ERDA/JPL 954343-76/1
DISTRIBUTION CATEGORY UC-63

PROCESS FEASIBILITY STUDY IN SUPPORT OF SILICON MATERIAL, TASK I

Quarterly Technical Progress Report (IV)

September, 1976

Keith C. Hansen, Jack R. Hopper,
Joseph W. Miller, Jr. and Carl L. Yaws

LAMAR UNIVERSITY
Chem. Eng. Dept.
P. O. Box 10053
Beaumont, Texas 77710

JPL Contract No. 954343

Contractual Acknowledgement

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, under NASA Contract NAS7-100 for the U.S. Energy Research and Development Administration, Division of Solar Energy.

The JPL Low-Cost Silicon Solar Array Project is funded by ERDA and forms part of the ERDA Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays.

CALIFORNIA INSTITUTE OF TECHNOLOGY
JET PROPULSION LABORATORY (JPL)
4800 Oak Grove Drive
Pasadena, California 91103

Approval
Signature Carl L. Yaws

(NASA-CR-149062) PROCESS FEASIBILITY STUDY IN SUPPORT OF SILICON MATERIAL, TASK 1 Quarterly Progress Report (Lamar Univ. Beaumont, Tex.) 60 p
N77-71189
Unclas
00/98 56878

Technical Content Statement

Graduate-Student Assistant Acknowledgement

The author wishes to acknowledge the valuable help and contributions of the following graduate-student assistants in the performance of this work:

ROBIN W. BORRESON
L. DAVID HOOD
PRAFUL N. SHAH
CECIL E. GORIN
MICHAEL P. PATRIZI
MAURICE M. STICKER, JR.

ABSTRACT

During this reporting period, major efforts were expended on process system properties, chemical engineering and economic analyses.

In Task 1, primary activities were devoted to properties analyses of silicon source materials and silicon tetrafluoride investigation. Experimental data were identified for critical temperature and pressure for silicon tetrafluoride. Data for the remaining critical constants-volume, compressibility factor and density-are lacking. Critical constants-volume, compressibility factor and density-were estimated for silane (SiH_4) in the absence of experimental data.

Investigations were initiated for the generation of silicon tetrafluoride (SiF_4) from hydrofluosilic acid (H_2SiF_6), a relatively inexpensive by-product from the fertilizer industry. Optimum reaction conditions for the precipitation of the SiF_4 precusor (Na_2SiF_6) were determined. Reactions using various sodium salts (NaCl, NaF, NaOH, Na_2CO_3) were carried out and yields of Na_2SiF_6 were determined. In several cases (NaF, NaOH, Na_2CO_3) side reactions occurred and the effects of these were noted.

The thermal decomposition of sodium hexafluorosilicate (Na_2SiF_6) to generate silicon tetrafluoride (SiF_4) was investigated. Parameters such as reaction temperature and reaction time were studied and it was determined that the reaction proceeds readily above 500°C. Essentially quantitative yields of $SiF4$ can be obtained by heating Na_2SiF_6 to temperatures from 550° to 600°C for periods of 15 to 30 minutes.

Major chemical engineering analysis activities in Task 2 were devoted to preliminary process design for a 1000 metric ton/yr plant (solar cell grade silicon) based on the Zn/$SiCl_4$ process (Battelle). Process flow diagram, material balance, energy balance and equipment design are essentially complete. Results are presented for the reaction chemistry, raw materials, utilities, major process equipment and production labor requirements.

A chemical equilibrium investigation was initiated for application to alternate processes under consideration for solar cell grade silicon. Initial results indicate reliability of the computational procedure for the multi-component (minimum Gibbs free energy) computer program. In addition, chemical equilibrium compositions at various conditions were determined for the Zn/$SiCl_4$ and SiI_4 alternate processes (Battelle).

In Task 3, economic analysis activities were continued including survey results for product cost estimation techniques. Nominal values-product cost subitems for application to alternate processes-were selected.

Economic results based on the preliminary process design are presented for the Zn/$SiCl_4$ process (Battelle). Capital investment (fixed) was determined at $10,100,000 for the 1000 metric/tons year plant. Total product cost was estimated at $9.49 per kg of silicon.

TABLE OF CONTENTS

I. PROCESS SYSTEM PROPERTIES ANALYSES (TASK 1)

A. PROPERTIES ANALYSIS

During this reporting period, major activities were continued on process system properties for silicon source materials for solar cell grade silicon.

Experimental data were identified (F4, F11, F19, F21, F24, F26, F30, F38, F39, F62, F64, F65) for the critical temperature and pressure of silicon tetrafluoride (SiF_4). However, all sources cite either Booth and Swinehart (F4) or Moissan (F64).

Booth and Swinehart did their work in 1935. They prepared silicon tetrafluoride by three methods: (1) Guy-Lussac's reaction of sulfuric acid upon ground calcium fluoride and quartz (2) the action of sulfuric acid upon sodium fluorosilicate and quartz, (3) fluorination of silicon tetrachloride by antimony pentafluoride. The silicon tetrafluoride samples were purified by fractional distillation. Qualitative analysis and molecular weight determinations were used to determine purities. Their values for critical temperature and pressure are shown in Table I. No data are available for the remaining critical constants-critical volume, compressibility factor, and density-for silicon tetrafluoride.

Moissan reported his work in 1904. His values for the critical temperature and pressure of silicon tetrafluoride (-1.5°C and 50 atm) are considered incorrect because his samples were not sufficiently pure (F4, F37).

Data source compilation for silicon tetrafluoride was accomplished for both domestic and foreign sources.

Investigation of estimation methods was initiated for critical properties of silicon source materials for which experimental critical property data are not available. The investigation will center on major silicon source materials-silane (SiH_4), silicon tetrachloride ($SiCl_4$), silicon tetraiodide (SiI_4) and silicon tetrafluoride (SiF_4)-under consideration for solar cell grade silicon production.

TABLE I PRELIMINARY DATA ANALYSIS - CRITICAL CONSTANTS AND PHYSICAL PROPERTIES OF SILICON TETRAFLUORIDE, SiF_4

Identification	Silicon Tetrafluoride SiF_4
State (std. cond.)	gas (colorless)
Molecular Weight, M	104.08
Boiling Point, T_b, °C	-95.7 (sublimes)
Melting Point, T_m, °C	-90.2 (1318 mm Hg) -86.8 (1679 mm Hg)
Critical Temp, T_c, °C	-14.15
Critical Pressure, P_c, atm	36.66
Critical Volume, V_c, cm^3/gr mol	--
Critical Compressibility Factor, Z_c	--
Critical Density, ρ_c, gr/cm^3	--

Experimental data for the critical temperature and pressure of silane are available [A2, A15, A20, A22, A23, A25, A27, A29, A45, A47, A49, A50, A51]. However, all sources cite Adwentowski (A51), who prepared his sample from Mg_2Si and used the fraction boiling at -116°C. Since the boiling point of silane is generally accepted as -112°C, these data may not be completely reliable.

The critical compressibility factor, Z_c, was estimated by the Garcia-Barcena method

$$Z_c = f(T_b) - g(T_b/M0 \qquad (1)$$

where T_b = boiling point, °K; and M = molecular weight, g/g - mol. The terms f (T_b) and g (T_b/M) are shown as a nomograph [A29]. Reid and Sherwood tested this equation using sixteen inorganic compounds with an average deviation of 1.8%. The accuracy of the correlation was tested by applying it to similar inorganic and organic compounds (NH_3, N_2H_4, B_2H_6, CH_4). Average deviation was 3.6% for compounds tested.

The critical volume was found by the real gas relation

$$V_v = Z_c \, RT_c/P_c \qquad (2)$$

using the Adwentowski data and the estimated value of Z_c.

The results for critical constants and physical properties of silane are given in Table Ia.

TABLE Ia PRELIMINARY DATA ANALYSIS - CRITICAL CONSTANTS AND PHYSICAL PROPERTIES OF SILANE, SiH_4

Identification	Silane SiH_4
State (std. cond.)	gas (colorless)
Molecular Weight, M	32.12
Boiling Point, T_b, °C	-111.9
Melting Point, T_m, °C	-184.7
Critical Temp, T_c, °C	-3.5 (Questionable Value)
Critical Pressure, P_c, atm	47.8 (Questionable Value)
Critical Volume, V_c, cm^3/gr mol	130.06*
Critical Compressibility Factor, Z_c	0.281*
Critical Density ρ_c, gr/cm^3	0.247*

*Estimated values

B. SILICON TETRAFLUORIDE INVESTIGATION

Work was initiated during this reporting period on the generation of silicon tetrafluoride (SiF_4). The initial investigations were concerned with defining the optimum conditions for precipitation of the SiF_4 precursor (Na_2SiF_6) from an aqueous solution of hexafluorosilicic acid (H_2SiF_6).

Experiments were conducted in which concentrated aqueous solutions of various salts (NaCl, NaF, NaOH, Na_2CO_3) were reacted with a 23% aqueous solution of H_2SiF_6 at room temperature:

$$2\ NaX + H_2SiF_6 \rightarrow Na_2SiF_6\downarrow + 2\ HX \qquad (3)$$

where X = Cl, F, OH or CO_3

Reaction under these conditions resulted in the immediate formation of a precipitate which could be readily filtered and dried. With each salt, several reactions were carried out with differing stoichiometric amounts of the reactant in order to determine the reactant ratio which would give maximum precipitation of Na_2SiF_6. The results of these investigations are shown in Figures 1 through 4.

Figure 1 shows that the precipitation of Na_2SiF_6 with NaCl solutions gives maximum recovery of the SiF_4 precursor at a reactant ratio of slightly greater than 1:1. Increasing the amount of NaCl does not improve the yield any further. The percent yield of Na_2SiF_6 never rises above the 90-95% region due to its slight solubility in water. The precipitate formed was shown to be Na_2SiF_6 by comparing its infrared spectrum with that of an authenic sample. Air drying of the precipitate was shown to leave approximately 1-2% water.

Figure 2 shows that precipitation of Na_2SiF_6 with NaF solution gives essentially the same results as was obtained with NaCl up to about 1.25:1 reactant ratio. At higher ratios the calculated percent yield of Na_2SiF_6 rises above 100% which indicates that something else is occurring other than the precipitation of Na_2SiF_6. Hydrofluoric acid (HF) is a by-product of this reaction and will form an insoluble adduct (NaF·HF) which results in the greater than 100% calculated yield. Analysis is now being carried out to determine exactly how much NaF·HF is being precipitated.

Precipitation using NaOH solutions (Figure 3) gives completely different results than that obtained with either NaCl and NaF. The calculated yields (based on Na_2SiF_6) are much above 100% and continue to rise up to a reactant ratio of 3:1. The use of NaOH (a strongly basic reagent) resulted in the hydrolysis of the Si-F bond as well as precipitation of Na_2SiF_6. The hydrolysis of $SiF_6^=$ under basic conditions results in the

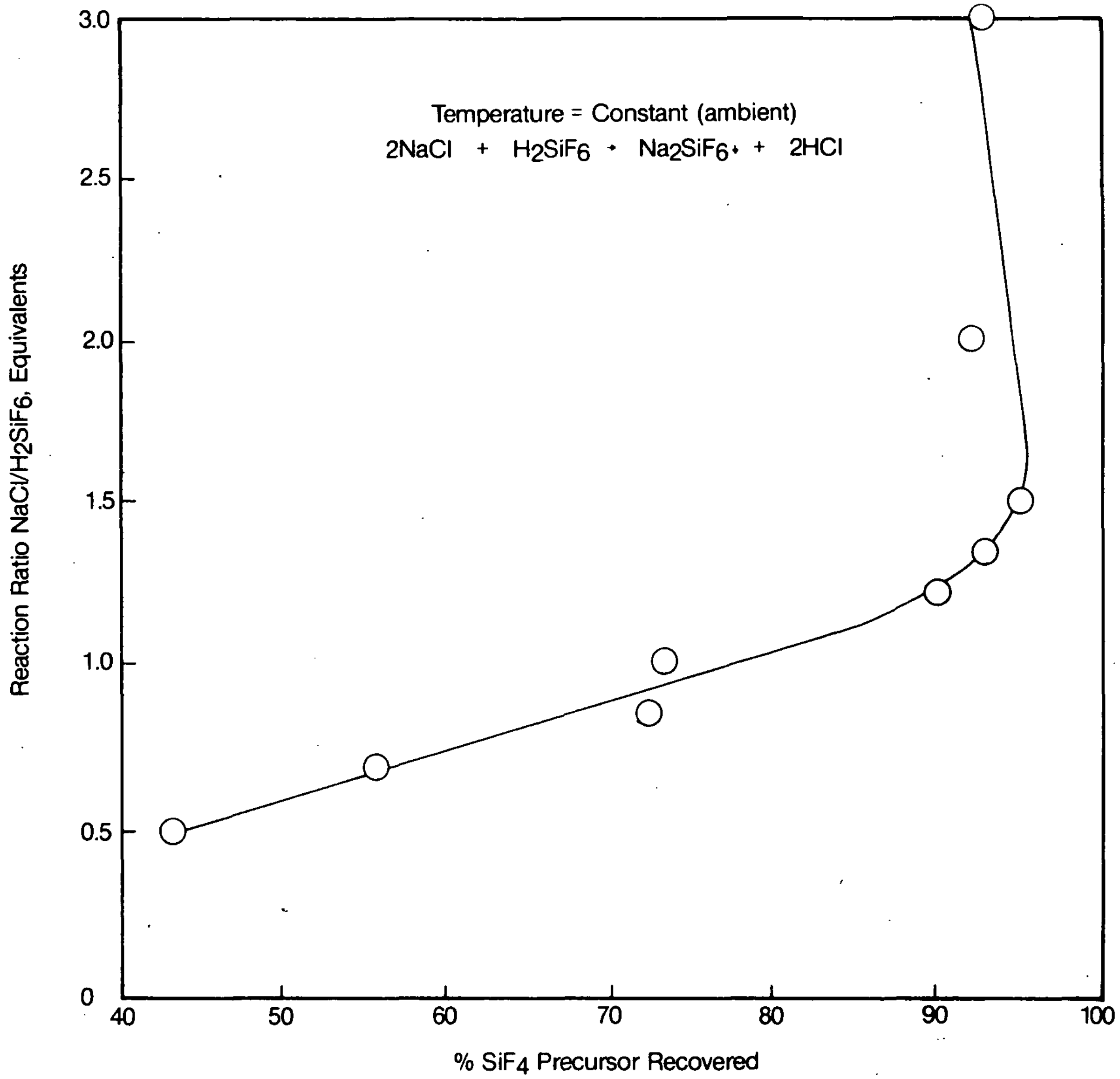


Figure 1. Variation of SiF_4 Precursor Recovery with Reaction Ratio (NaCl Reaction)

