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ESTABLISHMENT OF THE FEASIBILITY OF A PROCESS CAPABLE OF LOW COST, HIGH VOLUME PRODUCTION OF SILANE, SiH_4

Low Cost Silicon Solar Array Project, Task I
Quarterly Progress Report, October 1, 1976—December 31, 1976

MASTER

January 1977

Work Performed Under Contract NAS-7-100-954334

Union Carbide Corporation
Sistersville, West Virginia

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
Division of Solar Energy

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LOW COST SILICON SOLAR ARRAY PROJECT

TASK I

Establishment of The Feasibility of A
Process Capable of Low Cost,
High Volume Production of Silane, SiH_4

QUARTERLY PROGRESS REPORT

BY

W. C. BRENEMAN
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JANUARY 1977

Period Covered: October 1, 1976 - December 31, 1976

JPL CONTRACT 954334

UNION CARBIDE CORPORATION
CHEMICALS AND PLASTICS
SISTERSVILLE, WEST VIRGINIA

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TASK I

Establishment of The Feasibility of A Process Capable of Low Cost, High Volume Production of Silane, SiH_4

UNION CARBIDE CORPORATION
SISTERSVILLE, WEST VIRGINIA

W. C. BRENEMAN
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ABSTRACT

In the study of a process for the low cost, high volume production of silane (SiH_4) via redistribution of chlorohydrosilanes, the longevity and nature of the amine functional ion exchange resin catalyst was investigated. A modest decline in catalyst activity appears to be the result of loss of amine function during the initiallizing period. Long term activity remains quite high. In preparation for additional studies, deuterium labeled trichlorosilane is being prepared. The nominally 5 kg/day silane-from-dichlorosilane mini-plant has been constructed, leak tested and conditioned for start up. Approval for operation from a Pre-start Up Safety Review Team has been received in conjunction with an approved flameless method for venting silane. Laboratory studies of the hydrogenation of silicon tetrachloride co-product of the silane process are continuing along with the design of a mini-plant scale unit capable of pressurized operation. Preliminary design of a maxi-plant to integrate the entire process is also underway.

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INTRODUCTION

This research program commenced October 6, 1975. Its purpose is to determine the feasibility 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. 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 workers at Union Carbide have shown experimentally that pure chlorosilanes can be redistributed into an equilibrium mixture of other hydrochlorosilanes by contact with a tertiary amine ion exchange resin. Patents rights for that process and improvements there on have been filed.

Up through the previous quarter, laboratory work has determined the equilibrium composition and reaction rate for vapor redistribution of dichlorosilane and trichlorosilane as catalyzed by a macroticular tertiary amine functional ion exchange resin. At 80°C for example, the effluent vapor contained fourteen mole percent SiH_4 at equilibrium when the feed was pure dichlorosilane. The reaction half time was 0.25 seconds. In the case of trichlorosilane, the equilibrium composition was slightly less than ten mole percent dichlorosilane at 10 seconds half time.

Also studied was a method to remove traces of chlorosilanes from silane using a porous activated carbon.

The major co-product of the redistribution process is silicon tetrachloride as can be seen from the following chemical reaction path:

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

$$3\ H_2SiCl_2 \rightleftharpoons 2\ HSiCl_3 + SiH_4$$

$$\text{overall}\quad 4\ HSiCl_3 \longrightarrow 3\ SiCl_4 + SiH_4$$

A second phase of this program is to study the hydrogenation of silicon tetrachloride both as a method of recovering this co-product and as a means for consuming metallurgical grade silicon metal which, after all, is the object of the program, e.g. to convert impure silicon metal into high purity silicon metal by chemical means. The previous work showed that at circa 550°C silicon tetrachloride can be hydrogenated to trichlorosilane while consuming silicon metal according to the reaction:

$$3\ SiCl_4 + 2\ H_2 + Si \xrightarrow[Cu]{550°} 4\ HSiCl_3$$

The equilibrium composition at 1 atmosphere pressure and at 1 mole of H_2 per mole of $SiCl_4$ was about 20 mole percent $HSiCl_3$. Thus a close cycle process was possible for converting metallurgical silicon to high purity silicon using silane as the primary intermediate:

$$Si(M.G.) + 3\ SiCl_3 + 2\ H_2 \longrightarrow 4\ HSiCl_3 \qquad \text{Hydrogenation}$$

$$4\ HSiCl_3 \longrightarrow 2\ H_2SiCl + 2\ SiCl_4 \qquad \text{Redistribution}$$

$$2\ H_2SiCl_2 \longrightarrow SiCl_4 + SiH_4 \qquad \text{Redistribution}$$

$$SiH_4 \longrightarrow 2\ H_2 + Si\ (Pure) \qquad \text{Pyrolysis}$$

$$\text{net}\quad Si(M.G.) + 2\ H_2 \longrightarrow Si\ (Pure) + 2\ H_2$$

The impurities being removed, of course, in the process of refining the SiH_4.

A mini-plant is being constructed to study the conversion of dichlorosilane to silane. At the beginning of this past quarter the piping was 99+% complete and leak checking prior to insulation was in progress.

DISCUSSION

I. Laboratory Investigations

A. Disproportionation of H_2SiCl_2 to SiH_4

There was concern, expressed in the previous Quarterly Report on the long term activity of the Rohm and Haas A-21 ion exchange resin catalyst. The 10 grams of A-21 resin catalyst used in previous disproportionation studies was taken out of the reactor. The reactor was recharged with fresh amount of 40 grams of A-21 resin for further studies on the mechanism of the disproportionation reaction. The 10 grams spent A-21 resin catalyst was analyzed for total nitrogen in order to establish the amount of tertiary amines on the polystyrene-based A-21 resin. The original A-21 resin and another sample of spent A-21 resin withdrawn in earlier disproportionation experiments were also analyzed with the following results:

(a) Original A-12 resin before reaction

N = 6.3% by weight

(b) Spent A-21 resin after experiment 2825-69 (8 hours)

N = 4.8% by weight

(c) Spent A-21 resin after experiment 2982-76 (70 hours)

N = 4.5% by weight

The decrease of nitrogen contents in these A-21 resins was in agreement with the previously observed lowering of A-21 resin catalytic activity reported in the previous Quarterly Report. The "age" of these two spent A-21 resin catalysts could not be accurately determined since the A-21 resin was used in a number of different disproportionation experiments under various conditions. However, an estimate from the recrods in the notebooks showed that the spent A-21 resin in (a) had been reacted for a total of about eight hours while the A-21 resin in (c) had been reacted for a total of about seventy hours. The nitrogen analyses in (a), (b) and (c) showed that most of the nitrogen reduction occurred early in the run, via. from 6.3% to 4.8% after eight hours. Afterwards, the nitrogen content leveled off, viz., from 4.8% to 4.5% after seventy hours. The A-21 resin contained two types of tertiary amines. One was chemically bonded ("grafted") to the polystyrene resin base. The other was physically adsorbed on the polystyrene resin beads. The presence of low molecular weight, physically adsorbed tertiary amines was evident from the mild amine odor exhibited by the A-21 resin beads. Thus, the rapid loss of nitrogen content in the A-21 resin could be explained by evaporation of these low molecular weight tertiary amine species. The leveling off of the nitrogen content in the spent A-21 resin after seventy hours of reaction was explained by the chemically bonded tertiary amine which was retained on the polystyrene base. In conclusion, the lowering of A-21 resin catalytic activity was physical in nature. It is an inherent problem in the manufacturing of the A-21 resin beads. There was no evidence of degradation of the A-21 resin beads or other extraneous causes such as poisoning and surface contamination.

Naturally, questions were raised on what effect the reduced A-21 resin activity would have on the process of making SiH_4 from H_2SiCl_2. Taking the data given in Run Number 6, Table I, on the disproportionation of H_2SiCl_2 to SiH_4 at 80° with 2.05 g/minute H_2SiCl_2 feed and 12.6% (60.5 cc/minute) SiH_4 conversion from 10 grams, seventy hour old A-21 resin, the production rate of SiH_4 was calculated to be 0.48 pound SiH_4 per hour per pound A-21. In a hypothetical scale up situation, one would need a modest size column of A-21 resin bed 2 foot diameter by 15 foot height to make 500 pounds per hour of SiH_4 based on the above "reduced" A-21 resin activity. Thus, from a process point of view, even with this lower A-21 catalytic activity, the SiH_4 production rate would still be plentiful. Furthermore, these rough calculations do not include optimization of the SiH_4 process. For example one could substantially increase the SiH_4 output by running the disproportionation reaction under pressure instead of at atmospheric pressure on which the above calculations were based.

B. The Nature of The Amine Catalyst

Very little was known on the mechanism of the disproportionation reaction of hydrochlorosilanes with tertiary amine catalysts. One theory was that the amine hydrochloride was believed to be the true catalyst. Consequently, the A-21 resin used in previous experiments was treated with HCl gas prior to use. A series of experiments was carried out with a fresh sample of A-21 resin. No prior treatment with HCl was carried out. Furthermore, the reaction product mixture was analyzed as soon as H_2SiCl_2 was fed into the A-21 resin reactor.

