250
12-9-77

sh. 1658

ERDA/JPL/954334-77/3

LOW COST SILICON SOLAR ARRAY PROJECT

Establishment of the Feasibility of a Process Capable of Low Cost, High Volume Production of Silane (Phase I), and the Pyrolysis of Silane to Semiconductor-Grade Silicon (Phase II)

Quarterly Progress Report, April—June, 1977

By
W. C. Breneman
E. G. Farrier
J. Y. P. Mui
J. Rexer

MASTER

October 1977
(TIC Issuance Date)

Work Performed Under Contract No. NAS-7-100-954334

Union Carbide Corporation
Chemicals and Plastics
Sisterville, West Virginia

Carbon Products
Parma, Ohio

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
Division of Solar Energy

DISCLAIMER

NOTICE

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161

Price: Paper Copy $4.00 (domestic)
$6.50 (foreign)
Microfiche $3.00 (domestic)
$4.50 (foreign)

ERDA/JPL/954334-77/3
Distribution Category UC-63

LOW COST SILICON SOLAR ARRAY PROJECT

TASK I

SILICON MATERIAL TASK

Establishment of the Feasibility of a Process Capable of Low Cost, High Volume Production of Silane (Phase I), and the Pyrolysis of Silane to Semiconductor-Grade Silicon (Phase II)

QUARTERLY PROGRESS REPORT

Period Covered: April - June, 1977

JPL Contract 954334

Union Carbide Corporation

Chemicals and Plastics
P. O. Box 180
Sistersville, WV 26175

Carbon Products Division
12900 Snow Road
Parma, Ohio 44130

D. L. Bailey. .	Program Manager	E. G. Farrier.	Program Manager
W. C. Breneman.	Principal Scientist	J. Rexer . . .	Principal Scientist
J. Y. P. Mui. .	Research Chemist	R. J. Dufala .	Development Engineers
		M. R. Malay. .	

DISTRIBUTION OF THIS DOCUMENT IS [illegible]

EB

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

The purpose of this program is to establish the practicality of a process for the high volume, low cost production of silane and its subsequent pyrolysis into a semi-conductive grade silicon metal. A small process develop unit for producing silane from dichlorosilane (DCS) using a tertiary amine functional ion exchange resin as a catalyst for a redistribution reaction has been operated successfully on what is now a routine basis.

High quality silane has been produced in good yield and limiting equipment size has been identified. The silane gas product is essentially free of foreign compounds (to 5 ppm detection limit) and produces a silicon epitaxial film with a resistivity of 20 ohm cm and very strong "N" type character. Epi film quality was very good. The overall yield of silane was 92% of theory. The production rate, limited by the 2.66 cm diameter distillation column, was 112 g/hr. Design of a silicon tetrachloride (STC) hydrogenation reactor used to convert co-product STC to trichlorosilane has been completed and fabrication and installation are underway, as is a modification of the silane unit to permit use of trichlorosilane as feed, producing STC and silane.

The production of silicon by the pyrolysis of silane is currently being accomplished in a free space reactor. The free space reactor product is a very fine powder which is then consolidated by melting. The melt is cast into rods. Analysis of the product from earlier experiments indicated that metal or graphite liners in the reaction chamber region resulted in product contamination. A quartz liner is currently being evaluated in the reaction chamber. Other identified contamination sources are air borne particles and contamination during melting and/or casting. Equipment changes are being made to simplify the system and to minimize handling of the material. A troublesome dust collector was replaced by a simple porous metal filter, and an in-line operation is being evaluated.

As a partial demonstration of the system, the free space reactor was operated for 5 hours and was shut down on schedule. The silicon powder produced was transferred from the reactor to a holding chamber pneumatically, and in a sequential operation the silicon powder was transferred into a melting crucible. When sufficient melt was obtained, powder transfer was stopped and silicon rods were cast. Some contamination of the product is expected due to the use of a graphite liner in the reaction chamber and lack of control in the melting/casting operation. The product is currently being evaluated.

INTRODUCTION

The purpose of this research program is to determine the feasibility and practicality for the high volume, low cost production of silane (SiH_4) as an intermediate raw material for solar grade silicon metal. The process to be investigated is based on the synthesis of SiH_4 by the catalytic redistribution of chlorosilanes which would be produced by the reaction of hydrogen, metalurgical silicon and by-product silicon tetrachloride. The goal is to demonstrate the feasibility for a large scale (approximately 1000 metric tons per year) production cost of under $4.00 per kilogram of SiH_4.

Prior to the inception of this program in October, 1975, workers at Union Carbide have shown experimentally that pure hydrochlorosilanes can be redistributed into an equilibrium mixture of other hydrochlorosilanes by contact with a tertiary amine ion exchange resin. Patent rights for that process and improvements thereon have been filed. In addition, other workers at Union Carbide have shown experimentally that silicon tetrachloride, a by-product of the silane redistribution process, can be converted to trichlorosilane while at the same time consuming metalurgical silicon metal and hydrogen.

Thus, a closed cycle purification scheme has been proposed for converting metalurgical grade silicon into high purity solar grade silicon using volatile hydrochlorosilanes as intermediates. That process would conceptually appear in three steps as:

1. Hydrogenation of metalurgical silicon metal and by-product silicon tetrachloride to form trichlorosilane.

$$2\ H_2 + 3\ SiCl_4 + Si\ (M\text{-}G) \xrightarrow[Cu]{550^\circ} 4\ HSiCl_3 \qquad (1)$$

2. Redistribution of trichlorosilane to silane and silicon tetrachloride.

$$4\ HSiCl_3 \longrightarrow 3\ SiCl_4 + SiH_4 \qquad (2)$$

3. Pyrolysis of silane to high purity silicon.

$$SiH_4 \xrightarrow[\Delta]{} Si + 2H_2 \qquad (3)$$

Up through the previous quarter, laboratory investigations have defined the rate, equilibrium conversion and some aspects of the redistribution and hydrogenation reaction mechanisms. A small process development unit capable of pressure operation has been constructed and operated to demonstrate in a practicle manner the conversion of dichlorosilane to silane. A preliminary design of a hydrogenation unit was initiated to demonstrate the practical aspects of that key portion of the process. A preliminary design for an integrated process unit tying together both hydrogenation and redistribution was also prepared.

DISCUSSION

I. SILANE DEVELOPMENT UNIT

The small development unit for demonstrating the practical production of silane from dichlorosilane under went its initial start up last period producing silane of 97% purity at 92% yield. The goal of the present period was to upgrade the purity to "solar" grade and to stabilize unit operation. Both of these goals were accomplished. A cylinder of silane containing 1.1 kg at 1448 KPa pressure was produced, analyzed, and sent to J.P.L. as a progress sample. The material was essentially pure SiH_4. The chromatographic analysis indicated no foreign materials. (Figure 3) A 14 micron epitaxial layer of silicon deposited from SiH_4 on a 10 Ωcm "P" type silicon wafer resulted in 20 Ωcm "N" type silicon with good surface quality and relatively little compensating "P" type impurity.

The development unit was modified this quarter to assure routine production of high quality silane. (Figure 10) The silicon tetrachloride absorber/stripper unit originally designed to upgrade silane purity from 92 to 99% was replaced by a simple up flow refrigerated condenser. This unit did not perform as expected due to entrainment of $SiCl_4$ into the product gas and, more importantly, resulted in large losses of silane from the vent of the stripper used to devolatilize the silicon tetrachloride. The refrigerated condenser, operating at -60°C and 275 kPa pressure, yields an effluent silane >97% pure. The remaining impurities, chiefly monochlorosilane, would be removed by adsorption on activated carbon.

Other mechanical changes were made to improve system reliability and stability. These included: (a) isolating the on-line chromatograph carrier gas feed (b) installing a small superheater on the ion exchange reactor vapor feed line to prevent condensation (c) resizing the integral orifice differential pressure flow meter to provide a controlled, small differential pressure, and (d) removing a troublesome "liquid drainer" valve from the distillation column and reverting to a gravity system.

With these modifications the unit has operated routinely for 6 hours per day for five consecutive days, during which the product silane was collected and compressed into storage cylinders. The gas leaving the final carbon adsorption bed (operated at 25°C, 329 kPa) was always essentially pure SiH_4. Not all of the SiH_4 was compressed into cylinders. During system start up, the unit was vented to waste until all inert gas (nitrogen and helium) was purged from the system and until the gas composition leaving the final condenser had stabilized. This avoided inadvertantly overloading the relatively small carbon bed and contaminating the downstream system. It also served to identify a steady state operating situation so that the collected silane would be representative of longer term unit operation. This start up period normally lasted 1 to 2 hours each day.

The refrigerated upflow condenser functioned well to dampen flow and composition fluctuations. The composition of the gas entering and leaving the condenser were:

	Entering	Leaving
SiH_4	86.9	96.3
H_3SiCl	7.3	3.6
H_2SiCl_2	4.9	0.1
$HSiCl_3$	.9	-

Typical chromatograms are shown in Figures 1 and 2. For silane leaving the carbon bed, the chromatogram, Figure 3, indicated all chlorosilanes had been removed.

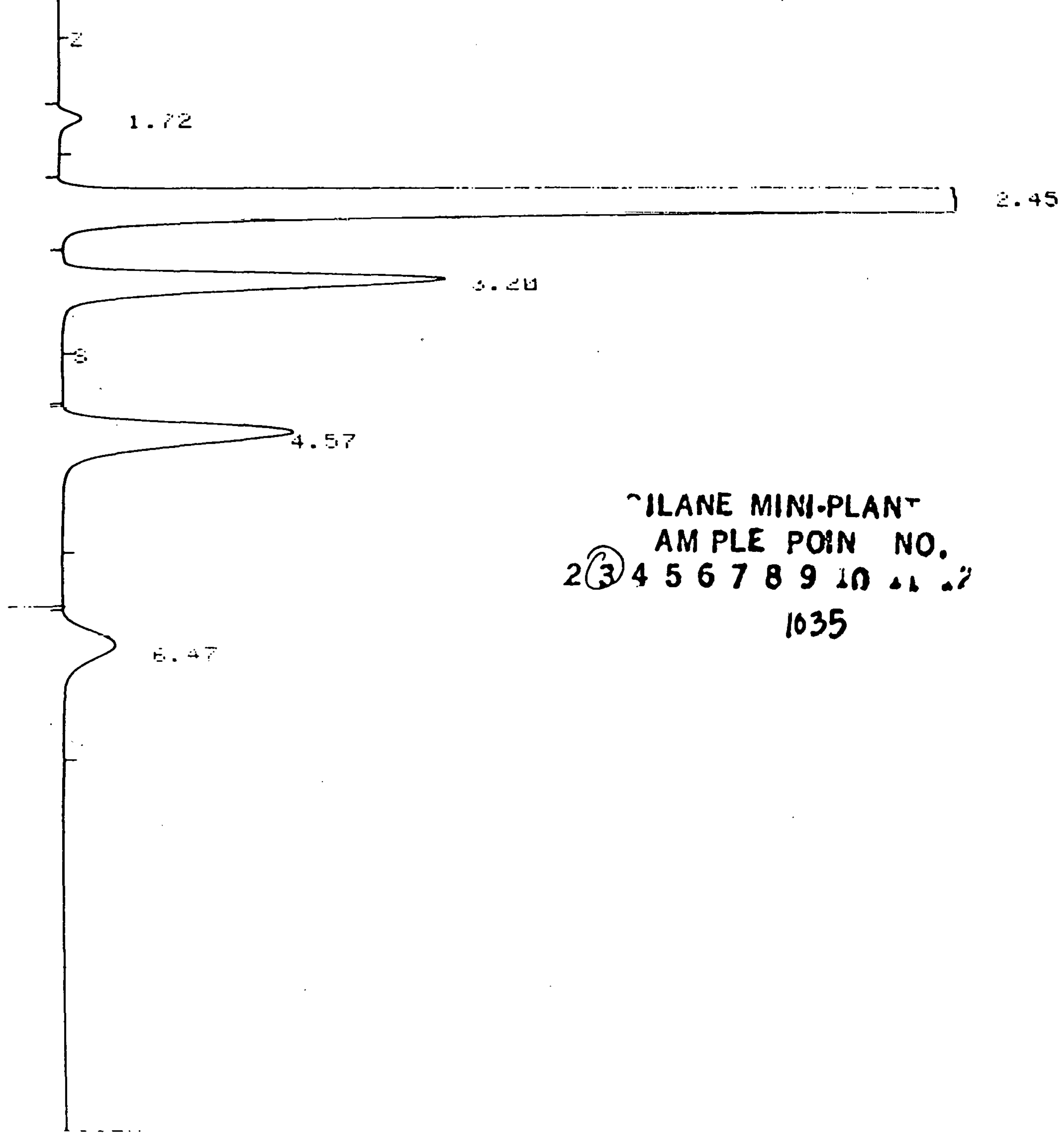
The compressor, a diaphragm style .3 cfm capacity unit, was used to pump the product silane into high pressure gas bottles. The cylinders had previously been baked under vacuum and maintained under a slight positive pressure with helium. After connecting them to the silane compressor, the helium was pumped off and the silane pumped in. The compressor system performed flawlessly boosting the pressure from 136 kPa to 1550 kPa. A pulsation damper was installed on the compressor suction pressure gauge to prolong gauge life and to permit more accurate measurement. No other modifications were required.

The carbon bed used to remove traces of chlorosilanes was 2.66 cm diameter by 122 cm high and contained 400 gram of activated carbon, Union Carbide JXC 6 x 8 mesh. This carbon had been previously characterized to absorb approximately 20 weight percent dichlorosilane at 25°C from a 5% concentration gas stream. (Figure 9)

FIGURE I

On-line Chromatogram

Crude Silane Gas from Distillation Column



SILANE MINI-PLANT
SAMPLE POINT NO.
2 [✓ 3] 4 5 6 7 8 9 10 11 12
1635

NORM

RT	EXP RT	AREA		CAL #	AMT
1.72	1.72	28140	Pressure Surge	2	0.703
2.45	2.45	5675000	SiH_4	3	85.779
3.20	3.20	368800	H_3SiCl	4	7.316
4.57	4.57	464700	H_2SiCl_2	1	4.884
6.47	6.47	174400	$HSiCl_3$	5	1.318

