pressure decreases. Again using the ideal gas law,

$$dN = -dP_1 (V/RT) \quad (\text{IB-5})$$

where V is the volume being evacuated. Substituting equation IB-5 into equation IB-4 gives equation IB-6

$$dP_1 = \frac{-\pi P_1^2 r^4}{16L\eta V} dt \quad (\text{IB-6})$$

The assumptions of the derivations are: constant volume of the system; ideal behavior of the gas, and laminar flow through the capillary. Since the pressure is measured with a U-tube manometer, the volume of the system will change by 10 to 21 ml. during an experiment. However, with a total volume of the viscometer of over 1 liter, this change can be neglected. The gases to be measured do not exhibit ideal behavior, but at pressures of less than 1 atmosphere their deviations should not be large. Laminar flow assumes zero velocity at the wall. A correction may need to be made for slip at the wall and this will be considered when the collection of data is begun.

From equation IB-6, the viscosity (η) of a gas can be calculated from the slope of the line obtained by plotting $1/P_1$ versus t . In order to avoid the necessity of careful measurements of the capillary dimensions and the volume of the system, a gas of known viscosity can be used to determine an apparatus constant which includes all the constant terms in equation IB-6. Alternatively, the calculation constant can be omitted and the viscosity of the unknown, relative to that of a reference gas, can be computed from the inverse ratio of the slopes of the $1/P$ versus t graphs (equation IB-7).

$$\frac{\eta}{\eta_{\text{ref}}} = \frac{\text{slope}_{\text{ref}}}{\text{slope}} \quad (\text{IB-7})$$

Using gases of known viscosity such as helium, argon, nitrogen, and hydrogen; evaluation and calibration of the apparatus has been initiated. Once these studies indicate that the method is sound and acceptable values can be obtained, work will be started on silicon source materials such as silane and some halogenated silanes.

Evaluation and calibration of the gas viscometer assembled and described above was initiated. Using argon as a reference to determine a viscometer constant, experimental values for gas viscosity of nitrogen have been determined between 40°C and 200°C. These values were compared to recommended values for the gas viscosity of nitrogen (36) in order to evaluate the accuracy of data obtained on this viscometer (IB-16). The recommended values used were those presented in "Thermophysical Properties of Matter", Vol. 11 on viscosity (TPRC), and were determined by an evaluation of available published data. It was stated that the published data correlated with the recommended values to within $\pm 2\%$. The viscosity values obtained for gaseous nitrogen in this study deviate from the recommended values by less than 2% from 40°C to 200°C (IB-16).

Figure IB-16. Viscosity of Nitrogen

II. CHEMICAL ENGINEERING ANALYSES (TASK 2)

A. SILANE PROCESS (UNION CARBIDE)

Major efforts were completed during this reporting period on the preliminary process design for the Union Carbide silane process (Case C-Revised Process). For Case C, Union Carbide engineering-research personnel revised their original flowsheet to provide a more optimum arrangement of major process equipment, raw material requirements and operations conditions.

A summation of the salient features of Case C is presented in a tabular format as follows:

CASE C

Process.....	Silane (Union Carbide)
Plant Size.....	1000 MT/yr of Silicon
Process Flowsheet.....	Original received from Union Carbide
Process Chemistry and Equilibrium.....	From Union Carbide
Silicon Production Method.....	Pyrolysis of Silane
Major Process Equipment.....	91 pieces of process equipment

The status of preliminary process design activities involving Case C, including progress since the last reporting period, is given below for key items:

	<u>Prior</u>	<u>Current</u>
.Base Case Conditions	97%	100%
.Reaction Chemistry	97%	100%
.Process Flow Diagram	95%	100%
.Material Balance	80%	100%
.Energy Balance	70%	100%
.Property Data	70%	100%
.Equipment Design	50%	100%
.Production Labor	30%	100%

The detailed status sheet is shown in Table IIA-1.0C, and is representative of the various subitems that make up the preliminary design activity. The flowsheet used for the design is shown in Figure IIA-1.0C. This flowsheet was received from Union Carbide.