TABLE I

TREATMENT OF A-21 RESIN WITH HCl GAS

Run Number	Date	Reaction Temperature °C	H_2SiCl_2 Feedrate cc/Minute	SiH_4 Production Rate cc/Minute	Production Composition, Mole %				
					SiH_4	H_3SiCl	H_2SiCl_2	$HSiCl_3$	$SiCl_4$
1	3-9-76	80	250	35.8	14.1	35.4	35.4	42.1	0.7
2	6-12-76	80	250	32.0	14.8	10.6	35.6	39.8	0.2
(A-21 treated with 250 cc/minute of HCl gas for 10 minutes.)									
3	6-13-76	80	250	36.8	14.9	10.6	34.3	40.1	0.2
4	3-9-76	80	500	64.6	12.9	10.0	33.6	42.9	0.5
5	6-12-76	80	500	47.0	10.8	12.6	41.7	34.8	0.08
(After HCl treatment.)									
6	6-13-76	80	500	60.5	12.6	11.9	38.1	37.3	0.09
7	3-9-76	80	1000	125	13.2	9.0	35.5	41.9	0.4
8	6-12-76	80	1000	58.3	7.3	14.1	49.8	28.8	0.03
(After HCl treatment)									
9	6-31-76	80	1000	72.6	8.7	13.2	47.4	30.7	0.03

Results of these experiments are summarized in Table II. Data in Table II showed that the fresh A-21 resin catalyst was very active. In comparison with previous experiment (Number 11, Table II) carried out with HCl-treated A-21 resin, the catalytic activity of the untreated A-21 resin (Number 3, Table II) was just as high. Therefore, it may be concluded that prior HCl treatment of fresh A-21 resin used in these experiments contained about 1% water. The above experimental data does not rule out the possibility of the amine hydrochloride being the active catalyst since one might argue that HCl could be generated in-situ by the hydrolysis of SiCl linkage with water adsorbed on the A-21 resin surface. Nevertheless, there was one piece of experimental evidence reported earlier[1] that addition of HCl gas did enhance the catalytic activity of A-21 resin catalyst. The effect of HCl on the disproportionation of hydrochlorosilanes catalyzed by A-21 resin will be the subject of investigation along with other studies on the mechanism of these reactions. More work is in progress.

C. Preparation of Deuterium Labeled DCl

As a means for studying the mechanism of the amine catalyzed redistribution reaction of chlorosilanes, it is planned to use deuterium labeled reactants. These will be prepared by reaction of DCl with silicon metal to form deuteriated trichlorosilane $DSiCl_3$.

The deuteriated compound, DCl, was prepared by the reaction of D_2O with dimethyldichlorosilane as shown in the following equation,

$$2\ Me_2SiCl_2 \quad + \quad D_2O \longrightarrow Me_2ClSiOSiMe_2Cl \quad + \quad 2\ DCl$$

TABLE II

RATE OF DISPROPORTIONATION OF H_2SiCl_2 TO SiH_4 IN 40 GRAMS A-21 RESIN WITH NO PRIOR TREATMENT WITH HCl

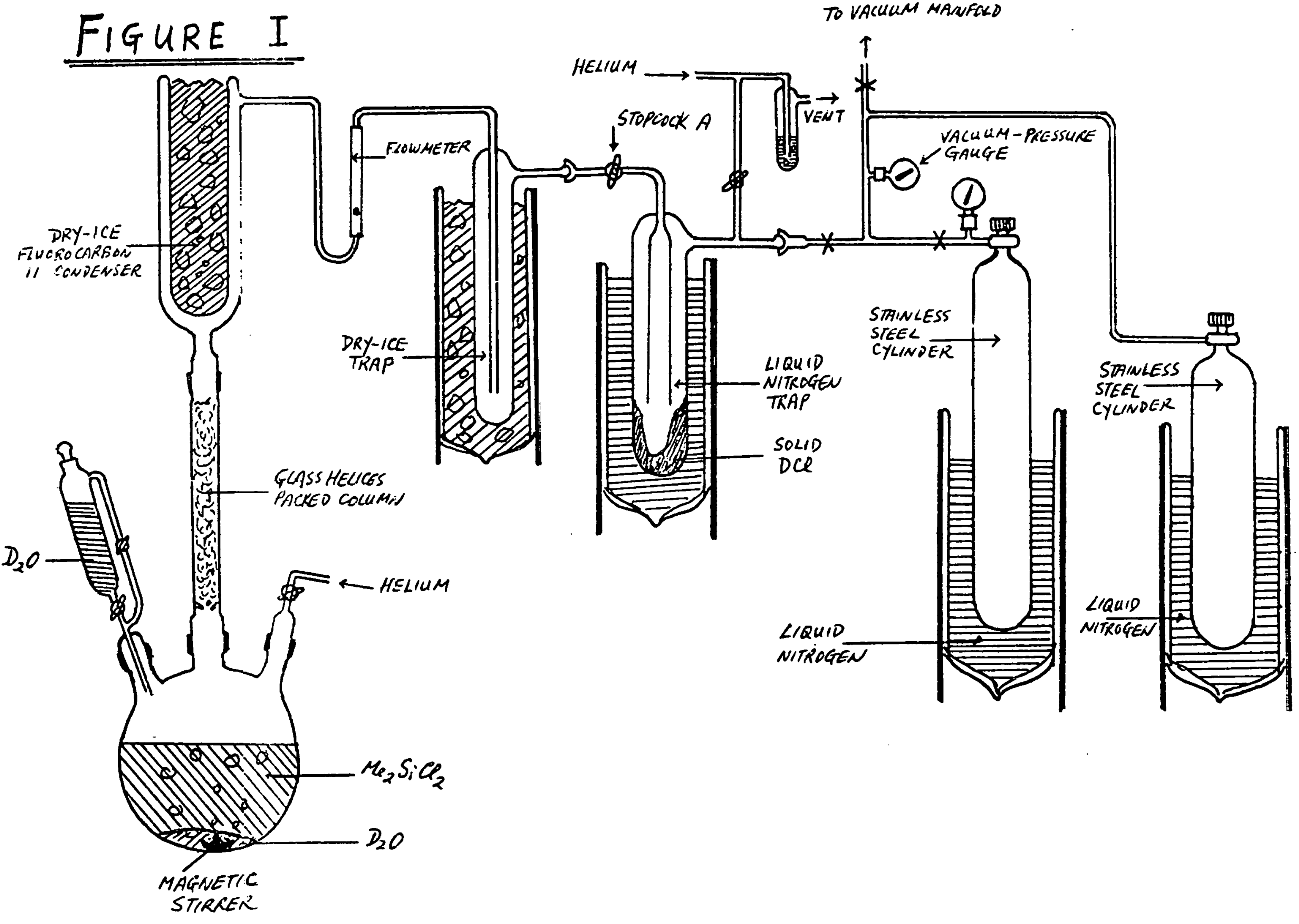
Experimental Number	Time Lapse Since H_2SiCl_2 Feed (Minute)	H_2SiCl_2 Feedrate (Grams/Minute)	Residence Time[1] (Second)	Product Composition, Mole %				
				SiH_4	H_3SiCl	H_2SiCl_2	$HSiCl_3$	$SiCl_4$
1	15	4.10	3.6	15.21	10.85	32.52	40.67	0.75
2	30	6.15	2.4	14.69	11.05	33.52	40.35	0.37
3	55	2.05	7.2	15.93	10.53	32.14	40.66	0.74
4	70	1.03	~~14.4~~	~~15.62~~	~~10.66~~	32.31	40.45	0.96
11[2]	--	0.52	7.3	15.9	9.6	32.9	41.1	0.48

[1] Based on void space in A-21 resin, i.e., 65% of bed volume.

[2] Data from Number 11, Table III, Monthly Report - April 1976, based on 10 grams A-21.

The apparatus was schematically shown in Figure 1. The reactor system was evacuated under vacuum for about thirty minutes to remove moisture which might be present. Then, the apparatus was filled with helium gas to atmospheric pressure. Dimethyldichlorosilane, 1980 grams, was placed in the 3-liter 3-necked flask equipped with a magnetic stirrer, a dropping funnel, a gas inlet tube and a glass helices-packed column topped with a dry-ice/Fluorocarbon 11 condenser. The Me_2SiCl_2 was heated slowly to reflux to drive off dissolved HCl gas in the liquid. The contents were cooled to room temperature while helium gas was passed into the apparatus to displace HCl gas which might be present. The dry-ice trap and the liquid nitrogen trap shown in Figure 1 were cooled with the appropriate coolants. Then, D_2O (180 grams) was placed in the dropping funnel and added dropwise into the flask with stirring. DCl gas produced passed through a flowmeter and into the dry-ice trap. The dry-ice trap was designed to remove Me_2SiCl_2 which might escape the dry-ice condenser. DCl, boiling point 81.6°, passed through the dry-ice trap and was condensed in the liquid nitrogen trap. After about one hour of reaction, the liquid nitrogen trap was filled with DCl. The condensed DCl was isolated from the reactor by closing off stopcock A as shown in Figure 1. Vent to the atmosphere was also closed. The DCl trap and the stainless steel cylinder were evacuated. Then, the DCl collected in the liquid nitrogen trap was distilled under vacuum into a stainless steel cylinder immersed in liquid nitrogen. After complete transfer of DCl into the cylinder, the reaction of D_2O and Me_2SiCl_2 was continued to produce more DCl. The procedure was repeated several times to collect about 550 grams of DCl in the stainless steel cylinder. The DCl collected was further

FIGURE I


TO VACUUM MANIFOLD
HELIUM
VENT
STOPCOCK A
FLOWMETER
VACUUM-PRESSURE GAUGE
DRY-ICE FLUOROCARBON 11 CONDENSER
DRY-ICE TRAP
LIQUID NITROGEN TRAP
SOLID DCl
STAINLESS STEEL CYLINDER
STAINLESS STEEL CYLINDER
GLASS HELICES PACKED COLUMN
D_2O
HELIUM
LIQUID NITROGEN
LIQUID NITROGEN
Me_2SiCl_2
D_2O
MAGNETIC STIRRER

purified by trap-to-trap distillation from one stainless steel cylinder to another. The distillation was carried out twice from one cylinder at -70° to another empty cylinder at -196°. This further removed trace of Me_2SiCl_2 which might be present. The purified DCl (552 grams) was stored at room temperature in a stainless steel cylinder for future application. An internal pressure of about 620 psig was developed.