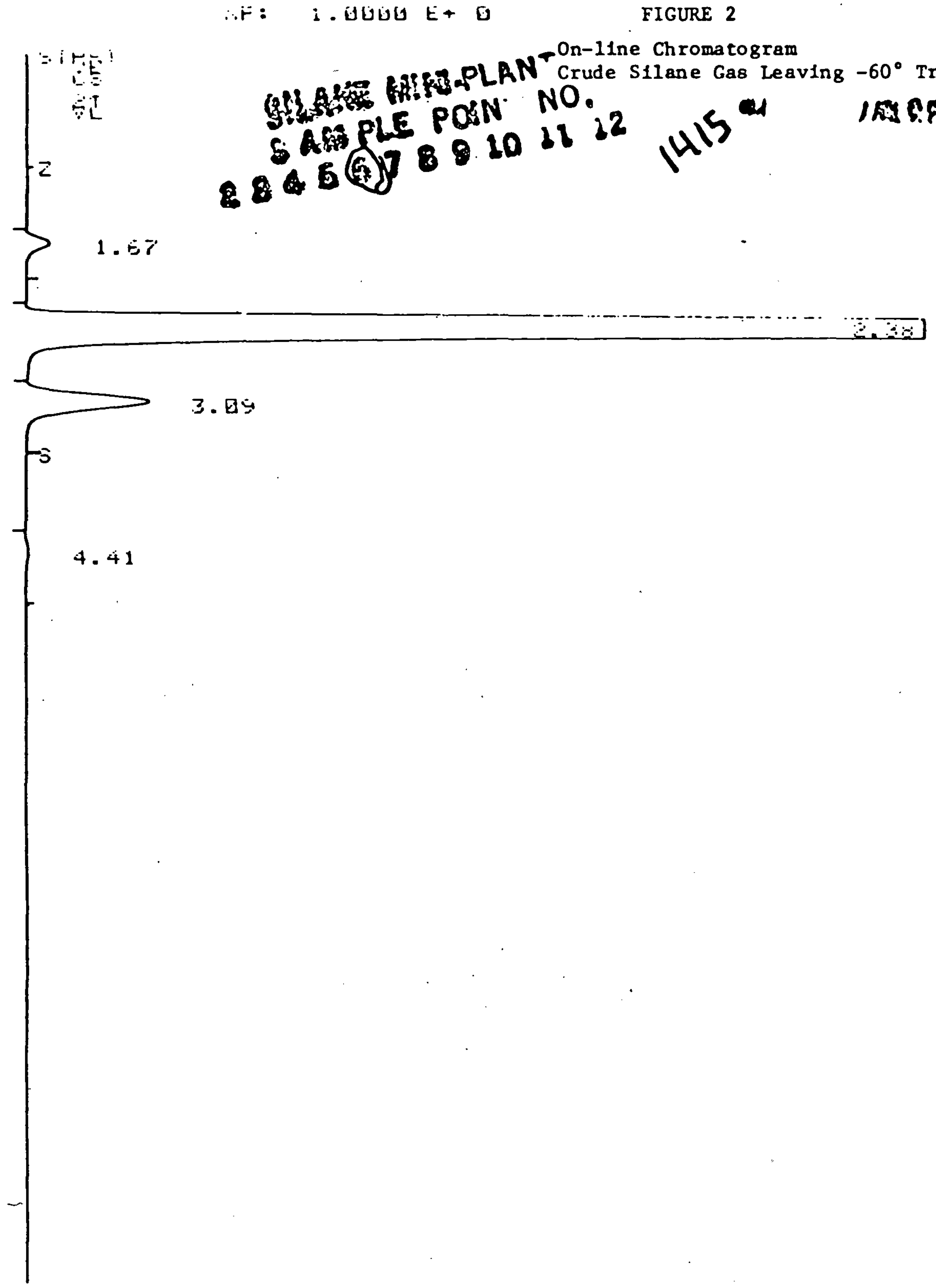
RF: 1.0000 E+ 0

FIGURE 2

On-line Chromatogram
Crude Silane Gas Leaving -60° Trap

SILANE MINI-PLANT
SAMPLE POINT NO.
2 3 4 5 [✓ 6] 7 8 9 10 11 12

1415 [illegible]

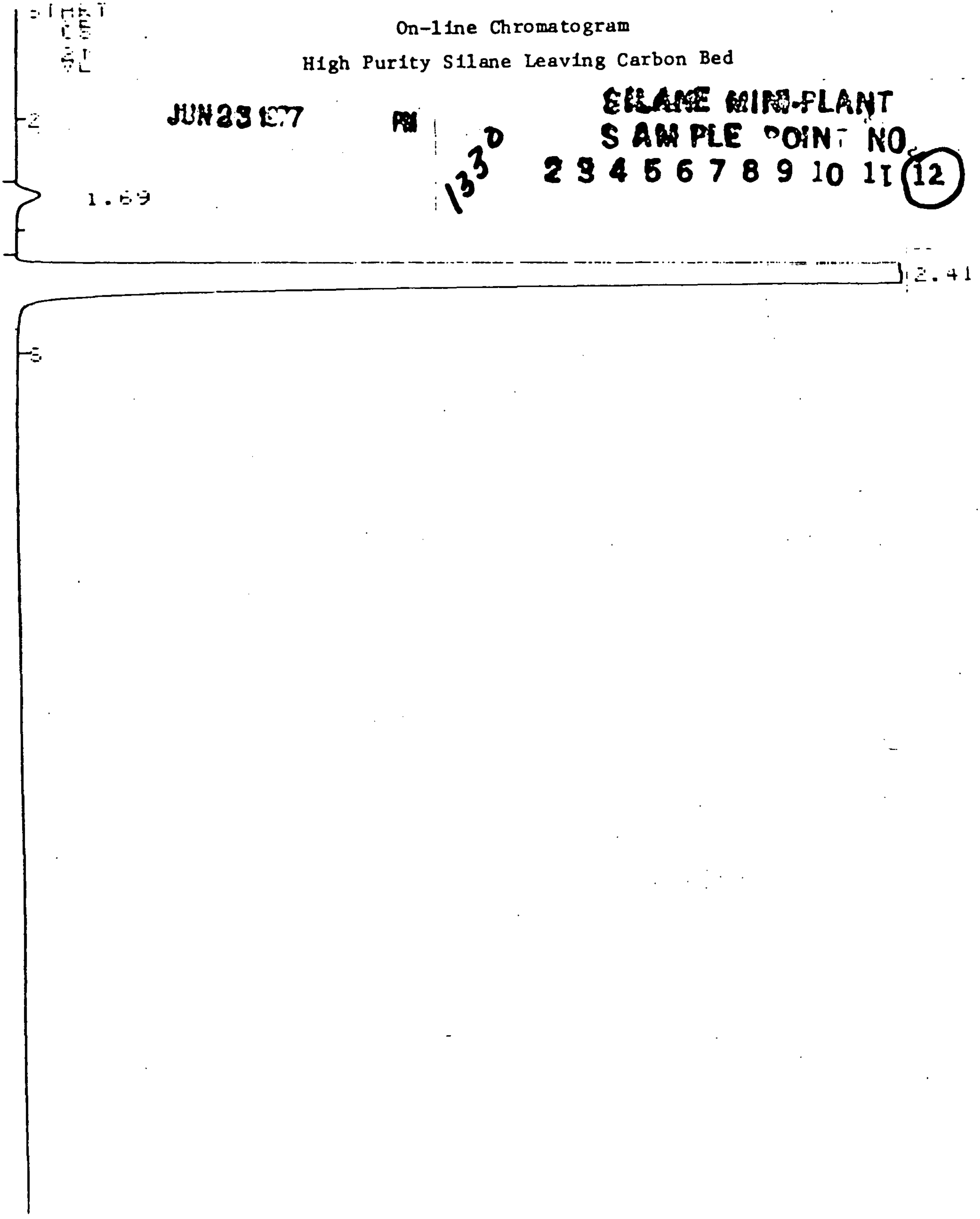


```
hp 5830A
NORM
  RT          EXP RT           AREA                      CAL #      AMT

  1.67          1.65           26890  Pressure Surge       2        1.065
  2.38          2.36         3901000  SiH4                 3       95.214
  3.09          3.08          177400  H3SiCl               4        2.608
  4.41          4.57            5691  H2SiCl2 R            1        0.093
```

FIGURE 3

On-line Chromatogram

High Purity Silane Leaving Carbon Bed



JUN 23 1977 PM

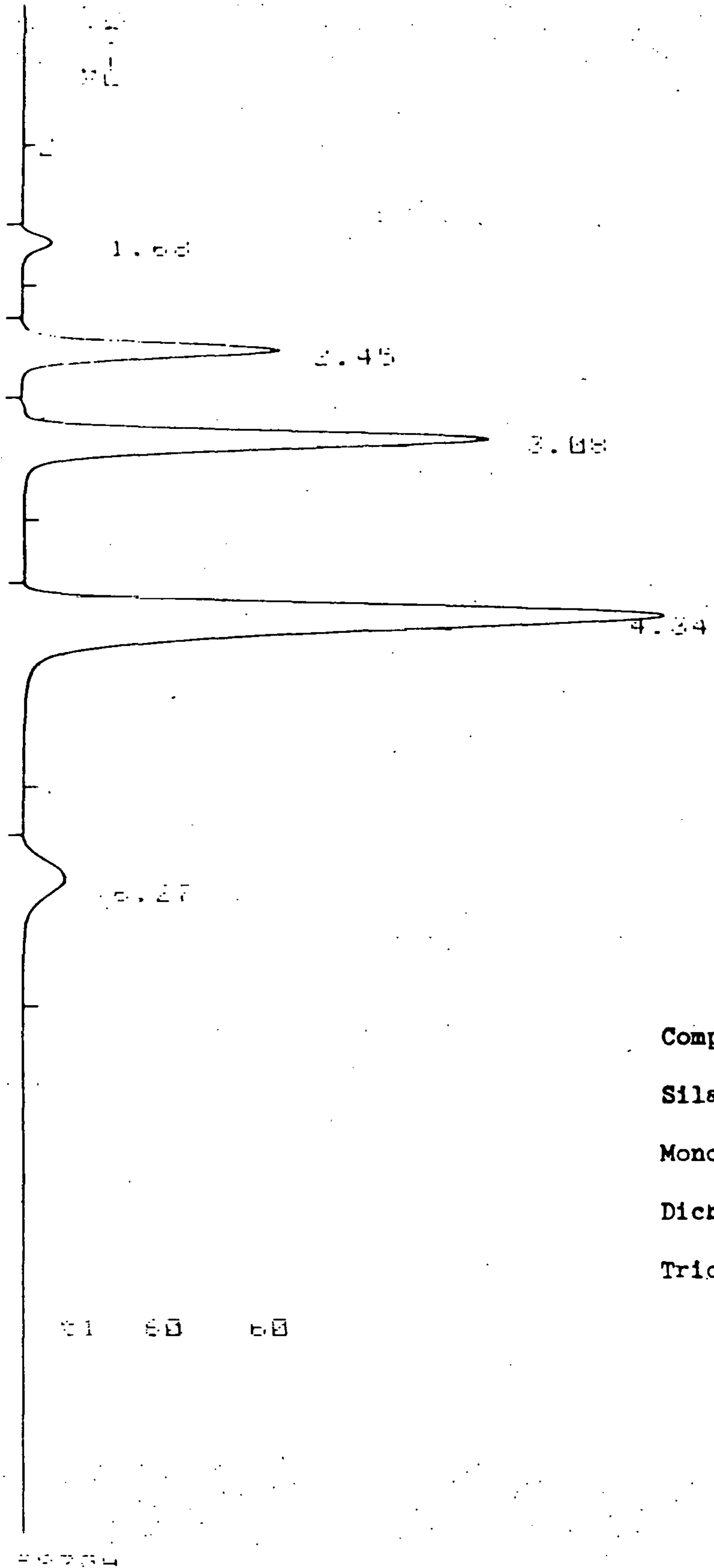
1330

SILANE MINI-PLANT
SAMPLE POINT NO.
2 3 4 5 6 7 8 9 10 11 ⑫

```
hp 5830A
NORM
    RT          EXP RT            AREA                    CAL #      AMT

   1.69          1.72            27440  Pressure Surge       2      1.101
   2.41          2.45          4076000  SiH4                 3     98.899

             AF:   1.0000 E+ 0
```

FIGURE 4
On-line Chromatogram
Gas Stream Entering Redistribution Reactor

SILANE MINI-PLANT
SAMPLE POINT NO.
2 3 4 5 6 7 8 ~~9~~ 10 ⑪ 12
JUN 28 1977 1430



Silane

Monochlorosilane

Dichlorosilane

Trichlorosilane

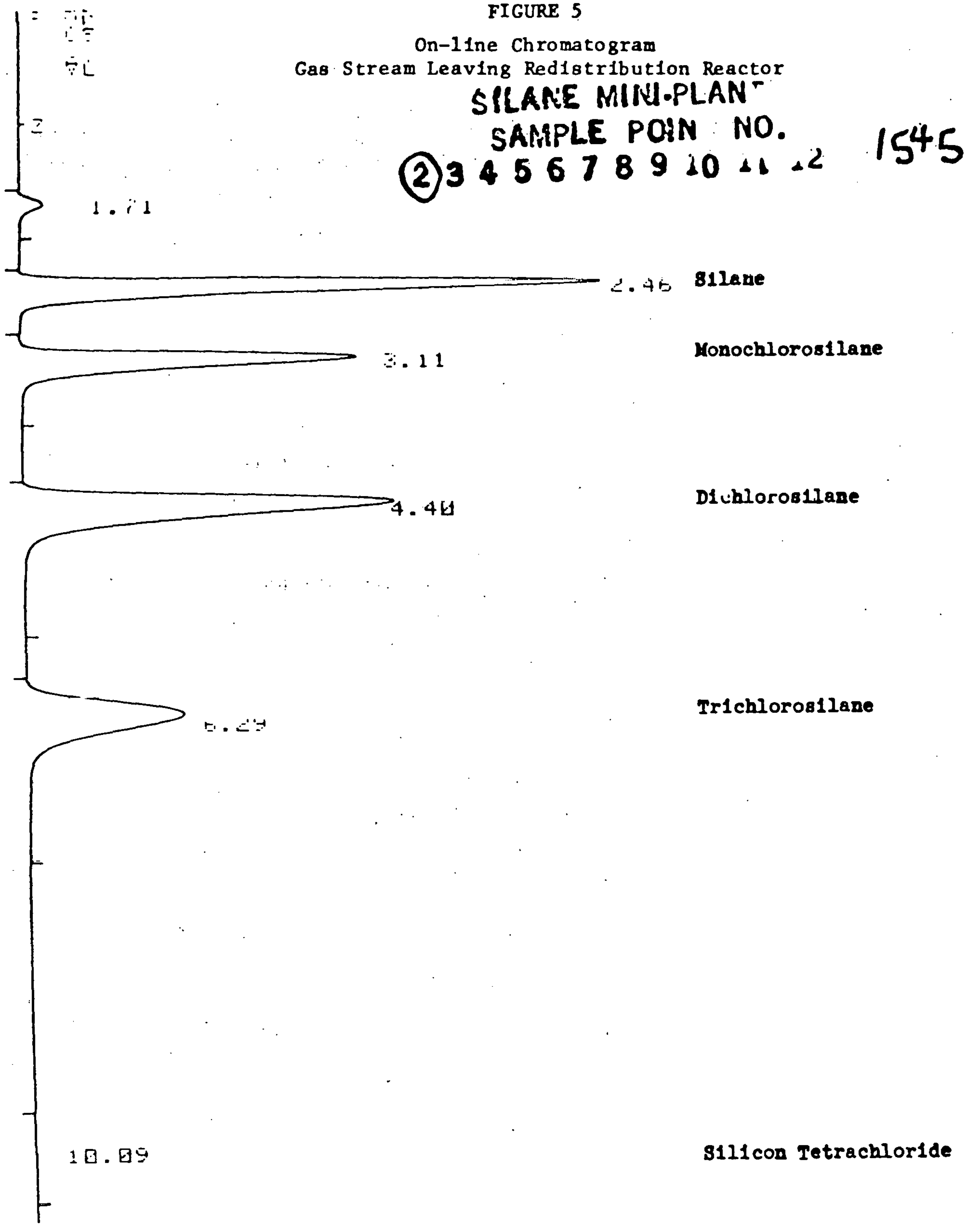
Compound	Mole %
Silane	18.6
Monochlorosilane	35.5
Dichlorosilane	43.1
Trichlorosilane	2.8