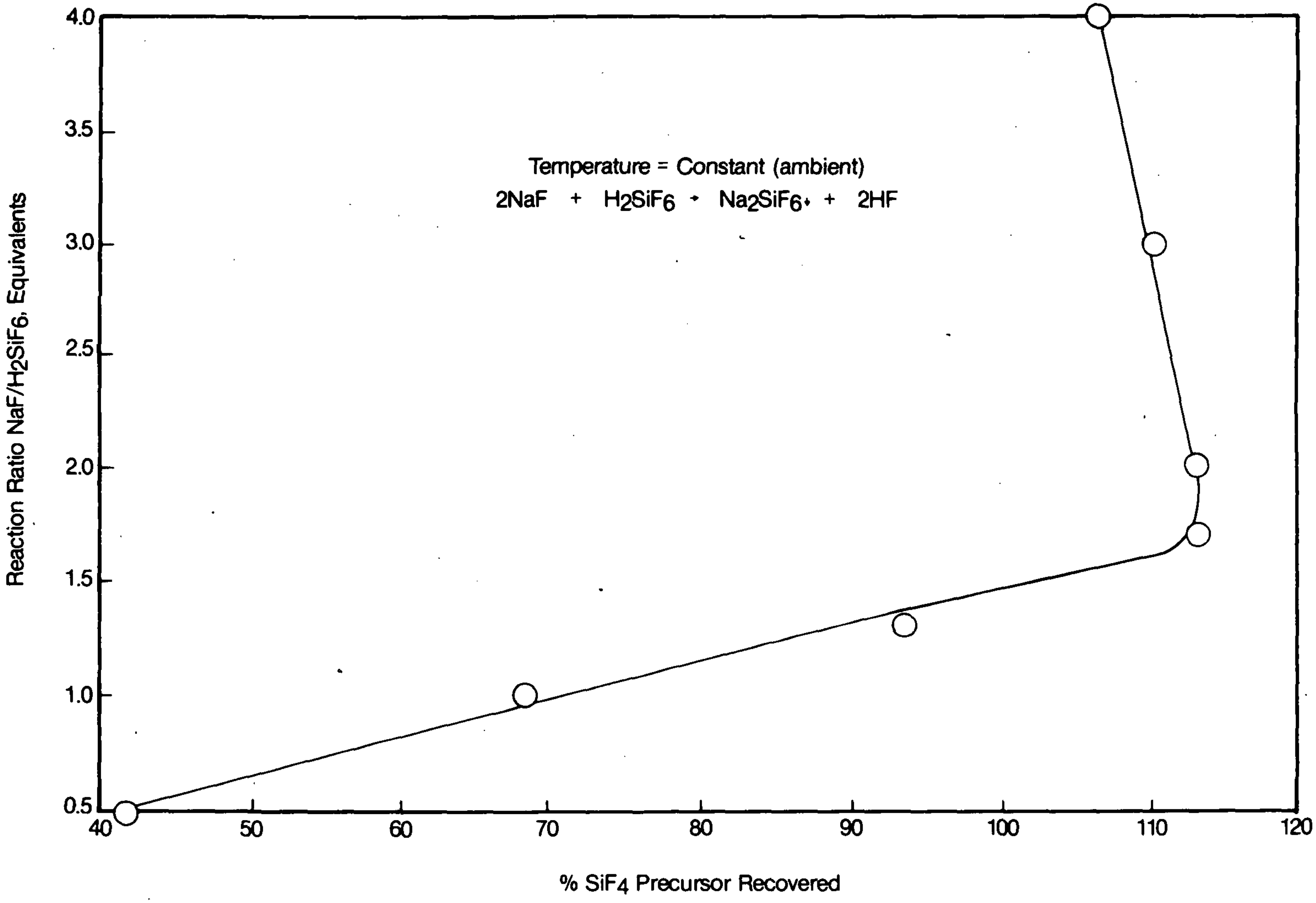


Figure 2. Variation of SiF_4 Precursor Recovery with Reaction Ratio (NaF Reaction)

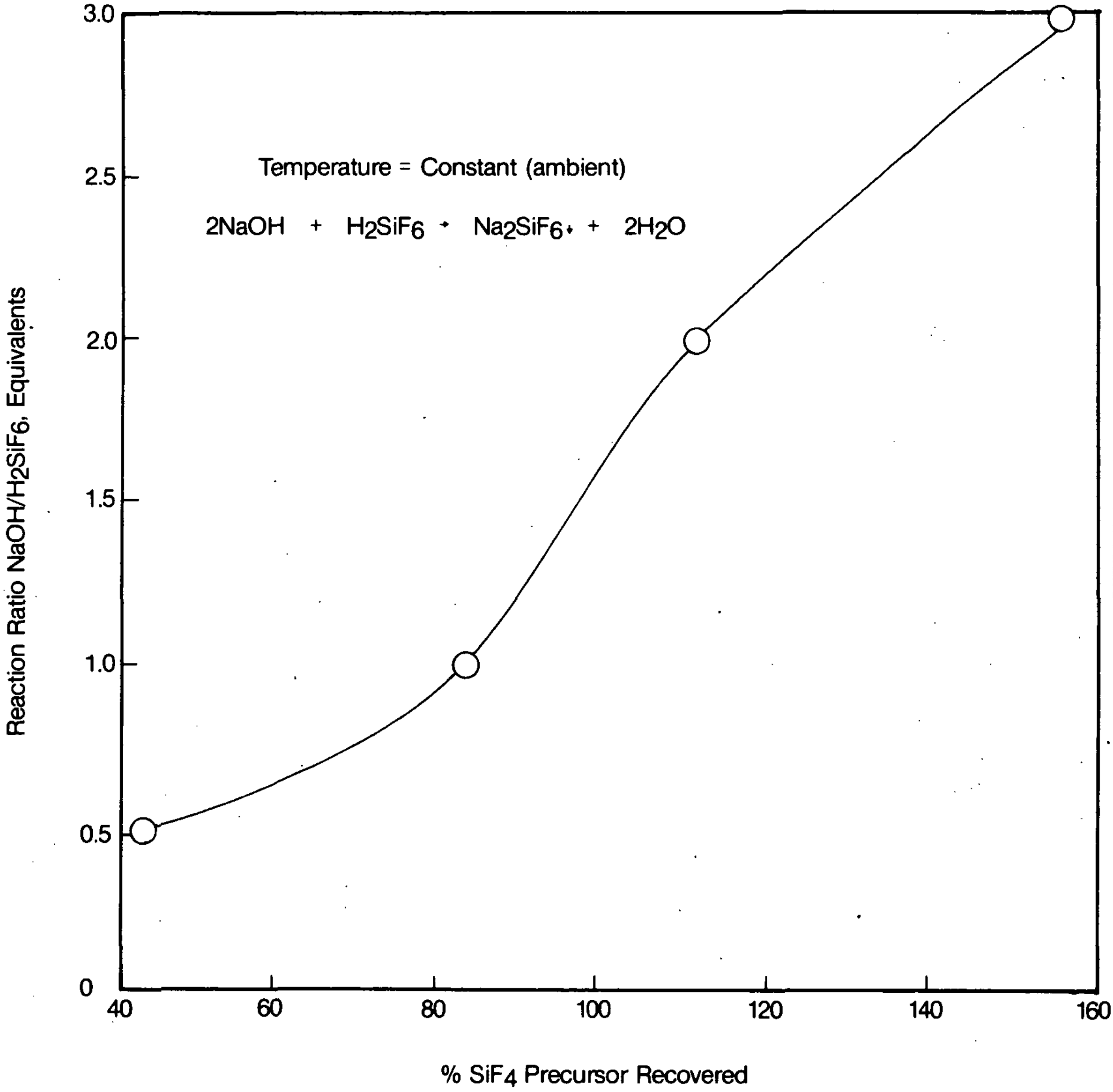


Figure 3. Variation of SiF_4 Precursor Recovery with Reaction Ratio (NaOH Reaction)

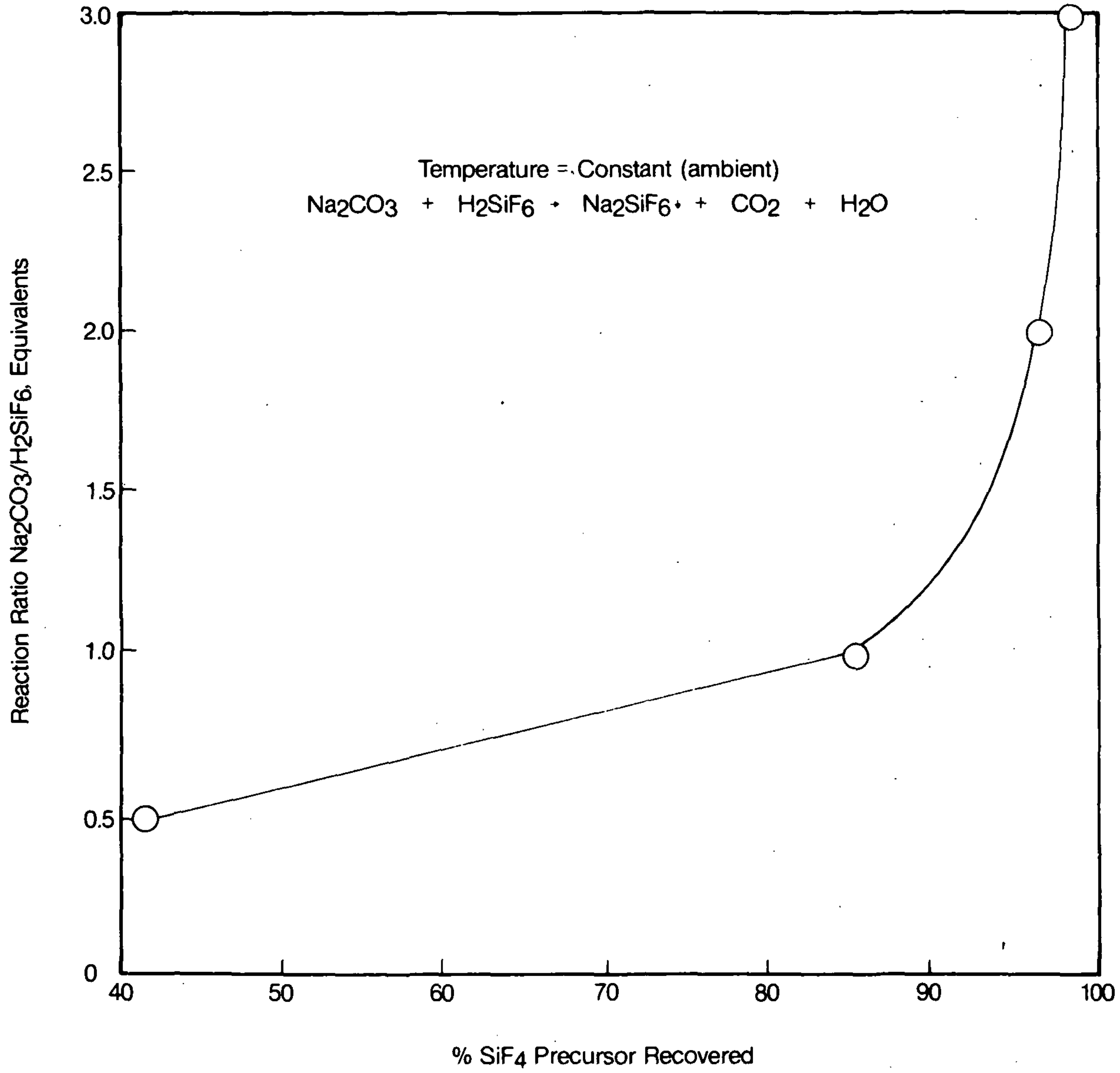


Figure 4. Variation of SiF_4 Precursor Recovery with Reaction Ratio (Na_2CO_3 Reaction)

formation of silicic acids which are hydrated oxides of silicon and these precipitate along with Na_2SiF_6. The formation of silicic acids in these reactions was confirmed by infrared analysis of the precipitate which showed characteristic absorptions for both silicic acid and Na_2SiF_6.

Figure 4 shows that reaction with Na_2CO_3 (a weakly basic reagent) gives results comparable to those obtained with NaCl solutions. Infrared analysis of the precipitate however, indicated the presence of some silicic acids which showed that hydrolysis was occurring with Na_2CO_3 as well as with NaOH.

Investigations were also initiated for the generation of silicon tetrafluoride (SiF_4) by the thermal decomposition of sodium hexafluorosilicate (Na_2SiF_6):

$$Na_2SiF_6 \overset{\Delta}{\rightleftarrows} SiF_4\uparrow + 2\ NaF \qquad (4)$$

Parameters such as temperature, reaction time, and general reaction conditions were examined in order to determine optimum conditions for efficient SiF_4 generation.

Anhydrous samples of Na_2SiF_6 were placed in a quartz tube and heated under various reaction conditions. The amount of SiF_4 generated was determined from the weight loss of the sample after heating based on the stoichiometry in equation 4.

Initially the samples were heated for 1 hour in a closed system of inert gas (N_2) maintained at 1 atmosphere and at constant temperatures ranging from 350°C to 600°C. In no instance was the generation of SiF_4 above 12%. This low yield of the SiF_4 was due to the fact that the thermal decomposition reaction is an equilibrium reaction (eq. 4) and when the decomposition is carried out under conditions which allow an equilibrium to be established, the reaction will proceed no further than the equilibrium point.

As a result of these initial results, the reaction conditions were altered such that a slow stream of N_2 (approximately 200 cc/min) was continuously passed over the sample during the decomposition. Figure 5 shows the results of these experiments. Heating the samples for 1 hour gave low yields of SiF_4 up to about 500°C. Above 500°C the percent generation of SiF_4 increased rapidly such that the generation of SiF_4 was essentially quantitative above 550°C.

Based on the above results, it is obvious that the decomposition of Na_2SiF_6 to generate SiF_4 occurs extensively at temperatures above 500°C. Since this data was obtained by heating the samples for an extended period (1 hour at each temperature), the per cent generation of SiF_4 was obtained as a function of reaction time in order to determine the minimum amount of heating required to produce high yields of SiF_4. Figures 6, 7 and 8 show the results of this type investigation at 500°C, 550°C, and 600°C. Figure 2 indicates that decomposition is not complete at 500°C even upon heating for a period of 1 hour. At 550°C the generation of SiF_4 approaches completion in 30 minutes (figure 7) and at 600°C the reaction is extentially complete in 15 minutes.