The results from the preliminary process design are presented in a tabular format similar to previous design results for alternate processes to produce silicon. The guide to the tables for Case C is given below:

.Base Case Conditions.....	Table IIA-1.1C
.Reaction Chemistry.....	Table IIA-1.2C
.Redistribution Equilibrium.....	Figure IIA-1.1C
.Raw Material Requirements.....	Table IIA-1.3C
.Utility Requirements.....	Table IIA-1.4C
.Major Process Equipment.....	Table IIA-1.5C
.Production Labor Requirements.....	Table IIA-1.6C

CASE C

TABLE IIA-1.0C CHEMICAL ENGINEERING ANALYSES:
PRELIMINARY PROCESS DESIGN ACTIVITIES FOR SILANE PROCESS-CASE C (UNION CARBIDE)

<u>Prel. Process Design Activity</u>		<u>Status</u>	<u>Prel. Process Design Activity</u>		<u>Status</u>
31	1. Specify Base Case Conditions	●	7. Equipment Design Calculations		●
	1. Plant Size	●	1. Storage Vessels		●
	2. Product Specifics	●	2. Unit Operations Equipment		●
	3. Additional Conditions	●	3. Process Data (P, T, rate, etc.)		●
			4. Additional		●
	2. Define Reaction Chemistry	●	8. List of Major Process Equipment		●
	1. Reactants, Products	●	1. Size		●
	2. Equilibrium	●	2. Type		●
			3. Materials of Construction		●
	3. Process Flow Diagram	●	8a. Major Technical Factors		●
	1. Flow Sequence, Unit Operations	●	(Potential Problem Areas)		●
	2. Process Conditions (T, P, etc.)	●	1. Materials Compatibility		●
	3. Environmental	●	2. Process Conditions Limitations		●
	4. Company Interaction	●	3. Additional		●
	(Technology Exchange)				
	4. Material Balance Calculations	●	9. Production Labor Requirements		●
	1. Raw Materials	●	1. Process Technology		●
	2. Products	●	2. Production Volume		●
	3. By-Products	●			
	5. Energy Balance Calculations	●	10. Forward for Economic Analysis		●
	1. Heating	●			
	2. Cooling	●			
	3. Additional	●			
	6. Property Data	●	○ Plan		
	1. Physical	●	● In Progress		
	2. Thermodynamic	●	● Complete		
	3. Additional	●			

CASE C

Figure IIA-1.0C Process Flow Sheet for Silane Process - CASE C (Revised Process)

CASE C

Figure IIA-1.0C (Continued)

CASE C

Figure IIA-1.0C (Continued)

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PLOT PLAN
1,000 METRIC TON
SILICON PLANT

Figure IIA-1.0C (Continued)

CASE C

TABLE IIA-1.1C

BASE CASE CONDITIONS FOR SILANE PROCESS-CASE C (Union Carbide)

1. Plant Size
 - Silicon produced from silane
 - 1000 metric tons/year of silicon
 - Solar cell grade silicon
2. Hydrogenation Reaction
 - Metallurgical grade silicon, hydrogen, and recycle silicon tetrachloride (TET) used to produce trichlorosilane (TCS)
 - Copper catalyzed
 - Fluidized bed
 - 500°C, 514.7 psia
 - 20% to 22.5% conversion of SiCl_4 (example)
3. TCS Redistribution Reaction
 - TCS from hydrogenation produces dichlorosilane (DCS)
 - Catalytic redistribution of TCS with tertiary amine ion exchange resin
 - Liquid phase 85 psia, 140°F
 - Conversion a function of inlet concentration (Union Carbide equilibrium)
 - Conversion from pure TCS feed is about 9.5% to DCS (example)
4. DCS Redistribution Reaction
 - DCS produces SiH_4 (silane)
 - Catalytic redistribution of DCS with tertiary amine exchange resin
 - Liquid phase 510 psia, 140°F
 - Conversion a function of inlet concentration (Union Carbide equilibrium)
 - Conversion from pure DCS feed is about 14% to Silane (example)
5. Recycles
 - Unreacted chlorosilanes separated by distillation and recycled
6. Silane Purification
 - Final purification by distillation
 - Designed to remove trace impurities (B_2H_6 , example)
7. Operating Ratio
 - Approximately 85% utilization (on stream time)
 - Approximately 7445 hour/year production
8. Storage Consideration
 - Feed materials (several week supply, approx. 1 month)
 - Product (two shifts storage)
 - Process (several hours to 1 shift)