FIGURE 5

On-line Chromatogram
Gas Stream Leaving Redistribution Reactor

SILANE MINI-PLANT
SAMPLE POINT NO.
② 3 4 5 6 7 8 9 10 11 12

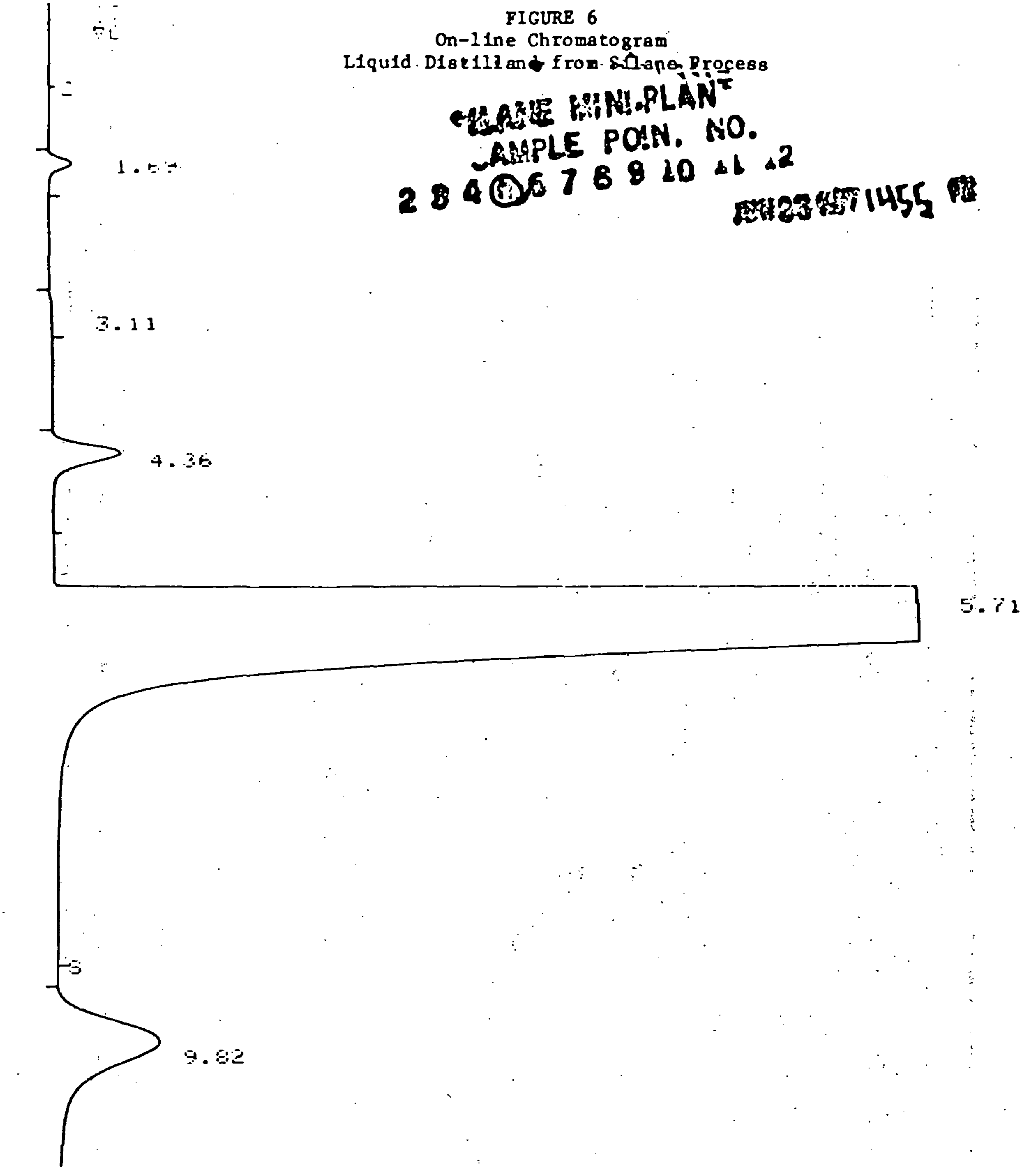
1545



```
HP 5830A
AREA %

  RT          AREA       AREA %
  1.71        22350       1.127
  2.46       554200      28.190
  3.11       472900      20.113
  4.40       747400      21.636
  6.29       444206      18.857
 10.09         1215       0.077
```

FIGURE 6
On-line Chromatogram
Liquid Distilland from Silane Process

SILANE MINI-PLANT
SAMPLE POIN. NO.
2 3 4 ⑤ 6 7 8 9 10 11 12
JUN 23 1987 1455

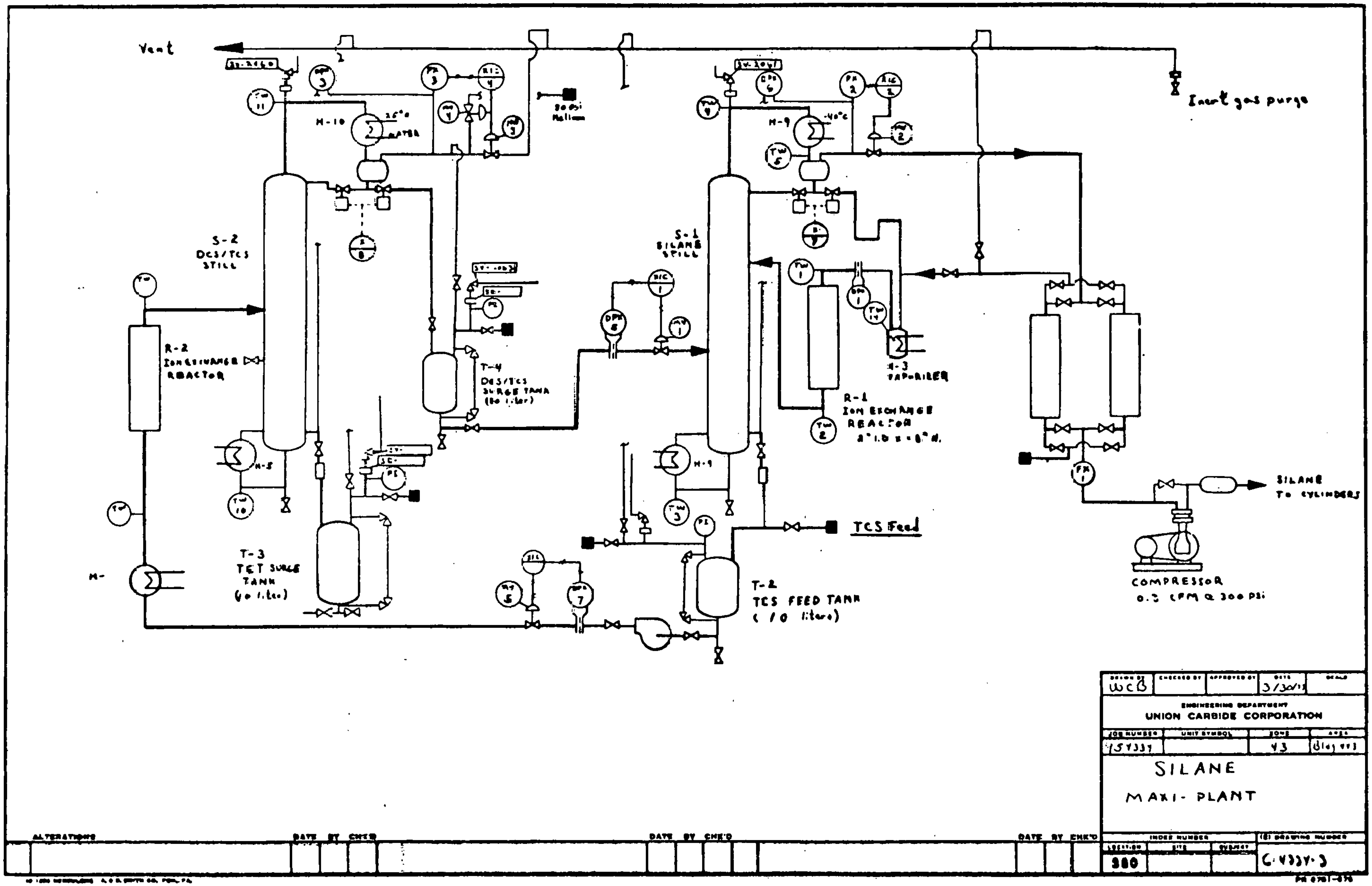


```
RP 5830A
AREA %

  RT          AREA      AREA %

 1.69        27130       0.258
 3.11         4064       0.039
 4.36       127500       1.213
 5.71      9860000      93.802
 9.82       492800       4.688

            RF:   1.0000 E+ 0
```

Monochlorosilane
Dichlorosilane
Trichlorosilane
Silicon Tetrachloride

SILANE MINI-PLANT

FIGURE 7


Vent
Inert gas purge
30 psi Helium
H-10
25°C WATER
H-9
-40°C
S-2
DCS/TCS STILL
S-1
SILANE STILL
R-2
ION EXCHANGE REACTOR
T-4
DCS/TCS SURGE TANK
(80 liter)
T-3
TET SURGE TANK
(60 liter)
H-8
H-7
H-
H-3
VAPORIZER
R-1
ION EXCHANGE REACTOR
T-2
TCS FEED TANK
(10 liters)
TCS Feed
SILANE To CYLINDERS
COMPRESSOR
0.5 CFM @ 300 psi
ALTERATIONS
DATE
BY
CHK'D
WCB
3/30/7
ENGINEERING DEPARTMENT
UNION CARBIDE CORPORATION
JOB NUMBER
UNIT SYMBOL
ZONE
AREA
157337
43
Bldg 443
SILANE
MAXI- PLANT
INDEX NUMBER
DRAWING NUMBER
LOCATION
SITE
SUBJECT
380
C-4334-3

The average silane production rate during the month was 80 gram/hr. This rate appears limited by the distillation column diameter, although the instantaneous maximum rate is somewhat higher. The residence time for the chlorosilane gases in the vapor phase redistribution reactor was maintained at 8.75 seconds. As shown in Figures 4 and 5 the chromatograms of the inlet and outlet composition shows the conversion of a stream rich in DCS and MCS into one containing significant SiH_4 and TCS and no foreign materials. The ratio of recycle flow to DCS feed through the reactor was 1.8:1. To date no significant catalyst deactivation has been noted and reactor pressure drop has held essentially constant at .020 KPa/cm at 5.57 cm/sec superficial gas velocity.

II. CARBON ADSORPTION OF CHLOROSILANES

The purification of silane using activated carbon as an adsorbent was studied this period. It had previously been determined (Quarterly Report, July, 1976) that carbon would remove monochlorosilane from an inert gas stream, but the ability to regenerate the carbon was not determined and the effect of temperature on carbon bed capacity at various concentrations of chlorosilanes was similarly not known.

An apparatus was constructed as shown in Figure 8 to allow heating or cooling of a two foot long bed of carbon. Calibrated flow meters were used to blend dichlorosilane with nitrogen at various concentrations. A bubbler filled with distilled water containing a small amount of bromothymol blue indicator was used on the bed effluent to sense the chlorosilane break through point. In each run, the bed was purged with pure nitrogen at 200°C until no chloride was detected by moist litmus at the bed outlet. Then the bed was adjusted to the appropriate temperature and the selected concentration of H_2SiCl_2 in N_2 allowed to flow until the indicator sensed chloride. The results at -40°C, 25°C, and 200°C are shown in Figure 9. The conclusion is that carbon (in this case Union Carbide JXC 6 x 8 mesh) can be effectively used to remove large concentrations of chlorosilanes from an inert gas (SiH_4 would be considered inert in this case). Furthermore, the carbon can be regenerated by a small reverse flow of inert gas at 200°C in about 1 1/2 hours. If pure SiH_4 were used as a purge gas, recovery and recycle of the di- and mono- chlorosilanes would be possible or periodic purging with helium could be used to expell electronically active impurities.

A summary of the development unit's operating parameters are listed in Table 1. The maximum silane production rate for the current system is 140 gram/hr. The limiting item is the diameter of the distillation column. The 2.5 cm column has a vapor rate

