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LSA SILICON MATERIAL TASK

CLOSED-CYCLE PROCESS DEVELOPMENT

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Interim Summary Report
August - December 1978

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The JPL Low-Cost Solar Array Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology by agreement between NASA and DOE.

ABSTRACT AND SUMMARY

This report summarizes the Jet Propulsion Laboratory Low-Cost Solar Array Project Contract 955006 "Closed-Cycle Process for Low-Cost Solar Silicon Using a Rotary Chamber Reactor," which was active from August 10, 1978 to December 8, 1978.

This program was Phase I of an effort to achieve production of low-cost solar-grade polysilicon from metallurgical-grade silicon in a closed-cycle process. Impure silicon would be converted to trichlorosilane by reaction with by-product silicon tetrachloride, and the trichlorosilane thermally decomposed in a rotary drum reactor. The technical restrictions to development of the program approach were based on minimizing new technology requirements by using existing technology to reduce the timing, risk, and cost of achieving production capability. The deficiencies in the established Siemens polysilicon process were identified and systematically eliminated to achieve a simple, continuous, easily scaleable, low-cost process. The process is closed cycle with high reactant concentration for material, equipment, and energy efficiency.

The initial effort on feasibility of the closed-cycle process was begun with the design of the two major items of untested equipment, the silicon tetrachloride by-product converter* and the Rotary Drum Reactor (RDR) for deposition of silicon from trichlorosilane. The design criteria of the initial laboratory equipment included consideration of the reaction chemistry, thermodynamics, and other technical factors. Design and construction of the laboratory equipment was completed. Preliminary silicon tetrachloride conversion experiments confirmed the expected high yield of trichlorosilane, up to 98% of theoretical conversion.

A preliminary solar-grade polysilicon cost estimate, including capital costs considered extremely conservative, of \$6.91/kg supports the potential of this approach to achieve the cost goal.

The closed-cycle process appears to have a very likely potential to achieve LSA goals.

*Development of the silicon tetrachloride to trichlorosilane converter was subcontracted to Battelle's Columbus Laboratories, Columbus, Ohio.

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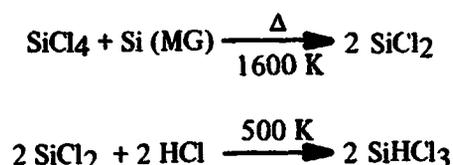
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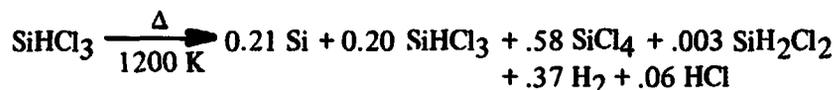
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SECTION I INTRODUCTION

This program had as its goal the demonstration of technical feasibility of a closed-cycle process for producing polycrystalline silicon to meet the objectives of the Material Task of the Low-Cost Solar Array (LSA) Project. Generally, the closed-cycle process would convert metallurgical-grade silicon to trichlorosilane, purify the trichlorosilane, then thermally decompose the trichlorosilane to form solar grade silicon and silicon tetrachloride. The silicon tetrachloride is used for the generation of trichlorosilane, via the silicon dichloride intermediate, by a high-temperature reaction with metallurgical-grade silicon:



The silicon tetrachloride and hydrogen chloride were formed as by-products in the thermal decomposition of trichlorosilane:



Based upon these chemical reactions, the program was directed toward demonstrating feasibility of silicon production in a closed-cycle reactor with in-situ exhaust stream regeneration using externally heated, large area gas-solid contact reactors. The Phase I program was structured to concentrate on answering the major technical aspects of this process; deposition of silicon in a rotary drum; and silicon tetrachloride conversion. The initial 12-month phase included demonstration of these two process steps and the engineering data required for design of a closed-cycle system. Phase II of this program would demonstrate the operation of a balanced closed-cycle process at a production level of ≈ 1 kg per hour polysilicon production rate. Engineering and operating data will be obtained to validate the production concept and allow more precise economic estimates.

Phase III of this program would involve an EPSDU* construction and operation at 25-100 T/y production level.

*Experimental Process System Development Unit

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SECTION II TECHNICAL DISCUSSION

A. DEFICIENCIES IN SIEMENS POLYSILICON PROCESS

An extensive analysis of potential polysilicon production processes was conducted to determine whether a suitable, economical polysilicon process could be defined to meet JPL/LSA goals. It was concluded that a lower technical risk alternative could be based on extension of the present Siemens approach for semiconductor silicon by systematic elimination of the significant cost-contribution factors. The Siemens process cost analysis done on JPL contract appears to be quite valid and will be used for baseline costs.*

1. Materials Costs

The standard Siemens process utilizes a reactor feed input of 5-10% SiHCl_3 in H_2 and achieves a conversion yield of <30% to silicon with exhaust by-products of HCl , SiCl_4 , H_2SiCl_2 , as well as unreacted H_2 and SiHCl_3 . The exhaust stream is separated, repurified and recycled for approximately the same cost as new chemicals. The cost of discarding the exhaust gases would be greater than their recycling. The conversion per pass then required ≈ 16 kg of SiHCl_3 per kg silicon, which at $\$0.80/\text{kg}$ contributes $\approx \$13$ cost/kg (without SiCl_4 by-product credit). Hydrogen and other material costs are probably less than $\$2/\text{kg}$.

2. Labor

The present Siemens process is a batch process in which silicon is deposited on several (often 3) "U" shaped rod, resistively-heated, filaments beginning at ≈ 0.5 cm and growing to 10-20 cm in diameter. The reactor deposition area varies continuously by $>10^2$ during a 100-200 hour run, requiring frequent manual or automatic changes in reactant flow, heater voltage, and current. Failure of a single filament can abort a run. The labor required to service a reactor during a run and between runs is 10-20 hours. Labor for silicon deposition contributes directly $\approx \$1.80/\text{kg}$ silicon with an additional $\approx \$2.60/\text{kg}$ labor cost to operate the remainder of the plant.

3. Overhead

Direct consumption of electricity, 385 kW/kg, is a major expense of $\$11.54/\text{kg}$ at $\$0.03/\text{kW-hr}$. Other utility costs for coolants and steam contribute $\approx \$2.72/\text{kg}$. The high electrical consumption results from the filaments radiating as giant light bulbs, from the requirement to heat

*"Process Feasibility Study in Support of Silicon Material Task I" JPL contract report ERDA/JPL 954343-77/3 (September 1977).

a large volume of reactant gas to deposition temperature, and from an even further reduced reaction efficiency when the filaments are small. The labor related portion of overhead including supervisory, clerical, maintenance, and laboratory is \approx \$3.69/kg.

Depreciation costs for a plant built in 1975 were estimated at \$8.05/kg based on a \$92.6 M plant investment cost.

A summary of the cost contribution for the present Siemens process is given in Table I. The additional costs of QA, Sales and Administration, and profit would establish a minimum selling price in the \$60+ range.

Table I. Estimate of Siemens Process Silicon Cost

	\$/kg
Material	15.34
Labor Direct & Indirect	4.20
Plant Overhead	3.82
Utilities	11.37
Supplies and Misc.	3.14
Depreciation, Taxes	10.47
General Expenses	6.23
By-product Credit	(6.23)
	<hr/>
Total Manufacturing Cost	48.34

This program approach entailed a systematic reduction of the various cost contributions, while remaining within the technology boundaries of known silicon chloride chemistry. The approach is based on several fundamental manufacturing concepts. *Continuous processing*: this concept reduces labor cost, facilitates scale-up to larger sized units, provides uniformity of product quality, permits a constant deposition area, and permits a steady-state operation that greatly reduces process control difficulties. *Total chemical recycle with minimum separation*: this concept factorially reduces material costs through efficient utilization of chemicals, reduces capital costs by reducing plant size, reduces necessity of by-product disposal, and alleviates environmental hazards. *High concentration of active chemicals*: this concept leads to improved investment utilization by higher throughput, and removes requirement for obtaining, handling, heating, and disposing of large quantities of diluent material. *Efficient energy utilization*: the processes and equipment will be designed to minimize energy losses to environment and nonproductive gas heating.

B. ANALYSIS OF BALANCED, CLOSED-CYCLE PROCESS

As shown by Hunt and Sirtl¹, SiCl₄(g), SiHCl₃(g), and SiCl₂(g) are the major silicon-bearing gaseous species in equilibrium with silicon in the temperature range (900-1100°C) used in producing silicon by thermal decomposition or hydrogen reduction of trichlorosilane (SiHCl₃). The SiCl₂(g)

tends to back react with the by-product HCl to give SiHCl₃, so that the major silicon-bearing compounds in the condensed by-product (in absence of polymer formation)* are SiCl₄ and SiHCl₃.

If SiHCl₃ (with or without hydrogen added) is used as the feed material for silicon deposition, SiCl₄ is a by-product. Further, the hydrochlorination of metallurgical-grade silicon to generate SiHCl₃ also yields SiCl₄ as a by-product. Thus conventional Siemens-process plants produce quantities of by-product SiCl₄ which impact an already limited market. At silicon production rates of thousands of metric tons per year, such as those contemplated for the silicon solar photovoltaic industry, the by-product SiCl₄ would have to be disposed of in another manner. Thus, for any large-scale process based on SiHCl₃ as a feed, it becomes of interest to develop a method for converting SiCl₄ to SiHCl₃ in a regenerator step.