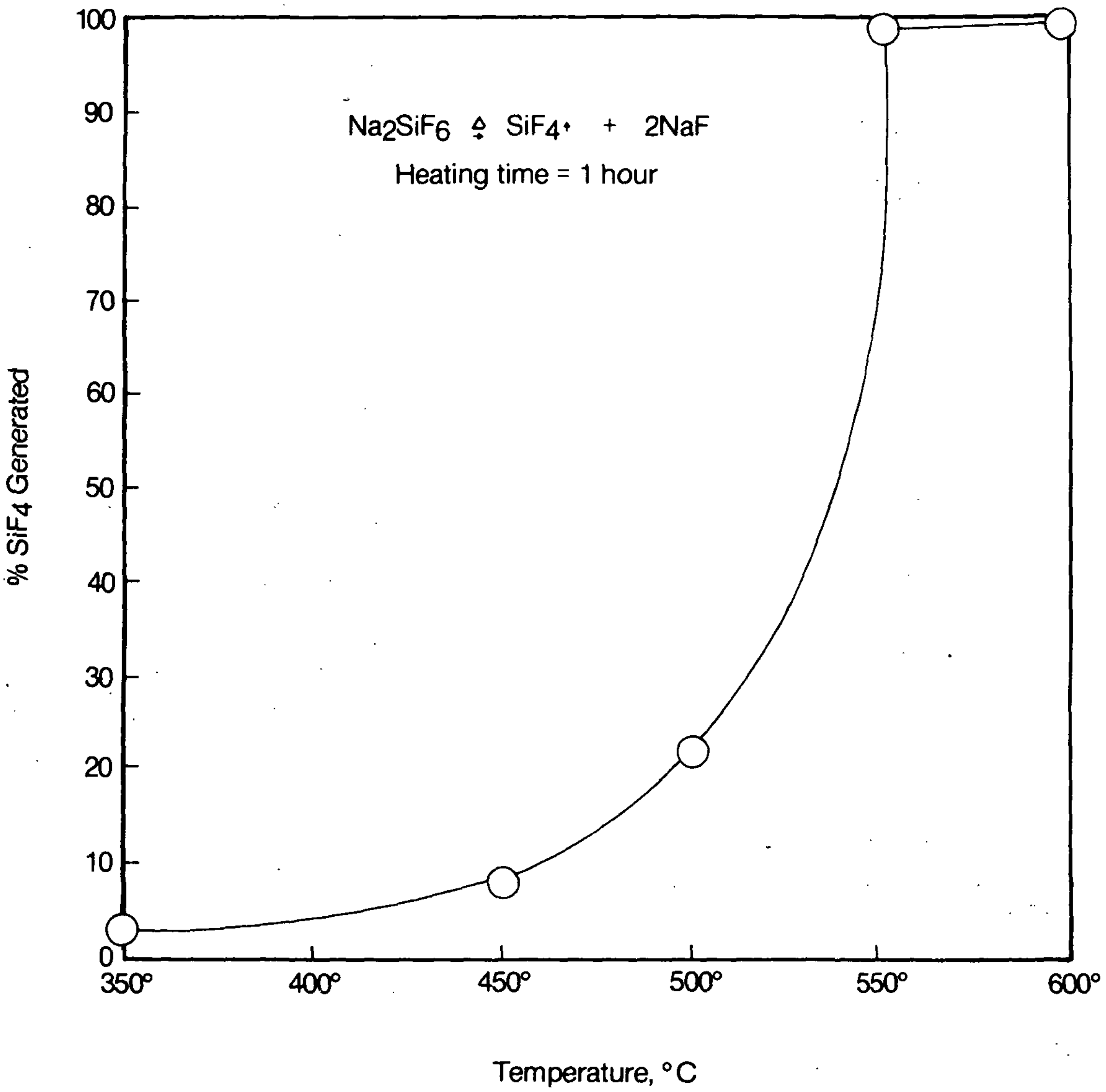


Figure 5 Variation of % SiF_4 Generated with Temperature

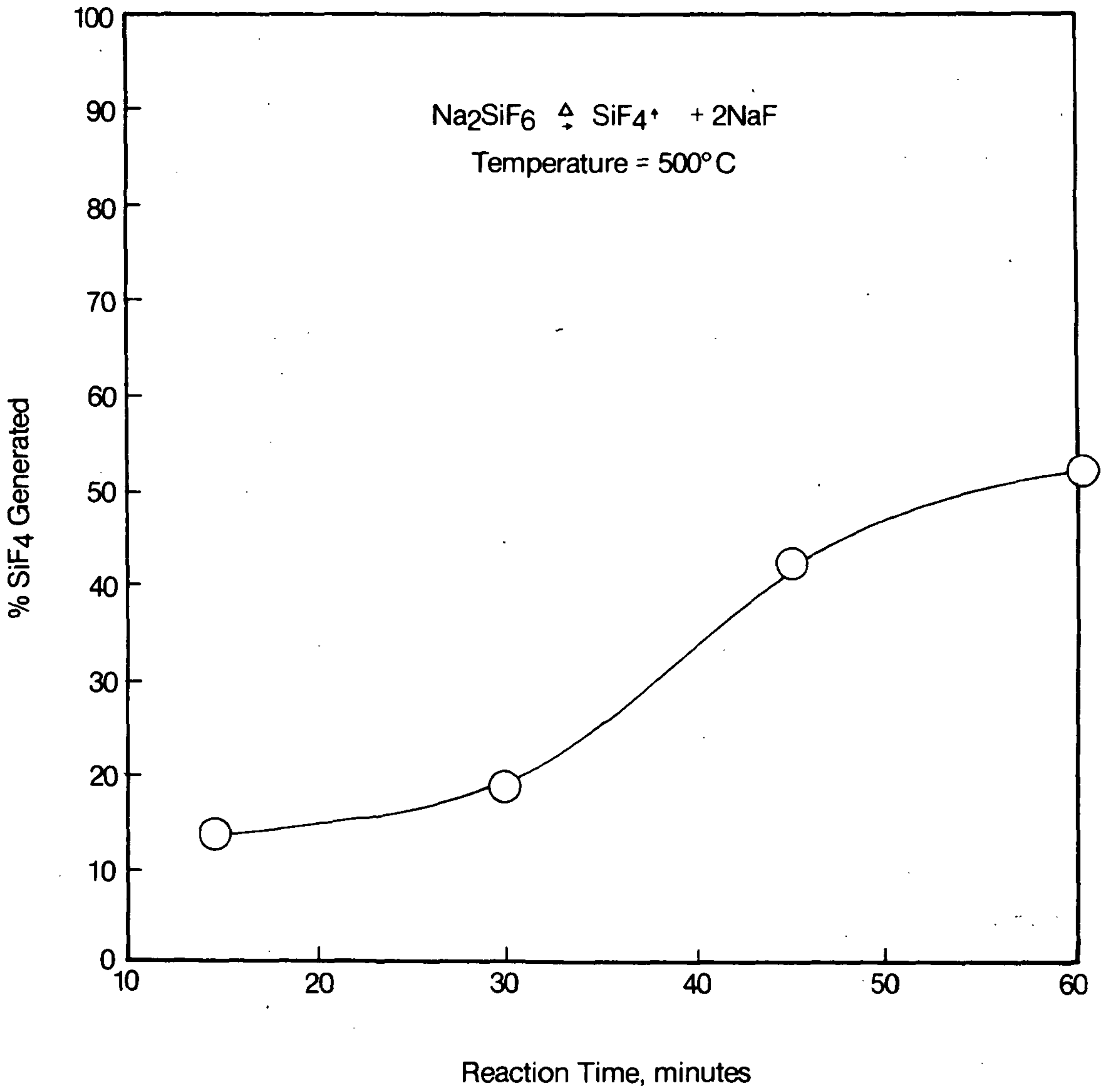


Figure 6 · Variation of % SiF_4 Generated with Reaction Time

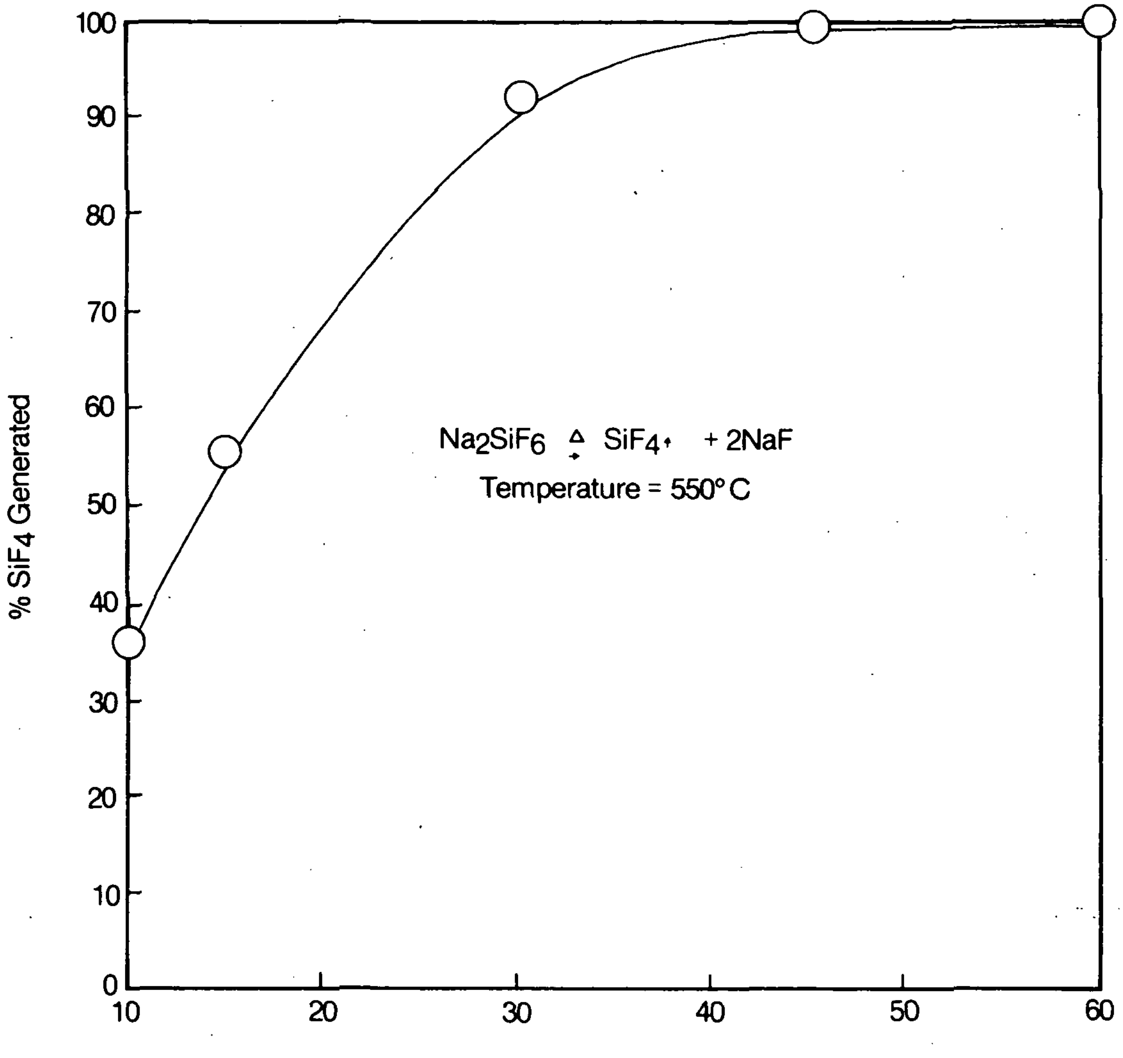


Figure 7 Variation of % SiF_4 Generated with Reaction Time

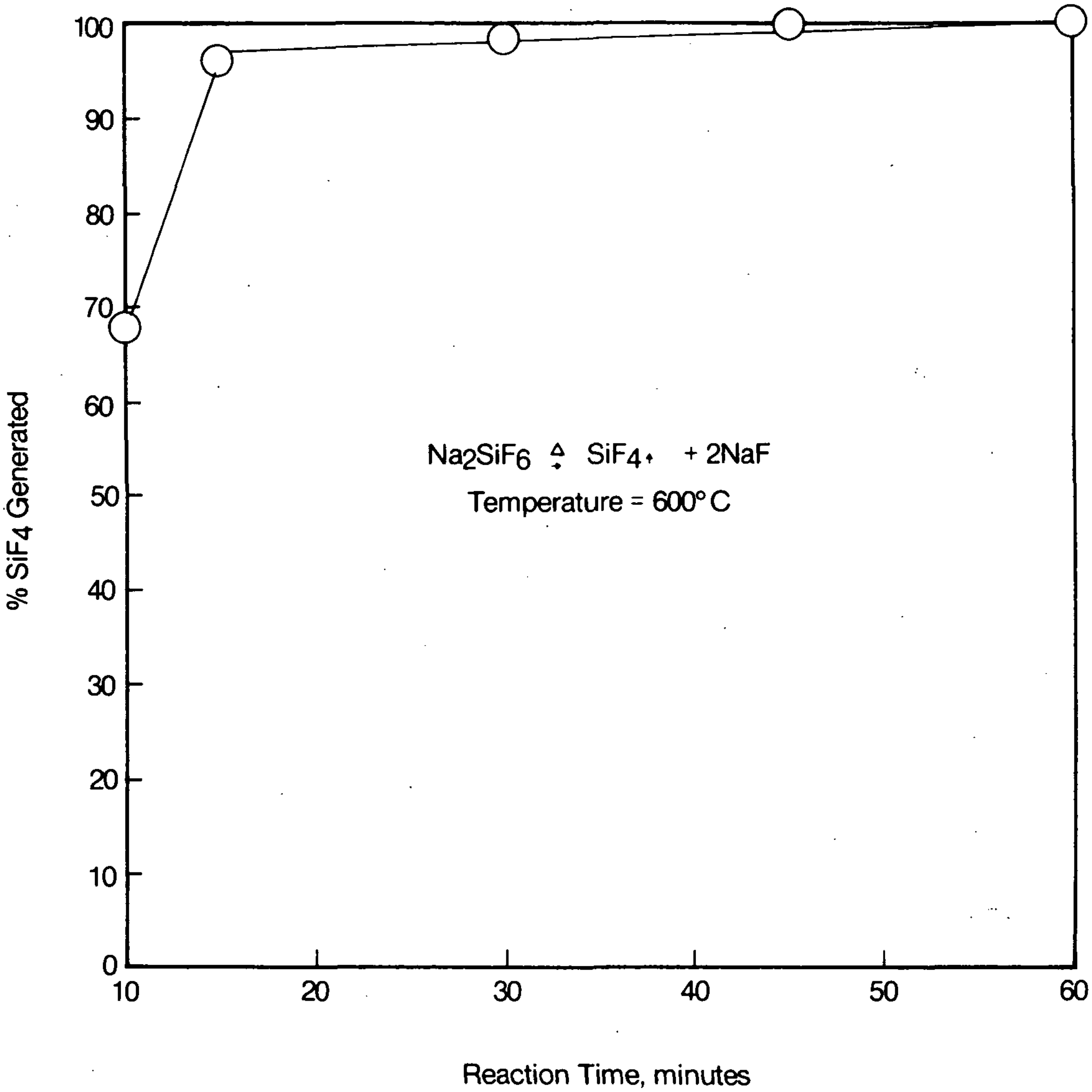


Figure 8 Variation of % SiF_4 Generated with Reaction Time

II. CHEMICAL ENGINEERING ANALYSES (TASK 2)

A. PRELIMINARY PROCESS DESIGN

Chemical engineering analyses were continued during this reporting period for alternate processes under consideration for solar cell grade silicon.