FIGURE 8

Carbon Adsorption Apparatus

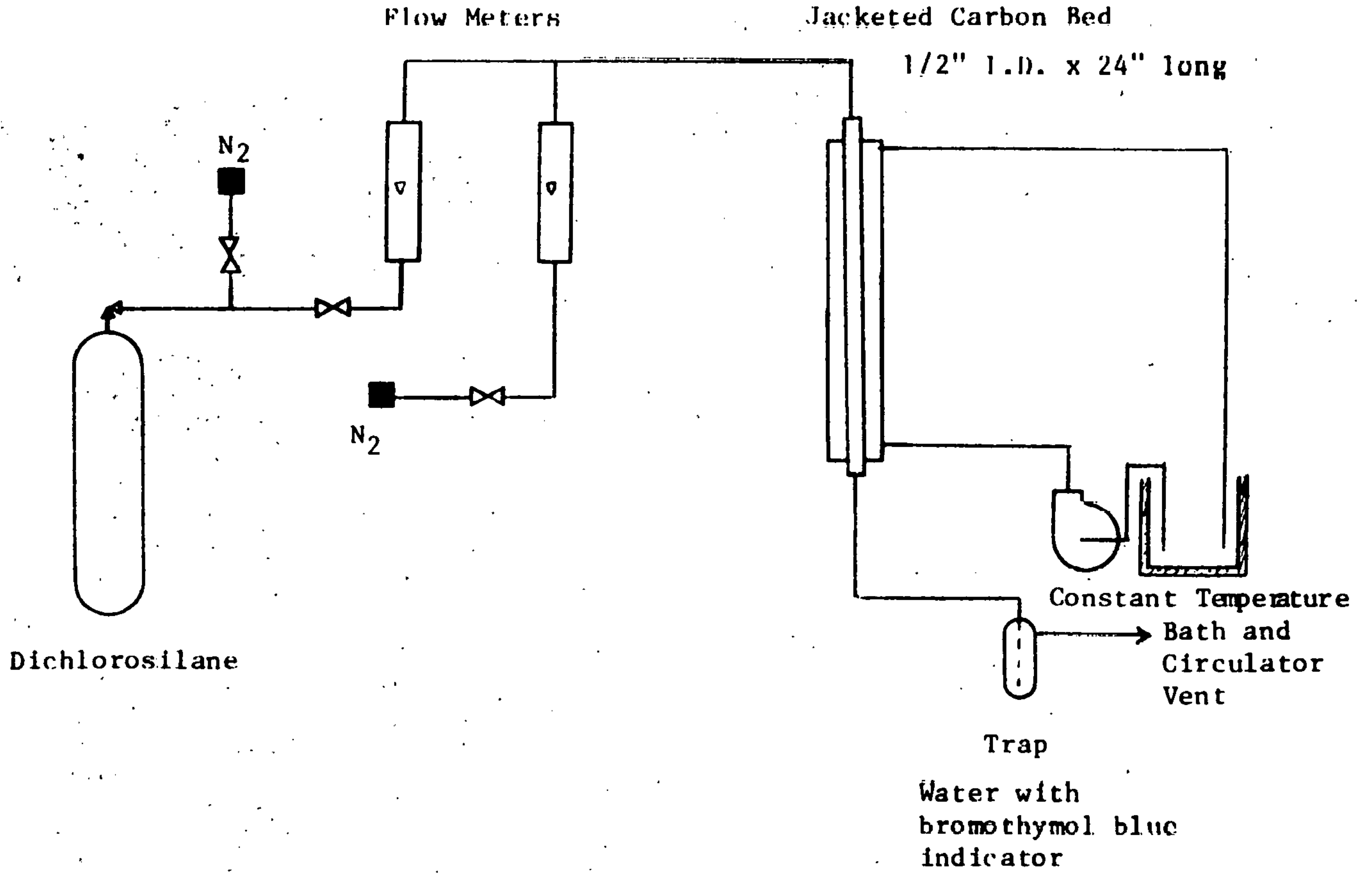


FIGURE 9

Adsorption of Dichlorosilane on Union Carbide JXC Carbon 6 x 8 mesh

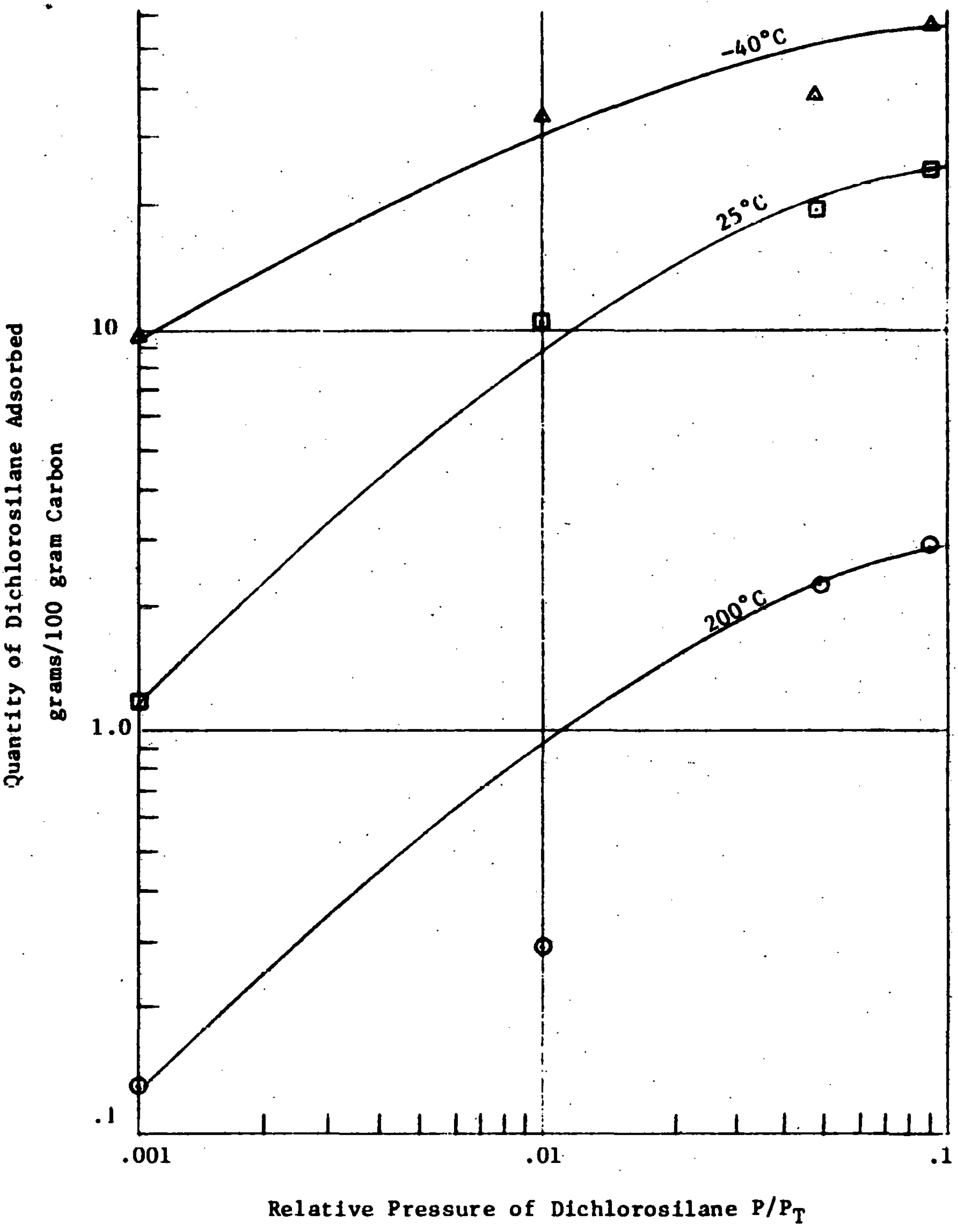


TABLE 1

OPERATING PARAMETERS
SILANE DEVELOPMENT UNIT

Dichlorosilane Feed Rate	760 gram/hr.
Silane Production Rate	80 gram/hr.
System Pressure	345 KPa
Reactor Residence Time	8.75 seconds
Reactor Temperature	55°C
Distillation Column Reflux Ratio	1.8:1
Theoretical Trays	24

limitation of 1.64 kg/hr/cm^2. At a reflux ratio of 2:1 and with the distillate being recycled through the reactor back to the column, this limit is approached at a silane production rate of 140 g/hr. In future work, now that unit operation has been stabilized, variations in reflux ratio (and corresponding variations in distillate and distilland compositions) will be compared with silane yield and production rate to more fully define the system operating sensitivity.

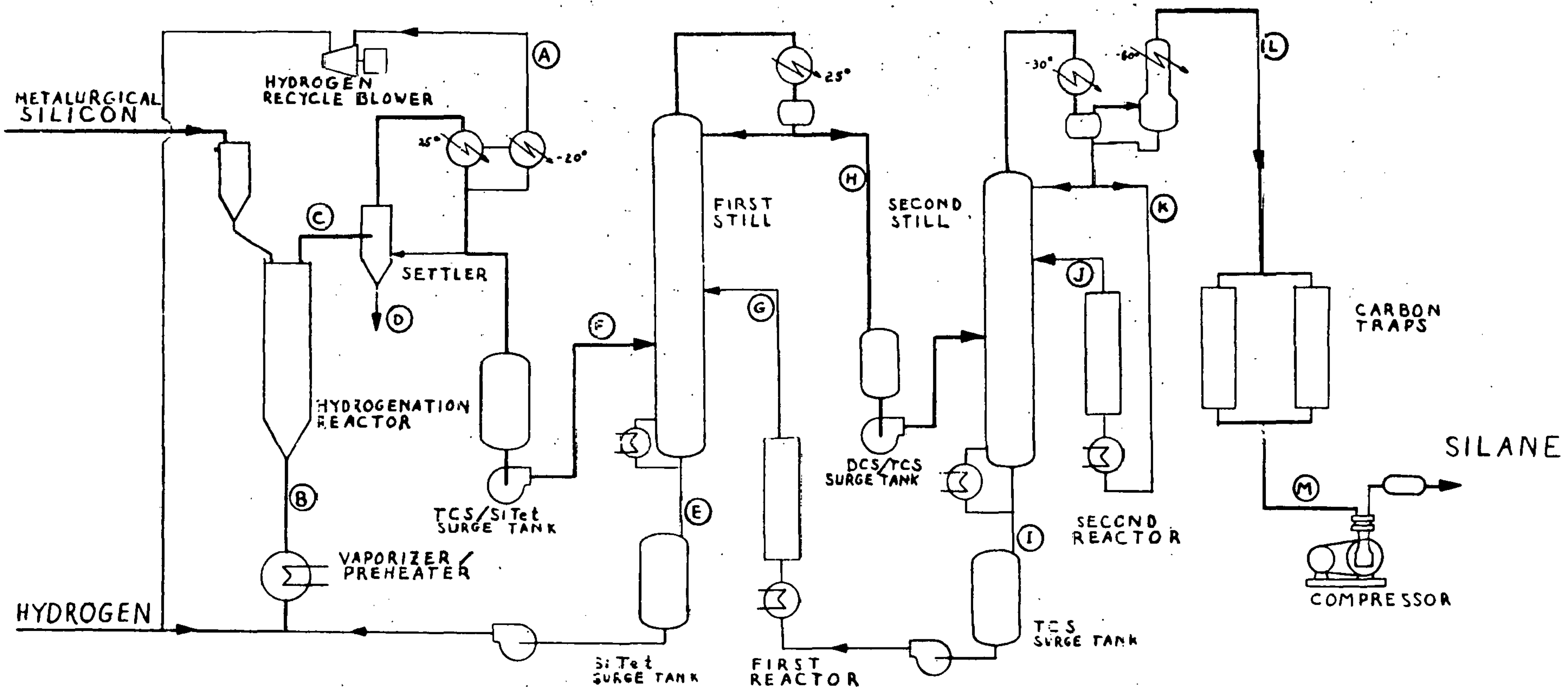
III. INTEGRATED PROCESS UNIT

The design of the modifications to the silane process development unit to permit use of trichlorosilane feed (or a tri-tet mixed feed) is in progress. The flow sheet (Figure 10) was described in last quarter's report and includes three basic items which will be added to the existing unit; a 5 cm diameter by 152 cm high distillation column, a 10 cm diameter by 152 cm high ion exchange resin reactor, and surge tank for a di/tri-chlorosilane distillate. Necessary accumulator tanks will be provided in the design to allow the various parts of the system to be operated independently of the others. Of course, in the integrated operation, these tanks would act to dynamically balance the system, but would not alter the purity of the streams.

The new distillation column, operating at 345 kPa will be fed a near equilibrium mixture of di-tri-and tetrachlorosilanes product of redistribution of a high purity trichlorosilane stream from the present silane development unit. Additionally, the tri-tetrachlorosilane product of the hydrogenation reactor will also be fed to the unit. In some preliminary runs, this may be a synthetic mixture. The column, 152 cm high is estimated to have 24 theoretical separation stages at a reflux ratio of 1.8:1 and will recover 99% of the trichlorosilane in the distillate. This distillate will be fed to the distillation column presently used to separate trichlorosilane from the lighter components including silane. Presently, this column, 2.5 cm diameter x 152 cm high operates at 1.8:1 reflux ratio and produces a distilland containing less than 1.5% dichlorosilane. Under the new flow scheme, the reflux ratio will be increased to 5:1 to achieve the same composition profile with the leaner 11% dichlorosilane feed.

Physically, the silicon tetrachloride absorber/stripper section of the process development unit will be removed and the supporting facilities, condenser, instruments, etc. utilized where applicable with the new reactor and distillation unit. The forecast completion date for the work is September 30, 1977.

FIGURE 10



	A	B	C	D	E	F	G	H	I	J	K	L	M
TEMP. °C	-17	550	550	110	124	25	80	25	75	60	-30	-60	-40
PRESS. psi	50	50	45	45	50	50	50	40	40	40	40	30	30
SiH_4 (H_2)	(91.7)	(49.4)	(45.9)	-	-	-	-	-	-	25.6	3.4	97	99.9+
H_3SiCl	-	-	-	-	-	-	-	-	-	16.3	24.4	2.5	-
H_2SiCl_2	-	-	-	-	-	-	9.9	11.0	0.9	37.8	68.2	0.5	-
$HSiCl_3$	1.7	.3	10.8	20	1.0	20	79.9	87.9	98.0	20.3	4.0	-	-
$SiCl_4$	3.6	49.2	43.3	80	99.0	80	10.2	1.1	0.1	-	-	-	-
FLOW	6.6	139.7	138.7	7.16	131	132	139.8	140.9	139.8	12.8	12.8	1.06	1.0

DATE BY CHK'D

DRAWN BY	CHECKED BY	APPROVED BY	DATE	SCALE
WCB			7/30/77	

ENGINEERING DEPARTMENT
UNION CARBIDE CORPORATION

JOB NUMBER	UNIT SYMBOL	ZONE	AREA
954334			

LOW COST
SILANE PROCESS

LOCATION	SITE	SUBJECT	DRAWING NUMBER
380			C-4334-5

A pre-start up safety team who will oversee both the hydrogenation and redistribution reactor systems has conviened and approved the preliminary design. Calling the team at this early date should largely eliminate any last minute safety oriented problem areas and permit smooth startup of the units.

IV. HYDROGENATION REACTOR SYSTEM

Fabrication has begun for a system to hydrogenate silicon tetrachloride in a fluid bed of metalurgical silicon. The detailed description of the reactor itself and the system flow sheet (Figure 11) was given in last quarter's report. The primary change since that date was to establish the reactor pressure rating at a nominal 2000 kPa (300 psig), up from the original 1000 kPa. This change will permit a more conclusive study of pressure effects on the equilibrium and kinetics of the reaction. This gas phase reaction is reportedly enhanced by pressure; a 2000 kPa rating is well within the ability of normal materials of construction at 500°C. The reactor design is shown in Figure 12. It consists basically of a 122 cm (48 inch) long 3 inch schedule 40 (7.8 cm I.D.) type 304 L stainless steel pipe equipped with standard ASA 300 lb. rated flanges. The flange seals will be of pure grafite "Grafoil" material. The gas entrance cone of 20° half angle as calculated for the particular feed conditions is provided by a machined graphite block resting inside the reactor. The first 60 cm of the reactor is heated by electric radiant heaters and the remainder well insulated. This design will permit studies over a range of temperatures (300-600°C) and pressures (100-2000 kPa) and residence time while making the system easy to disassemble and inspect or recharge for different experimental conditions. The downstream condenser system has been designed to produce liquid trichlorosilane silicon tetrachloride mixture free of settleable solid impurities. On-line chromatography used to analyze the products will permit accurate and rapid gathering of reaction data. Unreacted hydrogen will not be recycled, but will be analyzed to provide data for further engineering design.

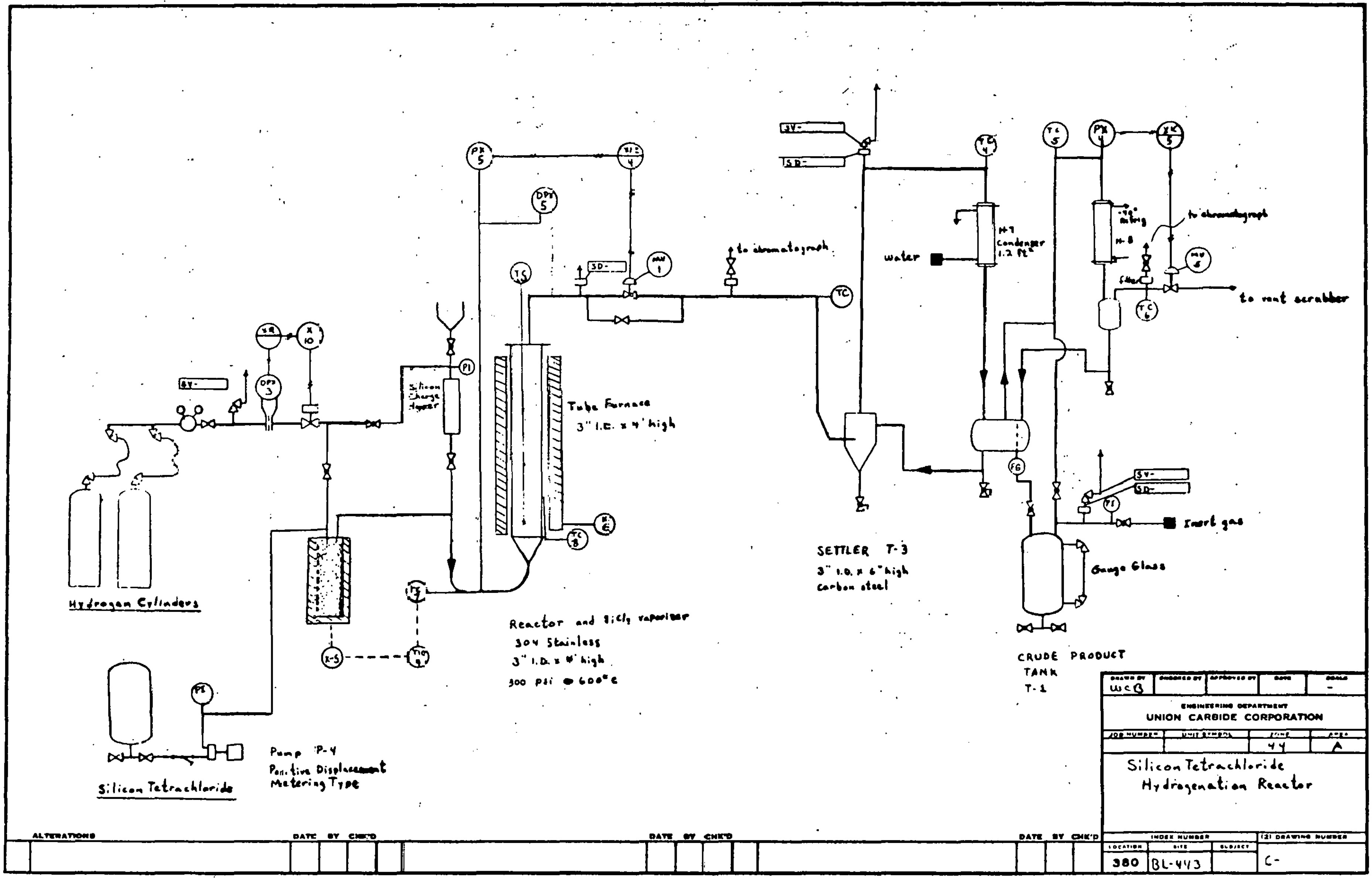
V. LABORATORY STUDIES

a) Reaction Rate Measurements on the Disproportionation of $HSiCl_3$ and $DSiCl_3$

The apparatus for the reaction rate measurements on the disproportionation of $HSiCl_3$ and of $DSiCl_3$ in a bed of A-21 resin catalyst was schematically shown in Figure 13. The reactor assembly was identical to the one used for the disproportionation of $HSiCl_3$ in the presence of DCl reported last period (see Quarterly Report, April, 1977). The reactor was recharged with a fresh sample of 10 g A-21 resin catalyst.