One of the options is to react SiCl₄ with metallurgical-grade silicon to give SiCl₂(g) and to quench the reaction product with HCl(g) to give SiHCl₃(g):



However, since two moles of SiHCl₃ are produced for every mole of silicon picked up in the regenerator, the process becomes a producer of by-product SiHCl₃ rather than SiCl₄.

It can be shown on the basis of the thermodynamic data of Reference (1) that by adding recirculated hydrogen to the SiCl₄ in the regenerator loop, the product can be controlled so that one mole of silicon is picked up for each mole of silicon that is produced in the SiHCl₃ decomposition step, and no excess of either SiHCl₃ or SiCl₄ is generated.

In all of the discussions that follow, the calculations by means of Battelle's EQUICA computer program² are based on the thermodynamic data of Reference (1), with the assumption (for the purposes of establishing a base) that equilibrium will exist, and that the reaction



occurs on quenching an equilibrium mixture.

1. Silicon Trichlorosilane Decomposition

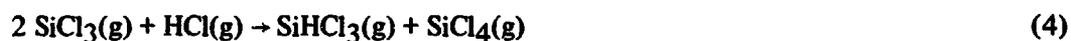
The first step in arriving at a balanced system is to establish the most desirable SiHCl₃ decomposition conditions.

*If the reaction mixture is quenched too rapidly, "polymers" based on (SiCl₂)_n chains can form, which are pyrophoric.

Figure 1 shows the effect of temperature on the efficiency of decomposition of $\text{SiHCl}_3(\text{g})$ at atmospheric pressure. It is noted that a broad maximum exists in the temperature range of interest. Figure 2 shows the effect of adding hydrogen to increase the efficiency at 927°C . Also plotted in Figure 2 is the number of moles of gas through the decomposer per mole of silicon produced. Clearly, the advantage gained in adding hydrogen is small, and for a decomposer limited by volumetric throughput, the optimum condition lies at 100% SiHCl_3 . Accordingly, this condition is chosen for the initial calculations for the balanced system.

Table II shows the equilibrium and "quenched" compositions for the production of 1.000 mole of silicon from 4.322 moles of SiHCl_3 plus 0.013 mole of SiH_2Cl_2 at 927°C . Recycling the almost negligible amount of by-product SiH_2Cl_2 at this point is a mathematical device for eliminating it from subsequent material balances.

In calculating the composition of the quenched (condensed) by-product, Reaction (3), which is known to occur, is used to eliminate $\text{SiCl}_2(\text{g})$. Elimination of SiCl_3 (although present only in the fourth decimal place) is done by the arbitrary reaction:



In the balanced system, the SiHCl_3 and SiH_2Cl_2 are recycled in the decomposer loop and the SiCl_4 , HCl , and H_2 are sent to the regenerator for conversion to SiHCl_3 . The key point is that in a balanced system 2.776 moles of SiCl_4 must be converted for every mole of silicon produced. Conversely, 1.000 mole of silicon must be picked up in the regenerator by the equivalent of Reactions (1) and (2) for every 2.776 moles of SiCl_4 fed to the regenerator.

2. Silicon Trichlorosilane Regeneration

In the regenerator step, it is assumed that the hydrogen and SiCl_4 from the decomposer are fed through a packed bed of silicon to form an equilibrium product whose composition depends upon that of the feed stream and temperature. The HCl is assumed to have been separated and is fed to the regenerator product in the quenching step. This has been shown to be of value in preventing the reversal of Reaction (1) which otherwise can lead to plugging of the quench system. Hydrogen and SiCl_4 are recycled in the regenerator loop to give the required balance.

In the calculations for the regenerator, $\text{SiCl}_2(\text{g})$ and $\text{SiCl}_3(\text{g})$ are eliminated from the quenched compositions as before. For convenience, $\text{SiH}_2\text{Cl}_2(\text{g})$ is eliminated somewhat arbitrarily, although present in small quantities, and its elimination is justifiable. This is done by the arbitrary reaction

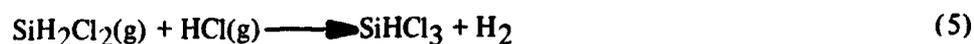


Figure 3 shows the effect of the hydrogen/ SiCl_4 composition of the regenerator feed on the mole ratio of SiCl_4/Si consumed in the regenerator. The target ratios for decomposer temperatures of 927°C , 1027°C and 1127°C are also shown. Operating the regenerator at H_2/SiCl_4 ratios above the decomposition target ratio results in the net production of SiHCl_3 . Net production of SiCl_4

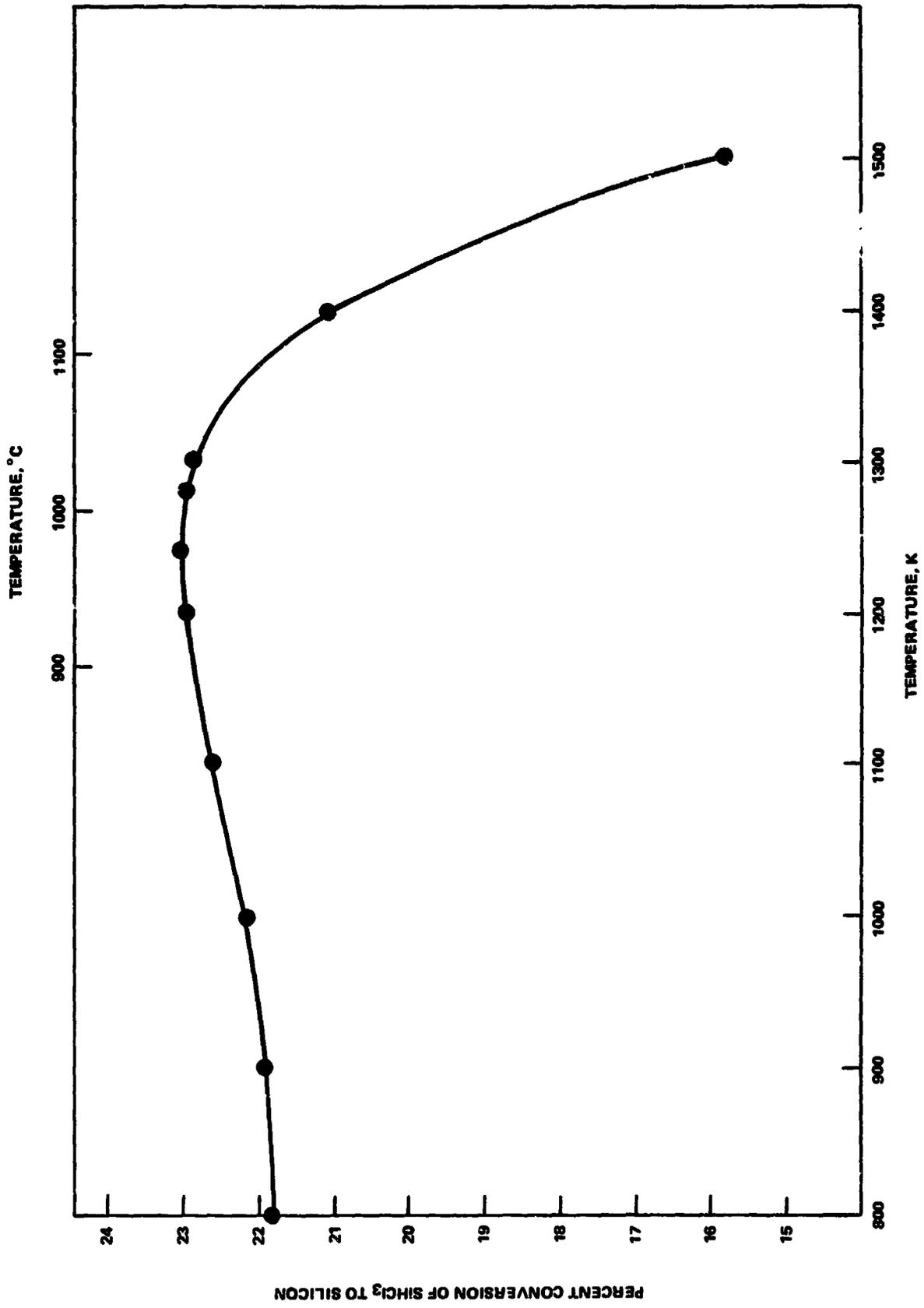


Figure 1. Effect of Temperature on the Equilibrium Thermal Decomposition of Trichlorosilane at 1 Atm. where

