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LOW COST SILICON SOLAR ARRAY PROJECT

Feasibility of Low-Cost, High-Volume Production of Silane and Pyrolysis of Silane to Semiconductor-Grade Silicon

Quarterly Progress Report, April—June 1978

By
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E. G. Farrier
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Work Performed Under Contract No. NAS-7-100-954334

MASTER

Union Carbide Corporation
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U.S. Department of Energy

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QUARTERLY PROGRESS REPORT

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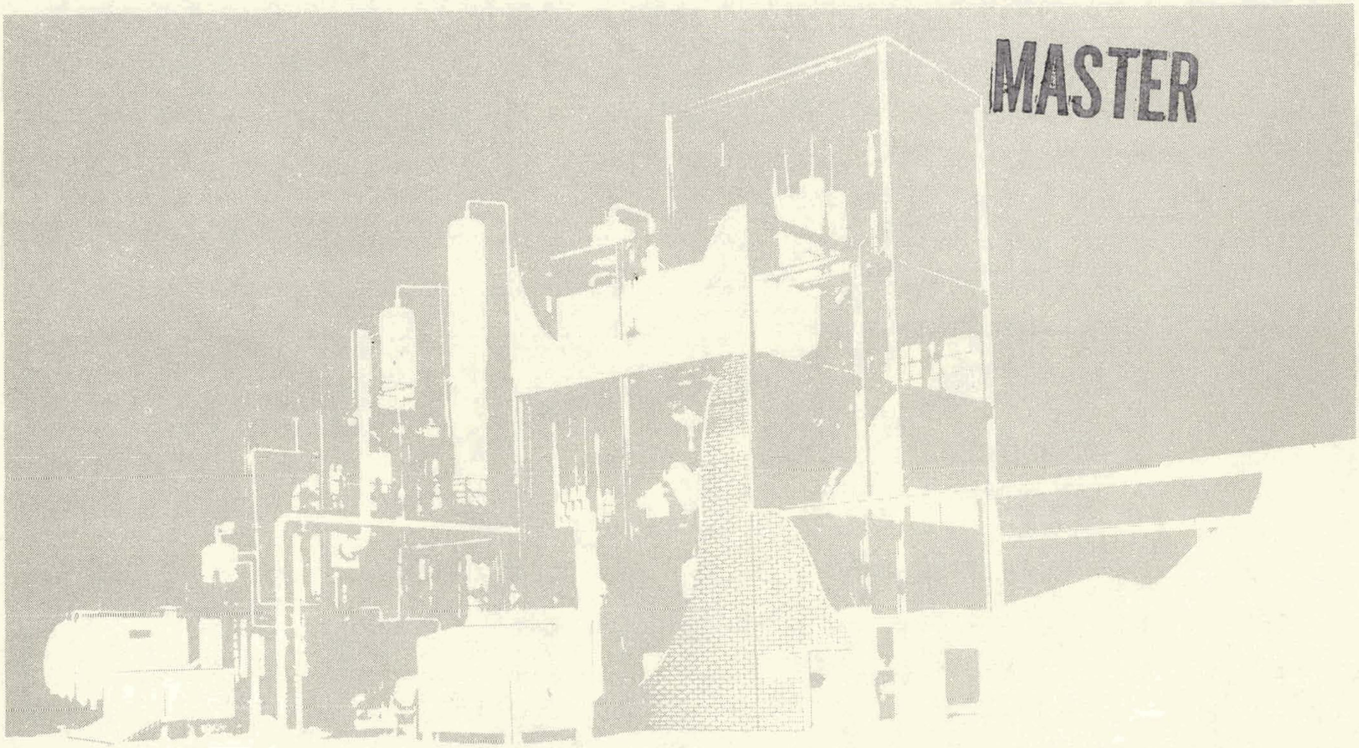
low cost silicon solar array project

FEASIBILITY OF LOW-COST, HIGH-VOLUME PRODUCTION OF SILANE AND PYROLYSIS OF SILANE TO SEMICONDUCTOR-GRADE SILICON



MASTER

W.C. Breneman E.G. Farrier H. Morihara

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ABSTRACT

SILANE PRODUCTION

The demonstration of continuous, integrated production of silane from metallurgical silicon and hydrogen has been accomplished and 3.2 kg of 99.8+% pure silane were prepared. Several minor changes are being implemented to improve the sampling system and to assure steady operation.

A material balance around the hydrogenation unit shows an 84% utilization efficiency and a 99.9% closure for silicon. A material balance for the major impurities in metallurgical silicon indicates that 90% of these were removed by a simple gas/liquid scrubber operating on the vapor stream of the hydrogenation reactor. Experimental programs are underway to obtain kinetic data for $SiCl_4$ hydrogenation and H_2SiCl_2 disproportionation at the latest design conditions of Union Carbide's Experimental Process System Development Unit sized for 100 MT/Yr of silicon.

SILICON PRODUCTION

A series of fluid bed reactor experiments was conducted with silane-helium gas mixtures. At low silane concentrations and a reactor wall temperature of 600°C, coherent silicon coatings were obtained on the seed bed particles. Only small amounts of powder were formed in 400 mm deep beds of silicon particles, when the bed was operated in a bubbling mode.

The fluidization behavior of silicon particles (with helium), having an average particle size of 200 μm, was studied at various temperatures and bed depths. Stable fluidized beds were obtained at room temperature over a wide range of gas velocities. The elevated temperature data were in good agreement with calculated values for the onset of fluidization and for the behavior predictable from the thermal expansion of the fluidizing gas.

A series of experiments was conducted to gain a better understanding of the mechanism of the silane pyrolysis reaction. In these experiments, silane/helium mixtures were directed both into empty transparent tubes and into transparent tubes packed with silicon particles. The products of the decomposition reactions were plate, powder, and fibers. The product forms were controllable, and the conditions favoring the formation of each form are being studied.

Silicon powder was produced in the free space reactor at a rate of 0.45 kg/hr for more than two consecutive eight-hour campaigns. The campaign was terminated during a third run after the induction coil was inadvertently deenergized and the reactor temperature dropped to a level that favored reactor wall formations. The silicon powder produced in these experiments was colored brown; previous results indicated that a dark-grey powder should have been formed. Components were found that were no longer functioning as designed, and the free space reactor was overhauled. After overhauling the reactor, the silicon produced was dark grey when the reactor wall temperature was 860°C. A run was made to demonstrate that high silicon production rates can be obtained at a moderate Reynolds number and reactor temperature by simultaneously increasing the gas flow and injector orifice.

PROCESS DESIGN

The preliminary SGS (semiconductor-grade silane/silicon) process design package for a 25 MT/Yr experimental unit was issued in April. Since the cost increase in going from 25 MT/Yr to 100 MT/Yr is only about 13%, JPL requested a process design for the larger size. All process design work was documented in an engineering memorandum to JPL before the 100 MT/Yr work was started.

Process design work in progress for the Experimental Process System Development Unit (EPSDU) sized for 100 MT/Yr includes a mass balance of major streams, incorporating recycle-purge streams and improved hydrogenation equilibrium data, P&I worksheets, and the free-space pyrolysis/melter design. Binary vapor-liquid equilibrium data and gas solubility data will be correlated and incorporated into process design computer programs.

A preliminary conceptual design for the fluid-bed pyrolysis in a EPSDU sized for 100 MT/Yr was completed. Product cost from this design appears to be in line with the cost from a free-space reactor/melter system. A re-evaluation of fluid-bed pyrolysis concluded that a single isothermal bed operated around 900°K appears technically feasible and economically attractive.

CAPACITIVE FLUID-BED HEATING

A model for the fluid-bed pyrolysis of silane was developed and is being used for estimating fluid-bed reactor design and performance. The model is based on the extrapolation of available data for epitaxial silicon deposition rate as well as on data for the heterogeneous and homogeneous decomposition of silane. The model was recently simplified by neglecting diffusion effects in the theoretical formulation. This simplified model is accurate within practical operating ranges.

The capacitive heating work originally planned was completed on schedule in May, and an interim technical summary will be issued shortly. Additional studies were initiated in June.

1.0 SILANE PRODUCTION

1.1 INTRODUCTION

The purpose of this program is to determine the feasibility and practicality of high-volume, low-cost production of silane (SiH_4) as an intermediate for obtaining solar-grade silicon metal. The process is based on the synthesis of SiH_4 by the catalytic disproportionation of chlorosilanes resulting from the reaction of hydrogen, metallurgical silicon, and silicon tetrachloride. The goal is to demonstrate the feasibility of a silane production cost of under $4.00/kg at a production rate of 1000 MT/year.

Prior to the inception of this program in October 1975, Union Carbide had shown that pure hydrochlorosilanes could be disproportionated to an equilibrium mixture of other hydrochlorosilanes by contact with a tertiary-amine, ion-exchange resin. In addition, Union Carbide had shown that silicon tetrachloride, a by-product of silane disproportionation, can be converted to trichlorosilane by reaction with metallurgical silicon metal and hydrogen.

Thus, a closed-cycle purification scheme was proposed to convert metallurgical-grade silicon into high-purity, solar-grade silicon using hydrochlorosilanes as intermediates. This process appears as:

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

   $$2\ H_2 + 3\ SiCl_4 + Si\ (M\text{-}G) \xrightarrow[Cu]{500^{\circ}C} 4\ HSiCl_3$$

2. Disproportionation of trichlorosilane to silane and silicon tetrachloride.

   $$4\ HSiCl_3 \longrightarrow 3\ SiCl_4 + SiH_4$$

3. Pyrolysis of silane to high-purity silicon.

   $$SiH_4 \xrightarrow{Heat} Si + 2\ H_2$$

Until now, laboratory investigations have defined the rate, equilibrium conversion, and certain mechanistic aspects of the disproportionation and hydrogenation reactions at atmospheric pressure. A small process development unit (PDU), capable of operating under pressure, was constructed and operated to demonstrate the conversion of dichlorosilane to silane. A high-pressure hydrogenation unit was constructed and the kinetics of the hydrogenation reaction were studied at elevated pressures. An integrated process development unit to demonstrate the closed cycle production of silane from metallurgical Si and H_2 was designed and constructed incorporating both the high pressure hydrogenation and redistribution reactor systems. This quarter, the integrated production of silane was achieved in the process development unit, and 3.2 kg of 99.8% pure silane were made. Experiments were started to obtain $SiCl_4$ hydrogenation and H_2SiCl_2 disproportionation kinetic data at the latest design conditions of Union Carbide's Experimental Process System Development Unit sized for 100MT/yr of Silicon.

1.2 DISCUSSION

1.2.1 HYDROGENATION of $SiCl_4$

The efficiency of the scrubber/settler portion of the hydrogenation system (Figure 1.1) for removing metallic impurities was evaluated. This unit is the primary means by which impurities in metallurgical silicon are removed from the process system. The unit used in the process development unit is shown schematically in Figure 1.2 and consists of a 7.75 cm diameter chamber 12.7 cm high. Hot vapors from the reactor enter the unit tangentially below the surface of a layer of liquid tri- and tetrachlorosilane. The liquid level is maintained by gravity flow of condensed product. The hot gases contact and heat exchange with the condensed product and leave the unit at equilibrium. Ideally, carry over metallic silicon, copper catalyst and other metallic dusts are scrubbed and settle in the liquid phase. Volatile impurities such as aluminum and iron chlorides would be condensed and settled also. The vapor stream leaving the unit would, therefore, contain those metals only to the extent of their equilibrium vapor pressure at the unit temperature.

The data were collected during a 22 hour operating period. The feed metallurgical silicon, the partially consumed material after reaction, settler liquid, and solid phases, and the final product chlorosilane mixture were weighed and analyzed. The silicon tetrachloride and hydrogen feed were assumed to contain no impurities - a reasonable assumption since both were from commercial sources of typical high purity.