Apparatus and analytical methods were devised to study the mechanism of the disproportionation of chlorohydrosilanes to SiH_4 by isotopic labeling.

D. Hydrogenation of $SiCl_4$

The hydrogenation of $SiCl_4$ to $HSiCl_3$ was carried out at 500° and at atmospheric pressure in a fluidized bed of Cu/Si contact mass for a total of 40 hours. The objective was to study the effect of prolong reaction time on the reactivity of the Cu/Si contact mass such as reaction rates. Furthermore, a material balance on the hydrogenation reaction was made in order to verify the stoichiometry as shown in the following equation.

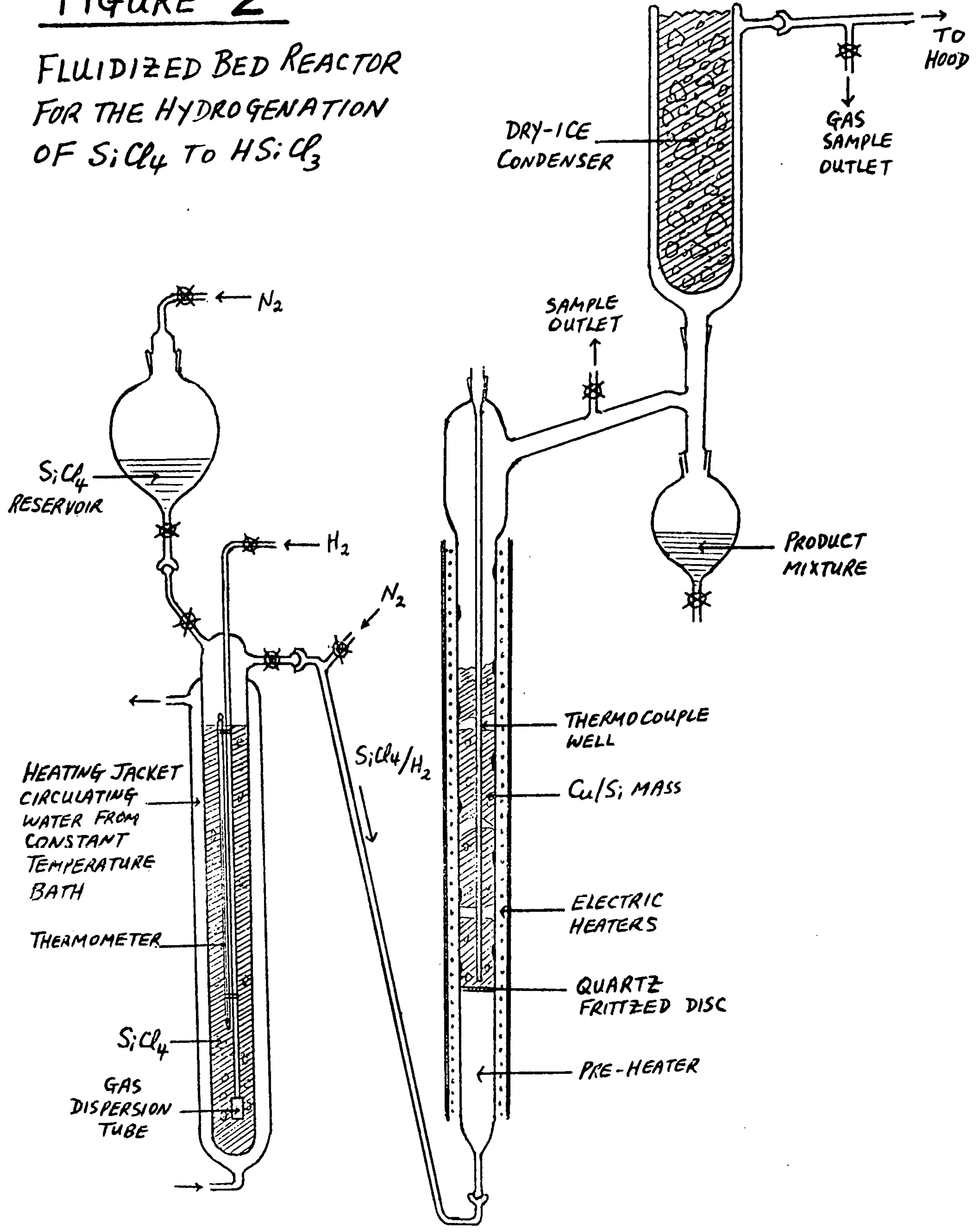
$$3\ SiCl_4 + 2\ H_2 + Si \xrightarrow{Cu} 4\ HSiCl_3 \qquad (1)$$

(a) Extended Reaction Time Studies

The experiment was carried out in a Vycor glass fluidized bed reactor as described in Figure 2. The reactor was charged with 220 grams of Cu/Si mass containing about 2.5% copper catalyst on the surface of the Si metal which had a particle size distribution of 65X150 mesh (208 x 104 microus). The Cu/Si mass was first reacted with HCl gas at 330° in order

FIGURE 2

FLUIDIZED BED REACTOR FOR THE HYDROGENATION OF $SiCl_4$ TO $HSiCl_3$



to remove surface contaminant, such as oxides. The surface cleaning procedure produced 47 grams of chlorosilane crude. The composition of the product crude was determined by gas chromatography (g.c.) and results were summarized in Table III. Next, the Cu/Si mass was heated to 550° while a 1:1 molar ratio of $SiCl_4$ and hydrogen was fed. The flowrate of H_2 was maintained at 160 cc/minute while the $SiCl_4$ feed was kept at 1.08 grams/minute or 154 cc vapor/minute. The residence time at 550° correspondence to 15 seconds based on empty tube and 7 seconds based on void space in the Cu/Si mass bed. After the reactor reached the selected reaction temperature of 550°, the chlorosilane product crude was collected and analyzed every hour. Results were summarized in Table III. The conversion of $SiCl_4$ to $HSiCl_3$ was about 14% in one pass through the Cu/Si mass bed. After 3 hours of reaction, the reactor was shutdown for the day. Nitrogen gas was introduced into the reactor at 550° to stop the reaction while the apparatus was cooled to room temperature. The reaction was continued in the following day. An appreciable drop of the Cu/Si mass activity was observed as indicated by the g.c. analysis of the hourly samples collected. The conversion of $SiCl_4$ to $HSiCl_3$ was decreased from 13.84% to 8.59%, representing an approximately 40% loss of reactivity. Furthermore, the chlorosilane product crude collected gave an orange color in contrast to the almost colorless liquid collected in the previous sample before the shutdown. Contamination of the solid surface was evident and the nitrogen gas was suspected to be the cause. The reaction temperature was lowered from 550° to 330° and the Cu/Si mass was again "cleaned" by reacting with HCl gas to collect 27 grams of product crude. Then, the reactor temperature was restored to 550° to continue the hydrogenation experiment. The cleaning procedure appeared to improve the activity of the Cu/Si

TABLE III

HYDROGENATION OF $SiCl_4$ TO $HSiCl_3$ AT 500° ATMOSPHERIC PRESSURE WITH 1:1 $SiCl_4$ TO H_2 OVER 220 GRAMS OF Cu/Si CONTACT MASS IN A FLUIDIZED BED REACTOR