FIGURE 11

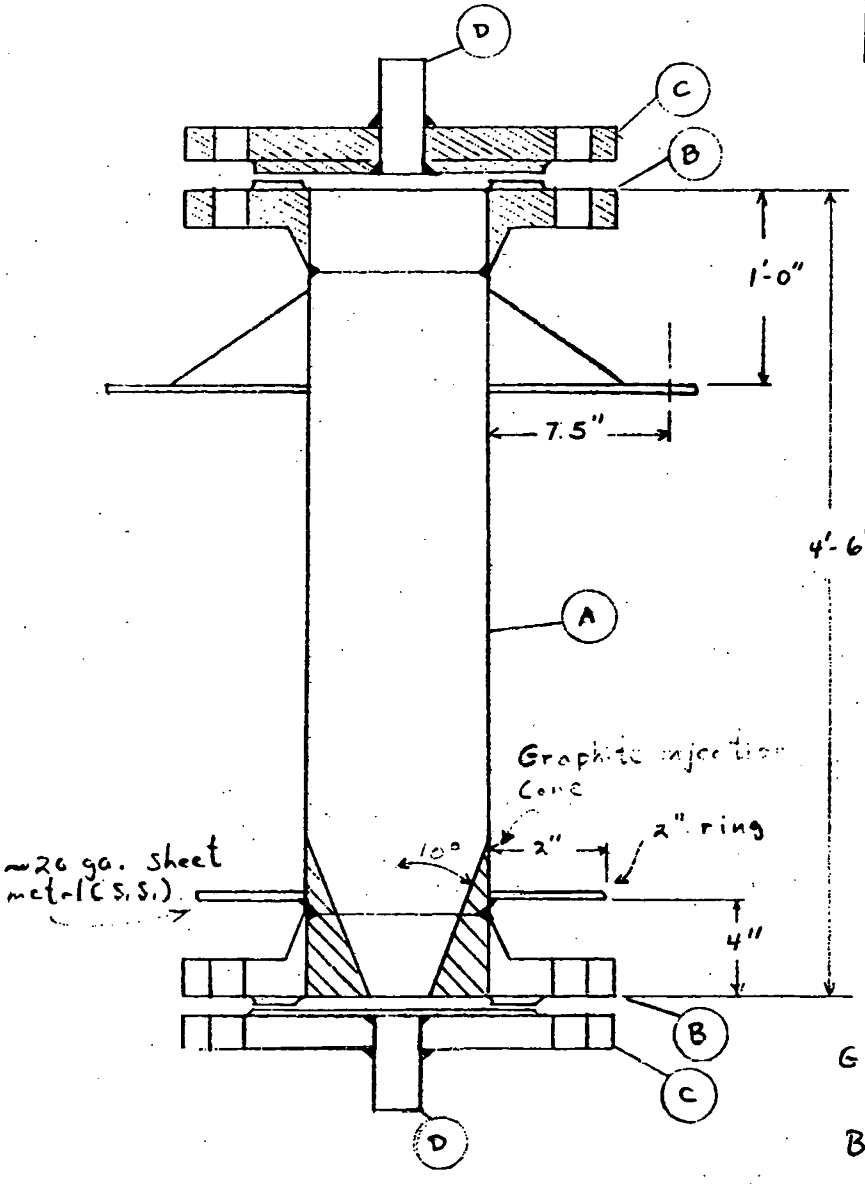
Hydrogenation Reactor System

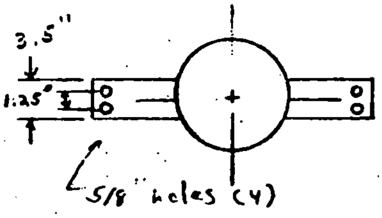


BY WCB DATE 5/26/77 SUBJECT Hydrogenation Reactor SHEET NO. OF
CHKD. BY DATE JOB NO.
W.O. 52556

FIGURE 12

300 psig @ 540°C
Hydrotest 925 psi





MOUNTING BRACKET

Gasket material:
.005" Grafoil
Bolt torque 40 ft-lb.

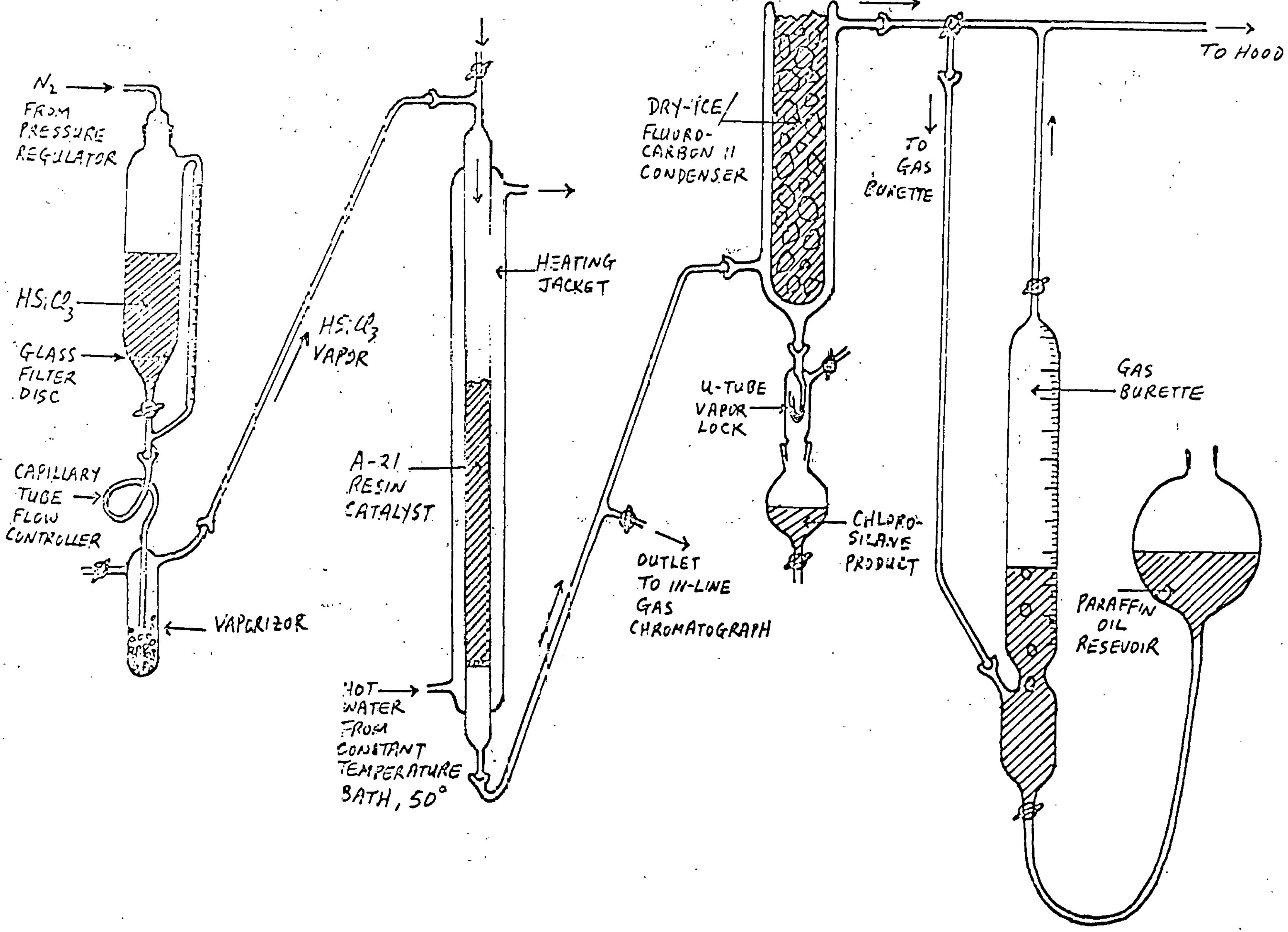
A. 3" Sched. 40 Pipe 54" long 304 S.S.
B 3" 300# W.N. Flange 304 S.S.
C. 3" 300# Blind Flange 304 S.S,
D. ½" 3000# Full coupling 304 S.S.

P.O. 511-240328
See W.C.B. for material

E. Alloy B-7 Stud Bolts for flanges

FIGURE 13

$$\begin{matrix} HSiCl_3 \\ DSiCl_3 \end{matrix} \xrightarrow{A-21} \begin{matrix} H_2SiCl_2 + SiCl_4 \\ D_2SiCl_2 + SiCl_4 \end{matrix}$$



Before the reaction rate measurements were made, the A-21 resin bed was conditioned by passing H_2SiCl_2 through the reactor at 60° for several hours. The purpose was to eliminate unknown variables such as moisture and volatile free amine which might be present in the A-21 resin. The conditioning of the A-21 resin with H_2SiCl_2 would minimize plausible variations of the A-21 resin catalytic activity during the reaction rate measurements on the disproportionation of $HSiCl_3$ and $DSiCl_3$. Dichlorosilane was fed into the A-21 resin reactor at 500 c.c./min. (2.1 g/min.) at 60° for 5 hours. Residence time was about 3 seconds. While the A-21 resin was conditioned with H_2SiCl_2, the composition of the products derived from the disproportionation of H_2SiCl_2 was also measured to collect more experimental data. Results of the gas-liquid partition chromatography (glpc) analyses were summarized in Table 2. The purpose of analyzing the chlorosilane products during the H_2SiCl_2 treatment of the fresh A-21 resin catalyst was to check if substantial amount of water was present in the polystyrene base resin. The A-21 resin was manufactured from an aqueous process and the commercial product contained 10% to 20% water. The A-21 resin used in all the disproportionation experiments had been pre-dried to remove water. Since chlorosilane would react with water to form HCl, the HCl gas produced would readily react with SiH-containing compounds as observed previously. The presence of substantial amount of HCl would shift the product compositions significantly and would generate larger than the normal amount of $SiCl_4$. As data in Table 2 indicated, there were no significant changes in product composition. The amount of $SiCl_4$ was only slightly higher in the first 25 minutes than those of the subsequent samples. However, the difference (0.6% versus 0.3%) was so small that it was insignificant. Thus, these data further proved that the method used to pre-dry the wet commercial A-21 resin was adequate.

b) Disproportionation of $HSiCl_3$

The vapor phase disproportionation of $HSiCl_3$ was carried out in the apparatus shown in Figure 13 at 50 and 60° and at various residence times determined by the feed rate of $HSiCl_3$. The reaction time was taken as the same as residence time which was based on the volume of the A-21 resin bed, 28.6 c.c. The liquid $HSiCl_3$ was fed through a capilliary flow meter. The flow rate was controlled by the nitrogen pressure applied to the $HSiCl_3$ container. The flow rate could be controlled and maintained very accurate this way, viz. 1.00 ± 0.02 c.c./min. The liquid $HSiCl_3$ was vaporized in the vaporizer. The $HSiCl_3$ vapor was fed into the A-21 resin reactor from the top. The reaction product mixture coming out of the reactor was condensed with a Dry-Ice/fluorocarbon 11 condenser. The gas burette assembly shown in Figure 13 was not used, since no non-condensable gaseous product would be produced as shown by earlier observations. An outlet was provided between the reactor and the Dry-Ice condenser. The outlet was connected to an in-line gas chromatograph which provided rapid quantitative analyses of the chlorosilane mixtures. A series of experiments was carried out at various feedrates of $HSiCl_3$ at 50° and 60° at atmospheric pressure. The feedrates were so chosen that the reaction product compositions was far from the equilibrium mixture composition. Results of the glpc analyses were summarized in Table 3. A plot of the $SiCl_4$ conversion versus reaction time was given in Figure 14.

The disproportionation of $HSiCl_3$ proceeded in a reversible reaction to give H_2SiCl_2 and $SiCl_4$ as primary products.

$$2\ HSiCl_3 \rightleftarrows H_2SiCl_2 + SiCl_4 \qquad (1)$$

As shown in Table 3, a small amount of monochlorosilane was also produced. H_3SiCl could be derived from subsequent disproportionation of H_2SiCl_2, viz.,

$$2\ H_2SiCl_2 \rightleftarrows H_3SiCl + HSiCl_3 \qquad (2)$$

Material balance for the overall reaction, i.e., (1) plus (2) would give

$$2 \times \text{mole}\ \%\ H_3SiCl + \text{Mole}\ \%\ H_2SiCl_2 = \text{Mole}\ \%\ SiCl_4$$

This relationship checked out quite well from data given in Table 3. A minor correction was necessary to calculate the $SiCl_4$ yield since the starting $HSiCl_3$ starting material contained a small amount of $SiCl_4$ and H_2SiCl_2. The $SiCl_4$ and H_2SiCl_2 conversion used in the graph shown in Figure 14 have been corrected by deducting the mole % of $SiCl_4$ and H_2SiCl_2 from the background level of 0.2% $SiCl_4$ and 0.2% H_2SiCl_2. Experiment No. C in Table 3 was a control experiment which was carried out after the $DSiCl_3$ experiment. The purpose of this experiment was to monitor the consistency of the A-21 resin catalytic activity. Experiment No. C was a repeated experiment of Experiment No. 3 in Table 3 after the subsequent $DSiCl_3$ experiment had been carried out. Analytical data on Experiment No. 3 and Experiment No. 3 in Table 3 showed no significant change in the catalytic activity of the A-21 resin bed throughout the reaction rate measurements.

c) The Rate of Disproportionation of $DSiCl_3$ in 10 g A-21 Resin Catalyst

Similarily, the rate measurements on the disproportionation of $DSiCl_3$ in the same 10 g A-21 resin bed were carried out under

BY	DATE	SUBJECT	SHEET NO. OF
CHKD. BY	DATE		JOB NO.