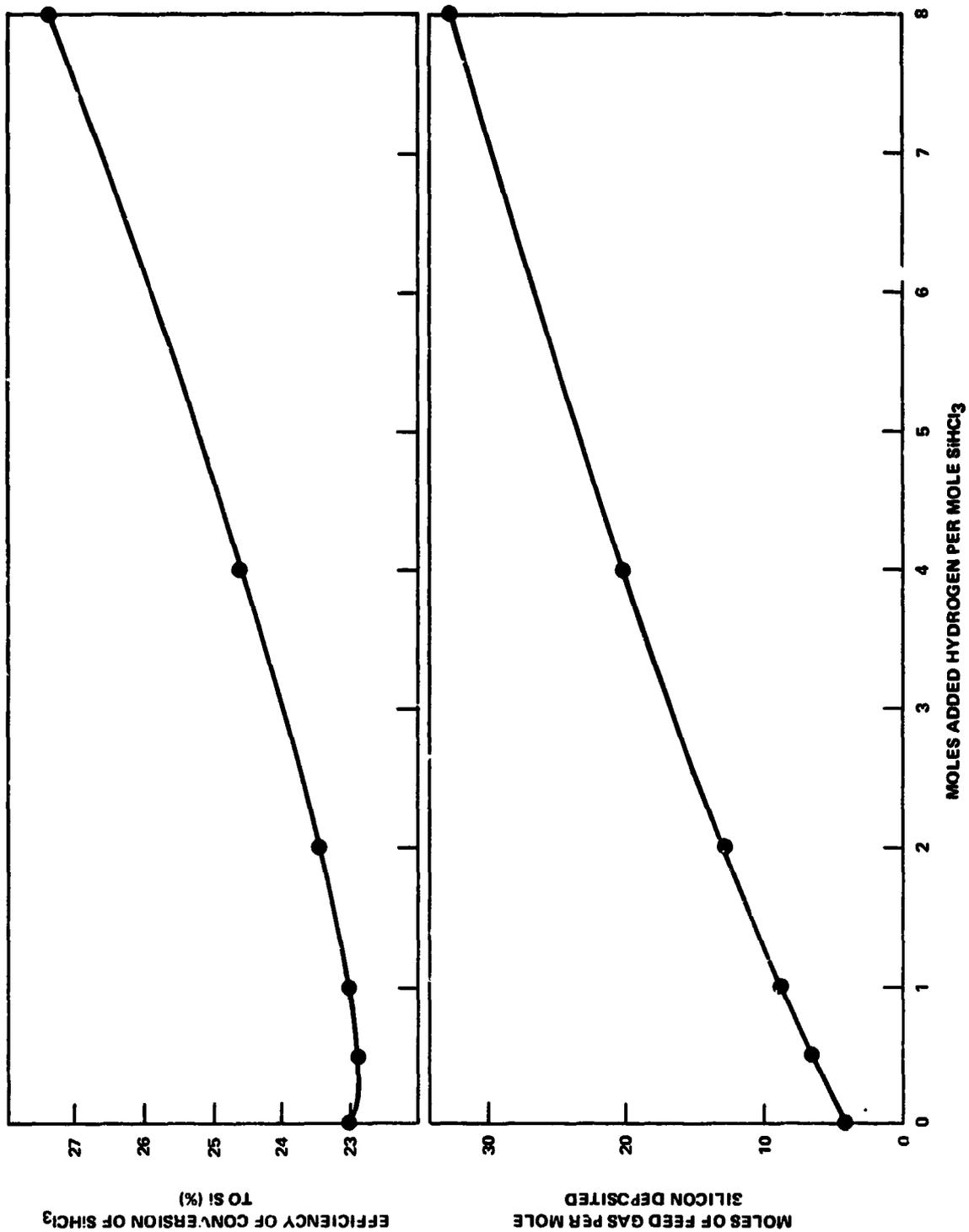


Figure 2. Effect of Hydrogen Addition on the Equilibrium Thermal Decomposition of Trichlorosilane at 927°C and 1 Atmosphere

Table 11. Equilibrium and Quenched Compositions (Moles) from Thermal Decomposition of 4.322 Moles SiHCl_3 + 0.013 Moles SiH_2Cl_2 at 927°C , 1.0 atm

Species	Equilibrium	Quenched
Si(s)	1.000	1.000
$\text{SiCl}_2(\text{g})$	0.046	0.000
$\text{SiCl}_3(\text{g})$	0.000	0.000
$\text{SiCl}_4(\text{g})$	2.776	2.776
$\text{SiH}_2\text{Cl}_2(\text{g})$	0.013	0.013
$\text{SiHCl}_3(\text{g})$	0.499	0.545
HCl	0.269	0.223
H_2	1.777	1.777

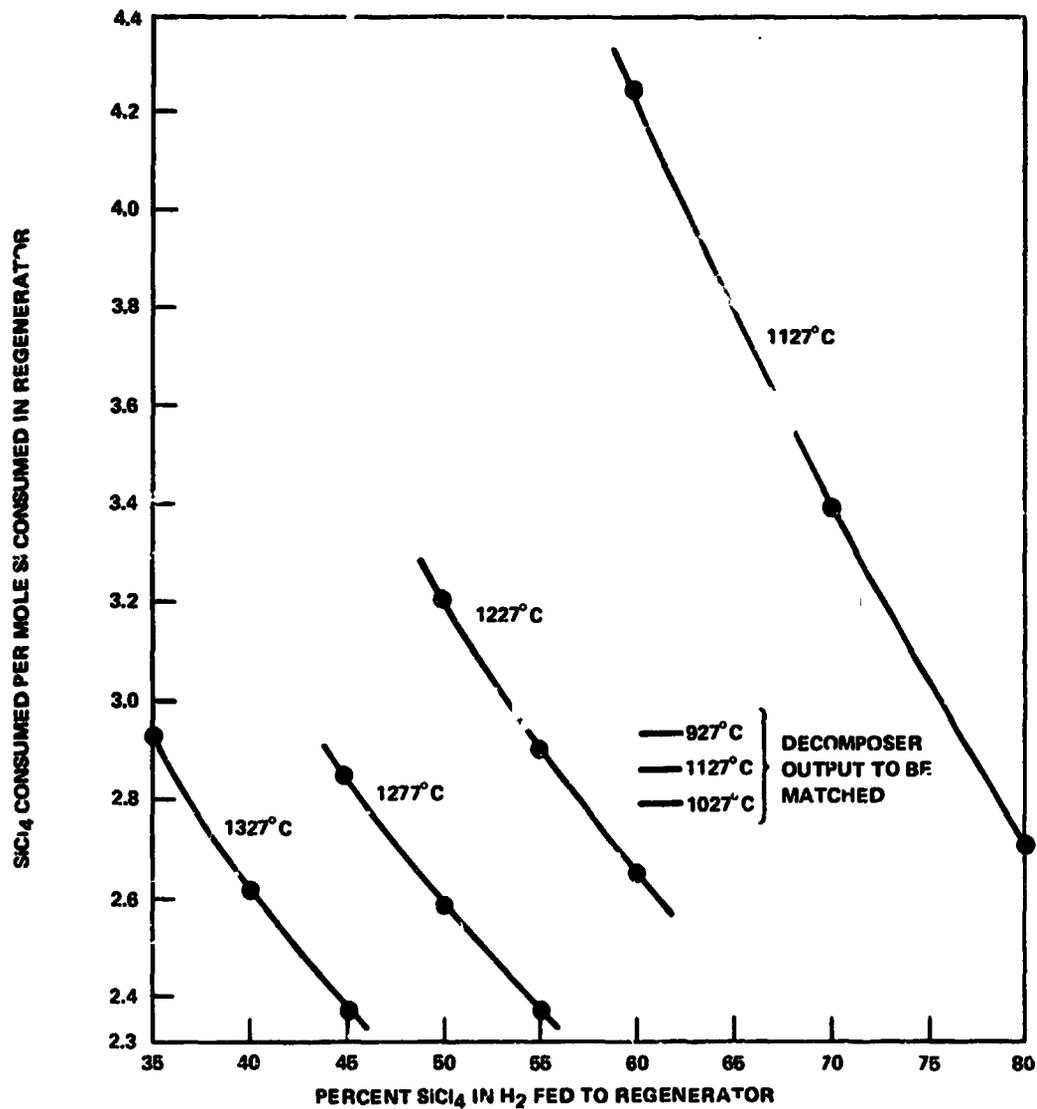


Figure 3. Effect of Composition on Reaction of Silicon Tetrachloride and Hydrogen with Silicon in Regenerator

occurs at ratios below target. It is clear from the target ratios given that the operating temperature of the decomposer has little influence on the requirements of the regenerator.

In seeking the overall decomposer/regenerator balance point, successive approximations are made with variable regenerator compositions, leading to data equivalent to that shown for the decomposer in Table II. Once the balance point has been established, an overall material balance can be drawn.

Figure 4 is a block diagram showing the functions of the various components of the balanced system. Table III gives the calculated process stream compositions for a balanced system with the decomposer at 927°C and 1.0 atm, and with the regenerator at various temperatures.

Residual inequalities in Table III and Figure 4 (in the third decimal place) are due in part to:

- 1) Insufficiently accurate approximation of the $H_2/SiCl_4$ ratio at the balance point
- 2) The great leverage of the low conversion efficiencies at 927°C and 1077°C
- 3) Rounding off.