CASE C

TABLE IIA-1.2C

REACTION CHEMISTRY FOR SILANE PROCESS - CASE C (UNION CARBIDE)

1. Hydrogenation Reaction

2. Trichlorosilane Redistribution Reaction

3. Dichlorosilane Redistribution Reaction

4. Waste Treatment (representative)

5. Silane Pyrolysis Reaction

Note

1. Reaction 1 product contains H_2 , HCl , SiCl_4 , SiHCl_3 , SiH_2Cl_2 (trace), other trace chlorides
2. Reaction 2 Product contains SiHCl_3 , SiCl_4 , SiH_2Cl_2 , SiH_3Cl
3. Reaction 3 Product contains SiH_2Cl_2 , SiHCl_3 , SiCl_4 , SiH_3Cl , SiH_4

CASE C

Figure IIA-1.1C Redistribution Equilibrium For Silane Process-CASE C
 (Provided by Union Carbide)

CASE C

TABLE IIA-1.3A

RAW MATERIAL REQUIREMENTS FOR SILANE PROCESS - CASE C (UNION CARBIDE)

<u>Raw Material</u>	<u>Requirements</u>	
	<u>lb/hr for 1000 MT/yr Silicon</u>	<u>lb/KG of Silicon</u>
1. M. G. Silicon (Si)	348.6	2.60
2. Silicon Tetrachloride (SiCl ₄ , make-up)	370.1	2.76
3. Liquid Hydrogen (H ₂ , make-up)	4.3	0.032
4. Copper Catalyst (Cu)	6.8	0.051
5. Hydrate Lime [Ca(OH) ₂]	326.3	2.43

Note:

Assuming all inert gas from D-01 is H₂

CASE C

TABLE IIA-1.4C

UTILITY REQUIREMENTS FOR SILANE PROCESS - CASE C (UNION CARBIDE)

<u>Utility/Function</u>	<u>Total Requirement</u>	<u>Requirement/KG Silicon</u>
1. Electricity	409.7 KW	3.050 KW/hr
2. Steam	23113 lb/hr	172.2 lbs.
3. Cooling Water	70,453 gal/hr	525 gallons
4. Process Water	9.52 gal/hr	0.0709 gallons
5. Refrigerant	0.130 MM Btu/hr	968 Btu
6. Fuel	3.640 MM Btu/hr	27,100 Btu

CASE C

TABLE IIA -1.5 C

LIST OF MAJOR PROCESS
EQUIPMENT FOR SILANE PROCESS - CASE C (UNION CARBIDE)

	<u>Equipment</u>	<u>Function</u>	<u>Duty/Type</u>	<u>Size</u>	<u>Material of Construction</u>
	<u>DISTILLATION COLUMNS</u>				
	1. D-01 Crude TCS/STC Stripping Column	To remove inert gases	24929 lb/hr of feed	24" diam. 20' tall, 10 sieve plates	CS
	2. D-02 TCS/STC Distillation Column	To remove STC at bottoms	64,213 lb/hr of feeds	4.63' diam., 74' tall, 22 sieve plates	CS
	3. D-03 DCS/TCS Distillation Column	To remove DCS at distillates	46,254 lb/hr of feeds	4.30' diam., 77.5' tall, 45 sieve plates	CS
41	4. D-04 Silane Distillation Column	To purify silane	6967 lb/hr of feed	24" diam., 50' tall, 30 sieve plates	316SS
	<u>REACTORS</u>				
	5. R-01 Hydrogenation Reactor (Fluidized Bed)	Hydrogenation of Si and SiCl_4	25,447 lb/hr of feed	6.5' diam. x 6.5' / 2.5' diam. x 10.5' cone	316SS
	6. R-02 DCS Redistribution Reactor (Fixed Bed)	To convert DCS to silane	6,967 lb/hr of feed	2' diam., 11.2' tall, with catalyst	316SS
	7. R-03 TCS Redistribution Reactor (Fixed Bed)	To convert TCS to DCS and STC	39,287 lb/hr of feed	3' diam., 17.3' tall, with catalyst	316SS
8. & 9.	R-04 Sludge Neutralization Reactor	Waste Treatment	Agitated Tank/Column	2' diam., 20' tall	316SS (for pricing)