Major effort was devoted to the preliminary process design for the $Zn/SiCl_4$ process (Battelle). The status including progress since the last reporting period for the process design is given below for key guideline items:

	Prior	Current
. Process Flow Diagram	30%	100%
. Material Balance	20%	100%
. Energy Balance	20%	100%
. Property Data	20%	100%
. Equipment Design	10%	100%

Additional details including activities accomplished, in progress and planned are shown in Table II for the preliminary process design.

The process flow diagram for the $Zn/SiCl_4$ process is given in Figure 9. The flow sequence includes facilities for storage of feed raw materials required for the production of solar cell grade silicon.

The flow diagram also provides for disposition of the by-product silicon tetrachloride streams (overheads, bottoms) from the purification step. The purification step assumes that technical grade silicon tetrachloride may be purified by distillation to meet purity levels required for solar cell grade silicon. The distillations yields a 5% overhead (non-spec), 90% heart cut (spec) and 5% bottoms (non-spec). The heart cut fraction is utilized for solar cell grade silicon production.

The results of the preliminary process design for the $Zn/SiCl_4$ process (Battelle) are summarized in a tabular format. The guide for the primary results in the accompanying tables is given below:

The base case conditions including plant size of 1000 metric tons/year production of solar cell grade silicon are given in Table III. The table also indicates that the process is based on purification of technical grade silicon tetrachloride ($SiCl_4$) by distillation. The conversion (72.4%) of the deposition reaction was determined thermodynamically by Battelle. Storage capacity was supplied to introduce independence from transportation delays and to allow individual functioning of various unit operations.

Table IV presents the reaction chemistry for the process. The silicon deposition is based on zinc (Zn) reduction of silicon tetrachloride ($SiCl_4$) in a fluidized bed reactor. The reaction chemistry is also given for electrolysis and waste treatment. The waste treatment reactions will be utilized to discharge aqueous SiO_2 and NaCl at neutral conditions as a plant efficient instead of waste $SiCl_4$.

The raw material requirements are listed in Table V. The list includes requirements for the basic feed materials ($SiCl_4$, Zn), waste disposal (caustic) and electrolysis (by-product chlorine). It should be noted that the present preliminary design starts with $SiCl_4$ (see Table III); therefore, Cl_2 is a by product. Future, improved, designs may utilize this Cl_2 to produce $SiCl_4$ from metallurgical grade silicon.

The utility requirements - including electricity, steam, cooling water, process water, high temperature coolant and nitrogen - are given in Table VI. The utility requirements on a per kilogram of silicon produced basis were determined from the energy balance for each major piece of process equipment. The electrolysis electricity requirements contain the theoretical amount plus 30% to allow for conversion to low voltage (D.C.). Further experimental work may show a larger electrical requirement for electrolysis. The heating requirements for various storage tanks (e. g., Electrolysis Feed Tanks) were determined by calculating heat losses resulting from the high storage temperatures (500°C) to the ambient . The primary utility is electricity with majority of the electrical requirements (approx. 14KW-HR of 15.3 KW-HR total being consumed in the electrolysis and vaporization processing.

The list of major process equipment is given in Table VII. Columns one and two give the equipment and function within the process. Colume three is the duty as taken from the appropriate material/energy balances. This information is used to calculate column four, the design size. Columns four and five are forwarded to economic analysis for determining equipment purchased cost. These last 2 columns represent the first trial design for this process from which a preliminary plant investment will be obtained. The material of construction is given as a guide primarily for costing purposes only.

The production labor requirements for the plant are listed in Table VIII. including both skilled and semi-skilled labor. The labor requirements are based on a combination of process types (A-batch, B-average and C-automated) normally encountered in a chemical process plant.

TABLE II CHEMICAL ENGINEERING ANALYSES: PRELIMINARY PROCESS DESIGN ACTIVITIES FOR $Zn/SiCl_4$ PROCESS

Prel. Process Design Activity	Status
1. Specify Base Case Conditions	●
1. Plant Size	●
2. Product Specifics	●
3. Additional Conditions	●
2. Define Reaction Chemistry	●
1. Reactants, Products	●
2. Equilibrium	●
3. Process Flow Diagram	●
1. Flow Sequence, Unit Operations	●
2. Process Conditions (T, P, etc.)	●
3. Environmental	●
4. Company Interaction (Technology Exchange)	●
4. Material Balance Calculations	●
1. Raw Materials	●
2. Products	●
3. By-Products	●
5. Energy Balance Calculations	●
1. Heating	●
2. Cooling	●
3. Additional	●
6. Property Data	●
1. Physical	●
2. Thermodynamic	●
3. Additional	●

Prel. Process Design Activity	Status
7. Equipment Design Calculations	●
1. Storage Vessels	●
2. Unit Operations Equipment	●
3. Process Data (P, T, rate, etc.)	●
4. Additional	●
8. List of Major Process Equipment	●
1. Size	●
2. Type	●
3. Materials of Construction	●
8a. Major Technical Factors (Potential Problem Areas)	●
1. Materials Compatibility	●
2. Process Conditions Limitations	●
3. Additional	●
9. Production Labor Requirements	●
1. Process Technology	●
2. Production Volume	●
10. Forward for Economic Analysis	●

○ Plan
◒ In Progress
● Complete

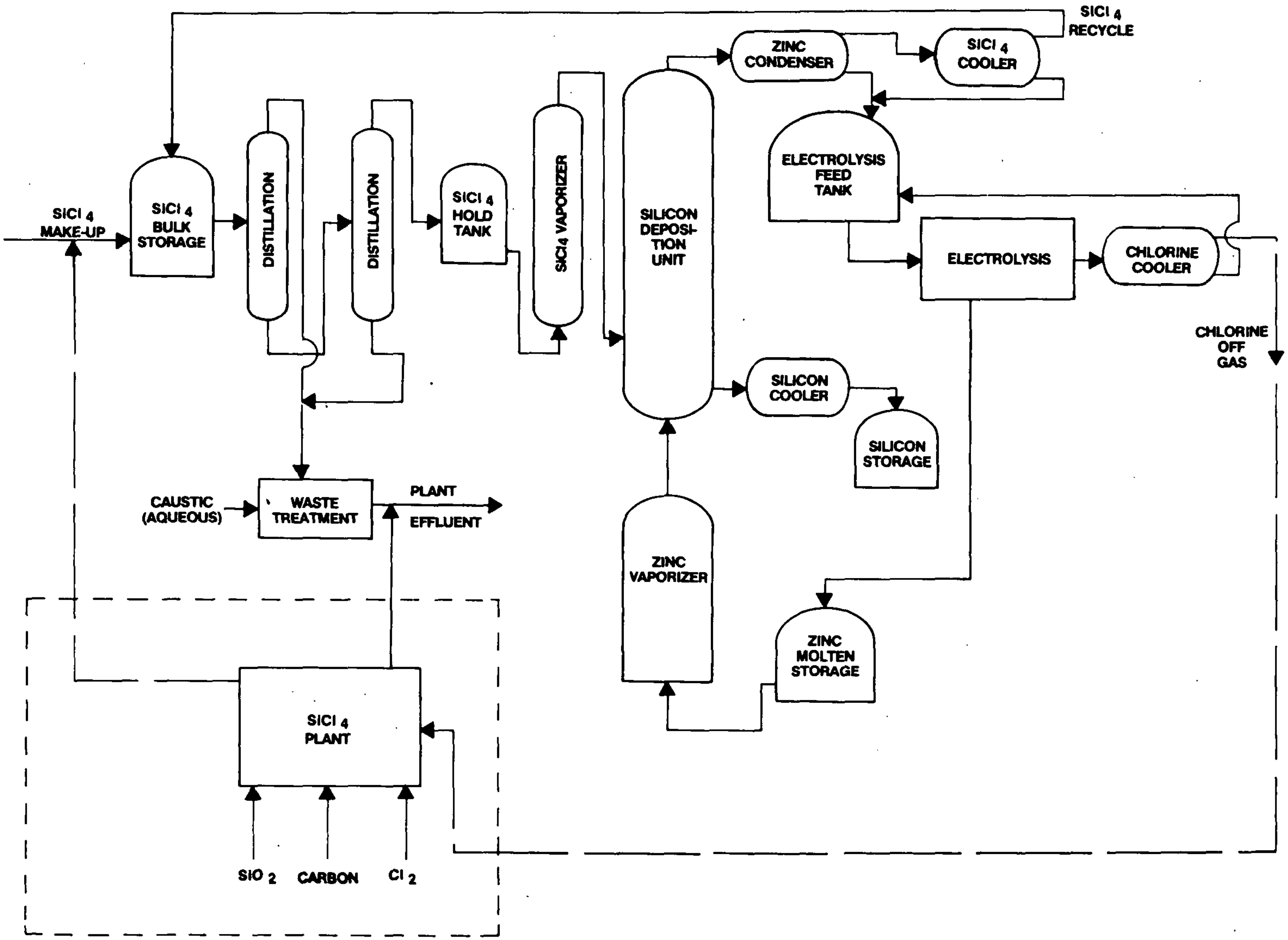


Figure 9 Process Flow Diagram for Zn/SiCl$_4$ Process (Battelle)

TABLE III

BASE CASE CONDITIONS FOR PROCESS Zn/$SiCl_4$ (BATTELLE)

1. Plant Size
   - Production of 1000 metric tons/year
   - Solar Cell Grade Silicon
2. Deposition Reaction
   - Zn reduction of $SiCl_4$
   - 1200°K, 1 ATM, 72.4% conversion (Battelle)
3. $SiCl_4$ Purification
   - Technical grade $SiCl_4$ purification by distillation
   - 10% waste (5% lights, 5% heavies)
   - 90% product (90% heartcut)
4. Electrolytic Recovery
   - Electrolytic recovery of Zn from $ZnCl_2$
   - Cl_2 is by-product
5. Operating Ratio
   - Approx. 80% utilization (79.3%)
   - Approx. 7000 hr/year production
6. Storage Considerations
   - Feed materials (two week supply)
   - Product (two week supply)
   - Process (several days)

Table IV

Reaction Chemistry for Process Zn/Cl_4 (Battelle)

1. **Silicon Deposition**

   $2Zn + SiCl_4 \rightarrow Si\downarrow + 2ZnCl_2$

2. **Electrolysis**

   $ZnCl_2 \xrightarrow{\text{electroly.}} Zn(l) + Cl_2(g)$

3. **Waste Treatment**

   $SiCl_4 + 2H_2O \xrightarrow{aq} SiO_2 + 4HCl(ag)$

   $NaOH(ag) + HCl(aq) \rightarrow NaCl(ag) + H_2O$

Table V

Raw Material Requirements for
Process $Zn/SiCl_4$ (Battelle)

	Raw Material	Requirement lb/KG of Silicon
1.	Silicon Tetrachloride, $SiCl_4$	15.37
2.	Zinc, Zn	1.42
3.	Caustic (50%), NaOH(ag)	3.85
4.	Chlorine, Cl_2	11.12 By-Product

TABLE VI UTILITY REQUIREMENTS FOR PROCESS Zn/$SiCl_4$ (BATTELLE)

Utility/Function		Requirements/Kg of Silicon Product
1. Electricity		15.25 Kw-hr
1. Low Voltage D.C. for Electrolysis	(10.098)	
2. Zinc Vaporizer Induction Heated	(3.837)	
3. Preheat Section of Deposition Unit Induction Heated	(.983)	
4. Electrolysis Feed Tank Heater	(.238)	
5. Molten Zinc Storage Heater	(.0986)	
2. Steam (100 PSIA)		10.24 Pounds
1. #1 Purification Column Calandria	(4.07)	
2. #2 Purification Column Calandria	(3.905)	
3. $SiCl_4$ Vaporizer	(1.695)	
4. Caustic Storage Heating	(.292)	
5. #1 Purification Column Preheater	(.277)	
3. Cooling Water		29.04 Gallons
1. #1 Purification Column Condenser	(14.47)	
2. #2 Purification Column Condenser	(13.88)	
3. Purified Tet After Cooler	(.592)	
4. $SiCl_4$ Recycle Cooler	(.1009)	
4. Process Water		6.41 Gallons
1. Diluant for Waste Treatment	(6.41)	
5. High Temperature Coolant		126.4 Pounds
1. Condense Zinc From Deposition Unit	(78.95)	
2. Chlorine Cooler/Stripper	(23.56)	
3. Cooling for Deposition Unit	(19.69)	
4. $SiCl_4$ Cooler/Stripper	(4.15)	
6. Nitrogen		55.75 Cu. Ft.
1. Cooling of Product Silicon	(55.75)	

TABLE VII LIST OF MAJOR PROCESS EQUIPMENT FOR PROCESS Zn/$SiCl_4$ (BATTELLE)

	Type	Function	Duty	Size	Materials of Construction
1.	Purified $SiCl_4$ Feed Tank	Feed for $SiCl_4$ Vaporizer	One Week Storage	39,250 Gallons	C.S.
2.	Silicon Storage Bin	Final Product Storage	Two Weeks Storage	10,970 Gallons	C.S.
3.	Electrolysis Feed Tank	Feed Tank for Electrolysis	One Day Storage, 1.062×10^5 BTU/hr or 31.1 K watts	3270 Gallons, 23.4 ft^2 of coils	316 S.S.
4.	Molten Zinc Storage Tank	Feed for Zinc Vaporizer	One Day Hold Up, 4.4×10^4 BTU/hr or 12.9 K watts	822 Gallons, 9.77 ft^2 of coil area	316 S.S.
5.	Raw Zinc Storage Tank	Raw Zinc Supply to Molten Storage	Two Weeks Storage	1151 Gallons	C.S.
6.	$SiCl_4$ Bulk Storage Tank	Raw $SiCl_4$ Storage and Feed for Purification	Two Weeks Storage	78,510 Gallons	C.S.
7.	Secondary Column Feed Tank	Hold-Up Between Purification Columns	Eight Hours Hold-Up	2130 Gallons	C.S.
8.	Waste Material Hold Tank	Collection of Purification Wastes. Waste Treatment Feed.	One Week Hold-Up	4708 Gallons	C.S.
9.	Caustic Storage Tank	Feed Caustic for Waste Treatment	Two Weeks Storage and 3.7×10^4 BTU/hr	14,895 Gallons	Heat Treated C.S.