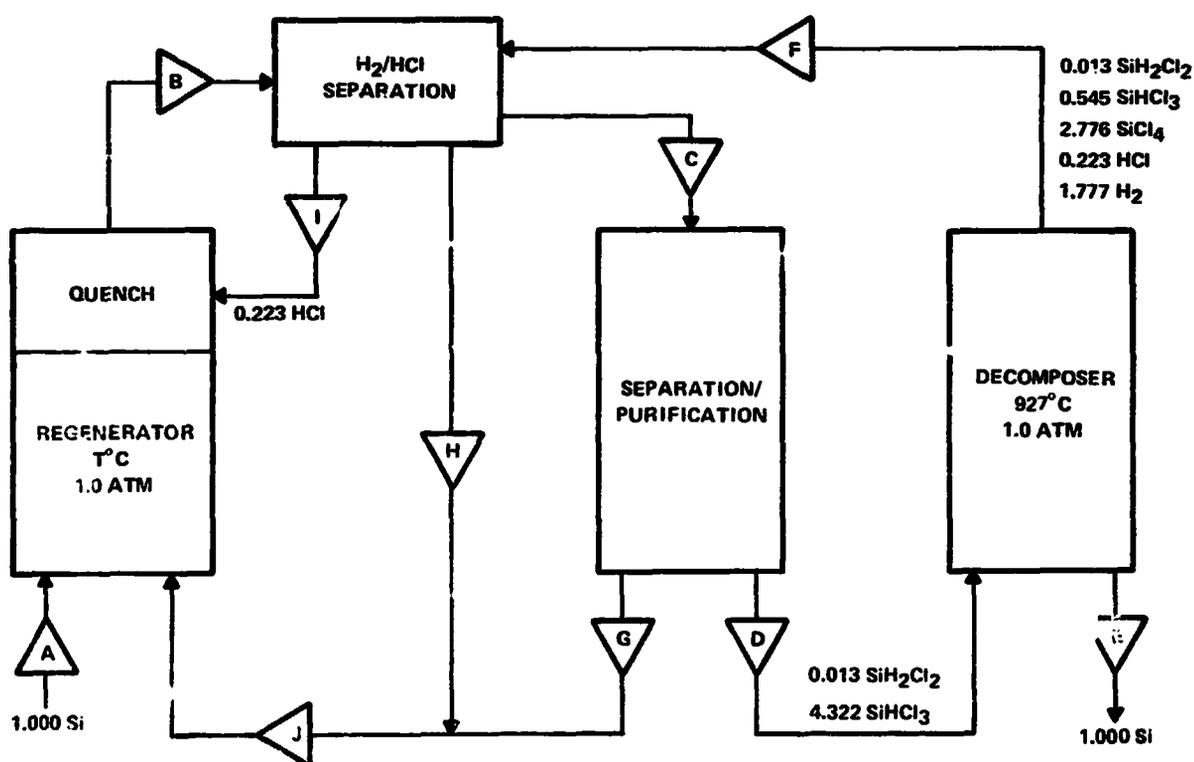


Figure 4. Block Diagram of Balanced System for Production of Pure Silicon

Table III. Materials Balance (Moles) for Figure 4 as a Function of Regenerator Temperature for Decomposer at 927°C and 1.0 Atmosphere*

Regenerator Temperature (C)	Variable Process Stream					
	Component	B	C	G	H	J
927	SiCl ₄	100.219	102.995	103.000	-	103.000 (97.43%)
	SiHCl ₃	3.774	4.319	-	-	-
	SiH ₂ Cl ₂	-	0.013	-	-	-
	H ₂	0.948	-	-	2.721	2.721 (2.57%)
1027	SiCl ₄	37.819	40.695	40.695	-	40.695 (91.94%)
	SiHCl ₃	3.772	4.317	-	-	-
	SiH ₂ Cl ₂	-	0.013	-	-	-
	H ₂	1.785	-	-	3.658	3.658 (8.06%)
1127	SiCl ₄	14.884	17.660	17.660	-	17.660 (78.85%)
	SiHCl ₃	3.778	4.323	-	-	-
	SiH ₂ Cl ₂	-	0.013	-	-	-
	H ₂	2.958	-	-	4.737	4.737 (21.15%)
1227	SiCl ₄	5.514	8.290	8.290	-	8.290 (57.25%)
	SiHCl ₃	3.778	4.323	-	-	-
	SiH ₂ Cl ₂	-	0.013	-	-	-
	H ₂	4.413	-	-	6.191	6.191 (42.75%)
1277	SiCl ₄	3.178	5.954	5.955	-	5.955 (46.13%)
	SiHCl ₃	3.778	4.322	-	-	-
	SiH ₂ Cl ₂	-	0.013	-	-	-
	H ₂	5.177	-	-	6.954	6.954 (53.87%)
1327	SiCl ₄	1.761	4.537	4.538	-	4.538 (37.14%)
	SiHCl ₃	3.777	4.322	-	-	-
	SiH ₂ Cl ₂	-	0.013	-	-	-
	H ₂	5.904	-	-	7.682	7.682 (62.86%)

*Constant process streams: A = 1.000 Si, D = 4.322 SiHCl₃ + 0.013 SiH₂Cl₂, E = 1.000 Si, F = 2.776 SiCl₄ + 0.545 SiHCl₃ + 0.013 SiH₂Cl₂ + 1.777 H₂ + 0.223 HCl, I = 0.223 HCl

3. Trade-Off Analysis

In developing a process based on the above rationale, one desires to minimize operating temperatures, minimize throughput, and maximize yield by taking advantage of the available options.

a. Regenerator Temperature

It is evident from the data of Table III that decreasing the operating temperature of the regenerator requires an increase in the number of moles of gas (SiCl₄ + H₂) in the feed by factors of

1.06, 1.18, 1.83, 3.61, and 8.65 in lowering the temperature from 1327°C to 1277°C, 1227°C, 1127°C, 1027°C, and 927°C, respectively. Thus, operating below 1127°C does not appear to be attractive. However, the decrease in operating temperature from 1327°C to 1127°C may be well worth the cost of handling the additional (1.83x) recycle.

b. Regenerator Pressure

It will be shown in the discussion of trade-offs in the decomposition section that because of the small change in molar volume (e.g., 24%) of reactants versus products in the Si/H/Cl system, the effect of pressure is not usefully significant.

c. Regenerator Composition

Because of the balance constraint, the compositional parameters are fixed at a given regenerator temperature and decomposer by-product composition and cannot be varied to improve the situation.

d. Decomposer Temperature

In a study of the trade-offs in the decomposer system which might lower the load on the regenerator, little is gained in changing the decomposer temperature, as shown in Figure 3.

e. Decomposer Pressure

The net increase in molar volume of products versus reactants, although only 24% for the data of Table II, makes it of interest to study the effect of decreasing the operating pressure of the decomposer to increase its efficiency. Table IV shows the effect of pressure on the conversion of SiHCl₃ to silicon and on the ratio of SiCl₄ generated per mole of silicon produced.

In the light of the data of Table IV, there exists no incentive for operating at reduced pressure.

Table IV. Conversion of 1.000 SiHCl₃ + 0.003 SiH₂Cl₂* to Silicon at 1200 K as a Function of Pressure

	Pressure (Atmospheres)						
	1.0	0.7	0.3	0.1	0.07	0.03	0.01
<u>Si Produced</u> SiHCl ₃ Fed	0.231	0.234	0.240	0.246	0.246	0.245	0.237
<u>Moles SiCl₄ Produced</u> Moles Si Produced	2.77	2.76	2.72	2.67	2.66	2.63	2.63

*The device of adding a constant 0.003 mole of recycled SiHCl₂ was retained here although the required addition varies with pressure from 0.003 mole at 1 atm to 0.002 mole at 0.03 atm, to 0.001 mole at 0.07 atm. Use of a pressure-dependent addition would make no significant difference in the results.

f. Decomposer Composition

With temperature and pressure ruled out as highly influential parameters in optimizing the decomposer cycle, one is left with two options based on compositional modification of the decomposer feed stream:

- 1) Adding recirculated hydrogen
- 2) Adding recirculated SiCl₄.

The hydrogen additions serve to decrease the SiCl₄ content of the by-product by favoring its reduction to SiHCl₃ and SiH₂Cl₂. Additions of recycled SiCl₄ decrease the net production of SiCl₄ suppressing conversion of SiHCl₃ to SiCl₄ by the "mass action" principles. As pointed out and shown in Figure 2, the addition of hydrogen is not as effective as one might have hoped in increasing the reaction efficiency, considering the large volumes of gas that must be recycled with accompanying pumping costs and energy losses (even with optimum heat exchange).

Figure 5 shows, as a function of the ratio H₂/SiHCl₃, the number of moles of SiCl₄ per mole of silicon produced, that must be ultimately discharged in the regenerator. Also shown is the total number of moles of gas that must pass through the decomposer per mole of silicon produced (equivalent to the curve that is shown in Figure 2). Again, the improvement (decrease of the load on the regenerator) is obtained at the cost of greatly increasing the recycle load in the decomposer.

Figure 6, the counterpart of Figure 5, shows the effects of recirculating SiCl₄ in the decomposer loop. Whereas the addition of hydrogen increased the SiHCl₃-to-silicon conversion efficiency, the addition of SiCl₄ decreases the conversion efficiency. Thus the total number of moles of gas passing through the decomposer per mole of silicon produced increases even more rapidly with dilution factor, and as can be seen from the data, even less of an improvement (decrease in net production of SiCl₄) is observed with SiCl₄ addition than was the case for hydrogen addition.