CASE C

TABLE IIA-1.5C (Continued)

HEAT EXCHANGERS

10.	H-01 Liquid Hydrogen Vaporizer	To provide H ₂ gas	7.22 lb/hr of Liquid H ₂	(Vendor supplied equipment)	
11.	H-02 STC Cooler	Exchange heats of STC streams	7.23 x 10 ⁵ Btu/hr shell-tube H. E.	893 ft. ² 514.7 psia	316SS/CS
12.	H-03 Quench Condenser	To condense chlorosilanes, 100°F	4.69 x 10 ⁶ Btu/hr shell-tube H. E.	676 ft. ² 514.7 psia	316SS/CS
13.	H-04 Recycle STC Vaporizer	To provide STC vapor to reactor	1.71 x 10 ⁶ Btu/hr kettle	65.9 ft. ² 514.7 psia	CS
14.	H-05 Recycle STC Superheater	To heat STC from 234 to 932°F	2.46 x 10 ⁶ Btu/hr Furnace Convection	1603 ft. ² 514.7 psia	316SS
15.	H-06 Recycle H ₂ Heater	To heat H ₂ from 100 to 932°F	6.78 x 10 ⁵ Btu/hr Furnace Convection	331 ft. ² 514.7 psia	316SS
16.	H-07 Stripper Recoiler	Reboiler of D-01, 242°F	9.06 x 10 ⁵ Btu/hr Kettle	39.8 ft. ² 95 psia	CS
17.	H-08 Stripper Condenser	Partial Condenser of D-01, 139°F	86,700 Btu/hr shell-tube H. E.	36.1 ft. ² 90 psia	CS
18.	H-09 TCS/STC Reboiler	Reboiler of D-02 216°F	7.83 x 10 ⁶ Btu/hr kettle	295 ft. ² 55 psia	CS
19.	H-10 TCS/STC Condenser	Total condenser of D-02, 120°F	6.24 x 10 ⁶ Btu/hr shell-tube H. E.	1315 ft. ² 55 psia	316SS/CS

CASE C

TABLE IIA-1.5C (Continued)

20.	H-11 DCS/TCS Reboiler	Reboiler of D-03	3.50×10^6 Btu/hr Kettle	333 ft. ² 320 psia	CS
21.	H-12 DCS/TCS Condenser	Total condenser of D-03, 234°F	3.99×10^6 Btu/hr shell-tube H. E.	429 ft. ² 320 psia	316SS/CS
22.	H-13 DCS Cooler	To cool DCS before redistribution reaction	1.88×10^5 Btu/hr shell-tube H. E.	22.1 ft. ² 550 psia	316SS/CS
23.	H-14 TCS Cooler	To cool TCS before redistribution reaction	2.01×10^6 Btu/hr shell-tube H. E.	161 ft. ² 85 psia	316SS/CS
24.	H-15 Silane Boiler	Reboiler of D-04 278°F	2.71×10^5 Btu/hr Kettle	15.4 ft. ² 360 psia	316SS/CS
25.	H-16 Silane Condenser	Total condenser of -44°F	1.30×10^5 Btu/hr Shell-tube H. E.	81 ft. ² 360 psia	316SS
26.	H-17 Silane Vaporizer/Superheater	To provide silane vapor for pyroly- sis, 200°F	25,000 Btu/hr Jacket/tubes	27.3 ft. ³ /12.0 ft. ² 355 psia	316SS/CS
27.	H-18 Pyrolysis Hydrogen Cooler	To cool H ₂ gas from 363 to 100°F	43,000 Btu/hr shell-tube H. E.	80.5 ft. ² 20 psia	316SS/CS
28.	H-19 First Stage H ₂ Intercooler	To cool H ₂ be- tween comp. stages 328 to 100°F	38,570 Btu/hr shell-tube H.E.	72.2 ft. ² 50 psia	316SS/CS
29.	H-20 Second Stage H ₂ Intercooler	To cool H ₂ be- tween comp. stages 328 to 100°F	38570 Btu/hr shell-tube H. E.	72.2 ft. ² 160 psia	316SS/CS