Table VII (Continued)

10.	Waste Neutralization Tank	Scrubber/Neutralizer For $SiCl_4$ Wastes		2500 Gallons	316 S.S.
11.	$SiCl_4$ Vaporizer	Vaporize Feed to Deposition Unit	2.199×10^5 BTU/hr	22.9 ft^2 of Surface Shell and Tube	C.S.
12.	Zinc Vaporizer	Vaporize Feed to Deposition Unit	1.713×10^6 BTU/hr or 502 K watts	2628 ft^2 for Hot Gas	Graphite
13.	Silicon Cooler	Cool Product to Ambient Temp.	1.02×10^5 BTU/hr	D = 1.02 ft, L = 3.05 ft	Graphite
14.	Zinc Condenser	Condense $Zn/ZnCl_2$ Gas From Reactor	2.068×10^6 BTU/hr	3458.2 ft^2 of Shell and Tube	Graphite Tubes and Shell
15.	#1 $SiCl_4$ Cooler/Stripper	Condense $Zn/ZnCl_2$ Gas From Zinc Condenser	3.73×10^4 BTU/hr	142 ft^2 of Shell and Tube	316 S.S. Tubes C.S. Shell
16.	#2 Cl_2 Stripper/Cooler	Condense and Recycle $ZnCl_2$ to Electrolysis	2.543×10^5 BTU/hr	1260 ft^2 of Shell and Tube	316 S.S. Tubes C.S. Shell
17.	$SiCl_4$ Recycle Cooler/Condenser	Condense and Recycle $SiCl_4$ to Bulk Storage	1.077×10^5 BTU/hr	29.38 ft^2 Shell and Tube	C.S.
18.	Column One Preheater	Preheat Feed to Distillation Column	3.55×10^4 BTU/hr	5.26 ft^2 Shell and Tube	C.S.
19.	Column One Condenser	Condense Overheads For Reflux	5.21×10^5 BTU/hr	379.5 ft^2	C.S.
20.	Column One Calandria	Reboiler for Column One	5.21×10^5 BTU/hr	54 ft^2 Shell and Tube	316 S.S. Tubes C.S. Shell

Table VII (Continued)

21.	Column Two Condenser	Condense Overheads for Reflux	5 x 10^5 BTU/hr	364 ft^2 Shell and Tube	C.S.
22.	Column Two Calandria	Reboiler for Column Two	5 x 10^5 BTU/hr	52 ft^2 Shell and Tube	316 S.S. Tubes C.S. Shell
23.	Purification After Cooler	Cool Hot Purified $SiCl_4$ to Ambient for Storage	3.2 x 10^4 BTU/hr	86 ft^2 Shell and Tube	C.S.
24.	Pump to $SiCl_4$ Vaporizer	Pump Liquid Tet to Vaporizer		3.9 gpm 200 ft of Head	C.S.; S.S. Impeller
25.	Electrolysis Vapor Recycle Compressor	Collect Vapors From Electrolysis; Feed Stripper		154.2 cfm at S.T.P.	316 S.S.
26.	Recycle $ZnCl_2$ Pump	$ZnCl_2$ From #2 Stripper/Cooler to Electrolysis		0.3 gpm, 100 ft Head	316 S.S.
27.	#1 Column Calandria Pump	Forced Convection Pump		16.12 gpm, 150 ft Head	C.S. 316 S.S. Impeller
28.	#2 Column Calandria Pump	Forced Convection Pump		11.44 gpm, 150 ft of Head	C.S.; S.S. Impeller
29.	Waste Material Pump	From Waste Hold Tank to Waste Treatment		.5 gpm, 50 ft Head	C.S.; S.S. Impeller
30.	Water Pump for Waste Treatment	Water to Waste Treatment for Dilution and Cooling		15.28 gpm, 100 ft of Head	C.S.; S.S. Impeller

Table VII (Continued)

31.	Caustic Pump	Pump 50% NaOH to Waste Treatment		3/4 gpm, 50 ft of Head	Heat Treated Steel
32.	Waste Treatment Pump	Find Treated Waste to Plant Effluent		16.6 gpm, 150 ft of Head	C.S. W/S.S. Impeller
33.	Pump to $SiCl_4$ Purification	$SiCl_4$ From Bulk Storage to Purification		4.4 gpm, 100 ft of Head	C.S. W/S.S. Impeller
34.	#1 Distillation Column, Overheads Pump	Reflux Pump		11.5 gpm, 100 ft of Head	C.S. W/S.S. Impeller
35.	#2 Distillation Column Overheads Pump	Reflux Pump		11.2 gpm, 100 ft of Head	C.S. W/S.S. Impeller
36.	Silicon Deposition Unit	Reactor to Produce Silicon	-5.3×10^5 BTU/hr Cooling + $1,107 \times 10^5$ BTU/hr Preheat or 128.7 K watts Preheat	15" Diameter, 30' High, 3.7 ft^2 of Area for Cooling (6 Units)	Graphite
37.	Electrolysis Cells	$ZnCl_2 \rightarrow Zn + Cl_2$ for Recycling Zn	1.166×10^3 K watts D.C. at 5.498×10^5 Amps, 2.12 Volts	6430 Metric Ton/Year of Zinc	Graphite
38.	$SiCl_4$ Purification, Column One	Removes Light Impurities		1.65 ft Diameter, 28.6 ft Tall	C.S.
39.	$SiCl_4$ Purification, Column Two	Removes Heavy Impurities		1.62 ft Diameter, 23.8 ft Tall	C.S.

TABLE VIII PRODUCTION LABOR REQUIREMENTS FOR PROCESS Zn/$SiCl_4$ (BATTELLE)

	Unit Operation	Type	Skilled Labor Man hrs/Day Unit	Semiskilled Labor Man hrs/Day Unit
1.	Deposition	A	36	
2.	Vaporization	B	23	
3.	Product Handling	A		36
4.	Vapor Condensation	B	23	
5.	Electrolysis	A	36	
6.	Tet Purification	C	16	
7.	Materials Handling	A		36
8.	Waste Treatment	B	23	
	Total		157	72

Skilled: .0573 Man-hrs/KgSi

Semiskilled: .00259 Man-hrs/KgSi

Notes

1. A Batch Process or Multiple Small Units
   B Average Process
   C Automated Process

2. Man hours/Day Unit from Figure 4-6, Peters and Timmerhaus (7).

B. CHEMICAL EQUILIBRIUM

Thermodynamic equilibrium compositions at various process conditions are to be determined as one of the key guide lines for the preliminary process design effort in the chemical engineering task.

The initial objective of this effort is to convert an available chemical equilibrium computer program (17) to the Lamar CDC 3300 computer. A second objective is to confirm the capability of our computational technique by evaluating a previously documented system. The primary effort will then be in applying the procedure to other alternate systems being evaluated as to the effects of process variables such as composition and temperature.

Concept

The basic thermodynamic criteria for chemical equilibrium is for the system to prosess a minimum Gibbs free energy for the reacting mixture. The chemical composition at the minimum Gibbs free energy is established by finding the conditions for which there is no change in the free energy with respect to composition. These conditions can then be shown to be related by the familiar(18) expression

$$\Delta G = -RT \ln K_a \tag{5}$$

where $\Delta G^o \equiv$ Standard-state Gibbs-free-energy change

$R \equiv$ universal gas constant

$T \equiv$ absolute temperature

$K_a \equiv$ thermodynamic equilibrium constant

This relationship is valid for each independent reaction in the system. If a system can be described by one or two reactions, the system composition can be obtained by solving this set of nonlinear simultaneous equilibrium constant equations. However if a large number of simultaneous reactions must be considered, direct minimization of the Gibbs free energy by one of the standard methods of nonlinear optimization is frequently more attractive computationally. The direct minimization of the Gibbs free energy has the advantage that it does not require the system of reaction equations to be specified, but only requires that all species in the system be specified.

Calculation Procedure

An outline of the basis for performing the calculations is as follows:

If we are given the Gibbs free energy function at a temperature and pressure

$$(F)_{T,P} = F(X_1, X_2, \ldots, X_N), \qquad (6)$$

We wish to find a set of X_i's which will minimize F for a constant temperature and pressure subject to the constraints of the material balances.

This can be accomplished with the following procedure:

1. Formulate the constraining stoichiometric equations.

$$\sum_{i=1}^{n} A_{ij} X_i + \sum_{i=n+1}^{l} A_{ij} X_i = b_j \qquad (7)$$

where A_{ij} = amount of gram-atoms of the j^{th} chemical element in the i^{th} species

X_i = moles of i^{th} species

b_j = gram-atoms of each element j

n = number of gaseous chemical species

n+1 to j = number of condensed species

2. Introduce Lagranian Multipliers, π_j, for each element in the constrained optimization problem.

$$\sum_{j=1}^{m} \Pi_j \left(b_j - \sum_{i=1}^{n} A_{ij} - \sum_{i=n+1}^{l} A_{ij} X_i\right) = L(x) \tag{8}$$

3. Formulate the equations for Gibbs free energy of a complex gas-solid mixture.

$$F(x) = \sum_{i=1}^{n} X_i \left[C_i + \ln X_i/\overline{X}\right] + \sum_{i=n+1}^{l} X_i \left(F_T°\right)_i/RT \tag{9}$$

where $$C_i = \frac{(F_T°)}{RT} + \ln P$$

$F_T°$ = Standard state Gibbs free energy

F_T = Gibbs free energy at T

$\overline{X}$ = total moles of reacting mixture

$F(x)$ = total Gibbs free energy of the mixture

4. Formulate the constrained function to be minimized.

New Function = Quadratic Approx. to Free Energy Function + Lagrangian Function

$$G(x) = f\ (F(x)) + L\ (x) \tag{10}$$

5. Find the minimum Gibbs free energy by determining the X_i which occur when partial derivatives of G with respect to X_i are zero.

$$\left(\frac{\partial G}{\partial X_i}\right)_{T, P, n_j} = \left(\frac{\partial f(f(x))}{\partial X_i}\right)_{T, P, n_j} + \left(\frac{\partial L(x)}{\partial X_i}\right)_{T, P, n} = 0 \qquad (11)$$

A flow chart showing the simplified steps for these calculations is given in Figure 10.

Results of Calculational Technique.

A computer program (17) for performing the previously outlined calculations was converted-over to Lamar's CDC 3300 system. The reliability of the program has been evaluated by performing calculations for the hydrogen-chlorosilane system which has previously been studied by Sirtl and Hunt (19). Sirtl and Hunt have used the approach of minimizing the Gibbs free energy directly as we are doing.

The input data required for the program are the heat of reaction at 298 °K, ΔH°_{298}, the entropy at 298 °K, S°_{298}, and the heat capacity, C°_p, for each of the possible species in the system.

A plot of the conversion of silicon in the feed to precipitated silicon, Si (solid), versus reaction temperature is shown in Figure 11. The conversion obtained in the present work is compared with the results of Sirtl and Hunt. Both calculational procedures are based on the same thermodynamic input data (All of our equilibrium calculations were made for a Cl/H molar ratio of 0.02 and a Si/Cl molar feed ratio of 0.33. This corresponds to a feed containing 98.7 mole % H_2 and 1.3 mole % $SiHCl_3$. Other combinations which satisfy the Cl/H and Si/Cl in the feed are also possible.) The present results agree very closely with the Sirtl and Hunt results. The shape of the curves are similar and the maximum occurs for both near 1500 °K.

A plot of the individual species in the gas phase at various pressures from 0.01 to 10 atmospheres at a temperature of 1200 °K is shown in Figure 12 to illustrate the information which may be generated. Individual composition data were not reported by Sirtl and Hunt and therefore a direct comparison could not be made.

It is felt that this evaluation of our calculation procedure has demonstrated the reliability and capability of our technique and thus we can proceed to analyze other alternate systems.