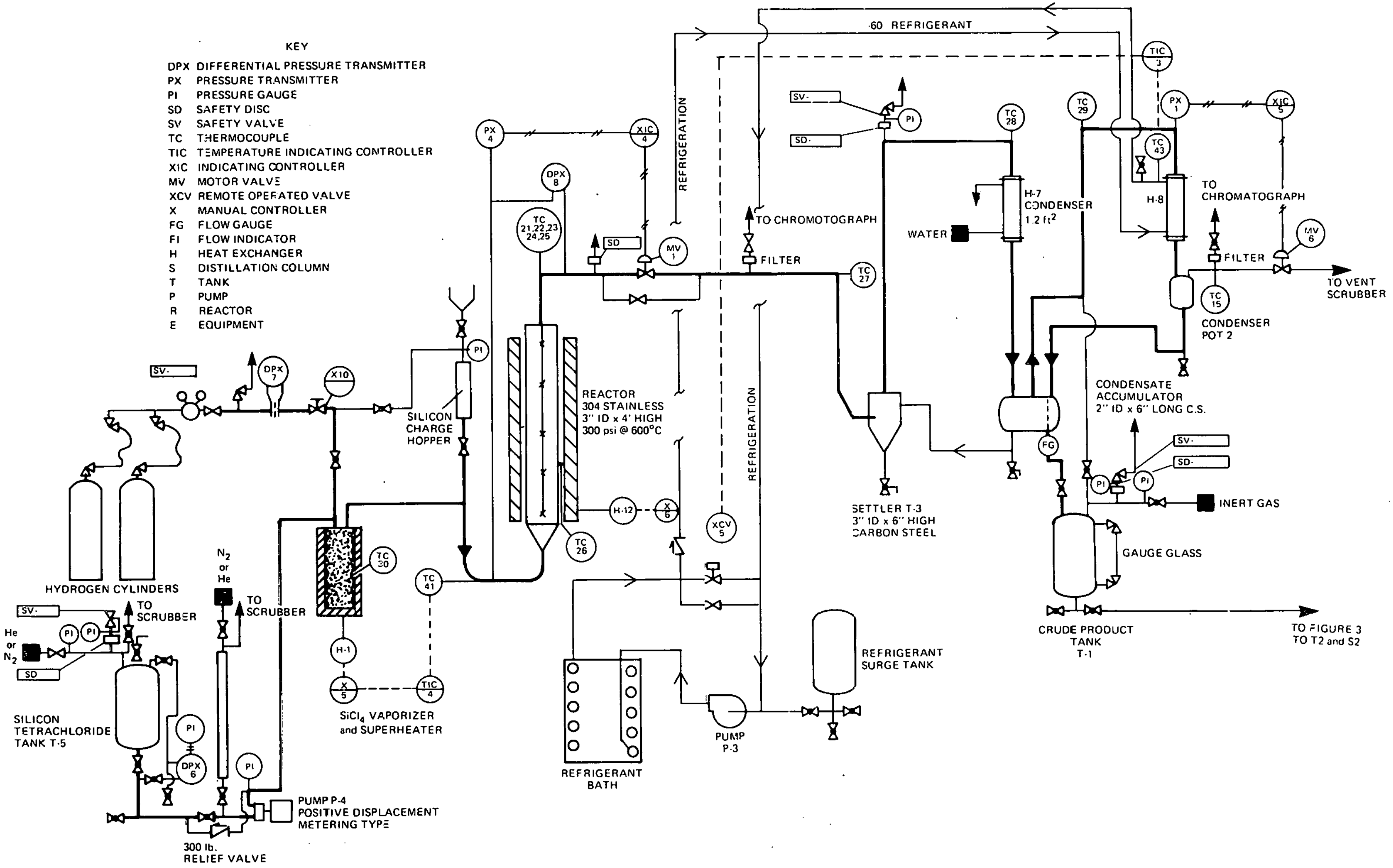

Figure 1.1
HYDROGENATION SECTION of SILANE PDU

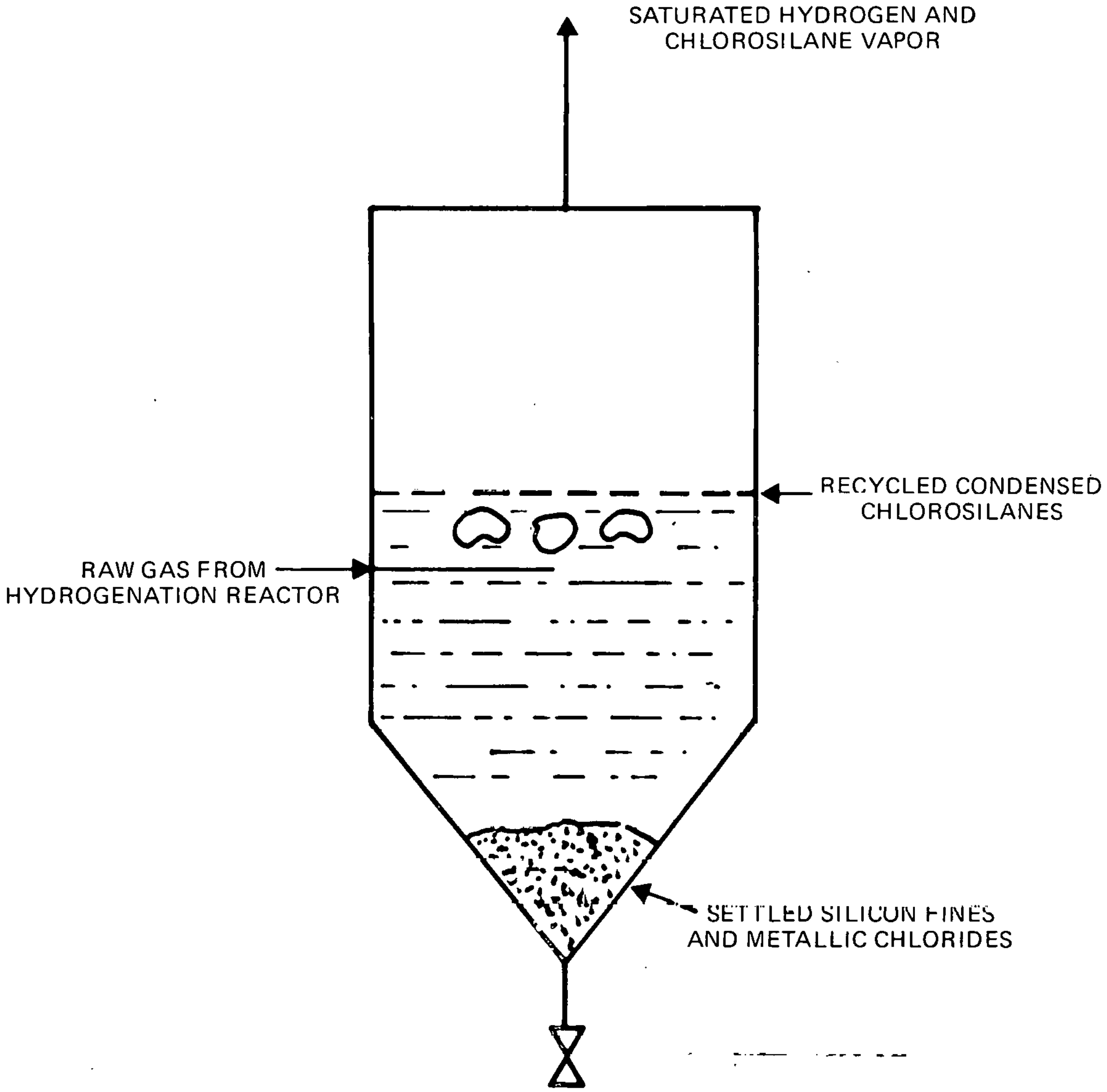

Figure 1.2
SCRUBBER/SETTLER for SILANE PDU

The analysis of the 150μ particle size silicon feed and partially reacted mass (Table 1.1) indicated only a slight change. Thus, impurities were all leaving the reaction mass at nearly the same rate as the silicon was being consumed. This is also significant as it indicates that impurities would not accumulate in the fluid bed reactor and cause poor performance.

Table 1.1

METALLURGICAL SILICONE/COPPER REACTION MASS

	Before Reaction	After 17% Conversion
Fe, %	0.60	0.60
Cu	0.42	0.44
Al	0.07	0.06
Ca	0.10	0.09
Mn	0.06	0.05
Pb, ppm	16	20

A material balance on silicon showed 99.99% accountability. The overall yield of silicon to useful products, di and trichlorosilanes, was 84% while the remainder consisted of solid silicon fines and liquid chlorosilanes collected in the settler. This value is close to the 85% figure used earlier to estimate large scale process economics.

The efficiency of the scrubber/settler for each of the impurities was calculated from the mass of the impurity which left the reactor, the mass collected in the solid and liquid phases in the scrubber, and the mass collected in the liquid product (Table 1.2).

Table 1.2

SCRUBBER/SETTLER EFFICIENCIES BASED ON PRODUCT EFFLUENT

	Grams Released in Reactor	Concentration in Product, PPM	Grams in Product	Settler Efficiency
Fe	4.70	0.28	.04	99.1
Cu	3.29	1.50	.20	93.9
Al	0.55	7.0	.93	-69.1
Ca	0.78	0.093	.01	98.7
Mn	0.47	0.33	.04	91.5
Pb	0.01	<0.02	$<3 \times 10^{-3}$	>70.0

$$\text{Efficiency} = \left[1- \frac{\text{mass of component in product stream}}{\text{mass of component leaving reactor}}\right] \times 100$$

These data show that, in general, the simple scrubber settler does work quite well. At the scrubber operating temperature of 60 - 80°C, the theoretical efficiency of the unit, based on the component vapor pressure would all be very close to 100%. A better mechanical design is being considered to improve gas liquid contacting.

These efficiency results are somewhat clouded by incomplete closure of the trace element material balance, most noteably aluminum. This is the result of trying to trace the presence of less than 5 grams of any component through the process chain where approximately 52 kg of chlorosilane product is involved.

The value for aluminum is obviously not reasonable showing aluminum being generated by the scrubbing procedure. Several possibilities can be considered here including a faulty analysis or a bad sample. The low value for lead is most likely due to the low levels originally present which approached the limits of detection of the analytical procedure (Flameless Atomic Adsorption).

1.2.2 PROCESS DEVELOPMENT UNIT

The integrated Process Development Unit (Figure 1.3) was operated continuously for periods exceeding 64 hours, producing high purity silane. From only the $HSiCl_3/SiCl_4$ mixture prepared earlier in the hydrogenation reactor, two cylinders containing a total of 3,191 grams of silane, analyzed on-line at >99.8% purity, was produced during 4 operating periods totaling 181.5 hours.

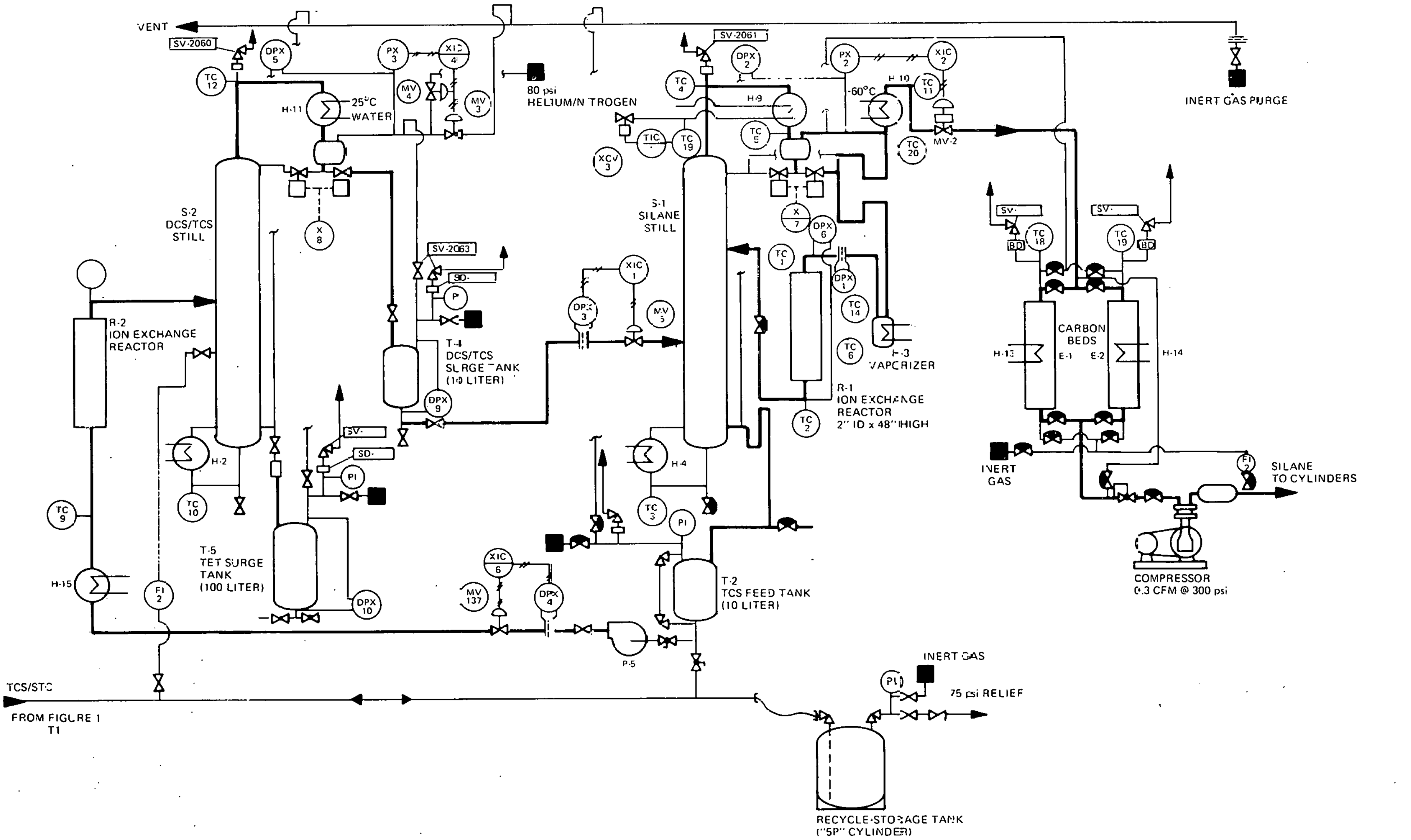

Figure 1.3

REDISTRIBUTION SECTION of SILANE PDU

The two cylinders of silane are undergoing a complete analytical workup including high sensitivity chromatography, mass spectrograph and a resistivity analysis of a deposited epitaxial film.