Only in the presence of an excess of hydrogen is the SiCl₄ addition really effective in suppressing net SiCl₄ generation. Figure 7 shows the effect of SiCl₄ addition in a mixture of (1-X) SiHCl₃ + XSiCl₄ + 8.0 H₂. At about 0.55 mole fraction SiCl₄ in the SiHCl₃ + SiCl₄ mixture fed, no net production of SiCl₄ occurs. Calculation of the equilibrium composition under these conditions confirms the a priori prediction that, except for the net generation of 0.15 mole of SiH₂Cl₂ per mole of silicon*, the overall reaction is effectively



Thus, if one is willing to accept the low efficiency (0.1563 mole silicon produced per mole fed) and the attendant large ratio (57.6) of moles of gaseous reactants needed per mole of silicon produced, the overall problem can be converted to one of having to recycle HCl instead of SiCl₄. Although this situation may be advantageous in some respects, it should be noted that the 57.6 moles

*The net SiH₂Cl₂ by-product could be decomposed at high conversion efficiency [e.g., ~50% (equilibrium) efficiency at 927°C] to produce silicon in a satellite unit.

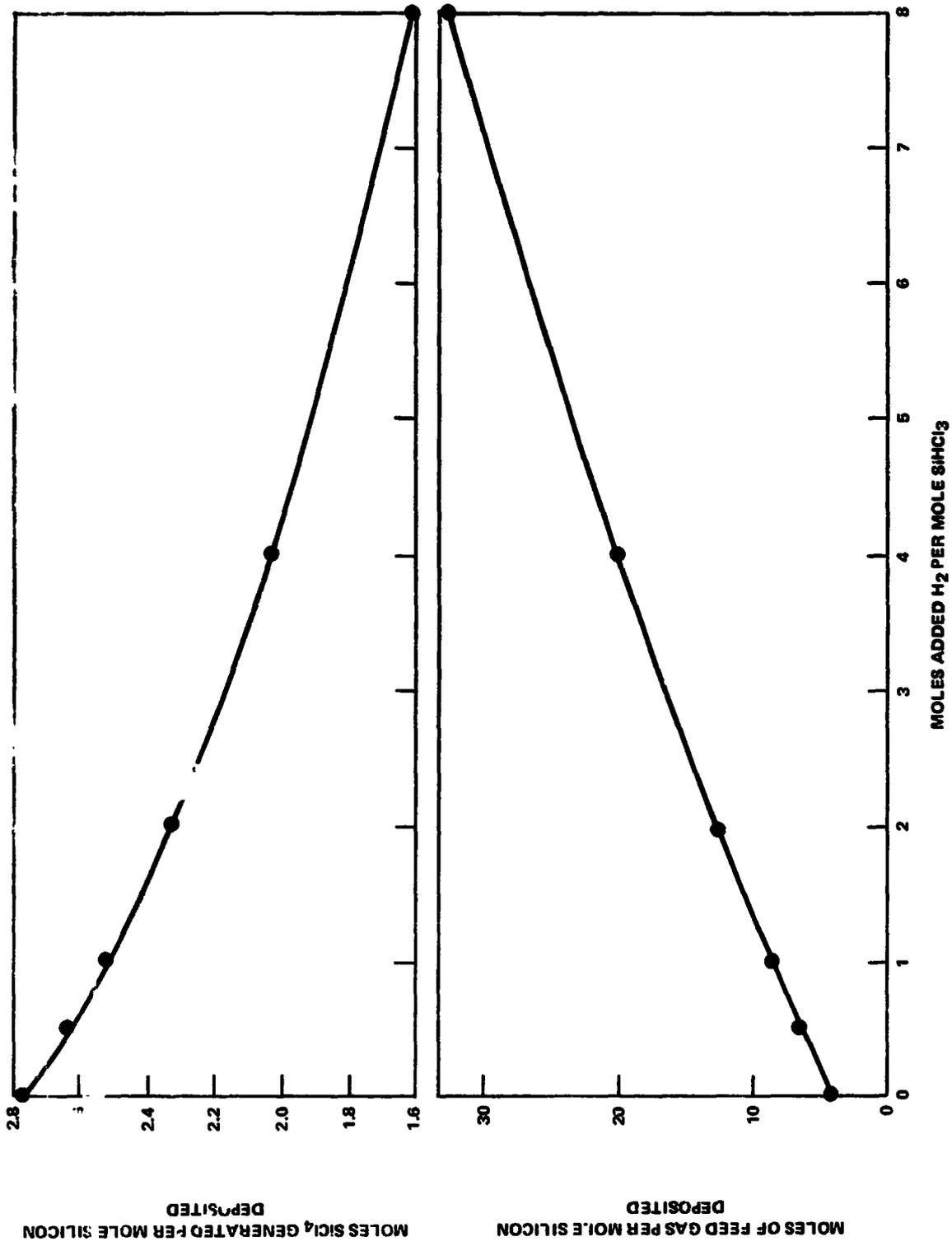


Figure 5. Effect on SiCl₄/Si Generation of Hydrogen Addition to Decomposer
 [1 SiHCl₃(g) + 0.003 SiH₂Cl₂(g) + X H₂(g), 927°C, 1 Atmosphere]

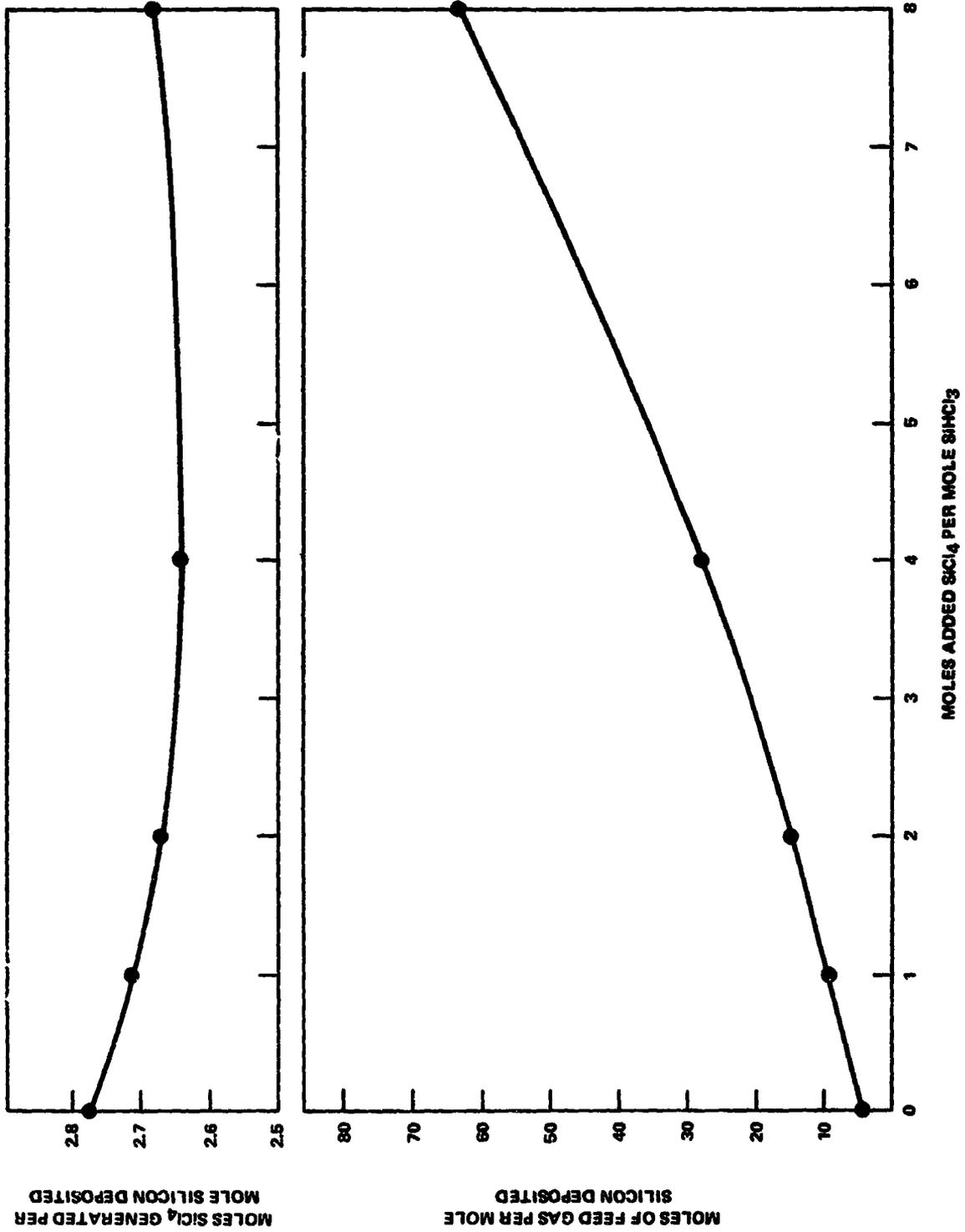


Figure 6. Effect on SiCl₄/Si Generation of SiCl₄ Addition to Decomposer
 [1 SiHCl₃(g) + 0.003 SiH₂Cl₂(g) + X SiCl₄, 927°C, 1 Atmosphere]