FIGURE 14

Rate of Disproportionation of $HSiCl_3$ and $DSiCl_3$ Vapor Over A-21 Resin Catalyst at Atmospheric Pressure

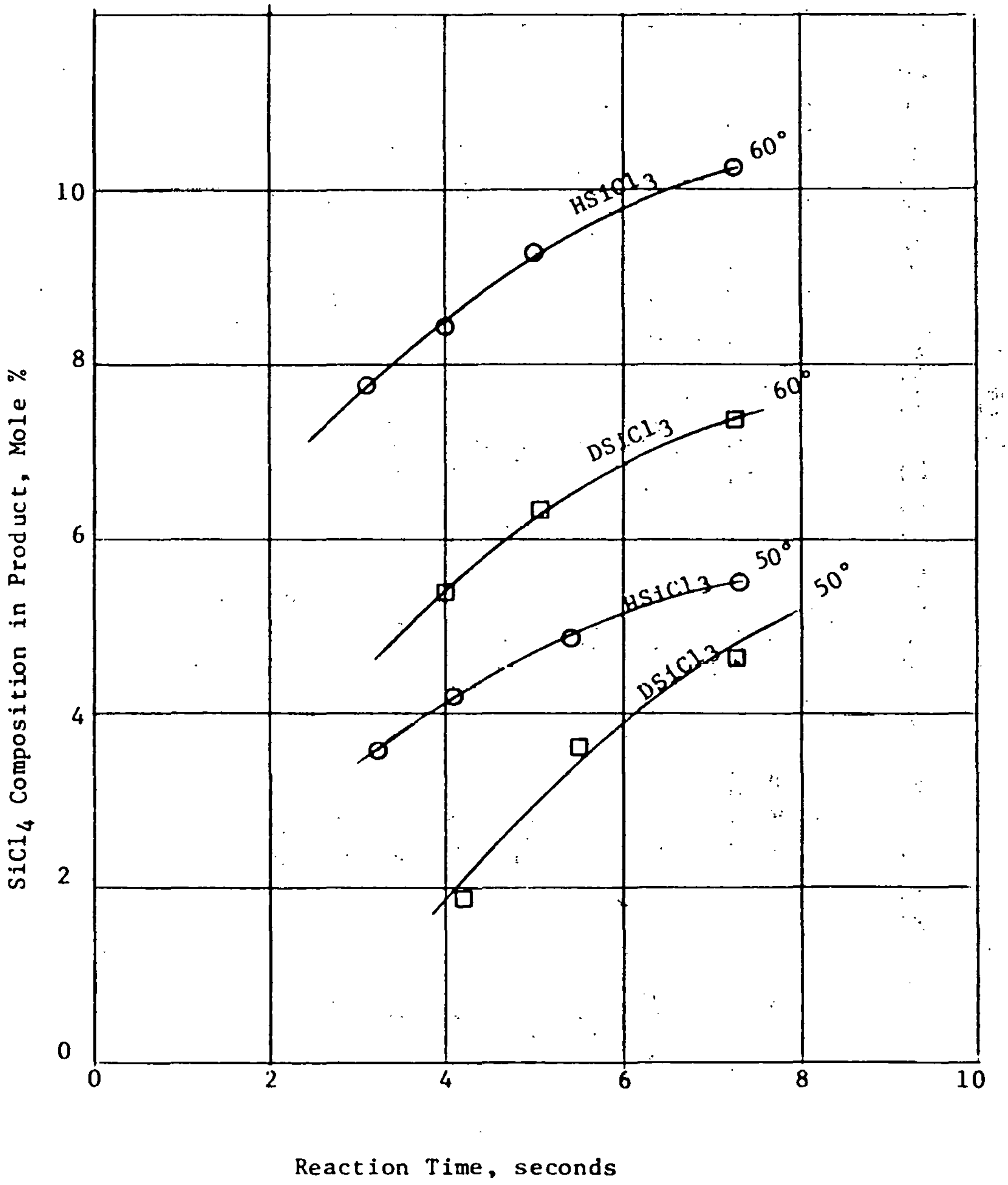


TABLE 2

DISPROPORTIONATION OF H_2SiCl_2 OVER A FRESH CHARGE OF 10g A-21 RESIN AT 60°

Reaction Time	H SiCl Feedrate c.c./min.	Residence Time sec.	Product Composition in Mole %				
			SiH_4	H_3SiCl	H_2SiCl_2	$HSiCl_3$	$SiCl_4$
10 Min.	500	3.0	14.14	11.00	34.12	40.09	0.65
25 Min.	500	3.0	14.23	11.01	33.55	40.80	0.42
1 hr.	500	3.0	14.05	11.46	34.62	39.60	0.27
2 hr.	500	3.0	13.99	11.38	34.54	39.82	0.27
3 hr.	500	3.0	14.11	11.40	34.67	39.54	0.29
4 hr.	500	3.0	14.43	11.26	34.17	39.84	0.29
5 hr.	500	3.0	14.56	11.18	33.67	40.28	0.32

TABLE 3

RATE OF DISPROPORTIONATION OF $HSiCl_3$ OVER 10g.A-21 RESIN AT 50° AND AT ATMOSPHERIC PRESSURE

Experiment Number	$HSiCl_3$ Feedrate c.c./min.	Residence(1) Time sec.	Product Composition, Mole %(2)				
			H_3SiCl	H_2SiCl_2	$HSiCl_3$	$SiCl_4$	Heavies
(Purity of Starting HSiCl)			0	0.20	99.55	0.20	0.021
1	0.89	7.36	0.13	5.42	88.66	5.72	0.08
2	1.21	5.43	0.05	4.91	89.94	5.04	0.05
3	1.60	4.11	0.07	4.16	91.40	4.28	0.08
4	2.00	3.29	0.05	3.73	92.42	3.75	0.05
(Repeat Experiment No. 3 after the DSiCl Experiment)							
C	1.61	4.08	0.07	4.22	90.98	4.67	0.05

(1) Based on A-21 Resin Bed Volume 28.6 c.c.

(2) Average of two measurements, except Experiment No. C.

TABLE 4

RATE OF DISPROPORTIONATION OF DSiCl$_3$ OVER 10g A-21 RESIN AT 50° AND AT ATMOSPHERIC PRESSURE

Experiment Number	DSiCl$_3$ Feedrate c.c./min.	Residence(1) Time sec.	Product Composition, Mole %(2)				
			D$_3$SiCl	D$_2$SiCl$_2$	DSiCl$_3$	SiCl$_4$	Heavies
(Purity of Starting DSiCl$_3$)			0	0.28	99.33	0.37	0.02
1	0.91	7.23	0.07	4.55	90.59	4.69	0.10
2	1.20	5.48	0.06	3.83	91.91	4.11	0.08
3	1.58	4.16	0.04	3.30	93.31	3.29	0.06

(1) Based on A-21 resin bed volume of 28.6 c.c.

(2) Average of two measurements.

the same experimental conditions as the $HSiCl_3$ case. Results were summarized in Table 4. A similar plot of $SiCl_4$ conversion versus residence time for the $DSiCl_3$ disproportionation reactions was given in Figure 14. The graphs in Figure 14 provided side-by-side comparison of the absolute reaction rates on the disproportionation of $HSiCl_3$ with those of $DSiCl_3$.The rate of disproportionation of $DSiCl_3$ was clearly slower than the rate of the disproportionation of $HSiCl_3$ under the same conditions.

These preliminary data showed a positive kinetic isotope effect in the redistribution of SiH and SiCl bonds. Also, it would indicate that the rate-determining step in the disproportionation reaction involved the breakage and/or the formation of the SiH and SiD bonds.

d) Temperature Effects in Disproportionation

As expected, the reaction rate of amine catalyzed disproportionation increases with increasing reaction temperature. Using the rate data at 50 and 60°, an Arrhenius activation energy was calculated to be approximately 14 kcal/mole. This value is in the range common for diffusion controlled reactions or those which are facile and which occur readily at modest temperatures. No variations in catalyst pore size or overall catalyst partical size have been made except that it is known that gell type resins are much less active than the macroreticular type such as Rohm & Hass A-21.

The temperature effect on the reaction using $DSiCl_3$ showed a result similar to that for $HSiCl_3$ except that the activation energy was modestly lower. (Figure 14).

e) Liquid vs Vapor Phase Disproportionation of $HSiCl_3$

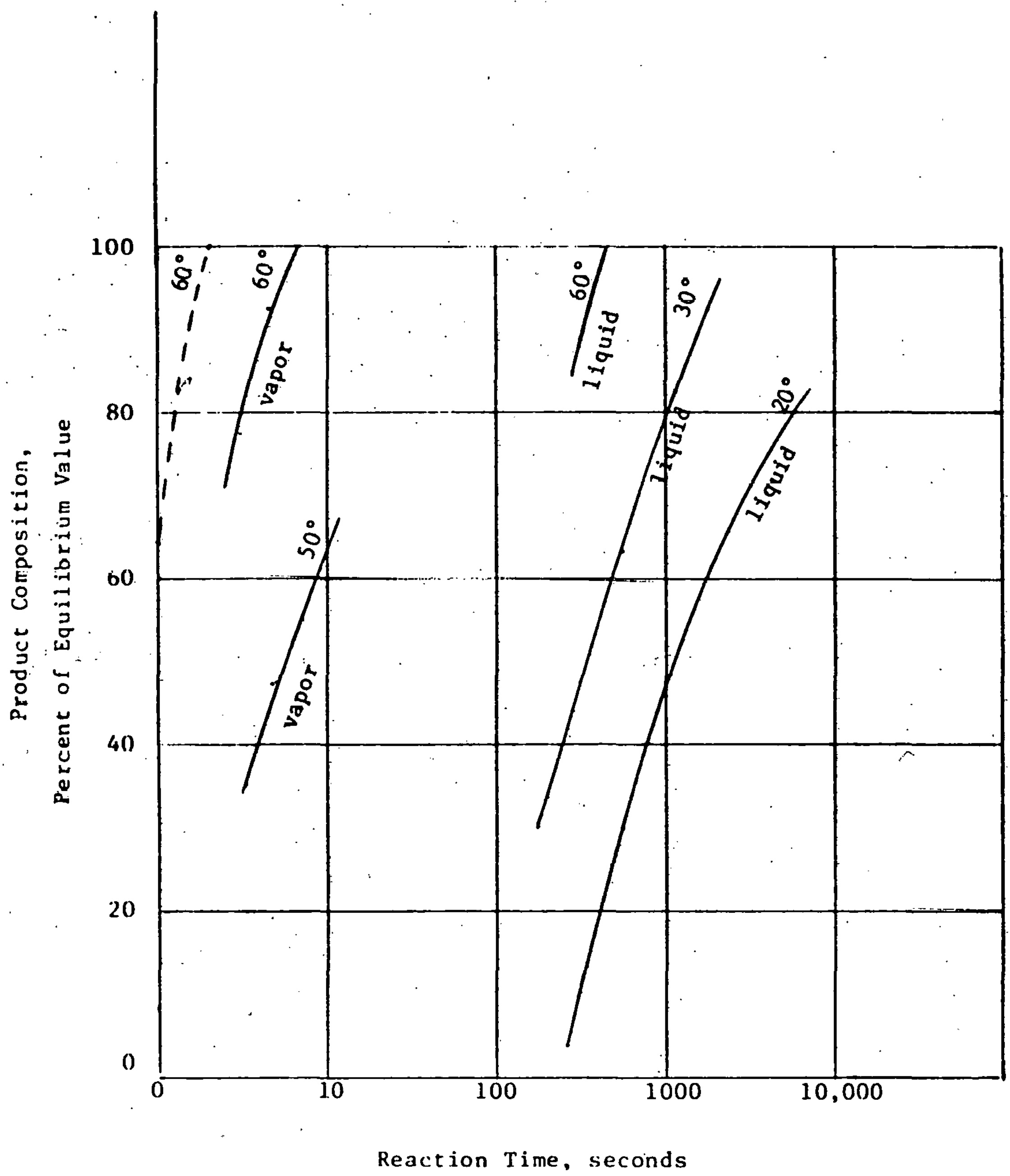
The synthetic scheme for the manufacture of SiH_4 involves a step to prepare H_2SiCl_2 by the disproportionation of $HSiCl_3$.

$$2\ HSiCl_3 \rightleftharpoons H_2SiCl_2 + SiCl_4$$

This reaction has been shown to occur both in the liquid and vapor phase when catalyzed by the A-21 amine functional resin. Figure 15 teaches that at 80% of the equilibrium conversion at 60°C, the vapor phase reaction is 80 times faster than the liquid phase reaction. However, the liquid density is 100 times higher than the vapor (at its dew point pressure at 60°C). The phase

FIGURE 15

Rate of Disproportionation of $HSiCl_3$ Over Amine Functional Resin Catalyst



in which the reaction is allowed to occur would likely not change the required size of the reactor by any large extent. Other criteria such as system hydraulics, energy costs, etc. would be more influential. For example, co-current liquid and vapor flow in the packed bed of resin would result in a pressure drop much higher than for vapor flow only. One idea explored by early workers at Union Carbide was to pack a small distillation column with the resin catalyst and by refluxing a sample of $HSiCl_3$, SiH_4 was detected in the condenser. The overall reaction was inefficient due to low operating temperatures at atmospheric pressure, but it did establish that a "reactive distillation" arrangement could be applicable to carry out just the reaction step in converting $HSiCl_3$ to H_2SiCl_2 in view of the good match of the boiling point of $SiCl_4$, $HSiCl_3$, and H_2SiCl_2 with the operating temperature of the A-21 resin bed reactor. For example, if one would carry out the disproportionation of $HSiCl_3$ in a distillation column packed with A-21 resin catalyst at, say, 200 to 300 kPa, the boiling point of $HSiCl_3$ would fall into a range of about 50° to 70° which would also be the operating temperature range for the disproportionation reaction to take place. Thus, one might be able to combine the disproportionation and the distillation in a single step by taking out lower boiling H_2SiCl_2 from the top of the column and by-product $SiCl_4$ from the bottom. The idea was to reduce the large volume of unreacted $HSiCl_3$ which would be recycled in a separated disproportionation reaction step followed by distillation. Since the disproportionation of $HSiCl_3$ by A-21 resin produced about 10% to 12% H_2SiCl_2 at near equilibrium in one pass, one needed to separate out the H_2SiCl_2 and $SiCl_4$ from the reaction stream by distillation and recycle the almost 90% unreacted $HSiCl_3$ back to the resin bed. The combined disproportionation and distillation concept might reduce much of the recycling load. Such combination of disproportionation reaction and distillation would be complex in nature and one would most likely not be able to obtain a clear-cut separation to get pure H_2SiCl_2. However, if one could obtain a reaction stream rich in H_2SiCl_2, say, about 70% to 80%, from this design concept, it would reduce much of the work load needed from a disproportionation reaction followed by a distillation design which produced a product stream containing only 10% H_2SiCl_2.

CONCLUSIONS

The feasibility of producing high quality silane via the disproportionation of hydrochlorosilanes has been demonstrated. The initial quantity of material prepared in a small process development unit has been shown to be of modest purity capable of conversion to that elusive commodity-solar grade silicon metal.

An integrated silane process development unit has been designed and initial construction is under way. The utility of activated carbon as an adsorbent for chlorosilane impurities in silane has been demonstrated. Laboratory studies have clearly shown the feasibility and relative reaction rates for liquid or vapor phase disproportionation of hydrochlorosilanes. This flexibility creates new trade-offs in the design of an optimum process. More engineering analysis is needed to gain the full benefit of this knowledge.

PROJECTED QUARTERLY ACTIVITIES

1. Complete construction of the hydrogenation reactor for converting $SiCl_4$ to $HSiCl_3$.
2. Complete installation of the integrated silane process development unit.
3. Continue studies on the synthesis and purification of silane.
4. Initiate studies of hydrogenation of $SiCl_4$ at elevated pressure.

PROGRAM STATUS UPDATE

The revised implementation plan is shown in Figure 16 attached. The program is on plan with the exception of the larger carbon bed installation which will be implemented as part of the general installation of the other process units. The labor hour and cost plans are shown in Figures 17.