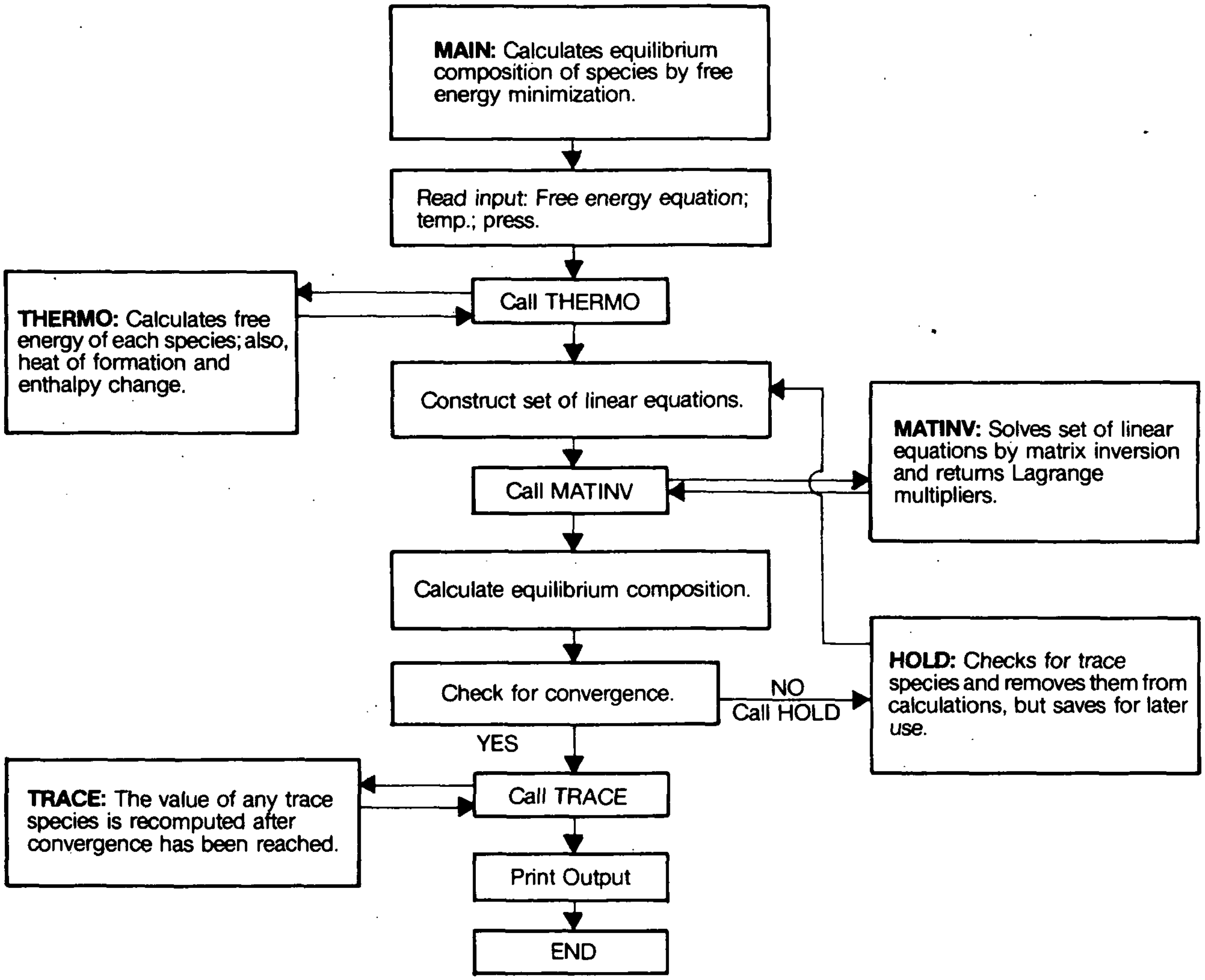


Figure 10 Flow Diagram of Chemical Equilibrium Composition Program

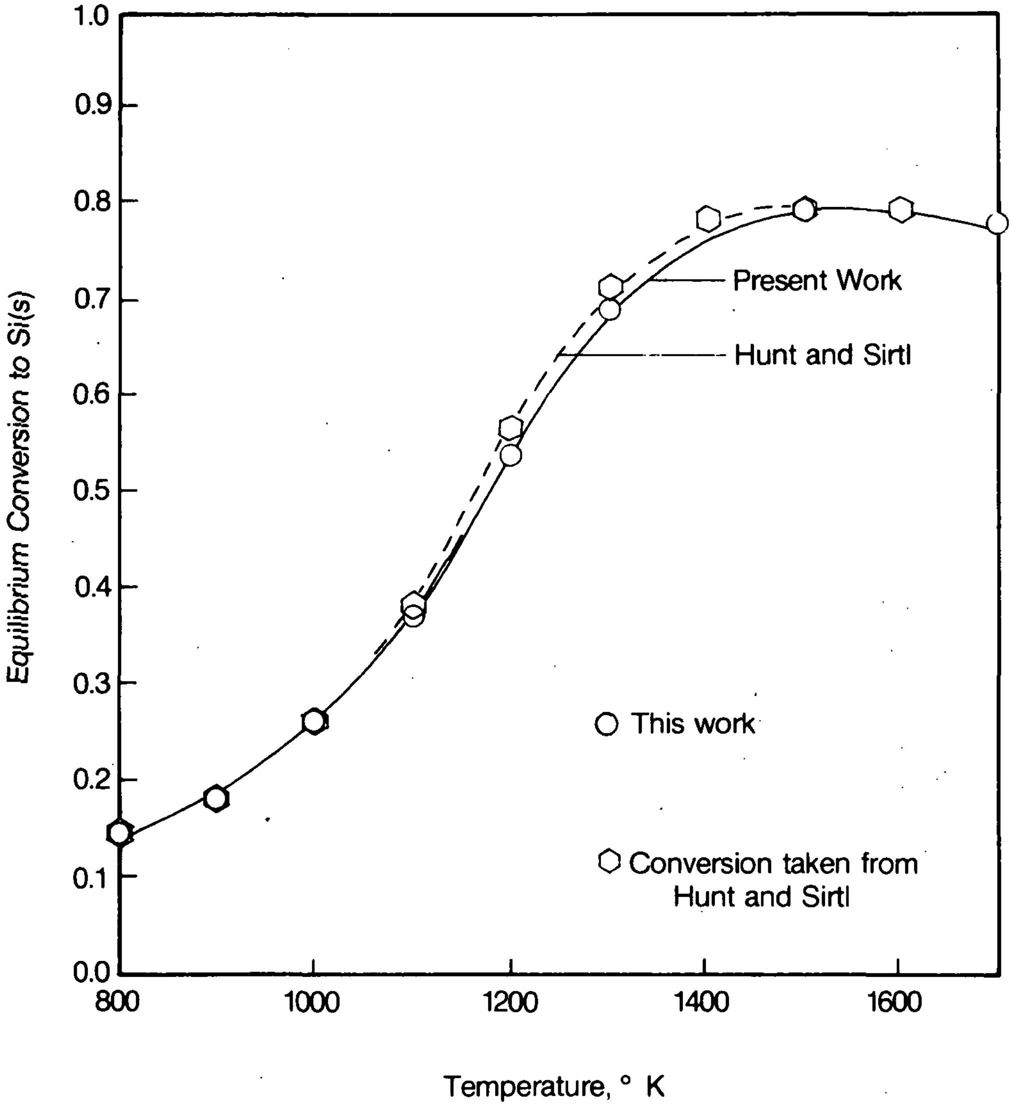


Figure 11 Equilibrium Conversion to Si(s) Versus Temperature

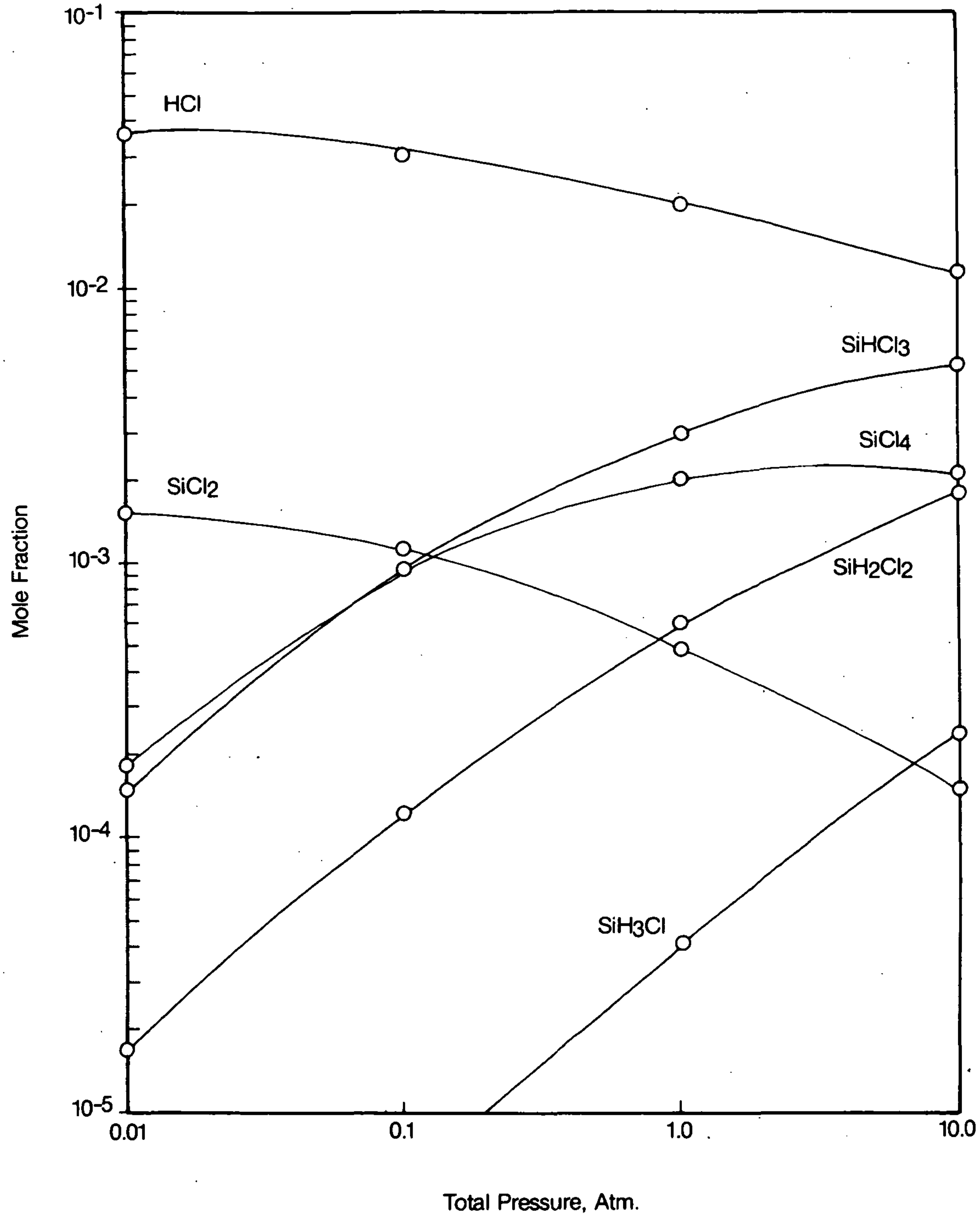


Figure 12 Mole Fraction of Each Specie Versus Total Pressure of System

Thermodynamic equilibrium compositions at various process conditions were also analyzed for the Zn/$SiCl_4$ (Battelle) and SiI_4 Decomposition (Battelle) processes.

Zn/$SiCl_4$

Determination of equilibrium compositions have been made at various conditions to support the preliminary process design for the Zn/$SiCl_4$ process (Battelle). Equilibrium conversion of $SiCl_4$ to Si(S) at pressures from 0.01 to 10 atmospheres are shown in Figure 13 at 1100 and 1200°K. Lower temperature and higher pressure favor the thermodynamic equilibrium conversion to Si(s). Comparison of results with Battelle for the same input data are shown in Figure 14. Good agreement is observed.

SiI_4 Decomposition

Equilibrium conversion of SiI_4 to Si(s) for the thermal decomposition of SiI_4 (Battelle) have been determined for various conditions in support of the preliminary process design for this process. Results are given in Figure 15 over the temperature range of 1200 to 1700°K at 0.001 and 0.01 atmosphere. Thermodynamic equilibrium conversion to Si(s) is increased at higher temperature and lower pressure.

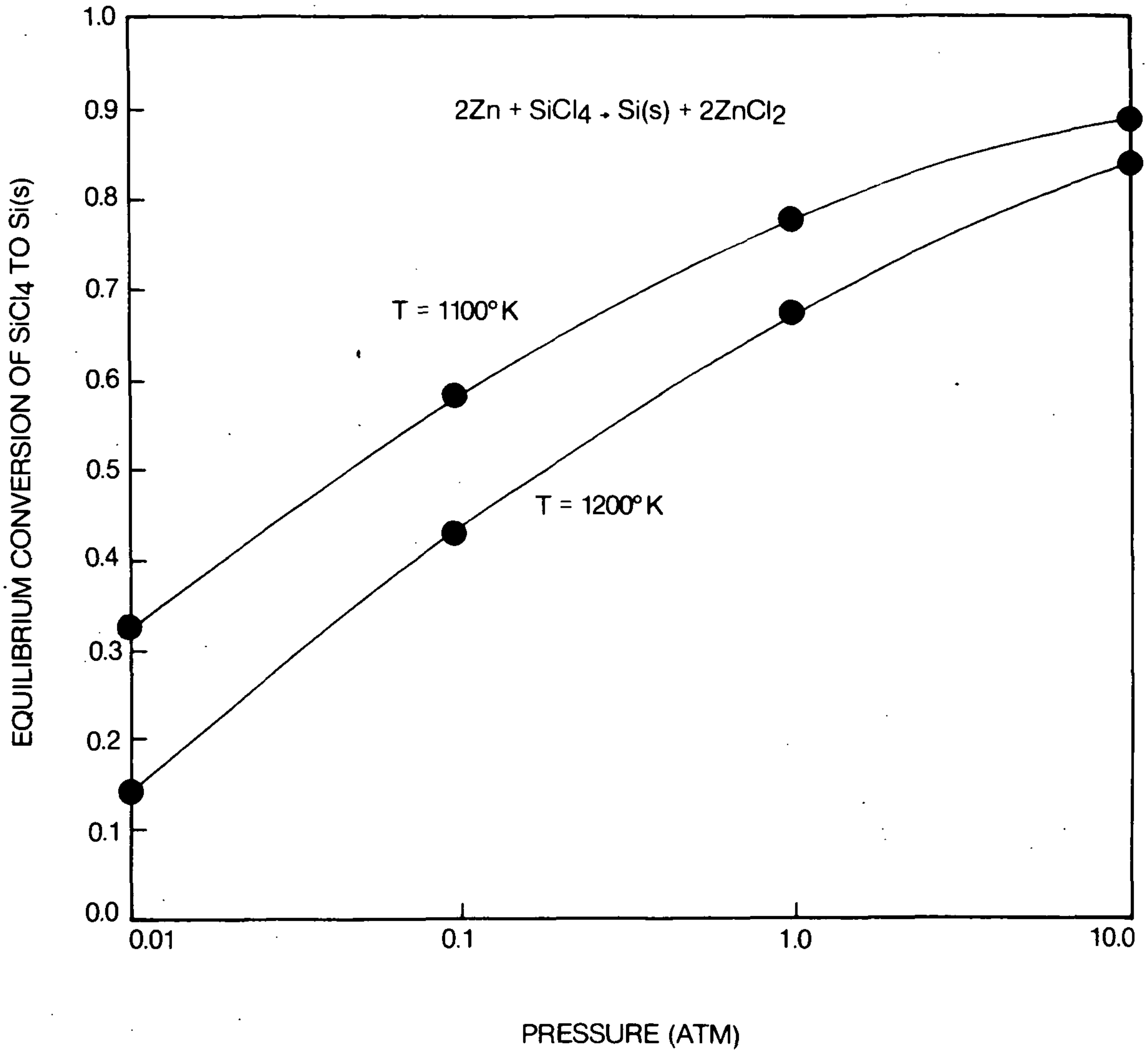


Figure 13 Equilibrium Conversion of $SiCl_4$ to Si(s) Versus Pressure For Zn/$SiCl_4$ Process (Battelle)