Reaction Time Hours	Weight of Crude Collected Grams	Product Composition, Mole %			
		H_2SiCl_2	$HSiCl_3$	$SiCl_4$	Heavies
0[1]	47	3.34	63.74	32.39	0.54
1	62	0.12	14.40	85.02	0.46
2	64	0.19	14.25	84.81	0.75
3	63	0.31	13.84	85.24	0.61
(Reactor under nitrogen at 550°, cooled and shutdown overnight.)					
4	64	0.14	8.59	90.72	0.55
5	65	0.14	9.97	89.52	0.36
(Clean Cu/Si mass again with HCl gas at 330° to collect 27 grams of crude.)					
-	27	5.55	70.77	23.57	0.12
6	65	0.22	12.13	87.57	0.07
7	66	0.25	11.51	88.15	0.09
(Shutdown overnight under $SiCl_4/H_2$.)					
8	64	0.16	11.22	88.56	0.06
9	65	0.14	11.60	88.18	0.09
10	64	0.16	12.15	87.65	0.04
11	63	0.19	13.79	85.94	0.08
12	64	0.11	13.92	85.92	0.05
13	63	0.22	14.74	85.03	0.02
(Shutdown over weekend under $SiCl_4/H_2$.)					
14	62	0.14	15.01	84.83	0.02
15	64	0.14	14.75	85.07	0.04
16	65	0.44	14.48	85.00	0.08
17	67	0.18	15.18	84.56	0.08
18	64	0.29	14.30	85.39	0.03
19	62	0.12	14.24	85.59	0.05
(Shutdown overnight under $SiCl_4/H_2$.)					
20	61	0.10	14.27	85.55	0.08
21	61	0.17	14.38	85.34	0.11
22	62	0.20	14.93	84.76	0.11
23	61	0.19	15.04	84.73	0.04
24	82	0.13	13.26	86.59	0.02
25	82	0.16	13.82	86.00	0.02
(Shutdown overnight under $SiCl_4/H_2$.)					
26	65	0.16	13.51	86.25	0.08
27	70	0.15	14.36	85.43	0.06
28	67	0.17	14.38	85.43	0.02
29	70	0.18	14.54	85.24	0.04
30	64	0.17	14.55	85.25	0.04
(Shutdown overnight under $SiCl_4/H_2$.)					
31	67	0.18	14.68	85.11	0.08
32	65	0.19	14.71	85.05	0.06
33	64	0.18	14.62	85.16	0.04
34	65	0.19	14.70	85.09	0.02
35	66	0.15	14.57	85.25	0.03
(Shutdown overnight under $SiCl_4/H_2$.)					
36	63	0.14	14.48	85.30	0.08
37	65	0.18	14.67	85.09	0.06
38	66	0.19	14.21	85.56	0.04
39	63	0.17	14.59	85.21	0.03
40	64	0.18	14.74	85.04	0.04

[1] Cu/Si mass was cleaned by reacting with HCl at 330° to collect 47 grams of crude. Then, temperature was raised to 550° to start the hydrogenation experiment.

mass which showed 12.13% conversion of $SiCl_4$ to $HSiCl_3$ in the following hourly sample (Number 6, Table III). At the end of the day, the reactor was shutdown. Instead of nitrogen gas, the Cu/Si mass was kept under an atmosphere of H_2 and $SiCl_4$ vapor while the mass was cooled to room temperature. The hydrogenation experiment was continued the next day. There was no change of the Cu/Si mass activity as shown by the conversion of $SiCl_4$ to $HSiCl_3$ before (11.51%, Number 7, Table III) and after (11.22%, Number 8, Table III) the shutdown. In the next 5 hours of reaction, the conversion of $SiCl_4$ to $HSiCl_3$ gradually improved from 11.22% to 14.74%. At this point, the original activity of the Cu/Si mass was restored. The hydrogenation experiment was carried out for a total of 40 hours. Results were summarized in Table III. There were five other shutdowns and start ups during the course of the experiment. In each instance, the Cu/Si mass was kept under an atmosphere of H_2 and $SiCl_4$ vapor. No measurable loss of the Cu/Si mass reactivity was observed as a result of these interruptions. The conversion of $SiCl_4$ to $HSiCl_3$ remained essentially constant at 14% to 15% throughout the experiment. Thus, the reactivity of the Cu/Si mass did not change after 40 hours of reaction. Results of these experiments also showed that nitrogen gas was not "inert" at 550° and, therefore, it should not be used as carrier gas at these temperatures.

(b) Material Balance

The apparatus was taken down and a total of 188.4 grams of Cu/Si mass was recovered. The spent Cu/Si mass appeared very much the same as the starting material. The fluidized bed reactor was clean except at the top where it was not heated and at the condenser assembly, where elutriated fine particles of silicon and by-product such as $AlCl_3$ and $FeCl_3$ were collected. Analyses of the starting Cu/Si mass for copper contents were in progress.

During the entire experiment, a total of 220 minus 188.4 equals 31.6 grams of silicon metal consumed. The amount of Si consumed in the HCl cleaning procedure was calculated to be 14.4 grams from the composition of the 47 grams and the 27 grams of chlorosilanes collected in the HCl plus Cu/Si reaction at 330°. Therefore, the hydrogenation reaction alone accounted for the remaining 31.6 minus 14.4 equals 17.2 grams of silicon consumed. A total of 2604 grams of product crude was collected in the 40 hours of hydrogenation reaction. Gas chromatography analysis showed that the 2604 grams of chlorosilane crude contained 291.9 grams $HSiCl_3$ and 4.04 grams H_2SiCl_2. According to the stoichiometry in Equation (1), for every four moles of $HSiCl_3$ produced, one mole of Si was consumed. Thus, 291.9 grams of $HSiCl_3$ were equivalent to

$$291.9 \times \frac{28.06}{135.5} \times \frac{1}{4} = 15.11 \text{ grams Si}$$

The formation of H_2SiCl_2 might be considered as hydrogenation product of $HSiCl_3$, namely

$$2\ HSiCl_3 + 2\ H_2 + Si \longrightarrow 3\ H_2SiCl_2 \qquad (2)$$

Thus, 4.04 grams H_2SiCl_2 were equivalent to

$$4.04 \times \frac{28.06}{101.0} \times \frac{1}{3} \times 4.04 \times \frac{2 \times 135.5}{3 \times 101.0} \times \frac{28.06}{135.5} \times \frac{1}{4} = 0.57 \text{ g Si}$$

From the amount of chlorosilane products collected, calculations showed 15.11 plus 0.57 equals 15.68 grams Si metal were consumed by the hydrogenation reaction. The observed Si consumption was 17.2 grams. Material balance on Si metal was

$$\frac{15.68}{17.2} \times 100 = 91.2\%$$

Thus, the agreement between the stoichiometry of the hydrogenation reaction [Equations (1) and (2)] and the observed material balance was quite good.

Analyses of copper in the Cu/Si mass bed before and after the 40 hour hydrogenation reaction are summarized below.

(1) Starting Cu/Si mass, sample number 2825-66-A,

Cu = 2.9% by weight

(2) Spent Cu/Si mass after 40 hours, sample number 2825-66-B

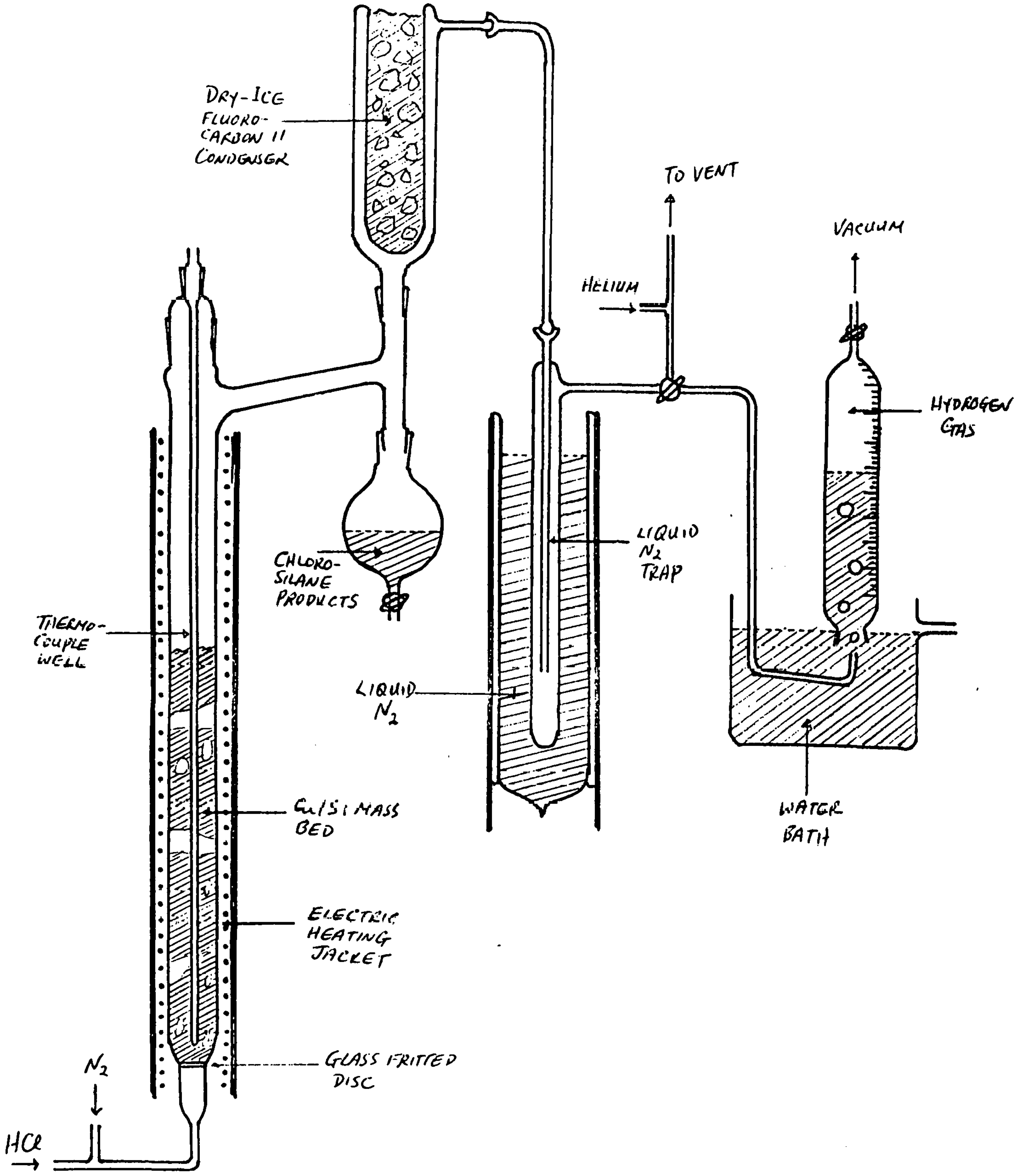
Thus, after 40 hours of reaction, the bulk of copper catalyst remained in the Cu/Si mass bed.