FIGURE 16

REVISED IMPLEMENTATION PLAN

May, 1977

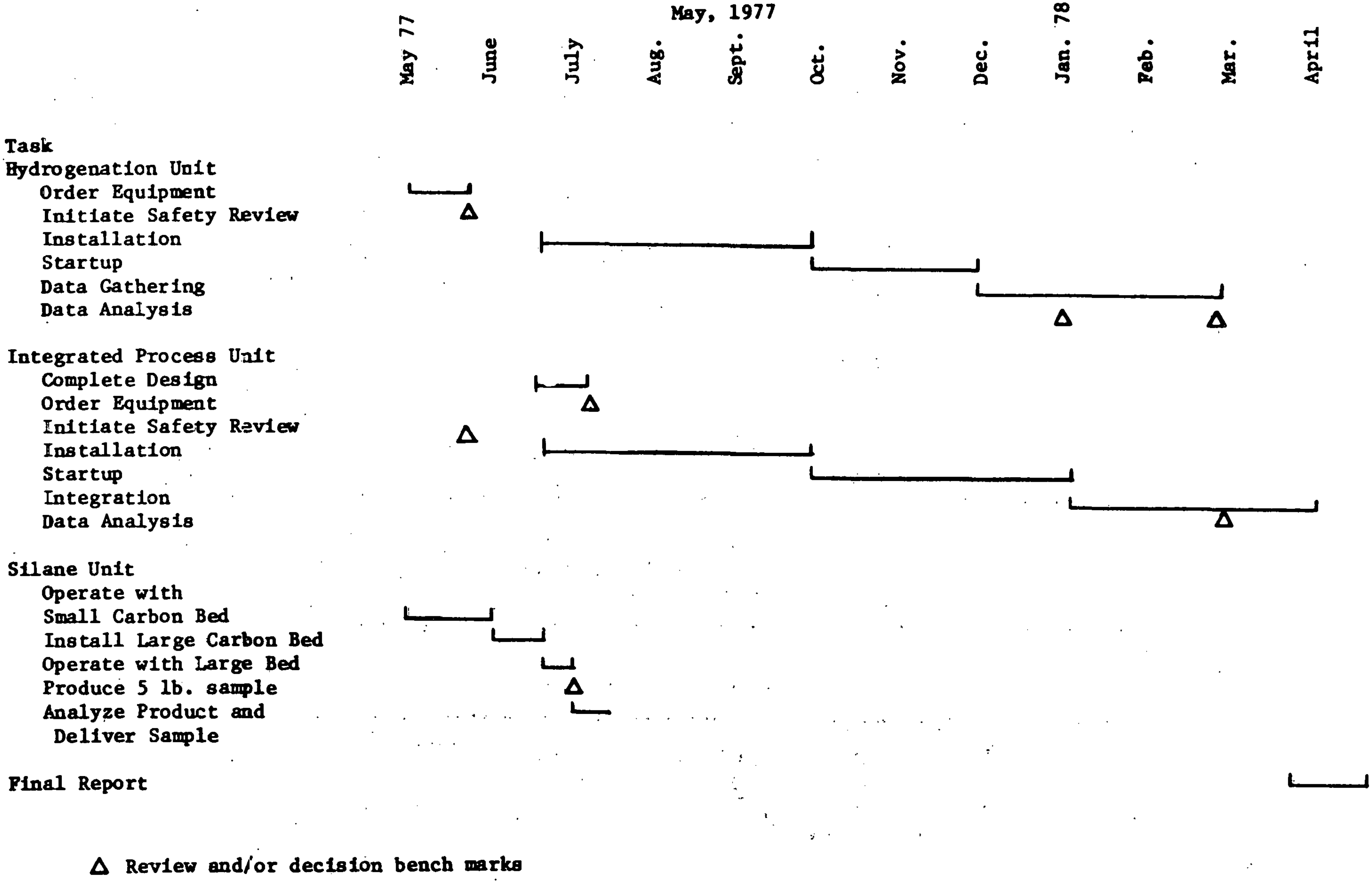
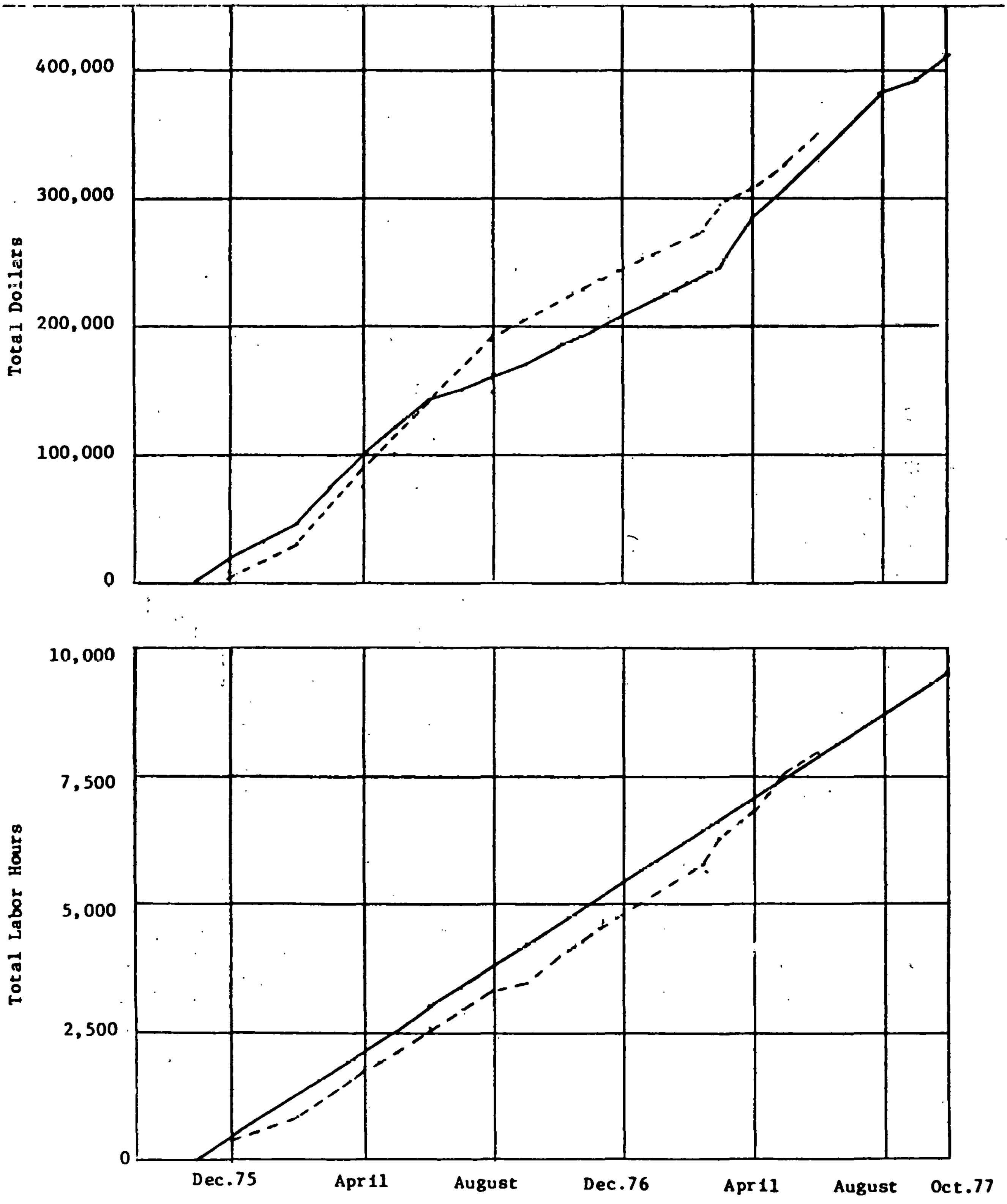


Figure 17

UNION CARBIDE CORPORATION

SISTERSVILLE PLANT

BY WCB DATE 2/28/77 SUBJECT Total Cost/Labor Hour SHEET NO. ____ OF ____
CHKD. BY ____ DATE ____ Plan for Low Cost Silane Project JOB NO. 954334
Revised



INTRODUCTION

The objective of the Parma Technical Center Program is to establish the economic feasibility of manufacturing solar and/or semi-conductor grade polycrystalline silicon through the pyrolysis of silane (SiH_4).

Union Carbide Corporation sponsored a program in which two low cost, high volume methods (fluid bed process and a free space process) of pyrolyzing silane to form polycrystalline silicon were pioneered. The technical and engineering feasibility of both methods was established experimentally. The free space pyrolysis process had the greatest potential for a low cost, high volume operation. In an effort to obtain design data for scale-up, a High Purity Reactor (HPR) was designed, constructed, and made operational.

The current program (under Contract 954334) was started in January, 1977. During the first quarter, silane was pyrolyzed in the free space of the HPR. Operating conditions indicated that high decomposition rates were attainable in a moderate size reactor. Equipment was installed for preheating the silane gas. Some of the engineering and design problems associated with powder transfer and thermal treatment were identified. This work was continued and expanded during the current quarter.

DISCUSSION

I. PRODUCT PURITY

A major goal of the silicon program is to demonstrate that the silicon produced in the free space reactor is of sufficient purity to meet all intended uses. To accomplish this goal, the impurity sources must be identified.

Analysis of the powder product from earlier free space reactor experiments indicated that the silicon product became contaminated when the reactor was lined with graphite. In experiments in which a nickel liner was used, a nickel-silicon reaction occurred. This contaminated the free space reactor powder with small pieces of nonmagnetic scale. The reactor was subsequently modified to accept a clear fused quartz liner. In a single trial experiment, the quartz liner successfully withstood the thermal and mechanical stresses without breaking. The quartz liner will be used in future experiments in which the product purity will be evaluated.

At the present time, each component of the free space reactor and consolidation apparatus is operated as a separate unit. Between operations, the product is exposed to air and air borne contamination. The individual components of this system are likewise exposed to similar contamination. Sources of gross contamination can be identified by analysis of samples from these components. A reduction in the level of contamination to the ppb range will require refined product handling procedures and the elimination of many current operations. An enclosed in-line system is being engineered that will include the current free space reactor, a powder transfer assembly, a powder storage vessel, and a powder consolidator. Trace impurity analysis of consolidated samples from the enclosed system should identify potential contamination sources that can be rectified during the development program. Additional experiments will be conducted to characterize the "state of the art," but it is believed that in-line processing will be required before high purity levels can be achieved.

A mass spectroscopic analyzer capable of detecting to 1 ppm for most elements is being used for the initial impurity analysis. A grid of powder samples from several pyrolysis experiments were submitted for impurity analysis in an effort to identify gross contamination sources and reproducibility of the test. The initial test grid included duplicate samples, samples of powder prepared from three different cylinders of silane, and samples from runs in which nickel or "Grafoil"* liners were used in the free space reactor. In addition to the powder samples, sections of cast silicon rods were submitted for analysis. Several of the rods were cast from free space reactor powder. Two control rod sections were also included for analysis. One of the control samples was of semi-conductor quality. The other control sample was a section of the semi-conductor quality silicon recast in the current casting apparatus. To date, the completed analytical results have not been obtained.

II. FREE SPACE REACTOR POWDER PRODUCTION

A critical engineering aspect of a process whose products are a gas and a finely divided powder is the efficient separation of these phases. For pollution control, the particulate matter must be separated from the exhaust gases. In a series of experiments, a prototype porous metal filter (having an average pore size of 30 μm) proved to be an effective means of preventing the fine silicon dust from entering the gas exhaust lines. As a consequence, the reactor assembly was simplified by replacing a troublesome dust collector with a simple porous metal filter. The new

---

*"Grafoil" is a Union Carbide Corporation trademark.

filter is a welded porous nickel tube (with welded end cap and flange) measuring approximately 70 mm O.D. x 305 mm long designed to fit inside of the settling chamber. No flame discoloration occurred in a test experiment. This indicated that silicon powder did not bypass the filter. In addition, there was no measurable quantity of powder in the exhaust lines after termination of the experiment and dismantling of the system. The current in-line filter assembly serves the dual purpose of separation of the silane pyrolysis products inside the reactor assembly and prevention of atmospheric pollution by particulate matter.

A closed system that operates continuously will eventually produce the highest purity silicon powder. As a partial demonstration of the capability of the current free space reactor to operate for extended periods of time, the reactor was operated continuously for 3 hours during two experiments and for 5 hours in a subsequent experiment. The silicon output was 0.3 and 0.6 kg/hr. for the 3-hour experiments, and 0.3 kg/hr. for the 5 hour one. All three experiments were terminated as planned with no indication of any component or operational problems.

The first critical step in the design of an enclosed in-line system was the demonstration of a powder transfer method. For the initial experiments involving powder transfer, the Monel reactor was removed from the settling chamber. The settling chamber was then sealed with a lid containing a gas inlet tube and a sight glass. For safety purposes, the powder in the settling chamber was fluidized and pneumatically transferred to a holding container using argon gas. An argon flow of 17 ℓ/min was used to convey in excess of 0.3 kg of silicon powder in 1/2 hour. Typical silicon production rates were between 0.3 and 0.6 kg/hr. At these rates, from 8 to 16 ℓ/min of hydrogen was produced from the pyrolysis of silane. It may eventually be possible to use the hydrogen by-product to transfer the powder, in an enclosed in-line system, in a continuous operation.

The agglomerated semi-solid cones that form during some of the pyrolysis experiments cannot be pneumatically transferred out of the settling chamber with the powder. Previous data showed that precise control of the reactor gas temperature near the injector orifice was effective in reducing the amount of semi-solids formed. During the current report period, two additional methods were evaluated. In two experiments, the injected silane was blanketed with equal volumes of argon by using a coaxial injector. The amount of agglomerated semi-solids formed was reduced from 41% (obtained in a previous silane preheat experiment) to less than 2%.

In a subsequent similar experiment, an electrically operated vibrator was attached to the injector and only 8% of the product was semi-solid. The combined use of the mechanical vibration, gas blankets and the gas temperature control should eliminate the semi-solids without hampering the reactor production capabilities.

The introduction of argon, together with silane through the coaxial injector, changes the composition of the injected gas. Dilution of the silane with 33 and 50 volume percent argon by this technique had no noticeable effect on the pyrolysis efficiency. The powder produced is being analyzed to determine the effects of dilution on the particle morphology.

Preheating the silane before injecting it into the free space reactor permits an additional degree of freedom in operation of the unit. The silane pyrolysis efficiency was evaluated at lower reactor wall temperatures (baseline is 1000° C) with preheated silane injected into the reactor. In the preheat experiments, the silane was injected into the reactor through an uncooled coaxial injector. The injector projected approximately 150 mm into the Monel reactor. A thermocouple was positioned inside the inner tube of the injector to monitor the temperature of the silane. In the first silane preheat experiment, heat transfer within the reactor brought the injected silane temperature to between 380° and 430° C (to prevent pyrolysis inside the injector, the maximum temperature that the silane should be heated is 450° C). The reactor wall temperature was between 900° and 950° C. There was no indication of undecomposed silane in the exhaust flame. In the second silane preheat experiment, the free space reactor wall temperature was controlled between 790° and 835° C. Heat transfer within the reactor brought the injected silane temperature to 285° to 335° C. A white discoloration of the exhaust flame was occasionally observed during the 70-minute experiment. By comparing the calculated amount of silicon expected with the amount actually recovered, a pyrolysis efficiency of 99% was obtained. One adverse result of the two silane preheat experiments described above was the production of large percentages (23 and 41, respectively) of agglomerated semi-solids. In the next series of experiments, attempts were made to reduce the amount of semi-solids formed by blanketing the silane with equal volumes of argon (results discussed separately). The injected silane temperature was controlled by: 1) passing the silane through an external heat exchanger, and/or by 2) wrapping heater tapes around the coaxial injector and the injector supply lines. In the only experiment in which the heat exchanger and heater tapes were used simultaneously, the silane decomposed inside both the injector and the gas lines causing blockage and cessation of gas flow. In a subsequent experiment, only the heater tapes were used to control the injector silane temperature. While the reactor wall temperature was intentionally varied between 905° and 930° C, the injected silane temperature was kept at approximately 320° C. Without the heater tapes, the injector silane temperature was approximately 150° C. Throughout this experiment, the exhaust flame was colorless, indicating an excellent pyrolysis efficiency. Preheating the injected silane offers two distinct possibilities: the reactor wall can be kept cooler to decrease wall reactions and to reduce heat losses, or the reactor wall temperature can be maximized with anticipation of higher production rates.