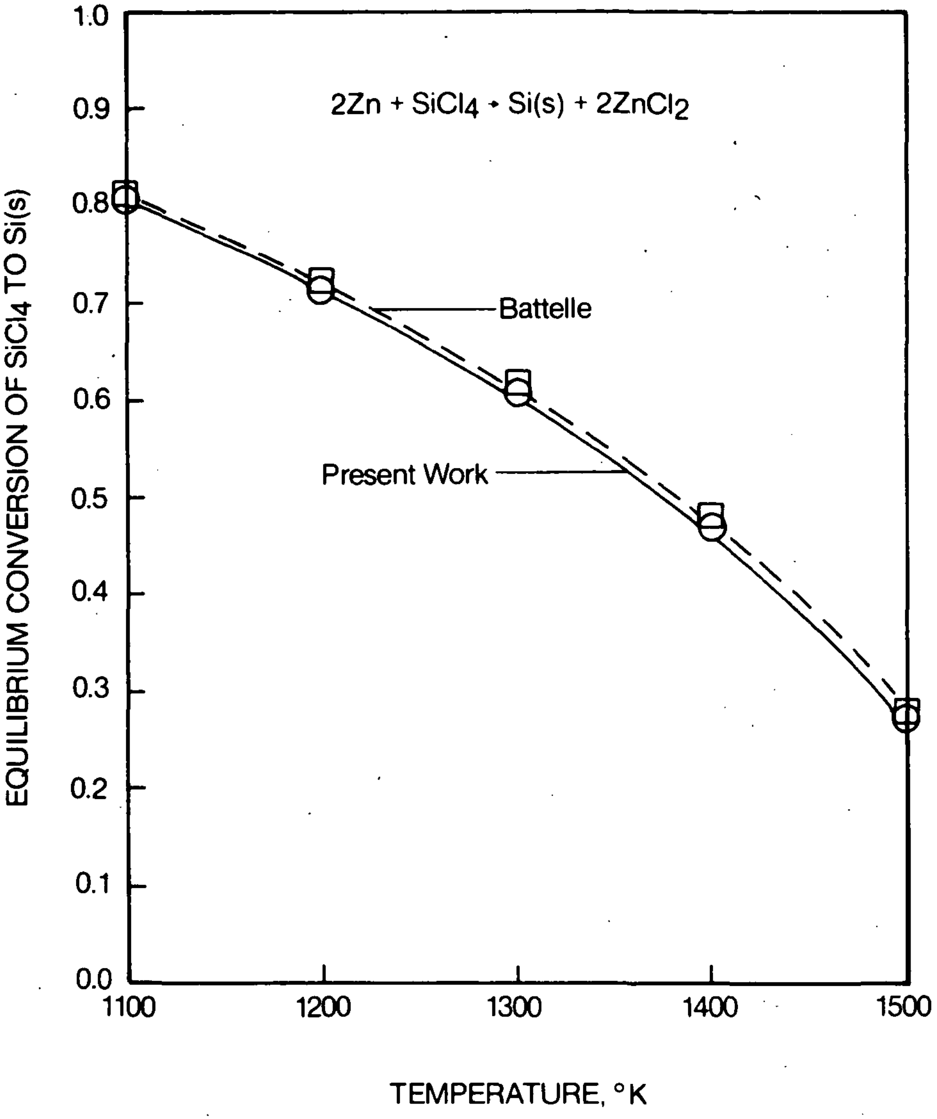


Figure 14 Equilibrium Conversion to Si(s) versus Temperature for Zn/$SiCl_4$ Process (Battelle)

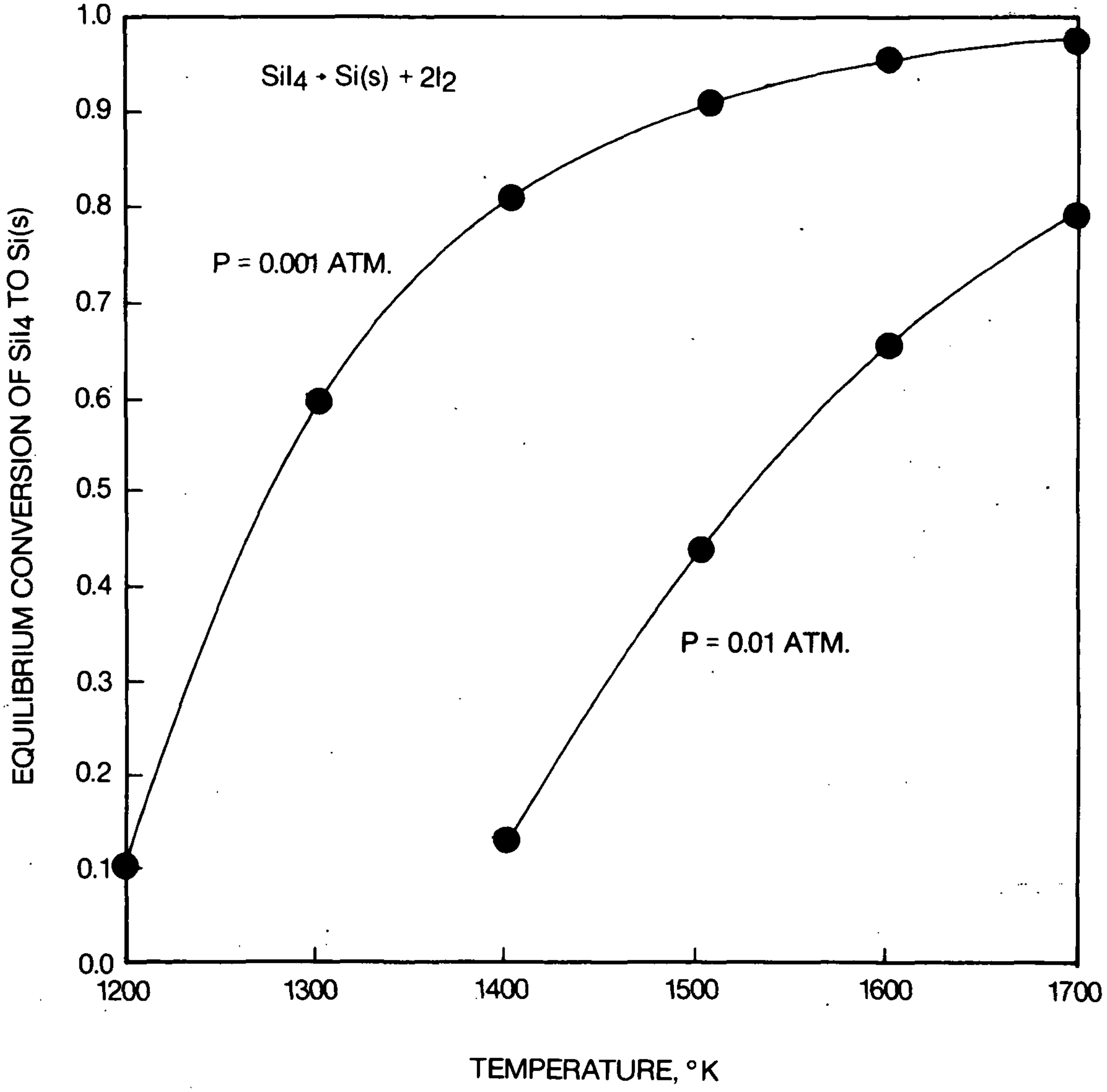


Figure 15 Equilibrium Conversion of SiI_4 to Si(s) Versus Temperature For SiI_4 Decomposition Process (Battelle)

III. ECONOMIC ANALYSES

Economic analysis activities for application to alternate processes under consideration for solar cell grade silicon were continued.

Results from a survey of methods for estimation of total product cost are shown in Table VIIIa. The typical range values for each subitem reflect the lower and upper limits.

Nominal values for the subitems were selected for application to the alternate processes. The first several subitems-raw materials, direct operating labor and utilities-will issue from the preliminary process design activity. Intermediate values between the lower and upper limits were selected on the most part for the remaining subitems. However, upper limit range values were selected on several subitems such as maintenance and repairs. The upper range values were selected on the basis of the more severe process conditions-corrosion characteristics and high process temperatures-for operations handling such silicon source materials (silane, silicon tetrachloride, silicon tetrafluoride, etc.) under consideration for production of solar cell grade silicon.

Major effort was devoted to the economic analysis for the Zn/$SiCl_4$ process (Battelle). The status including progress since the last reporting period for the economic analysis is given below for key guideline items:

	Prior	Current
• Factors for determining fixed plant investment	100%	100%
• Factors for determining total product cost	80%	100%
• Base case conditions	40%	100%
• Raw material costs	0%	100%
• Utilities cost	0%	100%
• Purchased equipment cost	40%	100%
• Production labor costs	0%	100%
• Estimation of capital investment	20%	100%
• Estimation of total product cost	10%	100%

Major conclusions and preliminary results are discussed by topic and presented in tables where appropriate.

- Base Case Conditions

All economic information has as its base January, 1975. All processes will be compared at this same time period. Important base conditions are summarized in Table IX.

- Raw Material Cost

Table X summarizes the raw material costs per kilogram of silicon in the last column, the total cost determined to be \$2.76/Kg of silicon with a credit of \$.368/Kg of silicon for by-product Cl_2. The second column is from the preliminary design (Table V), and the third column average costs per pound of material taken from reference 12 for January 1975. Column 3 times column 2 equals column 4. Only half credit was determined for Cl_2 to allow for purification costs.

- Utilities Costs

Table XI summarizes the utilities costs for this process with a total value of \$.882/Kg of silicon produced. Column 2 is taken from Table VI and column 2 from reference 7 with appropriate indices from reference 13 to establish January 1975 cost.

- Purchased Equipment Costs

The information from Table V is forwarded for determining the purchased cost for each piece of equipment. Cost information was obtained from references 1, 2, 3, 4, 5, 7, 8, 11, 14, 15, and 16. In each case the appropriate Marshall and Steven cost index ratio was used to bring costs to January 1975 values.

- Production Labor Costs

Table XIII gives a value of \$.524/Kg of silicon produced for total labor costs. Man hours are carried forward from Table VI and multiplied by the appropriate dollar/man-hour figure. The labor costs of \$6.90 and \$4.90 for skilled and semi-skilled labor were determined by averaging the labor figures from reference 17 for chemical and petroleum/coal products industries. This average is \$5.90/man-hr. By adding and subtracting \$1.00, the skilled and semi-skilled rates were estimated.

- Capital Investment

The method and factors used in Table XIV are discussed in previous reporting periods. The fixed capital investment is \$10,100,000 or \$10.1/Kg of silicon produced.

- Product Cost

The method and factors used in Table XV are taken from Table VIIIa. The total product cost is \$9.49/Kg of silicon.

Table VIIIa ECONOMIC ANALYSIS - SURVEY RESULTS FOR ESTIMATION OF TOTAL PRODUCT COST

			Typical Range	Selected Nominal Values
1.		Direct Manufacturing Cost (Direct Charges)		
	1.	Raw Materials - from prel. design	--	--
	2.	Direct Operating Labor - from prel. design	--	--
	3.	Utilities - from prel. design	--	--
	4.	Supervision And Clerical, % of 1.2	10-25%	15%
	5.	Maintenance And Repairs, % of fixed capital (50% labor, 50% materials)	2-10%	10%
	6.	Operating Supplies, % of 1.5	5-25%	20%
	7.	Laboratory Charge, % of 1.2	3-20%	15%
	8.	Patents And Royalties, % of prod. cost	0-6%	3%
2.		Indirect Manufacturing Cost (Fixed Charges)		
	1.	Depreciation, % of fixed capital	5-10%	10%
	2.	Local Taxes, % of fixed capital	0.5-4%	2%
	3.	Insurance, % of fixed capital	0.4-2%	1%
	4.	Interest, % of fixed capital	0.8%	8%
3.		Plant Overhead, % of Labor in 1.2 + 1.4 + 1.5	40-72%	60%
4.		By-Product Credit - from prel. design	--	--
4a.		Total Manufacturing Cost, 1 + 2 + 3 + 4		
5.		General Expenses		
	1.	Administration, % of manuf. cost	2.3-12%	6%
	2.	Distribution And Sales, % of manuf. cost	2.3-24%	6%
	3.	Research And Development, % of manuf. cost	2.4-6%	3%
6.		Total Cost of Product, 4a + 5		

TABLE IX BASE CASE CONDITIONS FOR PROCESS Zn/$SiCl_4$ (Battelle)

1. Capital Equipment
   - Jan. 1975 Cost Index For Capital Equipment Cost
   - Jan. 1975 Cost Index Value = 430

2. Utilities
   - Electrical, Heating, Cooling, Etc.
   - Jan. 1975 Cost Index (U.S. Dept. Labor)
   - Value = 181 (1967 Base = 100)

3. Raw Material Cost
   - Chemical Marketing Reporter
   - Jan. 1975 Value

4. Labor Cost
   - Average For Chemical, Petroleum, Coal And Allied Industries (1975)
   - Skilled 6.90 $/hr
   - Semiskilled 4.90 $/hr

TABLE X RAW MATERIAL COST FOR PROCESS $Zn/SiCl_4$ (BATTELLE)

	Raw Material	Requirement lb/Kg of Silicon	$/lb of Material	Cost $/Kg of Silicon
1.	Silicon Tetrachloride, $SiCl_4$	15.37	.135	2.075
2.	Zinc, Zn	1.42	.38	.538
3.	Caustic, NaOH 50% aqueous solution	3.85	.0382	.147
4.	Chlorine, Cl_2	-11.12	.0332	-.368
			Total Cost	2.76
			By Product Credit	-.368

TABLE XI UTILITY COST FOR PROCESS Zn/$SiCl_4$ (BATTELLE)

Utility	Requirements/Kg of Silicon	Cost of Utility	Cost $/Kg of Silicon
Electricity	15.25 Kw-hr	$.0324/Kw-hr	.4941
Steam	10.24 Pounds	$1.35/1000 Pounds	.0138
Cooling Water	29.04 Gallons	$.09/1000 Gallons	.0026
Process Water	6.41 Gallons	$.405/1000 Gallons	.0026
High Temperature Coolant	126.4 Pounds	$2.7/1000 Pounds	.341
Nitrogen	55.75 Cu. Ft.	$.50/1000 Cu. Ft.	.0279
		Total Cost	$.882/KgSi

TABLE XII PURCHASED EQUIPMENT COST FOR PROCESS Zn/$SiCl_4$ (BATTELLE)