F. Direct Synthesis of H_2SiCl_2 at Low Reactor Temperature

The reaction of HCl gas with Si metal is known to be a facile, strongly exothermic reaction. Indeed, the reaction was so rapid that even in a small, one-inch diameter fluidized bed reactor, it was difficult to obtain a uniform temperature distribution throughout the mass bed. Consequently, "hot spots" developed in the reactor, which usually occurred at the bottom of the mass bed. Copper was known to catalyzed the HCl + Si reaction to a still higher reaction rate. Thus, one would expect that the problem of hot spots in the fluidized bed reactor in the HCl + Cu/Si reaction would be more severe. A series of experiments was carried out to study the HCl + Cu/Si reaction at low reactor temperature ($< 270°C$) to avoid hot spot in the Cu/Si mass bed. Since H_2SiCl_2 was believed to be unstable at high temperatures, the idea was an attempt to increase the H_2SiCl_2 by eliminating the possibility of decomposing the H_2SiCl_2 formed at high temperatures. A hot spot in the fluidized bed reactor generally resulted from poor heat transfer from the reacting solid to the wall of the reactor. Since the rate of the HCl + Si reaction increased exponentially with temperature, all the HCl could be consumed in a small section of the reactor if proper mixing of the solid mass was not achieved. Indeed, a section of the Si mass bed has been observed to grow to red hot when this section of the mass bed remained static at the bottom of the reactor.

The appratus for the dichlorosilane synthesis was schematically shown in Figure 3. The fluidized bed reactor was the same as the one used in previous studies on the HCl + Cu/Si reactions.[2] Minor modifications were made to allow measurement of hydrogen gas generated in the reaction. The H_2 produced in the direct reaction was passed through a liquid nitrogen trap to remove impurities and was measured by water displacement as shown in Figure 3. Material balance for silicon has been made in previous experiments on the HCl + Si reaction.

FIGURE 3 APPARATUS FOR HCl + Cu/Si AT LOW TEMPERATURE



However, material balance for hydrogen and HCl was not studied and the present experiments were designed to do so. Into the fluidized bed reactor were charged 300 grams of 65X150 mesh Cu/Si contact mass containing about 1 weight percent of copper catalyst. The reactor was heated to 250° under nitrogen with an electric heater which provided uniform heating to the Cu/Si mass bed. The reactor temperature was controlled by thermocouple located at the mid-point of the mass bed. A thermocouple well extending from the top of the reactor to one-inch above the glass fritted disc allowed measurements of the reaction temperatures throughout the mass bed. Hydrogen chloride was then fed at the bottom of the reactor through the glass fritted disc at 1450 cc/minute at room temperature (22°). At this feedrate, the residence time corresponded to four seconds based on void space in the Cu/Si mass bed. The Cu/Si mass was fluidized vigorously and chlorosilane crude was produced at 250°. As shown in Figure 3, the reaction products were condensed with a dry-ice/Fluorocarbon 11 condenser and collected in a receiver. As soon as HCl gas was introduced into the reactor, temperature at the bottom of the reactor rose rapidly. The electric heater was completely turned off. The HCl + Cu/Si reaction became self-supporting without any external heating. The reactor temperature profile along the mass bed was recorded as follows.

Distance Above HCl Gas Inlet, Inch	1	3	5	7	9	11	13
Temperature, °C	270	264	256	250	230	210	200

The highest temperature in the Cu/Si mass bed at the bottom of the reactor one-inch above the glass fritted disc, despite the fact that HCl gas was fed in cold (22°) and about two inches of the Cu/Si mass bed above the glass fritted disc was exposed to the atmosphere with no insulations. The HCl + Cu/Si reaction was indeed very fast. The reaction was carried out for thirty minutes after a steady state was reached. The hydrogen gas production rate was measured four times at a constant HCl feedrate of 1450 cc/minute at 22°. The average of four measurements gave the H_2 production rate of 552 cc/minute at 22°. The chlorosilane crude collected in the receiver was analyzed by gasl-liquid partition chromatography (glpc). The experiments were repeated at various reactor temperatures. Results were summarized in Table IV. Data in Table IV showed no significant change in the H_2SiCl_2 yield with respect to reaction temperature. The yield of H_2SiCl_2 remained low at 1 to 1.5%. The composition of the reaction product mixture was essentially the same except that the amount of heavies, presumably Si_2Cl_6, increased substantially at lower reaction temperatures.

F. Material Balance for HCl and H_2

A balance equation (3) might be written to approximately accound for the product composition as shown in Table IV.

$$306\ HCl + 100\ Si \xrightarrow{Cu} H_2SiCl_2 + 88\ HSiCl_3 + 7\ SiCl_4 + 2\ Si_2Cl_6 + 108\ H_2 \qquad (3)$$

Thus, the calculated hydrogen production rate based on 1450 cc HCl/minute feed would be

$$1450 \quad x \quad \frac{108}{306} \quad = \quad 512 \text{ cc } H_2\text{/Minute}$$

TABLE IV

SUMMARY OF DATA ON THE HCl + Cu/Si REACTION AT LOW TEMPERATURES

Experimental Number	Reaction[1] Temperature °C	Hot Spots[2] °C	HCl Feedrate cc/Minute	Chlorosilane Crude Grams/Hour	Composition of Product Mixture-Mole %				
					H_2SiCl_2	$HSiCl_3$	$SiCl_4$	Lites	Heavies
1	250	270	1450	170	1.14	88.4	7.32	0.01	3.13
2	240	260	1200	128	1.26	86.0	9.81	0.01	2.91
3	280	310	1200	122	1.38	87.4	9.41	0.01	1.82
4	300	340	1200	124	1.38	88.6	9.19	0.01	0.82
5	330	365	1200	126	1.41	87.7	10.2	0.02	0.45

[1] At mid-point of the Cu/Si mass bed.

[2] At 1-inch above the glass fritted disc.

The observed H_2 production rate was 552 cc/minute. On the other hand, the calculated H_2 production rate based on 170 grams/hour of chlorosilane product crude (average molecular weight equals 139) was

$$\frac{170}{139} \times \frac{24,200}{60} \times \frac{108}{100} = 533 \text{ cc } H_2\text{/Minute}$$