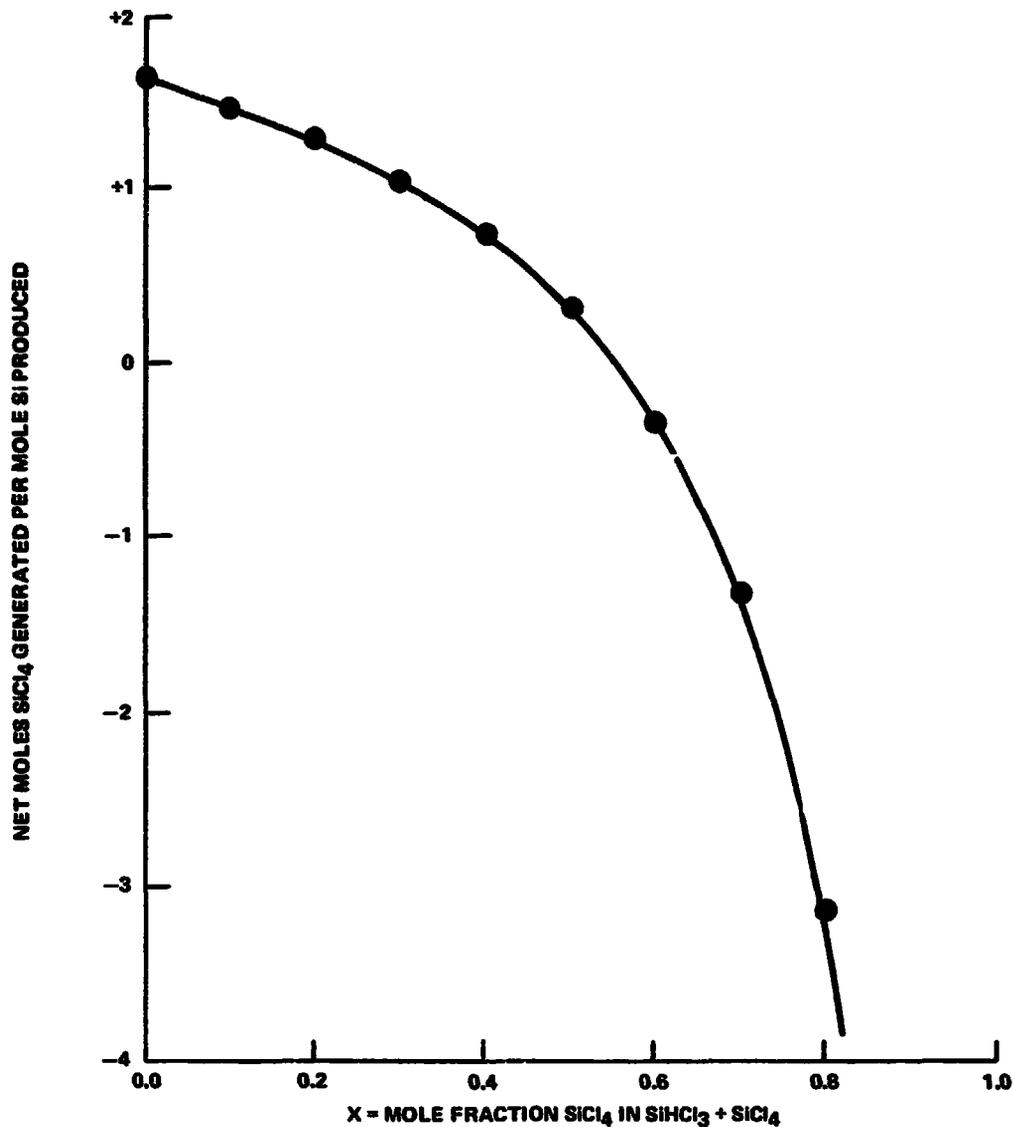


Figure 7. Effect of SiCl₄ Additions to SiHCl₃ on the Net Production of SiCl₄ in a Hydrogen Atmosphere [(1 - X) SiHCl₃ + X SiCl₄ + 0.003 SiH₂Cl₂ + 8 H₂] at 1200 K, 1 Atm, 0.1563 Moles Silicon Produced per Mole Silicon Fed

of feed gas per mole of silicon in the above case is ≈ 13 times the 4.335 moles of SiHCl₃ + SiH₂Cl₂ used in the reference case for a "pure" SiHCl₃ feed (Figure 4).

4. Kinetic Considerations

It should be emphasized that, except for the assumption that Reaction (3) predominates in cooling or quenching the decomposer and regenerator products, all of the above conclusions are based on the assumption that chemical equilibrium is attained. That is, the analysis predicts what *can* happen. What *will* happen depends upon kinetic factors which are more difficult to predict. Some conclusions can be drawn, however, which appear to be justified and can serve as guidelines.

The degree of approach to equilibrium will depend upon the nature of the decomposer, regenerator, and quenching equipment, as well as the process parameters.

With reference to the decomposer, Table V shows the equilibrium mole ratio of SiCl_4 generated to silicon produced from SiHCl_3 as a function of temperature. As seen earlier, this ratio does not change rapidly with temperature in the range of interest. Thus, for any observed departure from equilibrium in an experimental decomposer, one can assume that a fraction of the gas has come to equilibrium at the deposition temperature or some effective temperature approaching it, and the remainder has been unchanged. In this case, the SiCl_4 - HCl - H_2 stream going to the regenerator in Figure 4 would be of the same composition. On this basis, no change would be required in the regenerator loop of Table III. The only change required to account for nonequilibrium in behavior would be the additional quantity of unreacted SiHCl_3 and SiH_2Cl_2 to be recycled in the decomposer loop.

Table V. Mole Ratio of SiCl_4/Si Produced in the Equilibrium Decomposition of SiHCl_3 at 1 atm as a Function of Temperature

Temperature °C	SiCl_4/Si	Temperature °C	SiCl_4/Si
427	3.006	927	2.789 (2.776)*
527	3.001	1027	2.724 (2.717)*
627	2.982	1127	2.768 (2.755)*
727	2.942	1227	3.008
827	2.874	1327	6.994

*Parenthetical values are for SiHCl_3 containing 0.003 mole SiH_2Cl_2 per mole SiHCl_3 , presented earlier.

In the case of the regenerator, equilibrium conversion of the $\text{SiCl}_4 + \text{H}_2$ feed can undoubtedly be obtained in a packed bed of silicon at practical rates of throughput. However, the quenching of the reaction product depends on kinetic factors which cannot be predicted. Too rapid quenching can result in $(\text{SiCl}_2)_n$ -based polymer formation.¹ Too slow quenching can result in the deposition of silicon on available surfaces as the product of a given regenerator temperature tends to equilibrate at lower temperature.

The major objective of the quenching operation is to promote Reaction (3). Any reversion to equilibrium as the reaction product cools decreases the potential for SiHCl_3 production. As any equilibrium mixture contains some SiHCl_3 , it is the excess of SiHCl_3 over that amount that is indicative of the quenching efficiency.

In order to have a reference point for subsequent experimental work, calculations of the potential for quenching were made on the assumption that an equilibrium mixture from the regenerator is allowed to equilibrate at a lower temperature and then effectively quenched. A quenching index was then calculated, representing the fraction of $\text{SiHCl}_3 + \text{SiH}_2\text{Cl}_2$ in excess of

equilibrium that is recovered. Reactions (3) and (4) were assumed to occur quantitatively on quenching.

The regenerator feed mixture used for this calculation contained 37.3 mole percent SiCl₄ in H₂, which is fairly representative of the balanced concentration for decomposer outputs at 927°C and 1127°C and a regenerator temperature of 1327°C (see Figure 3). When this mixture is allowed to equilibrate with silicon at 1327°C, the product has the composition given in Table VI.

Table VI. Equilibrium Product of 37.3 Percent SiCl₄ in H₂ at 1327°C, 1 atm, per Mole Initial SiCl₄

Species	Moles	Species	Moles
SiCl ₂ (g)	0.7173	SiHCl ₃ (g)	0.1073
SiCl ₃ (g)	0.0022	HCl(g)	0.6724
SiCl ₄ (g)	0.3881	H ₂ (g)	1.2654
SiH ₂ Cl ₂ (g)	0.0055		

Table VII gives the results of quenching this mixture. It is seen that by the time the equilibrium mixture reaches 827°C, there is no potential for improving the yield by quenching, as no further SiCl₂(g) is available to participate in Reaction (3). It is also evident that equilibrium cooling of the initial (1327°C) mixture by even 100°C rapidly decreases the effectiveness of the regenerator system.

Table VII. Potential for Quenching Regenerator Product from Equilibration of 37.3 Mole Percent SiCl₄ + H₂ with Silicon at 1327°C, 1 atm

	Temperature to Which Mixture is Equilibrated and From Which It is Effectively Quenched, °C							
	1327	1227	1127	1027	927	827	727	627
E = Percent of SiH _x Cl _{4-x} Recoverable as SiHCl ₃ + SiH ₂ Cl ₂	68.1(*)	43.8	28.7	21.8	19.5	19.0	19.2	19.4
Q = Quenching Index = $\frac{E - 19.0}{68.1 - 19.0}$	1.000	0.505	0.198	0.057	0.010	0.000	-	-
Mole Percent SiHCl ₃ + SiH ₂ Cl ₂ in Quenched and Condensed Product (**)	68.1	48.6	33.9	26.1	23.1	22.3	22.3	22.4

(*) 67.6% SiHCl₃, 0.5% SiH₂Cl₂

(**) SiH_xCl_{4-x} components condensed out of residual H₂

C. SILICON TETRACHLORIDE TO TRICHLOROSILANE CONVERSION

The objective of the silicon tetrachloride conversion experimental studies was to:

- 1) Verify the thermodynamically predicted results
- 2) Develop an operable SiCl_4 -to- SiHCl_3 regenerator
- 3) Maximize yields in the SiCl_2 forming and quenching sections of the regenerator.