III. POWDER CONSOLIDATION

The tasks involved in engineering an enclosed in-line assembly capable of demonstrating product purity were: 1) to develop means of controllably transferring the free space reactor silicon powder from a reservoir to a melting crucible, 2) engineer the furnace equipment to melt the powder rapidly without bridging above the melting crucible and without reacting the powdered silicon with components of the furnace, and 3) engineer means of casting the liquid silicon into useful shapes. During the present report period, the equipment and procedures used to study the three tasks individually were engineered into a sequential operation capable of producing silicon rods for purity and resistivity analysis.

The consolidation of free space reactor powder comprises the transfer of powder to a holding chamber, melting of the powder in an acid (HNO_3 + HF) cleaned quartz crucible, and casting of the liquid silicon into rods. The powder transfer, melting behavior (fuming or dross formation), and rod casting can be visually monitored in the current apparatus. The powder transfer methods evaluated were pressure transfer techniques, vacuum transfer, and a combination of pressure and vacuum transfer techniques. The transfer technique engineered into the current apparatus involved fluidization of the powder in the holding chamber. Controlled flow transfer occurred through a tube leading from the holding chamber to the quartz melting crucible. The gas (argon) pressure in the holding chamber was slightly higher than the pressure surrounding the melting crucible. The temperature of the quartz melting crucible was maintained above the melting temperature of silicon. The silicon powder was continuously fed into the melting crucible until the desired liquid level was obtained at which time the powder transfer head (located above the melting crucible) was replaced by the rod casting head. During this exchange, the only silicon cooling that occurred was the result of a precautionary induction coil de-energizing measure. These experiments demonstrated that powder transfer, melting, and casting can be accomplished on a semi-continuous basis with the liquid silicon maintained under a protective atmosphere. Work is proceeding on preliminary design sketches of an enclosed in-line storage and melt casting facility that will be attached to the free space reactor.

Various means of transferring free space reactor powder from a storage vessel to the melting crucible were investigated. Pressure feeding of fluidized powder was adequate for the 51 mm diameter quartz crucible currently used for the melting and casting experiments. The powder entered the quartz crucible like falling snow at approximately 60 g/hr. The enclosed in-line system presently being designed will use a quartz crucible that is approximately 150 mm in diameter. The larger crucible is more amenable towards standard mass production powder transfer methods. A model that gravity fed fluidized powders to a simulated melting crucible was capable of transferring much larger quantities of powder. One drawback to this transfer method was the need for auxiliary fluidizing gases or pumps to utilize the hydrogen by-product as a fluidizing gas. A vibrating gravity feed system will also be modeled as an alternate transfer method before the design of the enclosed in-line system is finalized. Silicon rods were chosen as a convenient shape for evaluating the electrical resistivity and conductivity type. The casting procedure was to insert a clean quartz tube (i.d. is equal to the rod diameter wanted) into the melt after the desired liquid depth in the crucible was obtained. The silicon filled the tube by suction casting. The rapid cooling prevented the silicon from reacting and bonding to the quartz tube. Consequently, except for the small length of the tube that was submerged in the melt, the silicon rod can be pushed out of the tube. The quartz tube can be reused until it becomes too short to handle. In addition, the quartz melting crucible can be reused if most of the molten silicon is extracted.

A total of six silicon rods were cast from the above mentioned melt. The rods were either 6 or 9 mm in diameter and from approximately 45 to 75 mm long. Most castings had a small centrally located pin-hole defect that ran the length of the rod. This defect was attributed to improper casting temperatures. One of the castings was a thin silicon pipe (with a wall thickness of approximately 1/4 mm) that formed inside the quartz casting tube. This type of structure developed when the casting tube did not remain in the liquid silicon long enough for the core of the cast rod to solidify. This technique may provide a means of cladding the insides of gas and powder transfer tubes of the reactor to prevent impurity pickup. Three of the cast rods were sectioned with a water-cooled diamond cut-off wheel. The sections were submitted for chemical analysis and electrical resistivity measurements.

CONCLUSIONS

During this quarter, the entire effort concentrated on the production and consolidation of free space reactor powder. The tasks accomplished and/or initiated were as follows:

1. Identify and start to eliminate sources of contamination.

2. Consolidate the powder into a form that is less susceptable towards contamination, amenable towards purity and resistivity analysis, and readily acceptable to single crystal growers.

3. Demonstrate continuous operation capability.

4. Initiate the engineering effort needed for an enclosed in-line system that will include the current free space reactor, a powder transfer assembly, a powder storage vessel, and a powder consolidator.

PROJECTED THIRD QUARTER ACTIVITIES

I. FREE SPACE REACTOR

A. Continue to modify the free space reactor assembly to obtain a system in which powder samples can be extracted for analysis between experiments.

B. Modify the settling chamber to obtain a system in which the powder can be transferred to a holding vessel without opening the settling chamber.

C. Continue with the design and construction of a powder holding, melting, and casting apparatus that will be an integral part of the free space reactor.

D. Continue to investigate methods of transporting free space reactor powder.

E. Evaluate silicon nitride as a potential crucible material.

F. Study the sintering behavior of compact and loose powders.

II. FLUID BED REACTOR

A. Design and construct a glass fluid bed reactor for room temperature studies of operating and design parameters.

B. Design and initiate construction of a high temperature fluid bed reactor.

C. Study the effects of silicon crushing and grinding on the characteristics of the powder as potential fluid bed reactor seed.

PROGRAM STATUS UPDATE

The tentative implementation plan revised for the March, 1977, Progress Report is shown in Figure 1B. Updated direct labor hours and total cost plan for the Parma Technical Center are shown in Figures 2B and 3B, respectively.

IMPLEMENTATION PLAN*
JPL Contract No. 95[illegible]34 Modification No. [illegible]

Year	1977												1978											
Month of Year	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12
Month of Contract	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
I. Free Space Reactor Powder Preparation												Δ												
A. Reactor condition effects on particle morphology	~~1~~	~~2~~	~~3~~	~~4~~	~~5~~	~~6~~	7	8	9	10	11	12												
B. Output withdrawl criteria																								
1. Powder-gas separation	~~1~~	~~2~~	~~3~~	~~4~~	~~5~~	~~6~~	7	8	9	10	11													
2. Powder sample extraction		~~2~~	~~3~~	~~4~~		~~6~~		8		10														
II. Powder Consolidation by Fluid Bed and Alternate Means																								
A. Summarize Fluid Bed Reactor pyrolysis data		~~2~~	~~3~~	~~4~~																				
B. Study various consolidation methods							Δ																	
1. Powder compaction and sintering		~~2~~	~~3~~	~~4~~	5	6	7 }	8	9	10	11													
2. Powder melting and casting		~~2~~	~~3~~	~~4~~	~~5~~	~~6~~	7 }																	
C. Fluid Bed Reactor particle behavior tests						Δ																		
III. Study the Behavior of Most Promising System																								
A. Demonstrate eight-hour continuous operation																		18	19					
B. Demonstrate five-, eight-hour shift operations																			19	20	21			
C. Conduct engineering process studies																								
1. Minimize wall reactions													13	14	15	16	17	18						
2. Minimize injector cone formations													13	14	15	16	17	18						
3. Study operating parameter effects on rates													13	14	15	16	17	18						
4. Determine pyrolysis efficiency													13	14	15	16	17	18	19		21			
5. Determine current reactor product cost																							23	
D. Characterize product form and size													13	14	15	16	17	18	19		21			
E. Evaluate product purity															15		17		19		21			
IV. Preliminary Design for Pilot Plant Pyrolyzer																		18	19	20	21			
A. Engineering consideration for hydrogen recovery																				20	21			
B. Estimate pilot plant cost																					21	22		
C. Estimate pilot plant product cost																							23	
V. Reports																								
A. Monthly	~~1~~	~~2~~	~~3~~	~~4~~	~~5~~	~~6~~	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	
B. Quarterly			~~3~~			~~6~~			9			12			15			18			21			
C. Annual												12												
D. Final																						22	23	24

---

* Δ = Decision Milepost

Figure 1B

Direct Labor Hours Planned for the High Purity Silicon Project
Contract No. 954334

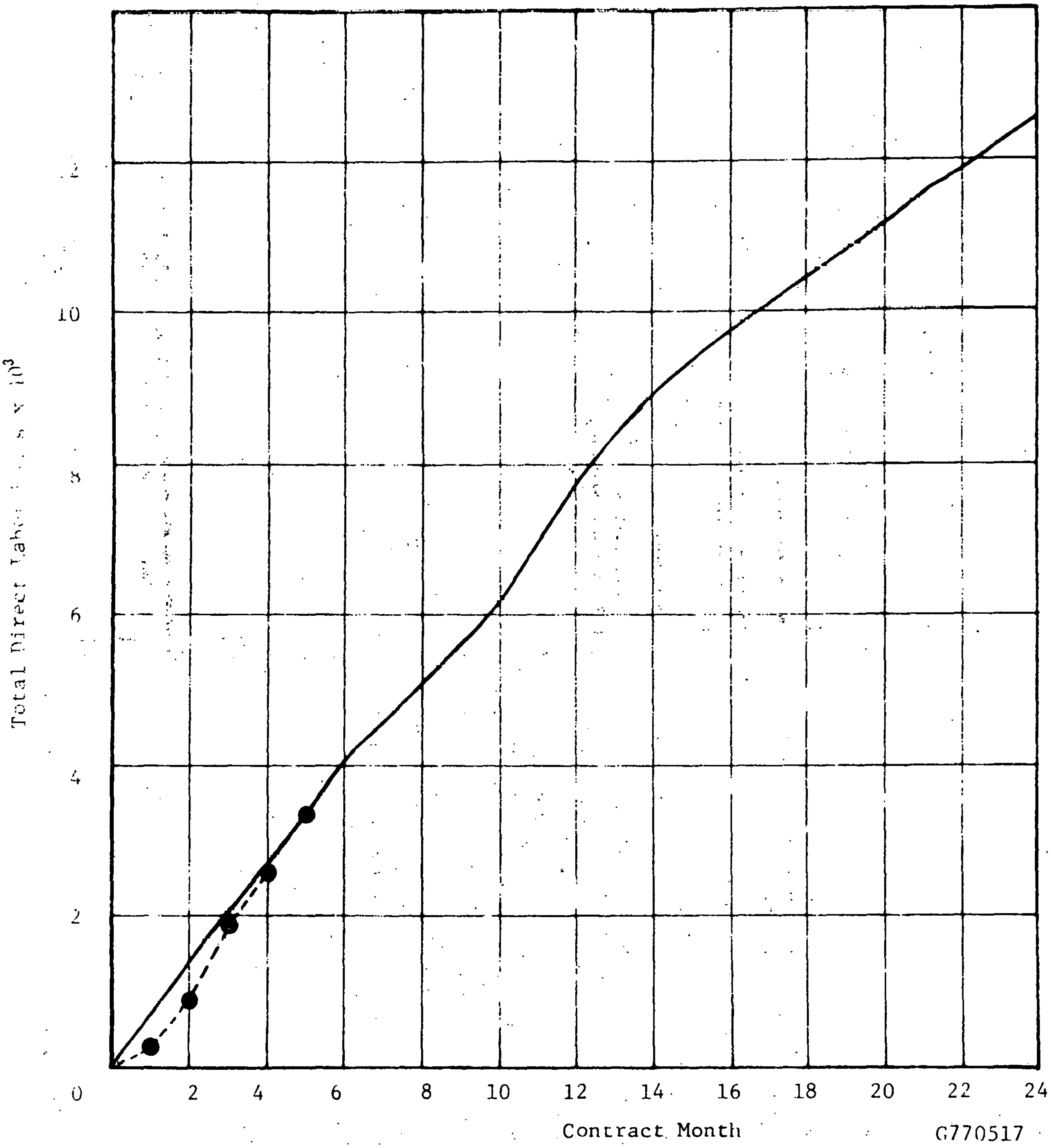


Figure 2B

Total Cost Plan for the High Purity Silicon Project
Contract No. 954334

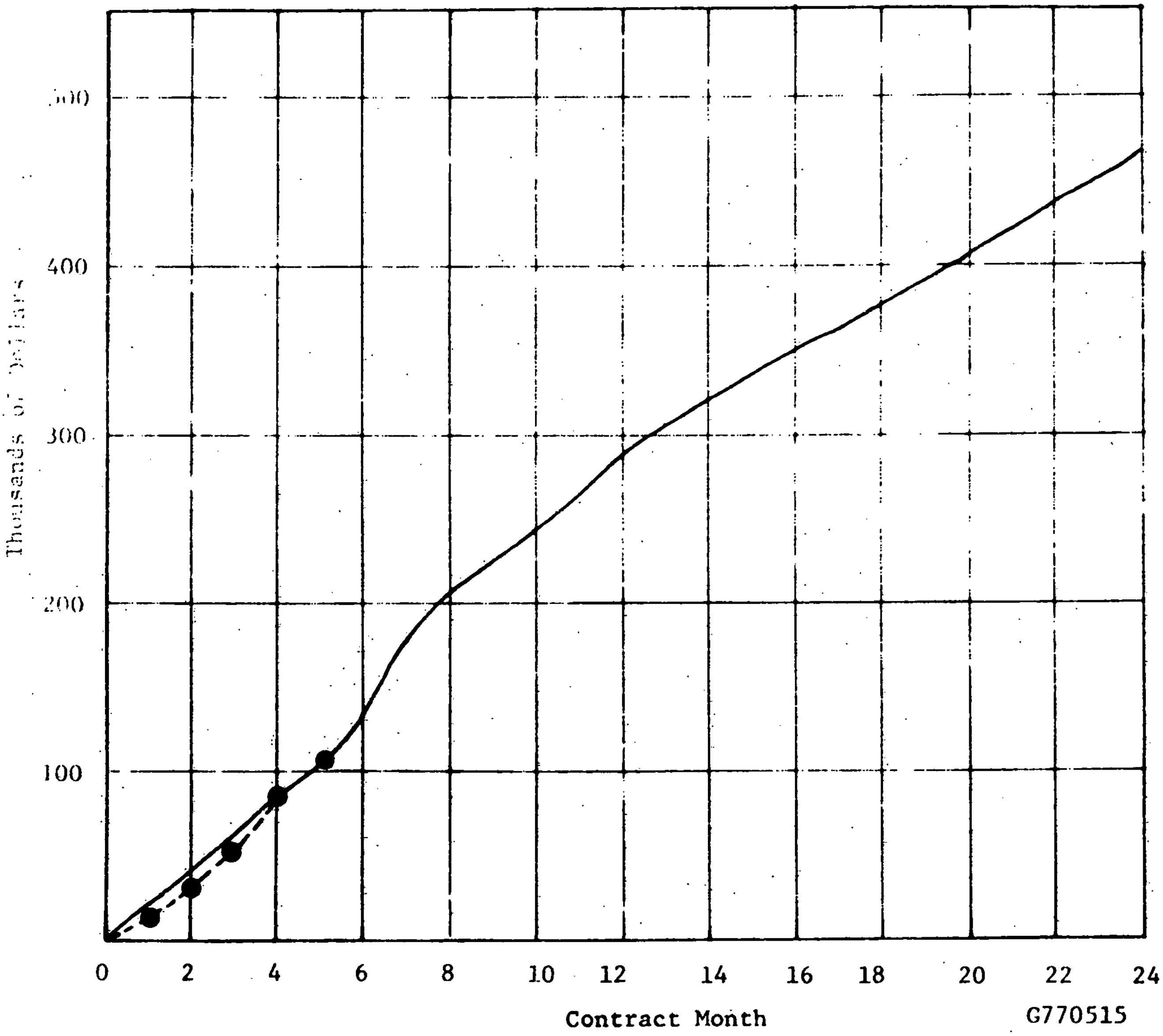


Figure 3B