The calculated HCl feedrate based on 170 grams/hour of chlorosilane crude was

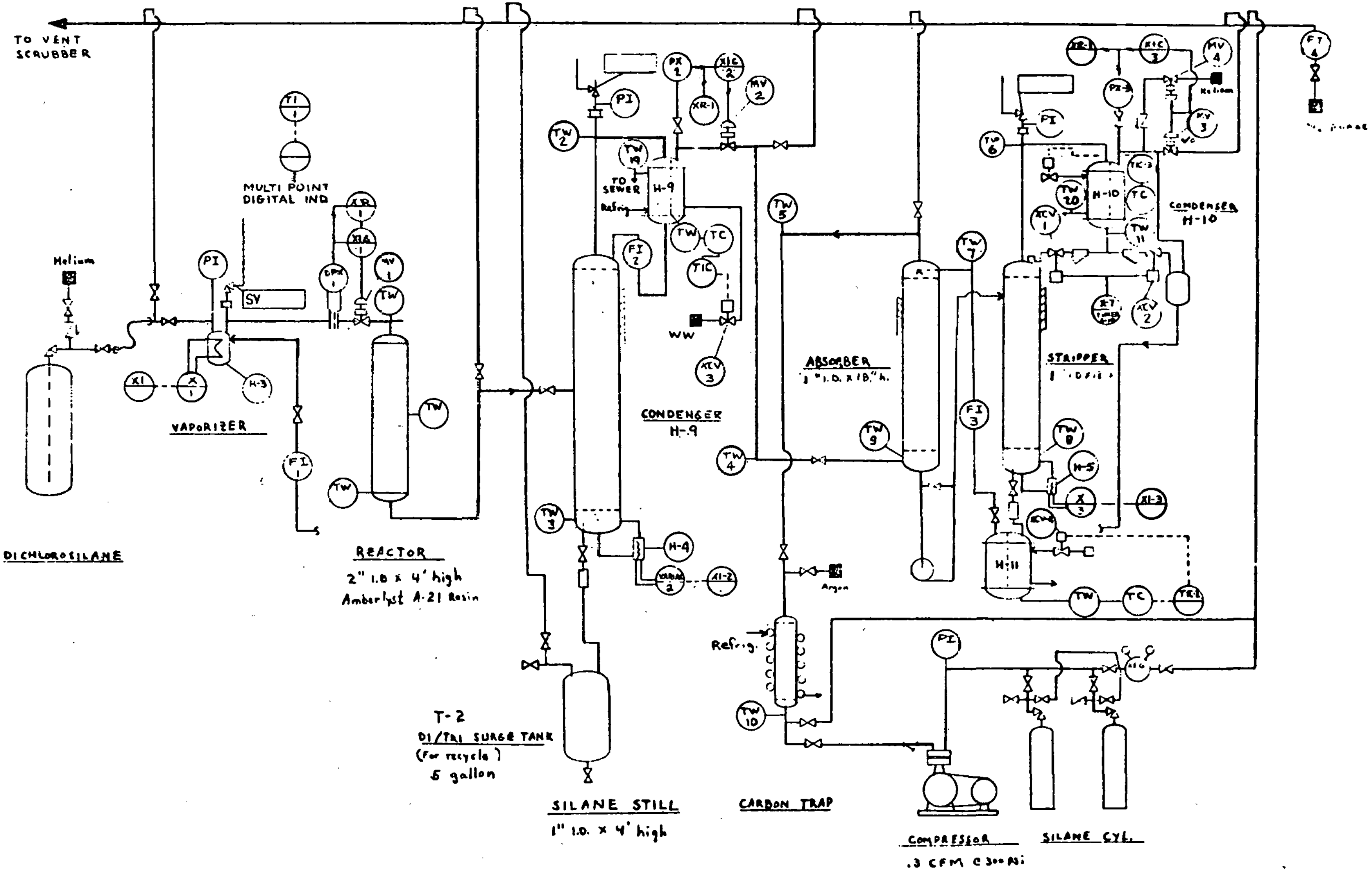
$$\frac{170}{139} \times \frac{24,200}{60} \times \frac{306}{100} = 1509 \text{ cc HCl/Minute}$$

The observed HCl feedrate was 1450 cc/minute. Thus, in addition to a good material balance for Si metal obtained in previous experiments, good agreement on the material balance for H_2 and HCl was also observed.

II. Pilot Plant Studies

A. Mini-Plant Operations

The Pilot Plant studies this period were concerned with the mechanical details of final assembly, leak testing and process safety review prior to system start up. A major problem which has been resolved is the leakage on the tube side of the shell and tube heat exchangers used as condensers and coolers on the silane mini-plant. Items H-9, 10 and 11 on the flowsheet C-075869



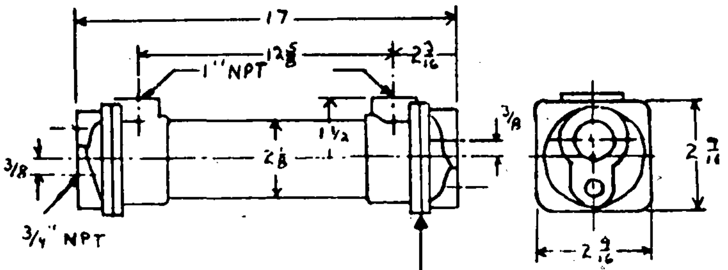
Silane Mini Plant

are standard fixed tube sheet, single pass, shell and tube exchangers constructed of 316 stainless steel. When installed these units were found to leak badly at the head gasket (Figure 4). Precision torque loading of the bolts, replacement of the original gaskets, lapping the tube sheet and head gasketing surfaces did not resolve the problem. Replacement units from the vendor were received this period. They also leaked although not so severely and not at all at the gaskets. Examination of these units indicated that the original gaskets were too hard and covered too much area to allow sufficient compression of the gasket to affect a seal within the tensile strength of the four 1/4-inch hold-down bolts. The problem has been resolved by changing to a softer gasket material and by precision torque tightening of the bolts. The units are now gas tight at 150 psig. (Normal operating pressure will be 60 psig.) The original heat exchangers did not respond to this technique and have been returned to the vendor.

The construction and initial check out of the mini-plant for producing SiH_4 from H_2SiCl_2 is complete. The completed unit has been successfully leak tested. A Pre-start Up Safety Review Team has critiqued the installation, operating procedures and safety considerations of the unit and with minor revisions has recommended approval to start the unit. The revisions have all been accomplished. These included installation of extra valves and check valves, an additional thermocouple in the vaporizer and a safety relief system on the absorber column. Venting flammable silane gas from the unit in a flameless fashion was also addressed and resolved to the satisfaction of the Review Team as will be discussed later.

FIGURE 4

TYPICAL HEAT EXCHANGER



Gasket, Compressed Asbestos

The unit was flushed thoroughly with Refrigerant 113 as a solvent to degrease and remove dirt, filings, tread dope and other assembly trash. The distillation columns were packed with 1/4-inch expanded metal contact packing and the absorber packed with 1/4-inch ceramic saddle packing, all of which had been cleaned in R-113 solvent. The resin reactor was filled with the Amberlyst A-21 ion exchange resin in the wet, as received condition. The water was removed by flushing with ethanol followed by a 50:50 ethanol/R-113 mixture until the water content was less than 0.01%. The entire process unit from the feed line through to the compressor discharge was purged with dry nitrogen. To complete the conditioning, the unit was flushed with silicon tetrachloride through all lines except the carbon trap and compressor.

B. Flammability of Silane

Silane is spontaneously flammable in air. This characteristic is both an asset and a liability in processing and handling the gas. While little or no accumulation of SiH_4 would be possible in the atmosphere surrounding the process unit or its vent stack, other flammable materials could be in the proximity such that leaking or venting SiH_4 could serve as an ignition source. This was of concern to the Pre-start Up Safety Review Team, especially in the case of the process and emergency vents. The alternates investigated were:

1) An incinerator/scrubber combination
2) A caustic scrubber
3) Vent gas dilution with nitrogen and/or steam

Of these alternatives, 1 and 2 were reported earlier. The early work on the flammability of silane oxygen mixtures[3 4] indicated that at temperatures below 120° that an induction period was possible but that a slow reaction took place yielding silicon. The ignition of silane-oxygen mixtures was dependent on the concentration, total system pressure, temperature and UV radiation. In actual practice, it has been observed that SiH_4 leaking from a point source into ambient air will show first a white stream of silica and then a flame if either the leak rate increases or a frictional disturbance of the leak is made. In venting SiH_4 through a nitrogen or steam diluted stream into ambient air, the presence of a flameless brown plume of presummable amorphous silicon has been observed.

To determine if a nitrogen and/or steam dilution could be used to flamelessly vent SiH_4 from the development reactor, the system shown in Figure 5 was constructed. It consisted of a system of three flow meters for metering SiH, N_2 and steam into a pipe which ended in a 3/4-inch or 1/2-inch nominal pipe in ambient air. The process vent line of the development reactor is 3/4-inch. A flow of N_2 and/or steam was established and the SiH_4 flow increased slowly until a visible flame was seen. Figure 6 illustrates the concentration of SiH_4 at which ignition occurred. At less than 3% of SiH_4 with N_2 alone or 7% with a 2:1 steam nitrogen mixture, venting was possible. When a 1/2-inch vent pipe was used, the upper concentration for flameless venting of silane-nitrogen mixture was increased to 10% silane.