CASE C

TABLE IIA-1.5C (Continued)

PUMPS AND COMPRESSORS

30.	C-01 Pneumatic Conveying Fan	Si feed transport	417 ACFM Centrifugal	5.1 psi Δp 12 BHP	CS
31.	C-02 Recycle H ₂ Blower	H ₂ gas blower	22.8 ACFM Centrifugal	518.7 psia 1.23 BHP	CS
32.	C-03 First Stage H ₂ Compressor	H ₂ gas compressor	164 ACFM; double action, reciprocating	48.1 psia discharge, 19.8 BHP	CS
33.	C-04 Second Stage H ₂ Compressor	H ₂ gas compressor action,	50 ACFM; double action, reciprocating	157 psia discharge, 19.6 BHP	CS
34.	C-05 Third Stage H ₂ Compressor	H ₂ gas compressor	15.3 ACFM; double action, reciprocating	515 psia discharge, 19.8 BHP	CS
35.	P-01 Quench Contact- tor Pump	Circulating liquid chlorosilanes	100 gpm, centrifugal/motor	36.7' head, 1.56 BHP	316SS
36.	P-03 Recycle STC Pump	To supply STC	33.1 gpm Centrifugal/ Turbine	847' head, 14.2 BHP	CS
37.	P-04 TCS Distillate Pump	D-02 Reflux/ Distillate	144 gpm Centrifugal/ Turbine	589' head, 33.5 BHP	CS
38.	P-05 DCS Distillate Pump	D-03 Reflux/ Distillate	144 gpm Centrifugal/ Motor	759' head, 26.2 BHP	316SS
39.	P-06 Lime Tank Pump	Circulating Lime Slurry	100 gpm Centrifugal/ Motor	103' head, 4 BHP	Cast iron

CASE C

TABLE IIA-1.5C (Continued)

TANKS AND BINS

40.	T-01 Crude TCS/STC Storage Tank	Storage/Feed to Silane production	8 hr. storage, horizontal	12' diam. x 27' 95 psia	CS
41.	T-02 STC Storage Tank	Storage/Feed to Hydrogenation	6 hr. storage, Vertical	14' diam. x 13.4' 14.7 psia	CS
42.	T-03 Liq. H ₂ Storage	Liq. H ₂ make-up storage	(Vendor supplied equipment)		
43.	T-04 Waste Settler Tank	To separate solid residues	Vertical cyl/cone bottom	6' diam., 12' tall 514.7 psia	316SS
44.	T-05 Waste Chlorides Tank	To remove solid residues	285 lb/hr Vertical	3' diam., 4' tall 25 psia (aprox.)	316SS
45.	T-06 Quench Condenser Receiver	Gas-liq. separa-	15 min. storage Horizontal	4' diam. x 11.3' 514.7 psia	CS
46.	T-07 Recycle Hydrogen Receiver	H ₂ gas surge tank	Vertical	3' diam. x 6' 514.7 psia	CS
47.	T-08 Stripper Reflux pot	D-01 Distillate/ gas	30 min. storage Vertical	2' diam. x 3.4' 90 psia	CS
48.	T-09 TCS/STC Reflux pot	D-02 Distillate	10 min. storage Vertical	5' diam. x 10' 55 psia	CS
49.	T-10 DCS/TCS Relux pot	D-03 Distillate	10 min. storage Vertical	4' diam. x 12' 320 psia	CS
50.	T-11 A, B Silane Shift Tanks	D-04 Distillate/ Feed to pyrolysis	4 hr. storage, each, Vertical	5' diam. x 9.4' 360 psia	316SS