These long term runs demonstrated the production of silane from metallurgical silicon and hydrogen in an integrated process and have produced a quantity of silane for more extensive analysis. While the chemistry of the process has been demonstrated as well as the overall longevity of the catalyst, several sampling and mechanical problems peculiar to the small process development unit prevented good material balances and other operating data from being obtained. The feed to the unit was metallurgical silicon and hydrogen. Some silicon tetrachloride was used to "prime" the system and to make up for losses of chloride value in the solid liquid waste stream from the scrubber/settler as discussed earlier. The operation of the hydrogenation portion of the process as described in the previous quarterly report (1) was decoupled from the redistribution section by storing the feed and product in separate tanks (50 gallon capacity). This permitted "integrated" operation, but allowed each unit to be operated separately.

The hydrogenation section was operated earlier to produce about 35 gallons of a mixture containing 25% trichlorosilane. This mixture was used as feed to the first distillation column of the redistribution unit.

The tri/tet distillation column operated routinely during most of the long term run. A failure of the electrically heated reboiler is discussed later. This column, as can be seen from Figure 1.3 has two feed streams - the tri/tet product from the hydrogenation reactor and a mixture of di-, tri-, and tetra chlorosilanes from the first redistribution reactor. The overhead material, comprising all of the dichlorosilane and most of the trichlorosilane is the feed to the second distillation column, while the distilland consists of all of the silicon tetrachloride and a minor portion of the trichlorosilane. The silicon tetrachloride is recycled to the hydrogenation unit.

The performance of the column was monitored by the top and bottom temperatures. The bottom temperature was controlled at the silicon tetrachloride boiling point by adjusting the heat input to the column while the head temperature was controlled by the reflux ratio to be as low as possible consistent with the bottom temperature. The normal head temperature at 40 psig operating pressure was 72 - 85°C depending on feed composition variations.

On-line analysis of the two outlet streams (Table 1.3) indicated non-representative sampling, which has been attributed to fractionation occurring in the sample lines themselves. While the samples are not representative of the composition, too rich in the more volatile compounds, the column temperature profile was in good agreement with the expected results and other upstream and downstream units operated as expected.

The trichlorosilane redistribution column is used to convert the distilland of the second distillation column, chiefly trichlorosilane with a minor amount of dichlorosilane, into a di-tri-tetrachlorosilane mixture. This unit, packed with Amberlyst* A-21 resin catalyst operated with a liquid chlorosilane feed at 40 psig, 55°C to produce an equilibrium mixture of chlorosilanes which were fed to the first column for separation. From the analysis of the liquid feed to this unit, it became apparent that the operating temperature and pressure was very close to the bubble point of the equilibrium product (Table 1.4). This resulted in partial vaporization and unreliable effluent analysis. However, it did not impair the overall operation - just our ability to precisely monitor it.

The second distillation column is fed with the nominally 10% dichlorosilane, 90% trichlorosilane distillate from the first column. The task of this second column is to reject trichlorosilane in the distilland. Any lower boiling silanes enter a partial condenser where a portion of the condensate is sent to a vaporizer and then through a second redistribution reactor before reentering the column. Silane produced in this second reactor leaves the partial condenser as a gaseous product. The second distillation column operated

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* Amberlyst A-21 is a trademark of Rohm & Haas Chemical Company.

Table 1.3

RESULTS of $HSiCl_3/SiCl_4$ STILL ANALYSIS

Stream	°C	Actual PSIG	Ideal Vapor Pressure PSIG	SiH_4	H_3SiCl	H_2SiCl_2	$HSiCl_3$	$SiCl_4$
Bottom	130	40	168.8	--	--	1.42	93.23	5.35
Overhead	72.0	40	69.7	0.89	6.52	33.61	56.99	1.99
Bottom	120	40	316.5	1.32	9.94	31.12	55.58	2.04
Overhead	85.5	40	95.0	7.36	4.00	30.00	57.45	1.19

Table 1.4

$HSiCl_3$ REACTOR INLET and OUTLET ANALYSIS

Stream	°C	PSIG	SiH_4	H_3SiCl	H_2SiCl_2	$HSiCl_3$	$SiCl_4$	H/Cl Ratio
Inlet	59.1	40	1.54	0.36	13.98	81.99	2.13	0.41
Outlet	55.6	40	76.22	0.01	0.64	22.46	0.67	4.61
Inlet	59.2	40	6.26	0.66	14.54	77.90	0.64	0.51
Outlet	61.1	40	19.24	0.02	2.42	76.18	2.14	0.65
Inlet	58.1	40	0.43	0.68	31.28	67.23	0.39	0.5
Outlet	58.0	40	10.53	80.57	7.96	0.92	0.02	3.0

relatively smoothly during the continuous runs. The bottom temperature was stable at 67°C (35 psig), the trichlorosilane boiling point, but the head temperature cycled from 45° to 60°C. The cycling results from coupling the redistribution reactor to the column distillate. A feed back loop is established which results in a cyclical variation in the column feed composition and corresponding variation in overhead product composition. Normally this fluctuation is damped out and a stable operation ensues. However, in this continuous run, the operating temperature and pressure of the second redistribution reactor were close to the dew point of the process stream. This resulted in a degree of condensation within the resin bed, short term accumulation of the higher boiling chloride rich silanes, high bed pressure drop and reduced through put.

When the through put was reduced, the effect was to increase the distillation column reflux ratio and separation efficiency, lowering the stream dew point. The lower dew point material in effect purged the reactor, reduced pressure drop, increased through put, decreased reflux, and began the cycle again. While all of this appeared to make the process unstable, the net result, the production of silane was never in doubt and did not change appreciably. However, stream compositions did fluctuate and intra unit material balances could not be obtained.

The design basis for the 100MT/year EPSDU discussed in Section 3.0 provides assurances for single phase flow in the redistribution reactors to prevent this type of instability. The process development unit has also been modified to assure non-condensing operation of the second redistribution reactor over a wider operating range. An equipment modification that permitted more reliable control of the reboiler liquid level in the second destillation column resulted in flashing, two phase flow at the distilland sample point which negated the analytical results. However, prior experience indicated that at the process conditions dichlorosilane levels in the stream would be below 5%. A revision to the sample point is underway.

The silane product gas from the second distillation column passes through an activated carbon bed to remove chiefly remaining chlorosilanes. The 2" I.D. x 4 ft. long beds packed with Union Carbide JXC 6 x 8 mesh carbon performed routinely. Adsorption was performed at 15 psig and temperatures from -3.5 to +25°C. Desorption was accomplished by heating to 200°C and letting the desorbed chlorosilanes return to the distillation system. Final stripping was done by purging with dry nitrogen to an atmospheric vent. A helium purge and cool down completed the sequence. On-line analysis of the effluent indicated relatively low values of mono- and di- chlorosilanes (Table 1.6) and no detectable hydrogen.

The purified silane was packaged into clean, helium purged high pressure gas cylinders using a diaphragm style compressor. The single stage compressor achieved 400 psi discharge at 15 psi suction. There were no problems with compressor or carbon bed operations.

Table 1.5

RESULTS of SILANE REACTOR INLET and OUTLET ANALYSIS

Stream	Flow % of Max.	ΔP, "H_2O	T, °C	PSIG	SiH_4	H_3SiCl	H_2SiCl_2	$HSiCl_3$	$SiCl_4$	H/Cl Ratio
Inlet	22	8	50.7	30	0.69	11.85	59.89	27.56	0.01	0.87
Outlet	22	8	49.0	30	40.41	23.08	26.96	9.52	0.03	1.56
Inlet	20	6	51.7	30	19.41	12.50	11.29	56.80	--	0.95
Outlet	20	6	49.1	30	0.01	0.65	26.39	72.94	0.01	0.47
Inlet	25	35	44.5	30	11.08	27.40	54.40	6.91	0.21	1.54
Outlet	25	35	43.2	30	41.63	21.04	25.88	11.41	0.04	2.73
Inlet	20	25	47.7	30	7.08	29.37	58.62	4.92	0.01	1.4
Outlet	22	25	48.0	30	40.40	21.30	26.39	11.85	0.06	2.64
Inlet	20	22	48.3	30	12.03	30.07	46.35	11.52	0.03	1.54
Outlet	20	22	47.3	30	44.26	20.33	24.40	10.94	0.07	2.91
Inlet	10	7	45.9	30	3.78	21.41	41.49	33.07	0.25	0.96
Outlet	10	7	41.4	30	26.68	18.30	41.15	13.83	0.04	1.81
Inlet	25	62	50.4	30	3.16	1.72	22.56	70.73	1.83	0.50
Outlet	24	41	50.2	30.	24.11	21.29	40.87	13.65	0.08	1.77
Inlet	15	4	47.6	15	25.0	12.95	35.19	26.69	0.17	1.44
Outlet	22	14	31.2	16	24.23	27.26	30.39	17.91	0.21	1.80
Inlet	15	56	53.1	30	42.50	13.72	20.52	22.81	0.45	2.25
Outlet	15	61	34.1	31	1.16	4.93	34.75	58.75	0.41	0.59

Table 1.6

TYPICAL CARBON BED OPERATING DATA

					Outlet Analysis		
Hours Onstream	PSIG	°C	%SiH_4	%H_3SiCl	%H_2SiCl_2	%$HSiCl_3$	%$SiCl_4$
0.08	15	24.5	99.87	0.04	0.01	0.08	--
6.5	15	- 3.5	99.96	0.04	--	--	--
7.0	15	- 3.5	99.96	0.04	--	--	--
16.5	15	- 3.5	99.00	0.80	0.19	0.01	--
18.5	15	29.6	98.82	1.03	0.15	--	--
20.5	15	28.3	99.91	0.09	--	--	--
4.0	15	20.9	99.97	0.01	0.01	0.01	--
6.0	15	16.3	99.77	0.19	0.01	0.03	--
9.0	15	9.9	99.86	0.09	--	0.05	--
9.5	15	13.1	99.78	0.19	--	0.03	--
14.0	15	9.1	99.84	0.15	0.005	0.005	--
15.0	15	17.9	99.82	0.18	--	--	--

The four periods of continuous operation were terminated due to mechanical failures. The first failure was due to a bad bearing in the condenser refrigerant circulation pump. The pump had logged several hundred hours operation. The second failure was the electric immersion heater reboiler on the first distillation column. The heater, designed for total liquid immersion, obviously had been boiled dry as determined by the appearance of the unit. The elements had formed a gray scale with traces of green material. It was estimated that skin temperatures on the order of 1000°C had been attained.

Silicon fines carried over from the hydrogenation reactor partially blocked flow to the still and when heat input was increased to maintain boilup, the overheating occurred. Film boiling in the reboiler was not a problem (2). To prevent reoccurrence, a filter has been installed in the feed line and heat input to the unit has been limited. Larger scale plants would of course utilize steam heated reboilers and solids carry over would be reduced using filters and a more efficient scrubber as discussed in Section 1.2.1.

The third run was terminated by copper-iron electrolytic corrosion, enhanced by a weak HCl solution, of a stainless steel trichlorosilane transfer line. A stainless steel tube carrying TCS was in physical contact with a copper vent line in a place where moisture could collect and in the proximity of the chlorosilane fume scrubber. This promoted a rapid external corrosion of the line. The replacement line was plastic wrapped to avoid reoccurrence.

The solenoid valves which provide timed reflux control on the silane and tri/tet stills began to have erratic behavior. This occurred after the break in the trichlorosilane line and was due to small pieces of hydrolyzate in the valve mechanism. Marginal operation was continued by controlling reflux manually. Replacement valves have been ordered. Several other minor problems which are ultimately traceable to the line failure were found and corrected including restriction of metering orifices and control valves. This first case of moisture inadvertently entering the system illustrates the effect small amounts of by-product silica can have on working parts, and close tolerance meters unavoidable in small equipment.

1.2.3 LABORATORY STUDIES

1.2.3a HYDROGENATION of $SiCl_4$

Two experimental programs are underway to obtain hydrogenation data at the design conditions (P=500 psi, T=500°C, $H_2/SiCl_4$ molar ratio = 1) of Union Carbide's EPSDU sized for 100 MT/yr. of silicon.

A 3" Process Development Unit reactor will operate at $T=500^{o}C$, $H_2/SiCl_4=1$ and $P \leq 300$ psi while a 1" laboratory reactor will operate at $T=500^{o}C$, $H_2/SiCl_4=1$, and $p \geq 500$ psi.