FIGURE 5

Silane Flame Apparatus

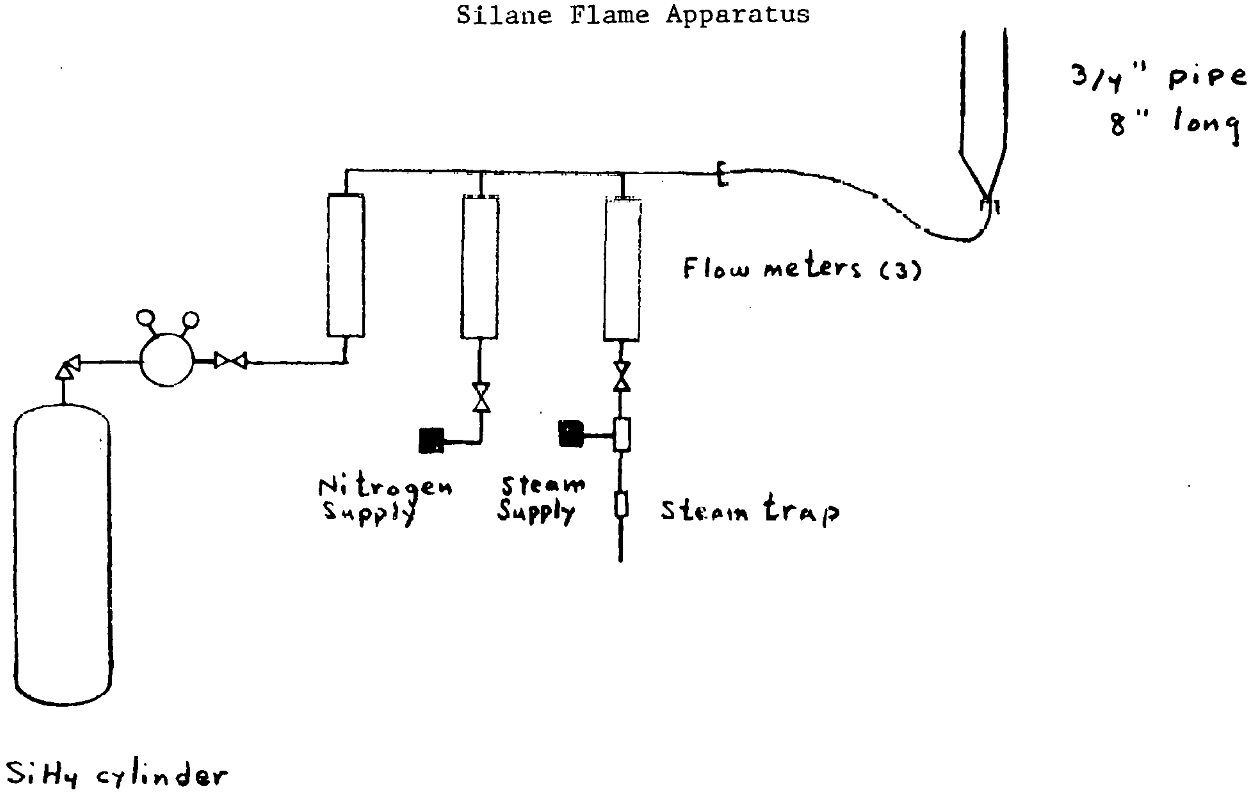
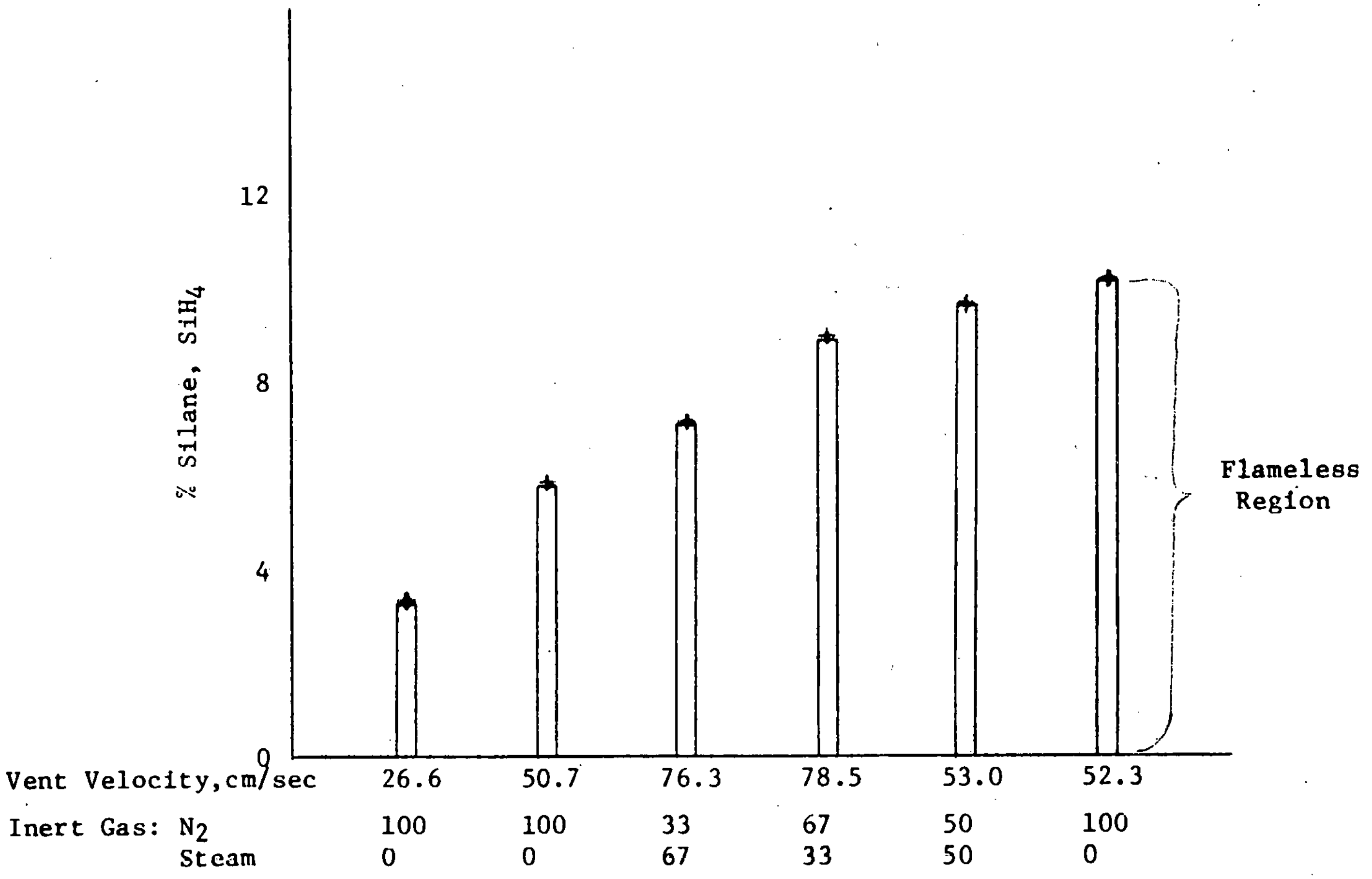


FIGURE 6

Flammability of Silane



In the development reactor unit, nitrogen is used to purge the process and emergency relief vent systems to maintain a dry, oxygen free condition. Based on the design capacity of the unit of 5000 cc/minute of SiH_4, a 200 cfh N_2 purge would provide 3% vent concentration if all of the SiH_4 were vented as produced. For controlled excursion of process conditions such as set-point changes, blowdown, etc., a 10 psi/minute change in system pressure would require 1000 scfh N_2 to maintain flameless venting. The vent system approved by the Safety Review Team consists of a 20 cfh N_2 purge of the process and emergency relief vent headers. In addition there are a 200 cfh and 1000 cfh critical orifice throttled additional N_2 purges which are manually opened during periods of silane venting as appropriate for the processing condition. This vent system is adequate for the 10 pound per day silane plant.

C. Hydrogenation of Silicon Tetrachloride

A preliminary process flowsheet has been developed for a hydrogenation reactor system (Figure 7). The heart of the system is a 3-inch ID x 4-foot high tubular reactor (316 SS) inside an electric resistance furnace. The reactor tube will be designed to facilitate study of fluidized or static beds of silicon of various particle size at pressures up to 150 psi at 500 to 600°C. The silicon tetrachloride fed liquid phase by a positive displacement metering pump will be vaporized in tubes around the reactor and mixed with hydrogen as they enter the reactor. The condenser system which could operate at a lower pressure will use direct contact of the hot gas with condensed chlorosilanes to quench the gas and collect volatile