	Equipment	Purchased Cost, $M
1.	Purified $SiCl_4$ Feed Tank	15.117
2.	Silicon Storage Bin	7.56
3.	Electrolysis Feed Tank	14.042
4.	Molten Zinc Storage Tank	6.887
5.	Raw Zinc Storage Tank	2.016
6.	$SiCl_4$ Bulk Storage Tank	21.836
7.	Secondary Column Feed Tank	3.023
8.	Waste Material Hold Tank	4.703
9.	Caustic Storage Tank	38.935
10.	Waste Neutralization Tank	16.797
11.	$SiCl_4$ Vaporizer	.513
12.	Zinc Vaporizer	104.045
13.	Silicon Cooler	2.496
14.	Zinc Condenser	136.679
15.	#1 $SiCl_4$ Cooler/Stripper	6.568
16.	#2 Cl_2 Cooler/Stripper	23.95
17.	$SiCl_4$ Recycle Cooler	1.68
18.	Column One Preheater	.756
19.	Column One Condenser	4.535
20.	Column One Calandria	2.263
21.	Column Two Condenser	4.535

Table XII (continued)

22.	Column Two Calandria	1.624
23.	Purification After Cooler	2.184
24.	Pump to $SiCl_4$ Vaporizer	1.822
25.	Electrolysis Vapor Recycle Compressor	8.398
26.	Recycle $ZnCl_2$ Pump	1.080
27.	#1 Distillation Column Calandria Pump	1.822
28.	#2 Distillation Column Calandria Pump	1.822
29.	Waste Material Pump	1.134
30.	Water Pump for Waste Neutralization	1.562
31.	Caustic Pump	1.300
32.	Waste Treatment Pump	1.822
33.	Pump to $SiCl_4$ Purification	1.562
34.	#1 Distillation Column Overheads Pump	1.562
35.	#2 Distillation Column Overheads Pump	1.562
36.	Silicon Deposition Units (6)	58.741
37.	Electrolysis Cells	1447.837
38.	#1 Distillation Column	14.613
39.	#2 Distillation Column	7.559
	Total Purchased Cost	1976.942

TABLE XIII PRODUCTION LABOR COSTS FOR PROCESS $Zn/SiCl_4$ (BATTELLE)

Unit Operation	Skilled Labor Man-hrs/KgSi	Semiskilled Labor Man-hrs/KgSi	Cost $/KgSi
1. Deposition	.01314	-	.0907
2. Vaporization	.008395	-	.0579
3. Product Handling	-	.01314	.0644
4. Vapor Condensation	.008395	-	.0579
5. Electrolysis	.01314	-	.0907
6. Tet Purification	.00584	-	.0403
7. Materials Handling	-	.01314	.0644
8. Waste Treatment	.008395	-	.0579
		Total	$.5241/KgSi

Notes
Based on labor costs of $6.90 skilled, $4.90 semiskilled.

TABLE XIV

ESTIMATION OF CAPITAL INVESTMENT FOR $Zn/SiCl_4$ PROCESS (BATTELLE)

			Invest. $1000
1.	Purchased Equipment Cost, E	100%	1977.
2.	Installation of Purchased Equipment	43%	850.
3.	Instrumentation and Controls (Installed)	13.5%	267.
4.	Piping (Installed)	41%	811.
5.	Electrical (Installed)	10.5%	208.
6.	Buildings with Services	23.5%	465.
7.	Yard Improvements	11.5%	227.
8.	Service Facilities (Installed)	55%	1087.
9.	Land	6%	119.
10.	Engineering and Supervision	32.5%	643.
11.	Construction Expenses	37.5%	741.
12.	Contractors Fee	19%	376.
		Subtotal	7769.
13.	Contingency	30% Subt.	2331.
14.	Fixed Capital Investment	➡ ➡ ➡ ➡	10,100.

TABLE XV

ESTIMATION OF TOTAL PRODUCT COST FOR Zn/$SiCl_4$ PROCESS (BALTELLE)

			$/KG
1.	Direct Manfacturing Cost (Direct Charges)		
	1. Raw Materials- from prel. design	--	2.76
	2. Direct Operating Labor- from prel. design	--	.52
	3. Utilities-from prel. design	--	.88
	4. Supervision and Clerical, % of 1.2	15%	.08
	5. Maintenance and Repairs, % of fixed capital (50% labor, 50% materials)	10%	1.01
	6. Operating Supplies, % of 1.5	20%	.20
	7. Laboratory Charge, % of 1.2	15%	.08
	8. Patents and Royalties, % of prod. cost.	3%	.29
2.	Indirect Manufacturing Cost (Fixed Charges)		
	1. Depreciation, % of fixed capital	10%	1.01
	2. Local Taxes, % of fixed capital	2%	.20
	3. Insurance, % of fixed capital	1%	.10
	4. Interest, % of fixed capital	8%	.81
3.	Plant Overhead, % of Labor in 1.2 + 1.4 + 1.5	60%	.66
4.	By-Product Credit- from prel. design	--	.37
4a.	Total Manufacturing Cost, 1 + 2 + 3 + 4		8.25
5.	General Expenses		
	1. Administration, % of manuf. cost	6%	.50
	2. Distribution and Sales, % of manuf. cost	6%	.50
	3. Research and Development, % of manuf. cost	3%	.25
6.	Total Cost of Product, 4a + 5	➡➡➡➡	9.49

IV. SUMMARY-CONCLUSIONS

Based on work efforts accomplished during this reporting period, the following summary-conclusions are made:

1. Task 1

Analysis of process system properties for silicon source materials was continued including initiation of investigation for estimation methods for critical properties. Critical volume, compressibility factor and density were estimated for silane in the absence of experimental data.

Experimental data were identified for critical temperature and pressure for silicon tetrafluoride (SiF_4). Data for the remaining critical constants--volume, compressibility factor and density---are lacking.

Investigations for generation of silicon tetrafluoride (SiF_4) from hydrofluosilic acid (H_2SiF_6) were initiated. The results for SiF_4 precursor (Na_2SiF_6) indicate that precipitation with concentrated NaCl solutions give maximum yield of Na_2SiF_6 (90-95%) without problems such as co-precipitation or hydrolysis which were encountered with other salts.

The results of investigations of the thermal decomposition of Na_2SiF_6 to generate SiF_4 indicate that the reaction proceeds readily above 500°C and that essentially complete conversion to SiF_4 occurs upon heating at 550-600°C for periods of 15-30 minutes.

2. Task 2

Major efforts were expended on the preliminary process design for the $Zn/SiCl_4$ process (Battelle). The preliminary design has been completed. Primary results for the process are presented including base case conditions, reaction chemistry, raw material requirements, utility requirements, list of major process equipment and production labor requirements. The preliminary design is based on a plant size of 1000 metric tons/year production of solar cell grade silicon.

A chemical equilibrium investigation was initiated for application to the alternate processes under consideration for solar cell grade silicon. Initial results indicate reliability of the computational procedure for the multicomponent computer program.

3. Task 3

Economic analysis activities were continued including results from a survey of methods for estimation of total product cost.

Nominal values for product cost subitems were selected for application to the alternate processes. The selected values indicate provisions for the corrosion characteristics and high process temperatures for operations handling silicon source materials such as silane, silicon tetrachloride or silicon tetrafluoride.

Major effort was devoted to the economic analysis of the Zn/Cl_4 process (Battelle). Based on the preliminary process design, capital investment (fixed) was estimated at $10,100,000 for a 1000 metric ton/year solar cell grade silicon plant. Total product cost was estimated at $9.49 per kg of silicon.

V. PLANS

Plans for the next reporting period are summarized below:

1. Task 1

Continue analyses of process system properties for silicon source materials including investigation of estimation methods for critical properties.

Investigations will be continued into the generation of SiF_4 by the thermal decomposition of Na_2SiF_6. The thermal decomposition of $BaSiF_6$ to give SiF_4 will also be investigated. The development of methods for the collection and analysis of SiF_4 will be initiated.

2. Task 2

Initiate preliminary process design for additional processes under consideration for solar cell grade silicon.

For the chemical equilibrium activity, support of the preliminary process design will be continued as needed.

3. Task 3

Continue economic analyses activities for application to processes under consideration for solar cell grade silicon.

References

1. Bauman, H. C., "Fundamentals of Cost Engineering In the Chemical Industry," Reinhold Publishing Corp., N.Y. (1964).

2. Chilton, C. H., ed., "Cost Engineering In the Process Industries," McGraw-Hill Book Co., N.Y. (1960).

3. Evans, F. L., Jr., "Equipment Design Handbook for Refineries and Chemical Plants," Vol. I and II, Gulf Publishing, Houston (1971 and 1974).

4. Guthrie, K. M., "Process Plant Estimating Evaluation and Control," Craftsman Book Company of America, Solana Beach, Calif. (1974).

5. Happel, J., and Jordan, D. G., "Chemical Process Economics," 2nd edition, Marcel Dekker, Inc., N.Y. (1975).

6. Perry, R. H., and Chilton, C. H., "Chemical Engineers' Handbook," 5th edition, McGraw-Hill Book Co., N.Y. (1973).

7. Peters, M. S., and Timmerhaus, K. D., "Plant Design and Economics for Chemical Engineers," 2nd edition, McGraw-Hill Book Co., N.Y. (1968).

8. Popper, H., ed., "Modern Cost-Engineering Techniques," McGraw-Hill Book Co., N.Y. (1970).

9. Winter, O., Ind. Eng. Chem., 61 (4), 45 (1969).

10. Perry, R. H., and Chilton, C. H., "Chemical Engineers' Handbook," 5th edition, McGraw-Hill, N.Y. (1973).

11. Jelen, F. C., "Cost And Optimization Engineering," McGraw-Hill, N.Y. (1970).

12. "Chemical Marketing Reporter," Schnell Publishing Company, New York (Jan. 1975).

13. "Wholesale Prices and Prices Indexes," U.S. Dept. of Labor, U.S. Government Printing Office, Washington D.C. (March 1975).

14. Anon. "Costs for Building and Operating Aluminum Producing Plants," Chem. Eng., 120 (Sept. 1963).

15. Zimmerman, O. T. and Lavine, I., "Cost Eng.," 6, 16, (July 1961).

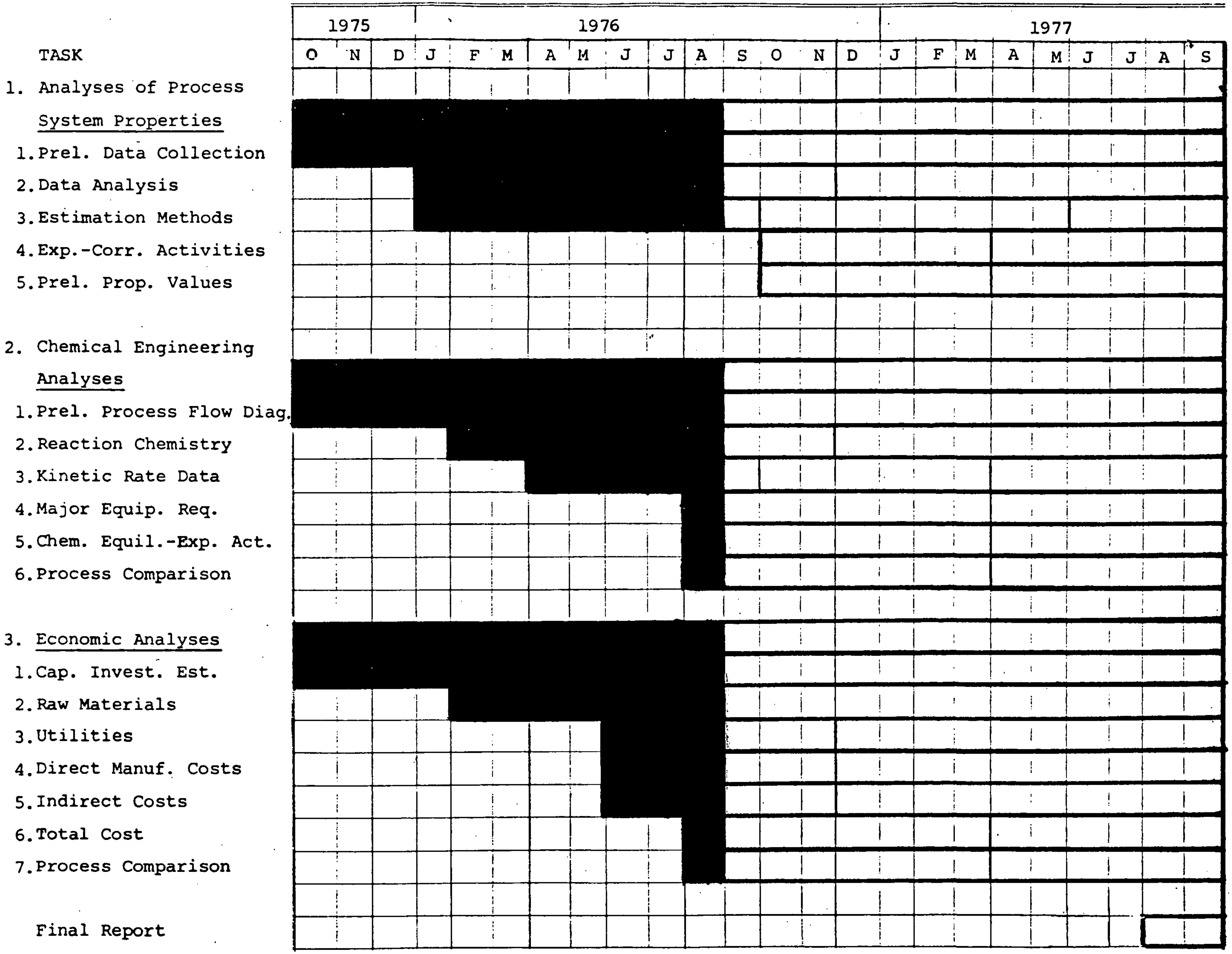
16. "Monthly Labor Review,"U.S. Dept. of Labor, Bureau of Labor **Statistics**, (June 1976).

17. del Valle, Eduardo G., "Evaluation of the Energy Transfer in the Char Zone During Ablution," Louisiana State University Ph.D. Thesis, December 15, 1974.

18. Balzhiser, R. E., Samuels, M. R. and Eliassen, J. D., <u>Chemical Engineering Thermodynsmics</u>, Prentice-Hall, Inc., 1972.

19. Hunt, C. P. and Sirtl, E., J. Electrochem Soc., <u>119</u> (No. 12) 1741 (December 1972).

MILESTONE CHART



PROCESS FEASIBILITY STUDY IN
SUPPORT OF SILICON MATERIAL TASK I

JPL Contract No. 954343