Each unit will obtain conversion versus residence time data by using varying bed heights. This information should help firm up the design of a larger reactor for Union Carbide's 100 MT/yr. EPSDU.

The 1" stainless steel reactor, which was hydrotested at 2350 psi, has a pressure rating of 1000 psi at 500°C. The hydro test includes a 50% safety factor since, for stainless steel, the strain at 2350 psi @ 25°C is equivalent to the strain at 1500 psi @ 500°C. A safety team will inspect the unit near the middle of July.

1.2.3b H_2SiCl_2 DISPROPORTIONATION

Figure 1.4 shows a flow diagram of the bench scale unit being constructed to study H_2SiCl_2 Disproportionation in the liquid phase at the design conditions (T=25-80°C, P=700 psi) of Union Carbide's EPSDU sized for 100 MT/yr. of Silicon. Completion will be near the middle of July and the unit will be hydrotested at 1500 psi. The kinetics of redistribution in the liquid phase have been determined previously for trichlorosilane by workers at Union Carbide. However, in the preferred design of the larger scale silane units, the second redistribution reactor will be operated by liquid phase only and reliable kinetic data are needed to size the larger units.

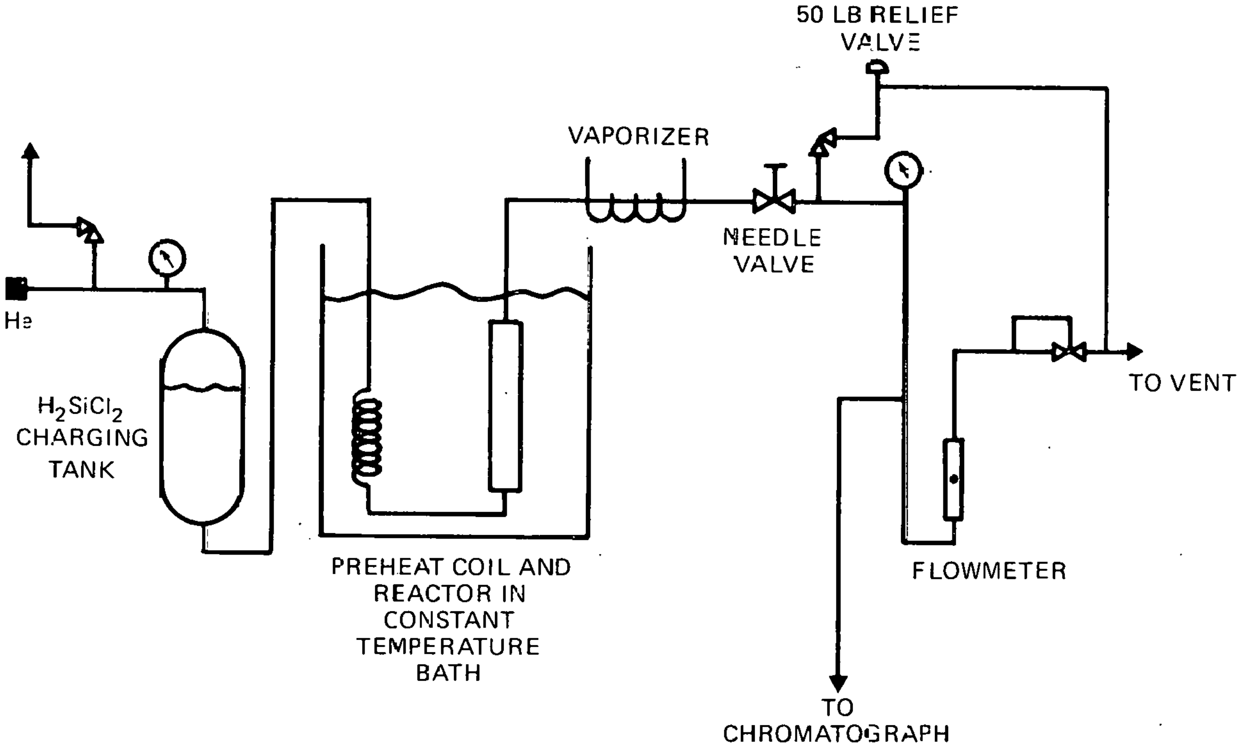

Figure 1.4
FLOW DIAGRAM of H_2SiCl_2 DISPROPORTIONATION UNIT

1.3 CONCLUSIONS

- The continuous operation of the Process Development Unit shows the feasibility and practicality of SiH_4 production from H_2 and metallurgical silicon using the low cost silane process.
- No fundamental problems associated with the chemistry or separations carried out in the process have been encountered.
- A material balance around the hydrogenation unit shows an 84% utilization efficiency at a 99.9% closure for silicon.
- The simple gas/liquid scrubber operating on the hydrogenation reactor vapor stream effectively removes the major impurities in metallurgical Si.
- The all-liquid or all-vapor operating mode for the redistribution reactors is required for stable operation and either is effective.

1.4 PROJECTED QUARTERLY ACTIVITIES

- Use of the 3" and 1" fluid-bed reactors to study the hydrogenation of $SiCl_4$.
- Study of the disproportionation of H_2SiCl_2 in the liquid phase using the bench scale fixed-bed reactor.
- Complete analysis of silane produced last quarter.
- Determine the vapor liquid equilibrium of diborane, phosphine, and argon in Silane at high pressures.

1.5 REFERENCES

(1) Breneman, W. C., Farrier, E. G., Morihara, H., Quarterly Progress Report, DOE/JPL 954334-78/5.

(2) Perry, J. H., "Chemical Engineers Handbook", 4th Edition, McGraw-Hill, New York 1963, Page 10-18.

2.0 SILICON PRODUCTION

2.1 INTRODUCTIONS

The objective of this program, which started in January, 1977, is to establish the feasibility and cost of manufacturing semiconductor grade polycrystalline silicon through the pyrolysis of silane. The silane-to-silicon conversion is to be investigated in a fluid bed reactor and in a free space reactor.

In the previous quarter, it was reported that silane, diluted with helium, was injected into a quartz fluid bed reactor in a spout-fluidized mode of operation. Experiments were conducted for up to two hours with no observable silicon or silane reaction occurring with the reactor wall and without locking up the bed. However, the spout and spout-fluidized beds were not stable at elevated temperatures. Through the use of a porous metal plate gas distributor, stable bubbling beds were obtained at elevated temperatures. The gas velocity range capable of maintaining a stable fluidized bed at 950° C was one-fourth that obtained at room temperature.

In the free space reactor, silane was converted into silicon powder at a rate of 0.45 kg/hr for eight continuous hours. The powder was subsequently pneumatically transferred out of the free space reactor assembly and melted at an average rate of 1.14 kg/hr to produce a dross-free casting. Free space reactor powder vacuum melted and cast into a high purity quartz crucible had an electrical resistivity of 120 ohm-cm.

2.2 DISCUSSION

2.2.1 FLUID BED REACTOR

A series of fluid bed reactor experiments, using a porous plate injector, was conducted in which silane-helium mixtures were introduced into beds of silicon particles whose average size was 335 µm. The experiments were conducted at reactor wall temperatures of 500° and 600° C. The fluid bed reactor was operated both as a slugging bed and as a bubbling bed. The slugging bed experiments were conducted at bed depths of 200 mm while the bubbling beds were 400 mm deep. The seed bed particles from these experiments were cross-sectioned and examined with an optical microscope. Coherent coatings were observed on the particles from all experiments conducted at 600° C. For experiments conducted at 500° C, the results were inconsistent. A portion of the silicon produced in all experiments was deposited on the wall of the reactor, and powder in varying amounts was produced. Substantially more powder was produced in the slugging beds than in the bubbling beds. In the bubbling beds, the higher temperature favored higher silane-to-silicon conversion efficiencies and less product in the form of silicon powder.

One experiment was conducted at a reactor wall temperature of 950° C using the porous plate gas distributor. The experiment was terminated after approximately one hour due to an increase in the gas line pressure. A close examination of the gas distribution system revealed that the increase in line pressure occurred when silane thermally decomposed in the pores near the upper surface of the porous metal plate. The plate was redesigned for more effective cooling and thermocouples contacting the top surface of the new gas distributor indicated that the surface temperature was below 300° C when the reactor wall temperature was 950° C.

The fluidization behavior of silicon particles having an average size of 200 μm was determined as a function of gas velocity and temperature for bed depths of 50 mm and 200 mm. The fluidizing gas, helium, was introduced through a porous metal gas distributor plate. The transition from a bubbling bed to a slugging bed was visually observed with increasing gas flow. The gas flows at which this transition occurred were within experimental scatter of the values previously obtained with the 335 μm particles. The gas injection velocities at which this transition occurred decreased with increasing temperature. A curve depicting this phase transition was drawn from values calculated from the observed room temperature data and the volume expansion of the fluidizing gas with increasing temperature. This phase transition appeared to be independent of bed depth and the average particle size. The mathematical expression given by Kunii and Levenspiel(1) accurately predicted that the minimum fluidization velocity decreased with increasing temperature and increased with increasing particle size.

2.2.1a SILANE PYROLYSIS STUDIES

To better understand the mechanism of the silane pyrolysis in the fluid bed reactor and the free space reactor, a simple horizontal pyrolysis reactor was evaluated. The experiments were conducted by directing silane-helium mixtures both into heated empty transparent tubes and into heated transparent tubes packed with silicon particles. The transparent tubes were used to visually observe the morphology of the silicon produced.

The experiments with the empty tubes were conducted at temperatures ranging from 440° to 900° C and silane concentrations ranging from 1/2% to 2%. In empty tube

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(1) Kunii, D., and Levenspiel, O., "Fluidization Engineering," John Wiley & Sons, Inc., New York, 1969, p. 73.

experiments conducted at 440° C and 490° C, most of the silane passed through the tubes without decomposing. However, the tubes were discolored indicating that some silicon did deposit. In all other empty tube experiments (temperatures ranging from 515° C to 900° C), gas phase decomposition into brown silicon powder occurred together with deposits on the tube that appeared to be dense. The initiation of these deposits was progressively closer to the gas inlet end of the tubes as the temperature of the furnace was increased. In general, powders that formed in the gas phase were carried out of the hot zone and deposited on the colder portions of the tubes.

For the packed tube experiments, two particle size cuts of metallurgical-grade silicon particles were used; an average particle size of 335 µm and approximately 1 cm chunks. Packing the tubes with particles enhanced gas mixing, heat transfer, and gas-to-solid collisions. By comparison to the open tube experiments, under similar conditions, the visual onset of pyrolysis in the packed tubes shifted closer to the gas inlet end of the tubes. Select seed beds were examined microscopically after the pyrolysis experiments. At temperatures of 540° C and 600° C, the silicon that deposited on the 335 µm seed particles resembled fibers or whisker growth and no powder was observed. Close examination of the fibers grown at 600° C revealed that they were extremely long and thin, whereas, the fibers grown at 540° C were much shorter. In experiments conducted at 540° C with 1 cm particles, fiber growth was reduced; and the primary growth appeared nodular. At 800° C using 1 cm particles, the product was primarily fine powder.

The data generated in the horizontal reactors explained some of the observed behavior in the more complex fluid bed reactor. This data permitted speculation as to what will be observed in future experiments. It was assumed that silane decomposition in a large bubble was comparable to decomposition in an empty tube; consequently, the data indicated that more fine silicon powder should have formed in the slugging bed than in the bubbling bed. This behavior was observed at both 500° C and 600° C. The horizontal reactor data suggested that lower reactor temperatures would result in the production of fewer fines but with reduced decomposition efficiency. The morphology of the silicon deposits on fluid bed reactor seed particles was not consistent with the morphology of the silicon obtained in the packed beds. This inconsistency indicated that a basic difference existed between the two systems. It is well known that temperature uniformity in fluid beds is better than in packed columns. However, the heat transfer and mixing in bubbles formed in the fluid bed is less than the heat transfer and mixing in the gas phase of the packed column. The morphology of the product from the fluid bed reactor was similar to that obtained in packed beds of substantially larger particles.

2.2.2 FREE SPACE REACTOR

An effort was made to operate the free space reactor for five consecutive eight-hour campaigns. A campaign consisted of producing silicon for eight continuous hours at a rate of 0.45 kg/hr. After cooldown, the system was purged with argon and the powder product was pneumatically transferred out of the settling chamber without dismantling the system. Two campaigns were completed. Shortly after starting the third campaign, the furnace power was inadvertently shut off and the reactor wall temperature dropped to approximately 790° C; 20 minutes lapsed before the reactor temperature was brought back up to approximately 850° C. The run was terminated after 90 minutes when the injector gas pressure had to be increased to maintain the desired flow meter setting. A post-mortem examination of the system after cooldown revealed that the reactor was blocked by a fairly dense (not friable) silicon formation, and the quartz reactor liner was shattered. It was previously demonstrated that when the reactor external wall temperature dropped below about 800° C, insufficient heat was transferred to the silane gas stream for complete pyrolysis. As a consequence, silane decomposed on the reactor wall and the silicon adhered to the wall.