CASE C

TABLE IIA-1.5C (Continued)

51.	T-13 Pyrolysis H ₂ Receiver	H ₂ Feed to Com- pressor	Vertical 25 psia	6' diam. x 12'	CS
52.	T-14 Lime Make-Up Tank	Lime solu. pre- paration	8 hr. storage Vertical, open	5' diam. x 9.2' 14.7 psia	CS
53.	T-15 Sludge Pump Tank	Sludge-solu. storage	4 hr. storage Vertical	5' diam. x 8'	316SS
54.	B-01 M. G. Silicon Storage Hopper	Feed to hydro- genation reactor	344 lb/hr Si	20' sq. x 5'/10' cone 14.7 psia	CS
55. & 56.	B-04 Pyrolysis Dust Bin	Solid residue	Small	3'diam. x 3' 25 psia	CS

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FILTERS

57.	F-01 Crude TCS/ STC Filter	In Line Filter	Small solid-liq.	50 gpm x 100μ	CS/316SS
58.	F-02 Waste Hydroxide Filter	Remove solid residues	100 gpm solid-liq.	Filtering area 67 ft. ²	CS/316SS
59.	F-03 Pyrolysis H ₂ Filter	Remove solid residues	Small Bag solid-gas	20 ft. ² x 5μ	CS/cloth
60.	F-04 M. G. Silicon Unloading Filter	Solid-air separa- tion in pneumatic conveyor	Small Bag solid-gas	20 ft. ² x 5μ	CS/cloth

CASE C

TABLE IIA-1.5C (Continued)

SOLID HANDLING EQUIPMENT

61.	S-01 M. G. Silicon Unloading Cyclone	Si feed transport	6" W. C. ΔP	417 ACFM	316SS
62.	S-02 Double Shell Blender	Si feed to reactor	Blending	20 ft. ³ /shroud	304SS
63.	S-03 M. G. Silicon Lock Hopper	Si Feed to reactor	Locking	20 ft. ³	CS

UNCLASSIFIED

64.	U-01 Quench Contactor Ejector	To withdraw gaseous products from reactor	6" W. C. Suction	100gpm 134 ACFM	316SS
65.	U-02 Lime Tank Agitator	Line solution preparation		3/4 HP	316SS
66.	U-03 Vent Gas Combustor	To burn vent gases from various units	20 ft. ³ , 0.5 MM Btu/hr load	1.22 ACFM	316SS
67.	U-04 Vent Gas Ejector	To withdraw gases from combustion chamber	10" W. C. Suction	100gpm 1.0 CFM (STP)	316SS

PYROLYSIS SECTION (Primary)

68.	R-05 Silane Pyrolysis Reactors (six)	To convert silane to silicon	25 KW Power supply	3' diam., 15' tall, cone shape (approx.)	Monel/ Quartz (pricing)
69.	X-01 Melters (six)	Melt silicon	60 KW Power supply		Graphite/ Quartz, etc.