In previous work at Battelle-Columbus, a regeneration reactor having a diameter of 38 mm was used. With some modification and extension of that earlier design, a 50-mm reactor was constructed which should yield roughly 500 g/hour of SiHCl_3 .

Two methods of quenching were considered: (1) fluidized bed and (2) liquid spray. Even though liquid spray was expected to give the most satisfactory results, the fluidized-bed system [schematically illustrated in Figure 8(a)] was constructed for use initially. This was done as an expedient since it could be assembled with materials on hand while the liquid-spray quenching system was designed and equipment ordered. Furthermore, it could be of considerable value in verifying previous results and gaining additional operating experience on utilizing new reactant compositions in a type of equipment with which some experience has been logged.

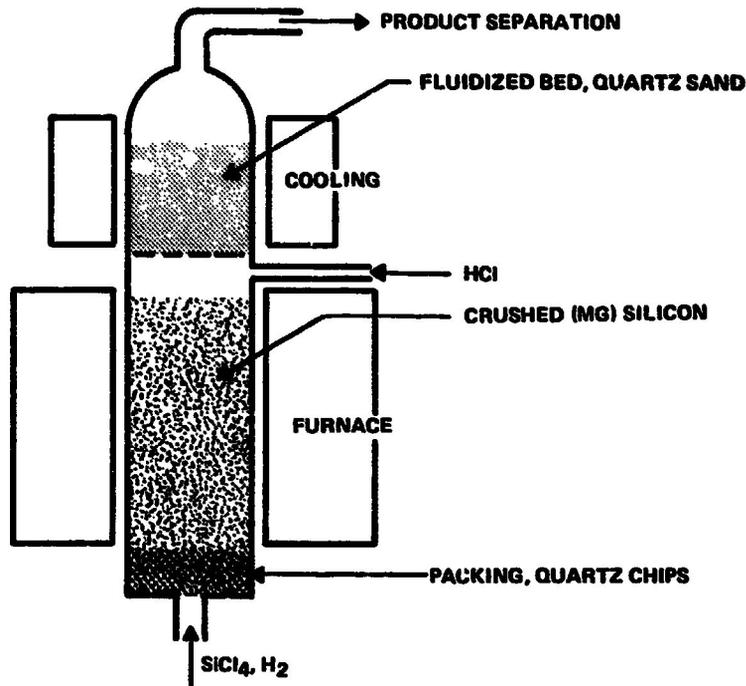
Concurrently with the fluidized-bed work, components for the spray-quenching system [schematically illustrated in Figure 8(b)] were designed and ordered to study this mode of quenching. A very limited work done with liquid-spray quenching in the past indicated the concept to have considerable promise. Furthermore, very efficient results are obtained with large-scale liquid-spray quenching in petroleum processing.

It was intended that both methods of quenching be pursued until conclusive data on the advantages (technical, operability, economic) of one over the other were ascertained.

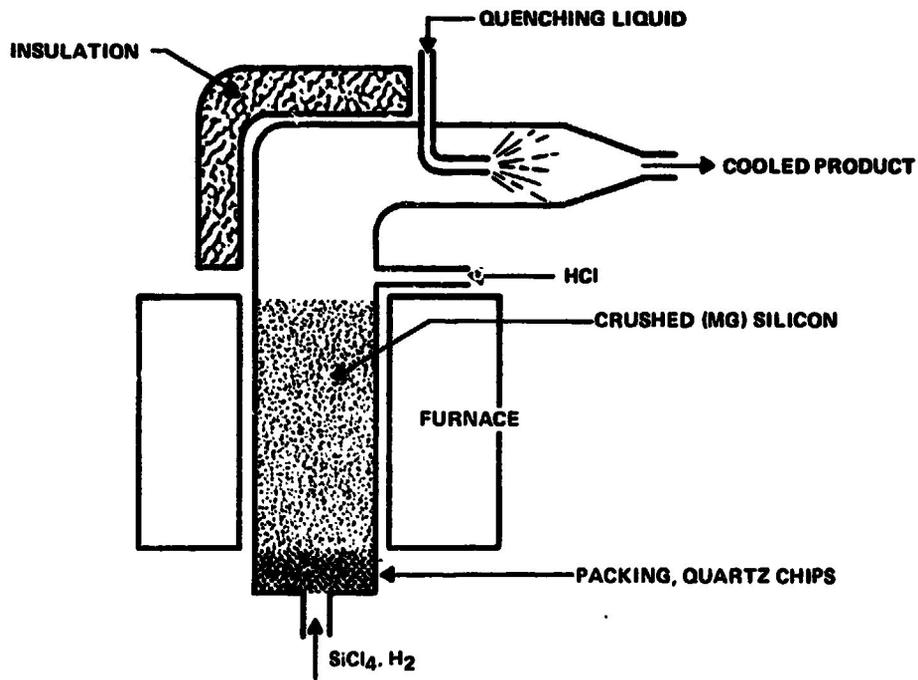
1. Fluidized-Bed Quenching

The SiCl_4 -to- SiHCl_3 -conversion reactor was fabricated of 50-mm ID quartz with an inner 40-mm quartz tube which contained a packed bed of metallurgical-grade silicon (1/4 x 3/8-inch lumps). About 11 inches of the silicon bed was inside a resistively heated furnace. Silicon tetrachloride vapor carried in hydrogen was passed upward through the bed of packed silicon and HCl admitted to the annulus between the 40- and 50-mm quartz tubes to join the reactant stream just above the packed bed of silicon. Temperature of the furnace was controlled by means of a thermocouple contacting the reactor at the midpoint of the furnace. The reactant stream passed into the quenching zone above the furnace and was conducted to three condenser/traps connected in series and cooled with dry ice/acetone. Noncondensables passed to an oil bubbler and were exhausted to a fume hood.

The fluidized-bed quenching zone consisted of a 50-mm-diameter bed of 70 x 80 mesh quartz sand fluidizing above a cone-shaped support with a 2-mm capillary tube at its apex through which the reactants from the packed-bed zone were introduced into the fluidized bed.



(a) FLUIDIZED BED QUENCHING



(b) LIQUID SPRAY QUENCHING

Figure 8. Schematic Diagram of Systems for Conversion of SiCl_4 to SiHCl_3 by Reaction with Si , H_2 and HCl

To understand this process, it was essential that temperatures be ascertained with reasonable accuracy. Therefore, thermocouple wells were installed on the central axis in the packed silicon bed and in the fluidized-bed quench section of the regenerator to permit temperature measurement at various positions within each of these zones.

In the packed bed of silicon under operating conditions, the temperature profile was such that, in the top 7 inches of the packed bed, only a 40°C increase was noted. The maximum temperature at the top of the bed was determined to be 43°C below the control temperature of the furnace as indicated by the thermocouple at the midpoint in the hot zone and against the outer wall of the reactor. The small temperature change noted in the top of the packed bed indicated that the actual gas temperature was approaching the packed-bed temperature.

The fluidized bed was cooled by means of a water-cooled coil immersed in the bed. Copper construction was used as an expedient to obtain information, recognizing that a noncontaminating material would eventually be required.

With maximum cooling of the fluidizing bed, i.e., using cold water through a 12-turn, approximately 4-inch-long coil of 3/16-inch tubing, the temperature of the fluidized bed ranged from 380°C, low in the bed (approximately 1/2 inch above the apex of the cone), to 90°C in the upper part of the bed 3 inches higher, under a heat load similar to that expected in an actual conversion experiment. These results indicated that the fluidized bed could be significantly cooled by this technique and thus offered the potential for greater conversion efficiencies over those resulting from an uncooled bed because of the probability of a more rapid quench. It is necessary to rapidly quench the reactor products from the packed-silicon bed to <750°C to maximize conversion of SiCl₄ to SiHCl₃. Consequently, it was decided to operate the fluidized bed at the lowest operable temperature.

After reference temperature data were obtained, a series of exploratory experimental runs was made primarily to gain experience and establish operability of the system. Operation of this system during conversion experiments using maximum cooling of the fluidized bed resulted in condensation on the cold coils, adherence of sand grains to the wet surface, and, finally, bridging and interruption of the gas flow as the bed agglomerated. In addition, a clear lemon-yellow liquid wet the walls of the reactor. This liquid was not vaporized by flaming with a hand torch. Upon cooling and dismantling the system, it was found that the material on the bed and in the reactor fumed in hydrofluoric acid (either 48% or approximately 10%) and the gas formed was spontaneously flammable in contact with air. It is understood that this is the classic behavior of polymers, which are not at present well identified or described.