A thorough inspection of all the components of the reactor was conducted. This inspection was prompted by the brown color of the powder obtained in the consecutive series of runs. Under similar furnace conditions, the silicon powder had previously been dark grey. It was found that the water-cooled injector had a constriction that severely limited the flow of water to the tip of the injector. In the critical hot-zone center, the original thermocouples were indicating temperatures approximately 20° lower than new thermocouples installed adjacent to the original ones. Since elevated temperatures favored the brown powder formations, the combined effect of a higher reactor temperature and restricted cooling of the injected gas may account for the powder color. It was believed that the restricted cooling was the major contributor. The free space reactor was overhauled.

A dry run was made to compare the behavior of the newly installed thermocouples with that of the original ones and simultaneously obtain a temperature profile inside the free space reactor. Three thermocouples were positioned at different elevations in each of three stainless steel tubes (thermocouple wires were insulated from one another and from the stainless steel tube). A hydrogen gas flow of 6 ℓ/min was maintained. Near the center of the induction coil, the thermocouples fastened to the reactor wall indicated higher temperatures (65° C) than the thermocouples in the confined gas stream inside the reactor. The turbulent gas behavior inside the reactor tended to reduce the temperature gradients sufficiently so that the internal gas temperatures near the ends of the induction coil were higher than the reactor wall temperature. Near the center of the induction coil, the newly-installed thermocouples indicated that the reactor temperature may be 20° C higher than is indicated by the original thermocouples. In preparation for five consecutive experiments (after overhauling the reactor), one short-duration (two-hour) run was conducted as a system checkout. Silane was injected through a 0.46 cm i.d. injector at 6 ℓ/min into the free space reactor whose outer wall temperature was maintained (at the center of the hot zone) at approximately 880° C. All systems appeared to be operational. Inspection of the reactor and settling chamber after cooldown substantiated previous results in which no semi-solid cone or wall formations occurred under identical experimental conditions. The powder produced had a bulk density of 0.11 Mg/m^3 and was dark brown to grey as anticipated. All components of the reactor appeared to be operating normally.

Data presented in the previous Quarterly Report showed that a silane-to-silicon conversion efficiency of at least 99% was obtained at a free space reactor wall temperature of 800° C if the Reynolds number of the injected gas was between 2000 and 6000. Significantly higher temperatures were required when the Reynolds numbers were higher or lower than the above values. It was postulated that the highly-efficient silicon production rate, at any select temperature, could be increased by simultaneously increasing the silane flow and the diameter of the injector orifice. This theory was evaluated in an experiment in which the injector orifice diameter was increased from the normal 0.46 cm to 1.59 cm. The silane flow rate was simultaneously increased to maintain a constant Reynolds number of 4000. With the reactor wall held at 860° C (hot zone center), a silane pyrolysis efficiency greater than 99% was obtained under steady state conditions. The run was terminated after 30 minutes as scheduled. The product of the reaction was a dark grey powder; no semi-solid reactor wall or injector formations were obtained. The bulk (as formed) density of the dark grey powder was 0.04 Mg/m^3. Additional experiments will be conducted to establish the maximum value of the injector-to-reactor diameter ratio for the current reactor. In most of the previous experiments, the injector diameter-to-reactor diameter ratio was 0.025. In the above run, the ratio was increased to 0.086. A new injector will be constructed that will increase the ratio to approximately 0.17. With this injector, 49 ℓ/min of silane (silicon production of over 8 kg/hr) must be injected into the free space reactor to maintain a Reynolds number of 4000.

2.2.3 SILICON CONSOLIDATION

It was previously demonstrated that the current equipment for fluidizing and pneumatically conveying the free space reactor powder was operational. Design improvements are being implemented to refine the present system. A larger capacity (minimum of 3.6 kg of silicon) storage hopper is being constructed for the melt consolidation apparatus. The storage hopper will contain a fluidizer plate to facilitate powder transfer and a porous metal filter system. An auger feed system is being built for controllably feeding powder into the 15.2 cm diameter quartz crucible, over a wide range of feed rates. After the powder conveying components are constructed, a series of experiments will be conducted to 1) demonstrate that the free space reactor can be operated for five consecutive campaigns without dismantling the reactor to remove the powder, and 2) establish the maximum melting rate of powder fed continuously into the current melter.

2.3 CONCLUSIONS

It was anticipated, based on literature data, that temperatures in the range of 900° to 1100° C would be needed to produce coherent coatings on fluid bed reactor seed particles. In the current fluid bed reactor, it was demonstrated that coherent particle coatings could be obtained at reactor wall temperatures as low as 600° C. At this temperature, the fluid bed reactor was operated for a scheduled four hours with a silane-helium mixture without the production of unacceptable quantities of fines. The newly-designed water-cooled gas distributor plate was used in the prolonged runs. There was no indication of silane pyrolysis in the pores of the plate, and no semi-solid growth formations were observed on the plate.

Data are being generated in the simple horizontal pyrolysis reactor that will provide an insight into the mechanisms of the reactions occurring in the more complex fluid bed reactor system.

It was demonstrated that the free space reactor could operate for more than two consecutive eight-hour campaigns producing powder at the rate of 0.45 kg/hr. The powder from each campaign was transferred to the hopper of the melt consolidation apparatus. Higher reactor production rates at moderate reactor wall temperatures were obtained by simultaneously increasing both the silane flow and the injector orifice to maintain a constant Reynolds number of 4000.

2.4 PROJECTED QUARTERLY ACTIVITIES

2.4.1 FLUID BED REACTOR

- Evaluate infrared analysis as a potential means of determining the composition of exhaust gases.

- Demonstrate that a long-duration silane pyrolysis experiment can be conducted in the fluid bed reactor.

2.4.2 SILANE PYROLYSIS STUDIES

- Continue to study the mechanism of the silane pyrolysis reaction both in empty transparent tubes and in static beds of silicon particles.

- Study the morphology of the silicon deposited on the seed bed particles and on the walls of the reaction tubes by optical and scanning electron microscopy.

2.4.3 FREE SPACE REACTOR

- Conduct five consecutive campaigns in which silicon powder is produced at the rate of 0.45 kg/hr for four hours and is then pneumatically transferred out of the settling chamber.

- Design and construct a water-cooled injector whose orifice diameter is approximately 3 cm.

- Continue to identify factors for optimizing the pneumatic transfer of silicon powder.

- Generate engineering data for plant design and scaleup.

2.4.4 CONSOLIDATION

- Construct a screw feed mechanism for controllably directing specified quantities of silicon powder from the storage hopper to the melter.

- Continue with the construction of a large hopper for storage of the free space reactor powder.

- Improve the design of the melter.

- Continue with experiments that will establish the optimum combined feed and melting rate of free space reactor powder in the melt consolidation apparatus.

3.0 PROCESS DESIGN

3.1 INTRODUCTION

This program, started in October 1977, originally was to provide JPL with engineering and economic parameters for an experimental unit sized for 25 metric tons of silicon per year and a product-cost estimate for silicon produced on a scale of 1000 metric tons per year.

The preliminary process design package for the 25 MT/Yr unit was completed. An analysis of the product cost from a 1000 MT/Yr unit indicated that the silicon selling price would be less than the DOE/JPL goal of $10/kg in 1986. Costs for 25, 50, and 100 MT/Yr units were then developed by scaling the 1000 MT/Yr estimate. It appears that the product selling price from a 100 MT/Yr EPSDU will meet the DOE/JPL intermediate goal of $25/kg in 1982. Since the plant-cost increase in going from 25 to 100 MT/Yr size is only about 13 percent, it was agreed to proceed with the process design for the larger unit.

All process design work associated with the 25 MT/Yr unit was documented. Using this as a basis, the process design for a EPSDU sized for 100 MT/Yr is currently in work.

3.2 DISCUSSION

3.2.1 SGS PROCESS DESIGN PACKAGE for the 25 MT/YR UNIT

The preliminary SGS (semiconductor-grade silane/silicon) process design package for a 25 MT/Yr experimental unit (3.1) was issued on April 28, 1978 and transmitted to JPL. A few items were added to the original package described in the January-March quarterly progress report.(3.2) The final package included the following items: process specifications, process description, heat and mass balance of major streams, equipment specifications, stream numbers and their descriptions, process flow diagram with major controls, layout drawings, electrical one-line drawing, pyrolysis/melting equipment list, and pyrolysis/melting assembly drawing.

Since the experimental unit size was changed from 25 MT/Yr to 100 MT/Yr, all process design work accomplished for the 25 MT/Yr unit was documented to serve as a basis for the 100 MT/Yr design. This documentation, described below, is in addition to the process design package issued in April.

A preliminary process design was assembled for pyrolyzing high-purity silane in a free-space reactor and melting the resulting fine silicon powder in quartz crucibles. Polycrystalline silicon rods can be suction-cast directly from the melt. This approach of free-space pyrolysis, powder melting, and suction-casting was applied to the process design of the 25 MT/Yr SGS facility since it is the only scheme demonstrated at present.

This work was documented as an engineering memorandum to JPL and it identifies principal design uncertainties requiring further development and describes new concepts for improving the present design.

A stream catalog giving a heat and mass balances for all streams was completed. It lists, among other things, the molecular weight of each component, mass flow rate, weight and mole fraction, pressure, temperature, liquid fraction, enthalpy, and average molecular weight. The stream volumetric flow rate and the specific heat will be added in the 100 MT/Yr process design and the stream viscosity may also be included later. The impurities entering in raw materials were estimated and an impurity mass balance shows the distribution of over 30 chemical species throughout the process. Computer-aided calculations were made to find the molar flow of each element at key areas of the process. This work contains the process description, rationale for selection of operating conditions, major process controls, process flow diagram, and a stream catalog.

3.2.2 SGS PROCESS DESIGN PACKAGE for the 100 MT/YR EPSDU

3.2.2a MASS BALANCE

Process design for the EPSDU sized for 100 MT/Yr was started. The unit is assumed to be on stream 70% of the time at an instantaneous silane production rate of 21 kg/hr. The product loss is assumed to be 10% during silane pyrolysis and subsequent melting and suction-casting into polycrystalline silicon rods. The instantaneous production rate for silicon rods is 16 kg/hr.

A preliminary mass balance of major streams for the 100 MT/Yr EPSDU was generated and recycle-purge streams and improved hydrogenation equilibrium data were incorporated. The previous hydrogenation reaction computer model had only two competing reactions:

$$Si + 3SiCl_4 + 2H_2 \rightarrow 4HSiCl_3$$

$$2HSiCl_3 \rightarrow H_2SiCl_2 + SiCl_4$$

The new hydrogenation reaction computer model balances the following five competing reactions:

$$Si + 3SiCl_4 + 2H_2 \rightarrow 4HSiCl_3$$

$$2HSiCl_3 \rightarrow H_2SiCl_2 + SiCl_4$$

$$SiCl_4 + H_2 \rightarrow HSiCl_3 + HCl$$

$$2H_3SiCl \rightarrow H_2SiCl_2 + SiH_4$$

$$2H_2SiCl_2 \rightarrow HSiCl_3 + H_3SiCl$$

Light-gas solubilities and and binary vapor-liquid equilibrium experimental data for chlorosilanes are becoming available.These data will be used in the next quarter to update the mass balance around the settler and distillation columns.

3.2.2b PIPING and INSTRUMENTATION WORKSHEETS

Detailed P&I worksheets are being prepared and are about 50 percent complete. These worksheets are used for initiating plant P&ID work and the detailed hardware selection effort. Problems associated with pump seals, valve selection, control logic, equipment sparing, environmental protection, and other design requirements will be resolved by contacting vendors to determine equipment availability, by learning from operating personnel of similar plants, and by exercising sound engineering judgement.

3.2.2c FSR PYROLYSIS/CONSOLIDATION DESIGN

Conceptual work is in progress on the design of an integrated free-space pyrolysis reactor/melter for the 100 MT/Yr EPSDU. The melter is being designed to operate in both argon and hydrogen environments. Initially it will be operated in argon, but eventually the entire pyrolysis/consolidation train will be operated in a hydrogen atmosphere. The design will be sufficiently flexible and concervative so that the pyrolysis reactor can be operated either intermittently, as presently demonstrated, or continuously.

The remaining experimental program at Parma should provide all presently identified data requirements for designing the 100 MT/Yr EPSDU. Based on the Parma R&D effort, it is believed that a first-generation 100 MT/Yr system can be built and operated successfully.

3.2.3 PROCESS DESIGN DATA

3.2.3a DATA ACQUISITION

The binary vapor-liquid equilibrium for H_2SiCl_2-$HSiCl_3$ at 100, 200, and 300 psia was completed and the resultant PTX data are shown in table 3.1. The binary system deviates somewhat from ideal behavior and shows some positive deviation from Raoult's law. Vapor pressures of H_2SiCl_2 and $HSiCl_3$ were also measured, and new vapor-pressure equations for these chlorosilanes were developed.