CASE C

TABLE IIA-1.5C (Continued)

70.	B-05 Powder Hoppers (six)	Pyrolysis Powder collection	96.1 lb/hr Si	8' diam. x 15' width cone bottom	316SS
71.	X-02 Hydrogen Cooler	Cool Hydrogen	42.4 lb/hr H ₂	See Economic Analysis	CS/Other
72.	X-03 Hydrogen Blower	Blow Hydrogen	127 CFM (STP)	See Economic Analysis	CS/Other
73.	X-04 Dust Filter	Filter Dust	127 CFM (STP)	See Economic Analysis	CS/Other
74.	X-05 Star Valve (six)	Flow Control		See Economic Analysis	CS/Other
75.	X-06 Conveyor	Transport Material	96.1 lb/hr Si and its containers	See Economic Analysis	CS/Other
76.	X-07 Drum Loader	Load Drums		See Economic Analysis	

CASE C

TABLE IIA-1.6C

PRODUCTION LABOR REQUIREMENTS FOR SILANE PROCESS - CASE C (UNION CARBIDE)

<u>Section/Unit Operation</u>	<u>Skilled Labor man-hr/KG Si (oper/shift)</u>	<u>Semiskilled Labor man-hr/KG Si (oper/shift)</u>
1. Hydrogenation	0.00745 (1)	0.00745 (1)
2. Silane	0.02230 (3)	----
3. Pyrolysis	0.02980 (4)	----
4. Waste Treatment	0.00745 (1)	----
5. Hydrogen Compression	<u>0.00745 (1)</u>	<u>----</u>
TOTAL	0.0745 (10)	0.00745 (1)

Note

Manpower estimate for production labor requirements based on:

1. Dividing plant into sections
 - type of unit operation
 - mark off working area
2. Specify work duties required in each section
3. Estimate operators required to perform work duties in each section
 - type of unit operation
 - size of working area
 - degree of automation (batch, semi-continuous, continuous, etc.)

B. OTHER PROCESS

The following technical progress reports are being screened with respect to chemical engineering analysis information for other processes under consideration for solar cell grade silicon.

1. Battelle Process (Zn/SiCl_4)
2. Motorola Process ($\text{SiF}_4/\text{SiF}_2$)
3. Westinghouse Process (Na/SiCl_4)
4. Dow Process (C/SiO_2)
5. SRI Process (Na/SiF_4)
6. Aerochem Process (H/SiCl_4)
7. J. C. Schumacher Co. (SiBr_4)

III. SUMMARY - CONCLUSIONS

The following summary-conclusions are made as a result of major activities accomplished during this reporting period:

1. Task 1

In analyses of process system properties, major activities were continued on properties of silicon tetrachloride; the source material for several alternate processes under consideration for solar cell grade silicon. The following property data are reported for silicon tetrachloride: critical constants, vapor pressure, heat of vaporization, gas heat capacity, liquid heat capacity, density, surface tension, gas viscosity, liquid viscosity, gas thermal conductivity, liquid thermal conductivity, heat of formation and free energy of formation.

In the viscosity investigation, the apparatus for the determination of gas viscosity values of silicon source materials has been assembled and the experimental method described. Initial evaluation and calibration studies were initiated using gases of known viscosity.

Calibration studies on the gas viscometer show that experimental values for viscosity of gases can be obtained which are accurate to $\pm 2\%$ in the temperature range 40°C to 200°C . This was determined by making measurements on argon and nitrogen, and then comparing the results with published values for the viscosity of these gases.

2. Task 2

Major efforts were continued on the Union Carbide Silane Process (Case C-Revised Process) involving an improved arrangement of major process equipment and operating conditions. The preliminary process design was completed including raw material usage, utility requirement, major process equipment list and production labor for a plant to produce 1000 MT/yr of solar cell grade silicon. The silicon powder is produced by pyrolysis of silane in the process. The powder is then consolidated to provide the silicon product.

IV. PLANS

Plans for the next reporting period are summarized below:

1. Task 1

Continue analyses of process system properties for silicon source materials under consideration for solar grade silicon.

Calibration of the viscometer will be continued with emphasis on increasing the temperature range of the study up to 350°C. Viscosity measurements will be initiated on halogenated silanes.

2. Task 2

Continue chemical engineering analysis of candidate processes under consideration for solar cell grade silicon.

3. Task 3

Complete cost analysis of the Union Carbide Silane process (Case C-Revised Process).

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PROCESS FEASIBILITY STUDY IN SUPPORT OF SILICON MATERIAL TASK I

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