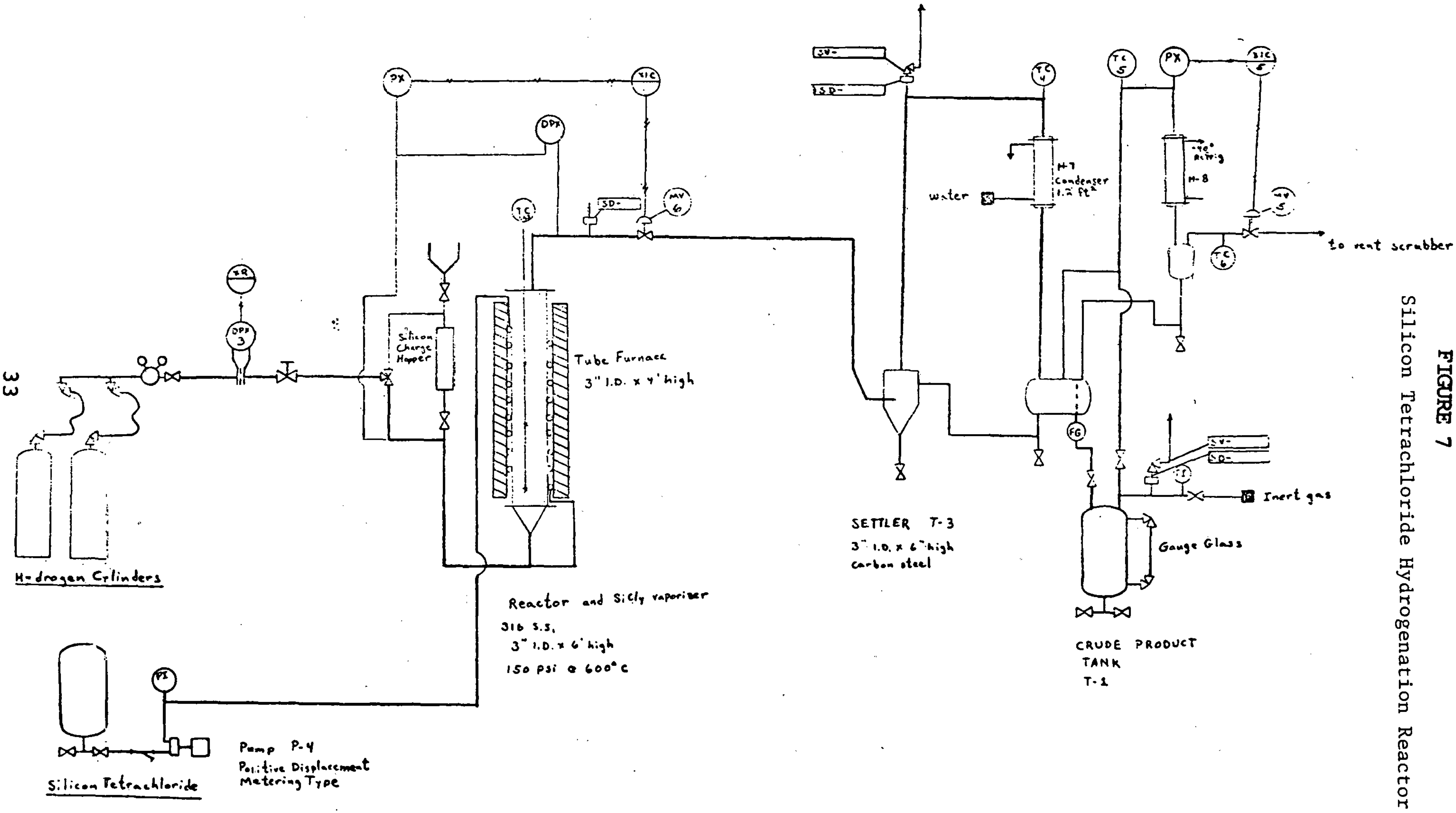


FIGURE 7
Silicon Tetrachloride Hydrogenation Reactor

metal halides in a settler. The excess hydrogen gas from the unit will not be recycled (as it would be in a production reactor) but appropriate chemical analysis will be made to characterize it. The crude $HSiCl_3/SiCl_4$ product mixture will be collected for eventual use as feed to the silane from trichlorosilane reactor system.

The condensers, settler, pressure controllers and valves have been assembled. The reactor design will be completed next month and the oven and reactor procurement and fabrication initiated.

D. Maxi-Plant

A preliminary flowchart for the trichlorosilane to dichlorosilane portion of the integrated maxi-plant has been prepared (Figure 8). This unit consists of a distillation column to separate $HSiCl_3$ from $SiCl_4$, a resin catalyst redistribution reactor and a distillation column to separate H_2SiCl_2 from $HSiCl_3$ and $SiCl_4$. The feed to this unit would be from the hydrogenation reactor. The H_2SiCl_2 product would go directly to the silane mini-plant while the $SiCl_4$ by-product would feed the hydrogenation unit.

E. Other Data

The analysis of silane stored absorbed on activated carbon[1] indicated that a change occurred in the purity of the gas. Asubstantial amount of hydrogen was indicated which was not present in the original gas (Table V). If 1.0% H_2 were present in the source SiH_4, this would not be adsorbed, concentrate

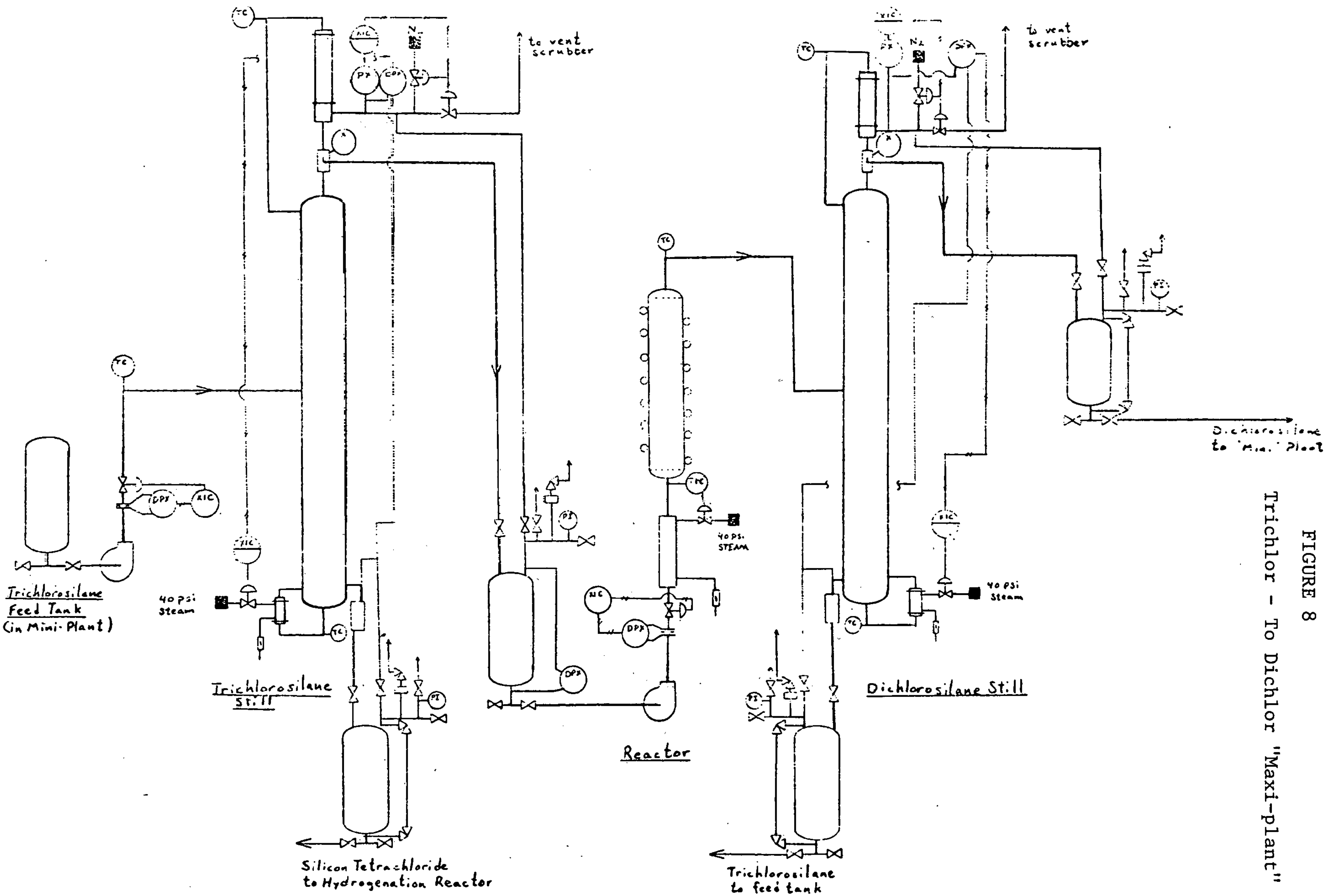


FIGURE 8
Trichlor - To Dichlor "Maxi-plant"

TABLE V

ANALYSIS OF SILANE ADSORBED ON CARBON

Hydrogen, %	20
Helium, ppm	20
Nitrogen, %	0.6
Argon, ppm	25
Disilane, ppm	1
Carbon Dioxide, ppm	10
Chlorosilane, ppm	1
Methane, %	0.15
Siloxane, ppm	2
Methyl Silane, ppm	2
Silane	Balance

in the void space and be manifest in an increased concentration in the initial gas eluted. It could also be due to a small decomposition of the SiH . The former is more likely.

To aid in data reduction and facilitate analysis of unit operation, a computer program has been written. The program will take the raw data of the various field instruments, convert them to a standard base and calculate the overall material balance. A second program uses the analytical results from the on-line chromatograph to calculate a component material balance around the main distillation column. The input data file for both programs are compatible and expandable to include energy input terms.

CONCLUSIONS

The laboratory investigation of the longevity of the amine catalyst for redistribution of chlorohydrosilanes indicates that with proper sizing of the reactor bed, good long term performance is to be expected. The initial decline in amine content and activity appear to level off after a short initialization period. The long term (40 hours) effects in the hydrogenation of silicon tetrachloride indicate that from a practical operations approach, nitrogen should not be used as an "inert gas". Argon would be a preferred second choice.

The mini-plant for producing silane from dichlorosilane is ready to start up. The pre-start up safety review process has proven of value the risk of operating new and/or unusual processes.

PROJECTED SIXTH QUARTER ACTIVITIES

- Operate the silane mini-plant and refine operation parameters.
- Continue fundamental process studies.
- Design and install a hydrogenation unit.
- Design an integrated maxi-plant.

PROGRAM STATUS UPDATE

The implementation plan has been modified to eliminate the pilot scale work on the direct synthesis of dichlorosilane and to substitute a study of the hydrogenation of $SiCl_4$. An updated baseline cost estimate will be presented in next quarter's report.

NEW TECHNOLOGY

There were no reportable items of new technology this quarter.

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