Gas solubility data for N_2, CH_4, and CO_2 in dichlorosilane and trichlorosilane have been measured at 30° and 60°C. Henry's constants (atm/mole fraction) computed from these data are listed in Table 3.2. Henry's constant, H, is defined as,

$$H = \lim_{X_2 \to 0} (f_2/X_2),$$

where X_2 is the solute (gas) mole fraction in the liquid phase and f_2 is the fugacity of the gas (approximately equal to the gas partial pressure). Table 3.3 contains Henry's constants recast into the unit ppmw/atm to allow calculation of the partial pressures required for small amounts to be dissolved in the liquid phase.

Table 3.1

PTX DATA for DICHLOROSILANE and TRICHLOROSILANE

X	T(°C)	P(psia)	T(°C)	P(psia)	T(°C)	P(psia)
0.0	102.4 102.7	101.0 102.0	137.0 136.9	201.0 201.0	159.7 159.9	299.4 299.4
0.1995	94.3	104.0	126.6	201.1	150.1	302.4
0.3395	88.6	102.0	121.2	201.0	143.5	298.4
0.3992	85.6	103.0	119.2	204.0	141.1	299.4
0.5043	83.6	104.0	114.9	202.0	137.6	302.4
0.8003	75.3	103.0	107.1	203.0	128.3	301.4
0.9004	73.7	103.0	104.6	201.0	125.6	299.4
1.0	71.8 71.4	102.0 102.0	102.6 102.7	202.0 202.0	123.6 123.6	299.4 299.4

NOTE: X is the mole fraction of DCS in the DCS-TCS solution.

Table 3.2

HENRY'S CONSTANT for N_2, CH_4, CO_2, B_2H_6, and PH_3

	Dichlorosilane H(atm/mole fraction)		Trichlorosilane H(atm/mole fraction)	
	30°C	60°C	30°C	60°C
N_2	933	745	899	794
CH_4	247	253	238	260
CO_2	72.4	92.0	76.3	98.7
B_2H_6*	33.0	47.0	31.8	46.0
PH_3*	25.5	30.0	24.5	29.0

Table 3.3

SOLUBILITY of N_2, CH_4, CO_2, B_2H_6, and PH_3 In Di-and Trichlorosilane

	Dichlorosilane k		Trichlorosilane k	
	30°C	60°C	30°C	60°C
N_2	297	373	230	261
CH_4	645	630	499	457
CO_2	6070	4770	4300	3320
B_2H_6*	8490	5920	6590	4520
PH_3*	13600	11500	10600	8880

* Estimated Value

k = ppmw dissolved/atm partial pressure

Since it is dangerous to study the solubility of B_2H_6 and PH_3 due to the toxic and pyrophoric nature of these gases, only an estimate of B_2H_6 and PH_3 solubilities was included in Tables 3.2 and 3.3 The estimate is based(3.3) on the fact that, although gas solubility varies considerably from solvent to solvent, the ratio of the solubilities of two gases remains relatively constant. Data were obtained from the literature for the ratio of B_2H_6-to-N_2, B_2H_6-to-CH_4, PH_3-to-N_2, and PH_3-to-CH_4 solubilities in various solvents. These ratios were then applied to the experimental di- and trichlorosilane N_2 and CH_4 solubilities to produce the estimates for B_2H_6 and PH_3. Experimental B_2H_6 and PH_3 solubility data will be obtained.

The HCl experiments on di- and trichlorosilane will be performed next, followed by N_2, CH_4, CO_2, and HCl solubilities in silicon tetrachloride.

3.2.3b DATA MODELING

We are currently investigating a Wilson equation route to K-value determination. The advantage of the Wilson equation is that it permits evaluating systems having three or more components using parameters derived from binary data. An in-house computer program VLEFIT accepts experimental vapor-liquid data (P, T, X) and computes parameters in the Wilson equation for the liquid activity coefficient. Other parameters required for generating th K-value may be obtained in the following manner: Poynting correction to the vapor pressure is made in obtaining the liquid fugacity and the Prausnitz-Chueh modified Redlich-Kwong equation of state is used for the vapor fugacity coefficient. This vapor-liquid data reduction procedure was incorporated into the in-house distillation column design computer program (MDCC).

The deviation from ideality for chlorosilane mixture equilibrium will increase distillation-column traffic and reboiler and condenser duties. The accurately measured experimental equilibrium data coupled with powerful multi-component data correlation techniques will permit design of the 100 MT/Yr EPSDU distillation train with confidence.

3.2.4 FLUID-BED PYROLYSIS

3.2.4a FUNCTIONAL DESIGN and ECONOMICS

A preliminary conceptual design of the fluid-bed pyrolysis system for a 100 MT/Yr EPSDU was completed. Two base cases involving isothermal beds one with high silane concentration in the feed and the other with low silane concentration in the feed were studied as shown below:

	Case I	Case II
Inlet Silane Concentration	51%	5%
Bed Temperature	800K	908K
Mean Particle Diameter	250μ	600μ
Fluid-bed Diameter	16 in.	20 in.
Fluid-bed Height	5 ft	4 ft
U/Umf	1.5	1.5

Figure 3.1 presents the conceptual schematic diagram of the fluid-bed pyrolysis system. A preliminary functional design of each piece of equipment was prepared and, where necessary, vendors were contacted to obtain equipment cost. The total equipment cost for Cases I and II are \$70,500 and \$190,500, respectively. The installed costs are \$337,000 and \$909,000, if the 4.77 multiplier is used. The incremental product costs for the two cases are \$3.63 and \$8.48/kg, respectively (Table 3.4). These costs appear to be in line with the free-space reactor/melting system.

3.2.4b TECHNICAL RE-EVALUATION

The fluid-bed pyrolysis reevaluation program initiated in March 1978 was completed. During the study, discussions were held with JPL consultants O. Levenspiel and T. Fitzgerald at Oregon State University on May 5, 1978. Discussions centered on our analytical modeling work and on a base-case, single isothermal bed design. The meeting was beneficial and the general conclusion was that, given time and effort, the fluid-bed pyrolysis of silane can be accomplished.

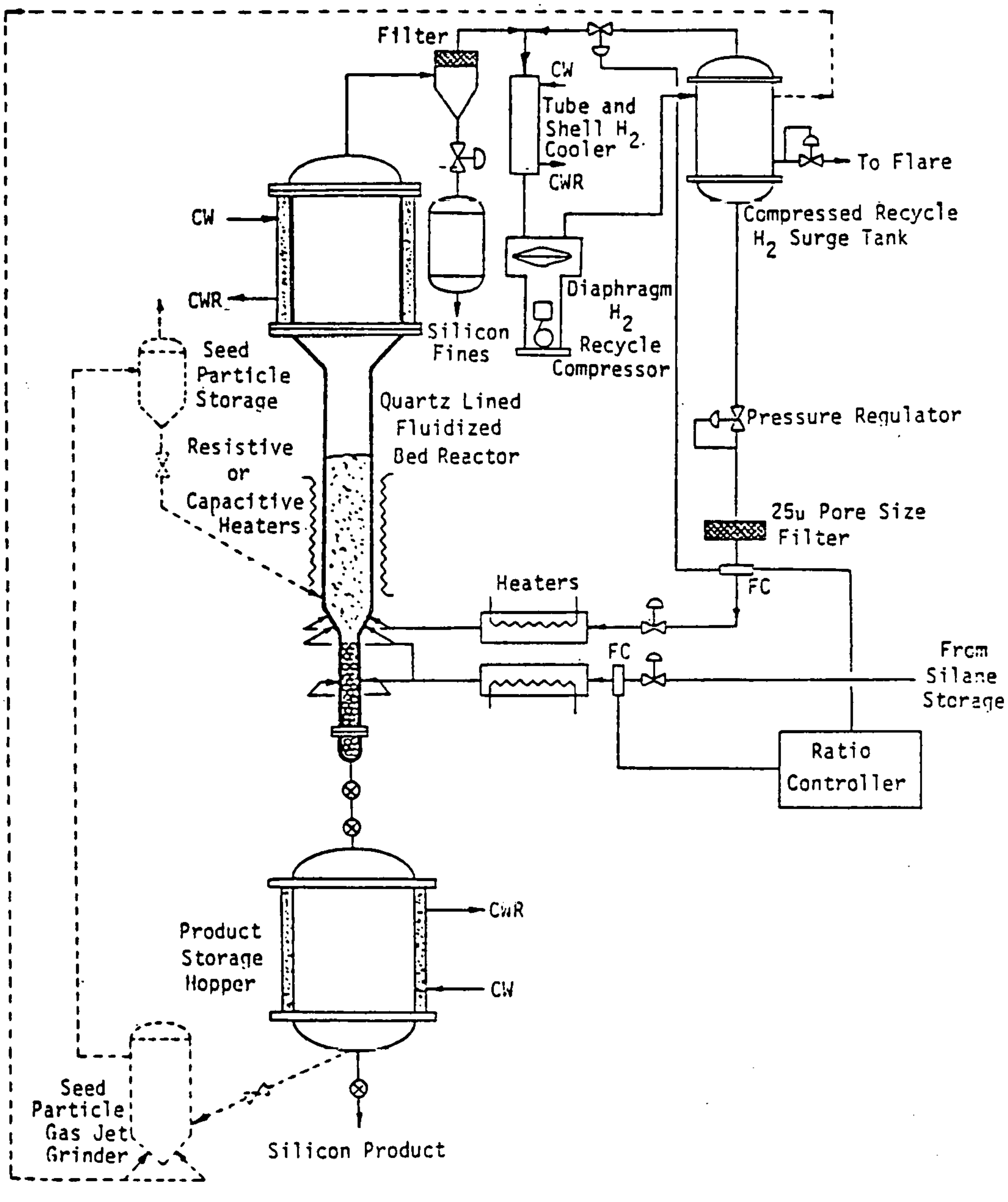


Figure 3.1
CONCEPTUAL SCHEMATIC DIAGRAM of FLUID-BED PYROLYSIS

Table 3.4

INCREMENTAL PRODUCT COST from a 100 MT/Yr FLUID-BED PYROLYSIS STEP

	$/kg Case I	 Case II
Raw Materials (silane & starter bed)	.01	.01
Labor	.79	.79
Utilities (electricity & cooling water)	.04	.15
Maintenance (7% plant cost)	.24	.64
Property taxes (5% plant cost)	.02	.05
Insurance (1% plant cost)	.03	.09
Annual Operating Cost	1.13	1.73
Capital Charges*	2.50	6.75
Incremental Product Cost	3.63	8.48

* (15-year project life, 10-year SOD depreciation, 48% federal income tax, 100% equity financing, 2-year construction time, 25% DCF rate)

The assessment of silane pyrolysis in a fluid-bed reactor indicates that at temperatures of about 900°K the concept is technically feasible and cost effective. This assessment is based on a bed design obtained from the theoretical model and an evaluation of plant, equipment, and installation costs. The data upon which the model is based were developed from epitaxial deposition experiments and are, therefore, representative of a temperature range considerably higher than the one of interest. Several related experiments conducted by JPL and UCC-Parma indicate that extrapolation of epitaxial data by the model yields conservative operating conditions for avoiding homogeneous gas-phase decomposition.

A single isothermal bed with hydrogen recycle is recommended as the design objective of a 2-year R&D program. The estimate of product costs pertaining to this concept were developed and the R&D program was outlined. The probability of success for demonstration of fluid-bed pyrolysis at the conclusion of this program appears to be excellent.

3.3 CONCLUSIONS

All process design work associated with the 25 MT/Yr unit was documented to supplement the preliminary process design package. This design was used as a basis for starting the process design for the 100 MT/Yr EPSDU which will include the additions and refinements that were planned for the second-iteration design of the smaller facility.

Experimental thermodynamic data, now becoming available, are being incorporated into the process design computer programing. This will enable complete characterization of the process streams and more precise specifications for major equipment.

3.4 PROJECTED QUARTERLY ACTIVITIES

3.4.1 PROCESS SPECIFICATIONS

Process specifications for Union Carbide's EPSDU sized for 100 MT/Yr will be established and these will be used as the basis for all subsequent process design effort.

3.4.2 HEAT and MASS BALANCE

A mass balance of all major streams including trace components will be made. A heat balance will then be accomplished across all major pieces of equipment for the 100 MT/Yr EPSDU.

3.4.3 PFD and STREAM CATALOG

A preliminary process flow diagram with major controls will be prepared for the 100 MT/Yr EPSDU. A stream catalog of all streams will be prepared; the impurity mass balance will be made separately, but will be printed out as an integral part of the stream catalog.

3.4.4 KEY EQUIPMENT DESIGN

Designs will be started for key equipment such as the hydrogenation reactor, redistribution reactors, distillation columns, adsorption beds, and the free-space pyrolysis reactor/melter system.

3.4.5 PRELIMINARY P&I DIAGRAM

P&ID worksheets, designed to be used as a basis for preparing the test facility P&ID, will be completed. Work on the P&ID will be started.

3.5 REFERENCES

3.1 "Preliminary Process Design Package for a 25 MT/Yr Semiconductor-grade Silicon Experimental Facility", JPL Contract 954334, Union Carbide Corporation, Linde Division, Tonawanda, New York, April 28, 1978.

3.2 W. C. Breneman, E. G. Farrier and H. Morihara, "Feasibility of a Process for Low-Cost, High-Volume Production of Silane to Semiconductor-grade Silicon", Quarterly Progress Report, JPL Contract 954334, Union Carbide Corporation, January-March 1978.

3.3 M. B. King, Phase Equilibrium in Mixtures, Pergamon Press, N.Y. 1969, p. 237.

4.0 CAPACITIVE FLUID-BED HEATING

4.1 INTRODUCTION

The purpose of this program is to explore the feasibility of using electrical capacitive heating to control the fluidized silicon-bed temperature during the heterogeneous decomposition of silane. In addition, a theoretical fluid-bed silicon deposition model was developed for use in the design of a fluid-bed pyrolysis scheme.

The effort originally planned for the program was completed the end of May. The model for the fluidized-bed pyrolysis of silane was developed for both single and multiple beds and is operative as a design tool.

An extension program was started in June to supplement the original work. The planned work includes:

Obtaining experimental data on the mechanics of a fluid-bed.

Demonstrating high-frequency electric heating of fluidized silicon particles to high temperatures.

Modifying analytical model by incorporating fluid-bed test data as it becomes available.

4.2 DISCUSSION

4.2.1 ANALYTICAL MODEL

A model for the fluidized-bed pyrolysis of silane was developed. The fluidized-bed reactor design and performance are estimated using this model which is based on the extrapolation of available silicon deposition-rate data and data on heterogeneous and homogeneous decomposition. This model was constructed to assess the potential performance of a fluidized-bed system, and to determine the conditions under which a novel bed-heating technique could be valuable. It predicts the diameter and depth of a fluidized bed as well as the energy and heat disposal required per kilogram of silicon produced.

The model was extended to consider multiple fluid-beds in series. This scheme becomes important when the bed temperature is low and the average bed particles are large. Low bed-temperatures afford high silane concentration in the feed, thereby reducing or even eliminating the need for hydrogen recycle. Figures 4.1 and 4.2 compare the bed dimensions of single-bed and three-bed schemes. The single-bed reactor requires a bed height of 14.2m, while the three-bed reactor has a total bed height of only 3.5m.

There are, however, several factors weighing against using multiple beds. The primary ones are:

1. A single, isothermal bed is simple and can be relatively compact with moderate hydrogen recycle. The bed height can be reduced substantially by employing small bed particles in the 100 to 200μ range.

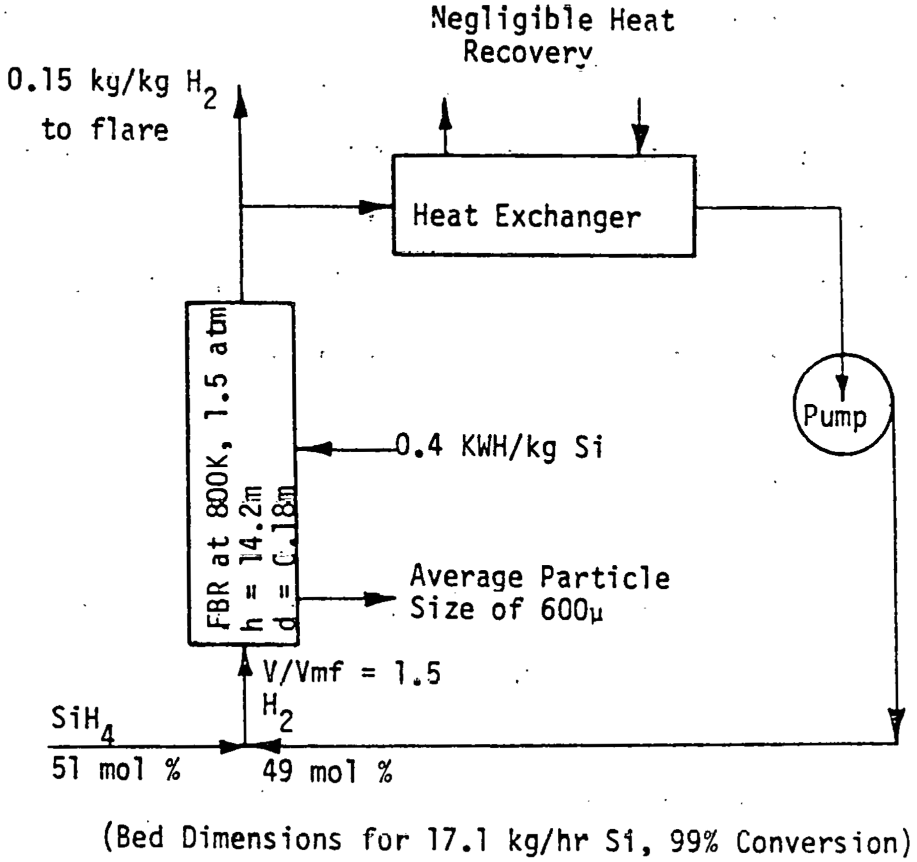
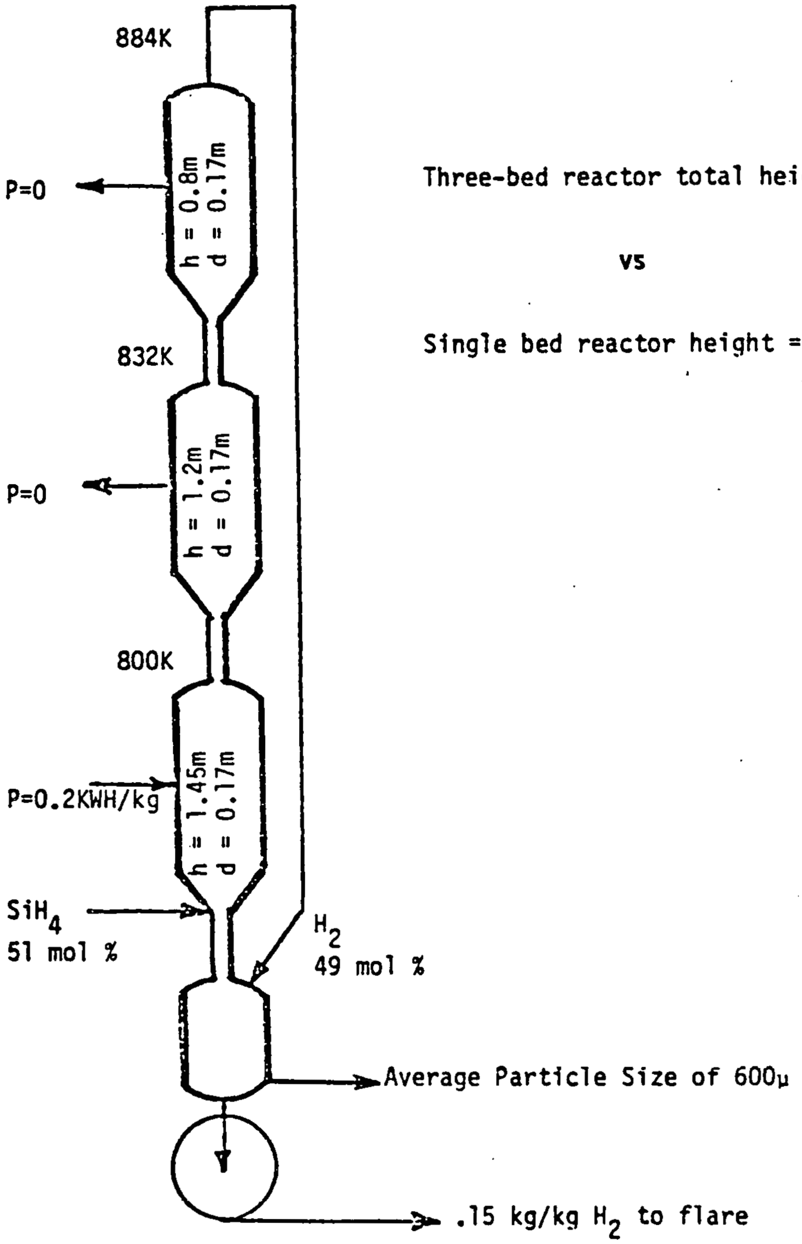


Figure 4.1

SIZE of a SINGLE-BED REACTOR
with LARGE PARTICLES OPERATED at 800K



Three-bed reactor total height = 3.5m

vs

Single bed reactor height = 14.2m (Figure 4.1)

(Bed Dimensions for 17.1 kg/hr Si, 99% Conversion)

Figure 4.2

SIZE of a THREE-BED REACTOR
with LARGE PARTICLES, 800–884K

2. Movement of solids from bed to bed is traditionally a difficult operation.

3. To obtain a real advantage in using a multiple-bed reactor, the first bed must operate at a very low temperature and this condition is relatively unexplored.

The model has been applied over a wide range of operating conditions to obtain a better physical feeling for the behavior of the fluid-bed system. This lead to the conclusion that we may be able to neglect diffusional effects in the theoretical formulation, as suggested by JPL consultant O. Levenspiel of Oregon State University. The diffusional terms were subsequently dropped and the fluid-bed peformance computed from this simple analysis was compared with that from the complete formulation. In the desired operating range, the performance difference was neglibible. The simple formulation showed a significant error at very high temperatures as shown in Figure 4.3. This figure shows the required length of the fluid-bed reactor as a function of the bed temperature. The simplified model, lacking the diffusional terms, underestimates the required bed length at high temperatures.

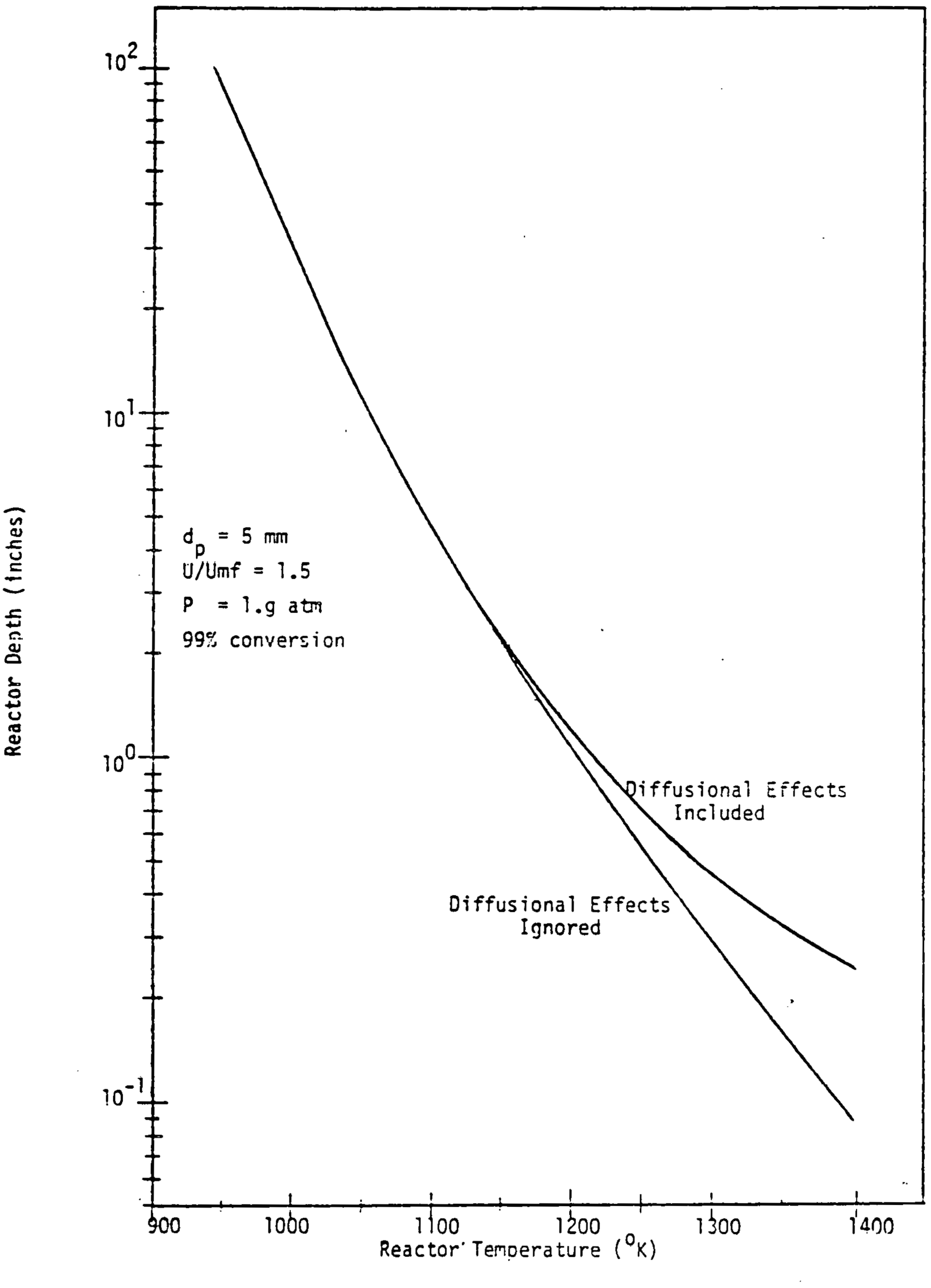


Figure 4.3

DIFFUSIONAL EFFECT on FLUID-BED DEPTH with TEMPERATURE

4.2.2 INTERIM TECHNICAL SUMMARY

The originally planned program was completed on May 31, 1978, and extension work was initiated in June. An interim technical summary of the work accomplished in the past eight months was written and will be issued shortly.

4.2.3 PLANNING of EXTENSION WORK

The work for the extension was planned with three fundamental objectives. The first is to obtain experimental data on the mechanics of a fluid-bed. There are two experimental set-ups for this task. The first test system will use the existing 2-inch glass reactor to simulate high-temperature operation using the scaling laws(4.1) obtained from T. Fitzgerald of Oregon State University. The scaling laws take into account the length, geometric similarity, pressure, gravity, viscosity, and inertial forces. They indicate that lead particles fluidized with helium at room temperature can model silicon particles fluidized with hydrogen at 900K. The size of the cold bed must be one-third that of the hot bed, and the lead particles must be smaller than the silicon particles by the same ratio. The 2-inch cold-bed reactor, therefore, can model a 6-inch hot-bed reactor. The second experimental set-up includes a reactor that is 6 inches in diameter and 6 feet high. We believe that this size is optimal for future developmental work. The fluidization characteristics of both lead shot and silicon particles will be obtained in this reactor.

The second objective is to demonstrate high-frequency electric heating of fluidized silicon particles to high temperatures. A key feature of the design is the use of a guard outer heater that will be controlled to make the insulated reactor wall nearly adiabatic.

The final objective is modification of the analytical model. The model will be updated by incorporating fluid-bed test data as they become available from the JPL and UCC laboratories.

4.2.4 EXPERIMENTAL WORK

4.2.4a HIGH-FREQUENCY ELECTRICAL HEATING APPARATUS

The apparatus for demonstrating high-frequency electrical heating to high temperatures is shown in Figure 4.4. It is well insulated to minimize the heat losses through the walls, top, and bottom flanges. There are several layers to the side walls including an inner layer of ceramic insulation surrounded by a cylindrical stationing (guard) heater, and a thick outer layer of insulation. By controlling the temperature of the outer surface of the inner insulation by the guard heater, the heat flux across the walls can be controlled. This feature makes possible accurate measurements of the temperature difference between the bed walls and the bed particles.

Calculations show that at the bed temperatures and gas flow rates of interest, the 1500W high-frequency power supply that has been specified is sufficient. All necessary parts for assembly of the apparatus were ordered except for the power supply which requires JPL approval.

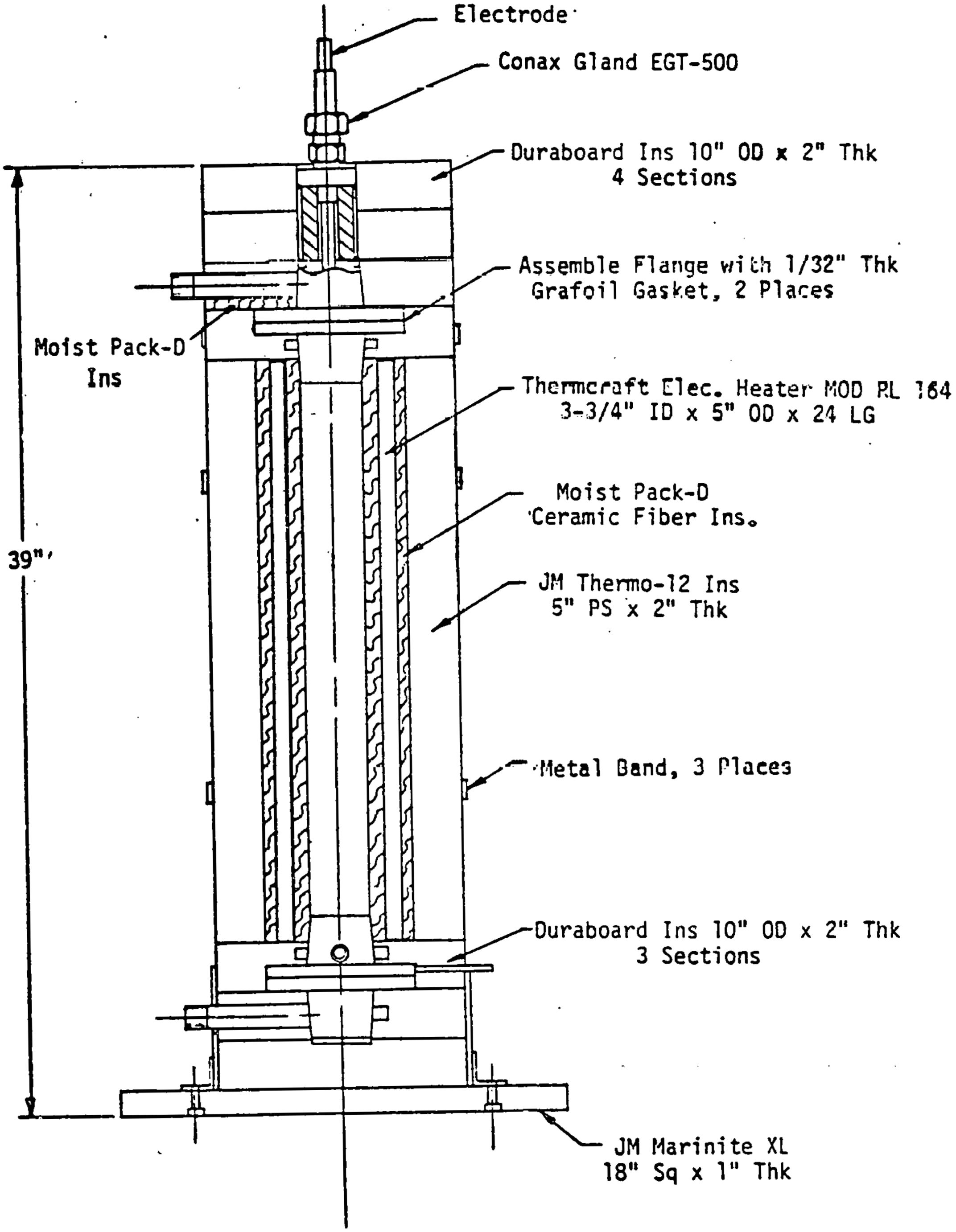


Figure 4.4

700°C CAPACTIVE HEATING REACTOR ASSEMBLY

4.2.4b STUDY of the MECHANICS of PARTICLE MOTION

Two beds will be used to study the mechanics of particle motion and develop bed hardware. The existing 2-inch diameter glass bed will be used for studying small lead particles fluidized with helium. The scaling laws discussed in Section 4.2.3 indicate that this system, operated at room temperature, should behave similar to a hot 6-inch diameter process development system.

In addition, a 6-inch diameter cold bed is being constructed to study solids handling and gas distributor design. The fluidized portion of the column is a Pyrex pipe. The design facilitates easy replacement of the distributor plates and bed particles. With the appropriate size of lead particles fluidized by helium, a 100 MT/Yr reactor can be modeled.

4.2.4c PARTICLE ATTRITION STUDY

The attrition of silicon particles will be examined in a very small bed as shown in Figure 4.5. The quartz tube containing the particles can be heated to the desired temperature by an electrical heater. After the gas leaves the fluid-bed section, it is cooled in a series of heat exchangers before being exhausted through a filter. This apparatus will also be used to test the durability of different reactor materials by placing sample coupons in the bed.

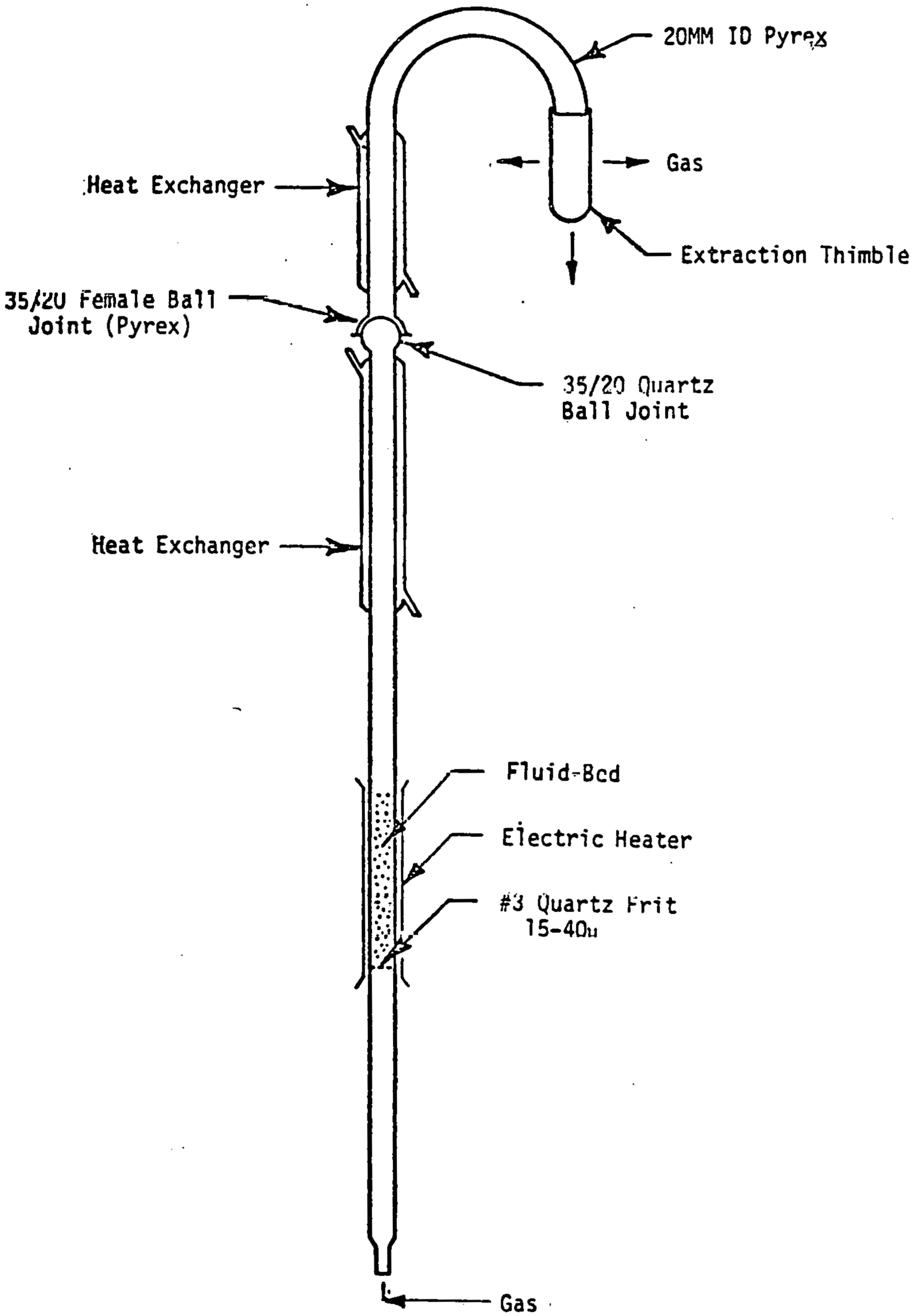


Figure 4.5
ATTRITION REACTOR

4.3 CONCLUSIONS

The effort originally planned for the capacitive heating program was completed at the end of May, and an interim summary report will be issued shortly. The high-frequency capacitive heating of a fluid-bed was demonstrated, although the bed-temperature rise was small due to power-generating limitations. An analytical model for the fluid-bed pyrolysis of silane was developed. Based on this model, a preliminary conceptual design of the fluid-bed pyrolysis system for a 100 MT/Yr EPSDU was developed. The design appears technically feasible and economically attractive. Extension work just started is aimed at increasing our confidence in the fluid-bed design by reducing certain key assumptions.

4.4 PROJECTED QUARTERLY ACTIVITIES

4.4.1 ELECTRICAL HEATING of FLUID-BED

The apparatus is assembled and the bed will be heated to 700°C. Fluid-bed characteristics will be studied at elevated temperatures.

4.4.2 FUNDAMENTAL FLUIDIZATION TESTS

The 6-inch diameter, cold-bed reactor will be constructed. The bed will be operated at U/Umf of 1.2 to 2.0 and bed-particle attrition will be studied during the run. Particle attrition will also be studied in a small quartz apparatus at elevated temperatures. The 2-inch reactor will also be run with lead particles fluidized by helium to simulate the 6-inch hot-bed.

4.5 REFERENCES

4.1 A private communication with Dr. T. Fitzgerald of Oregon State University on May 5, 1978.

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