Less vigorous cooling by use of a shorter, four-turn, approximately 1-inch-long coil of 3/16-inch tubing, gave bed temperatures in the range of 400°C and polymer formation was somewhat less noticeable but runs were still terminated by plugging after about 10 minutes. Operation of the quenching bed without an internal cooling coil, i.e., cooling only through the external walls of the reactor, gave bed temperatures ranging from 800°C in the center-bottom to about 600°C, 3 inches higher.

Reactants were fed to the system in the proportions expected to result from SiHCl₃ decomposition at $\approx 950^\circ\text{C}$, i.e., H₂ 11.370 moles/hour, 61.4 vol %; SiCl₄ 6.764 moles/hour, 36.6 vol %; and HCl 0.369 moles/hour, 2.0 vol %. At full thermodynamic efficiency, this would yield 762 g/hour SiHCl₃ or 63 weight percent SiHCl₃ in the product.

Operation under rapid quenching for short periods yielded a product having about 29%* SiHCl₃. Even at this relatively low quenching efficiency, the rate of SiHCl₃ production was 350 g/hour in the 50-mm system used. However, these experiments are not considered to be a valid evaluation of conversion because of varying conditions associated with plugging. Furthermore, much higher conversions have been obtained in similar previous work but the results are not directly comparable because of compositional differences. With only the cooling coil in place but no fluidized bed, the product contained 32% SiHCl₃.

Thus, operational problems prevented a definitive evaluation of the fluidized-bed quenching concept. At least two limitations are inherent in this system:

- 1) Necessity for adjusting total flow to achieve optimum bed action.
- 2) The restriction to flow offered by the required capillary or other means of bed support.

It should be noted on fluidized-bed quenching, that the benefits of operation at a lower temperature could yet be realized if localized subcooled surfaces, upon which polymers can form, were eliminated. This could probably be accomplished by replacing cooling water with air or a controlled-temperature, heat-transfer fluid.

However, rather than to concentrate on problems peculiar to the fluidized-bed quenching technique, the alternative spray-quenching system was developed simultaneously.

2. Spray Quenching

Spray quenching utilized the reactant-delivery system and heated silicon packed bed used with the fluidized-bed quenching. However, the top of the reactor was altered to direct a quenching spray into the exit tube. Addition of a product receiver and circulating system completed the equipment.

The spray-quenching technique offers several potential advantages both in efficiency of heat transfer from hot vapors to the vaporizable mixture of SiCl₄-SiHCl₃ and in operability by elimination of the fluidized bed with its inherent limitation on gas flows and requirement for a restricting capillary or other type of bed support. Calculations show that for a reactant flow capable of yielding 500 g/hour SiHCl₃, recirculation of cold product through a spray nozzle of about 1 gallon per minute provides a comfortable excess of cooling capacity. Therefore, nozzles providing spray at this flow and moderate pressures (20 to 40 psig) were obtained. An inexpensive gear pump was used in this initial design with the recognition of ultimate limitation in regard to durability and product purity.

*Based on thermodynamic calculations, a product containing $\approx 19\%$ SiHCl₃ should be obtained in the absence of quenching.

From the outset, the spray-quenching system was operated without major problems. However, adequate cooling had not been installed on the product/spray receiving tank and more volatile components were continually lost to the final trapping system. The length of conversion experiments was thus limited to the time required to lose by vaporization from the recirculation system sufficient $\text{SiCl}_4/\text{SiHCl}_3$ mixture to force termination. Runs were about 40 minutes long. The quenching liquid was analyzed for trichlorosilane before each run by comparing the solution density with that of mixtures of known composition. Afterward, the quenching liquid was combined with the condensate from the final dry ice-acetone cooled trap and analyzed again.

In the only run* in which reliable data were obtained, the respective density measurements of the $\text{SiCl}_4/\text{SiHCl}_3$ mixtures converted to 13.5 weight percent SiHCl_3 before the run and 16.0 weight percent SiHCl_3 afterward.

Some difficulty was encountered in obtaining a reliable final $\text{SiCl}_4/\text{SiHCl}_3$ inventory. Consequently, the final inventory was determined from the weight of the initial $\text{SiCl}_4/\text{SiHCl}_3$ mixture (549 g) and the SiCl_4 feed (286 g) along with a calculated silicon and hydrogen addition assuming theoretical pickup of both elements. It was found that 0.81 mole of SiHCl_3 was generated per mole of SiCl_4 fed at 37.3% in hydrogen, which is very near (98%) that calculated (0.83 mole) on the basis of thermodynamic equilibrium having been obtained in the 1600 K silicon bed and 100% quenching [$\text{SiCl}_2(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{SiHCl}_3(\text{g})$] of the product.

The consumption of silicon for this run and another in which product was inadvertently lost was collectively 148% of that predicted by thermodynamic calculations. This would suggest that (1) the temperature of the silicon reaction zone was in error by 60°C, (2) a larger quantity of SiCl_4 was introduced into the system than was indicated by the flowmeter, or (3) an error in determining the elemental silicon material balance was made. The latter is the most likely occurrence. However, if the quantity of SiCl_4 feed is adjusted to the higher value (Case 2 above), one would conclude that ≈ 0.55 mole of SiHCl_3 was generated per mole of SiCl_4 fed which is $\approx 66\%$ of that predicted thermodynamically, still a very favorable result.

Improvements in the condensing system on the reservoir/product receiver, and in more accurate measurement of conditions of operation and analysis are needed to provide for more reliable conclusions. However, it is felt that for so brief a program, the spray-quenching results were most encouraging.

D. LABORATORY ROTARY DRUM REACTOR

The limitations of the Siemens-type "hot rod" reactor with its high power consumption and batch operation are well known. The fluidized-bed reactor alternative under study in several JPL polysilicon programs, has its production rate basically limited by the reactant throughput attainable short of elutriating particles from the bed and by the rate heat can be put into the bed. Mechanically

*1600 K, 37 vol % SiCl_4 in H_2 .

agitated particulate beds obtainable in a rotary-kiln-type reactor has the strong incentives of simplicity, versatility, and improved thermal input.

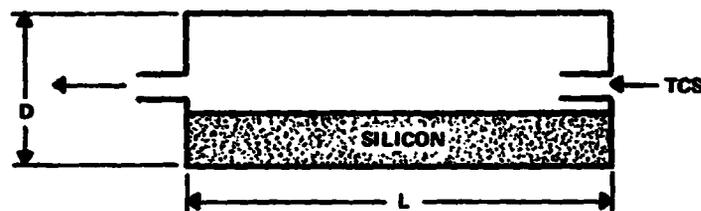
The Rotary Drum Reactor (RDR) was selected as the most promising technical approach based on the simplicity of equipment and operation, independence of rates of agitation and gas flow, improved thermal characteristics, higher potential throughput with long gas residence time, lower capital costs, and ease of scaling to large production capacity as compared with a fluid-bed reactor. The major problems expected in development of a silicon deposition rotary drum reactor are homogeneous gas phase reaction, deposition on reactor walls and gas-solid contacting.

The laboratory RDR was designed around a radiantly heated tube furnace. The initial design objective was to operate in a batch mode for deposition of 100 gms of silicon per hour, consistent with an easy scale-up to continuous mode operation at a higher (5X) deposition rate. A reactant supply system was constructed to allow trichlorosilane to be precisely metered into the bed of silicon granules.

1. Reactant Feed Rate

The chemistry of deposition by thermal decomposition of one mole of SiHCl_3 (TCS) yields 0.21 mole of silicon and by-products. A product rate of 100 gms per hour requires 16.95 moles or 2.296 kg per hour of TCS. Using 1.35 g/cc at the density of TCS at 25°C, a liquid flow rate of 28.35 ml/min which expands to 6.33 liters/min (STP) of gaseous TCS upon introduction into the heated reaction chamber is required.

2. Drum Dimensions, Si Bed Volume, Estimated Reactant Residence Time



$$D/L = 1/3, D = 10.16 \text{ cm}, L = 30.48 \text{ cm}$$

Drum Volume, $V_D = 2470 \text{ cc}$

Bulk Bed Volume, $V_B = 823 \text{ cc}$ (1/3 the drum volume)

Bulk Density of Bed = 1.5 gms/cc

Weight of Silicon Bed = 1235 gms.

Estimated time for 6.33 liters/min gas to flow through the unheated drum would be ≈ 23 seconds. Corrected for expansion of the trichlorosilane gas with temperature and for volume occupied by the silicon granules in the bed the residence time of the hot gas in the reactor would

be ≈ 12 seconds. This is an approximation of the average time the silicon in the bed will be in contact with the flowing trichlorosilane gas. Fluid bed residence times are usually ≈ 0.1 second since bed agitation depends on a high gas flow rate.

3. Reactor Power Requirement

- 1) Heat required to vaporize 38.27 gms/min TCS will be ≈ 1.9 kcal/min.
- 2) Heat to raise TCS vapor from 39°C to 1000°C will be ≈ 5.2 kcal/min.
- 3) Heat to raise 1.24 kg Si granules to 1000°C will be $\approx 2^{03} 8$ kcal/min.
- 4) Estimated heat required to maintain elevated temperature would be ≈ 3.4 kcal/min.

$$\begin{aligned}\text{Total Estimated Heat Required} &= 1.9 + 5.2 + 3.4 \\ &= 10.5 \text{ kcal/min (excluding heat of reaction)}\end{aligned}$$

or 733 Watts

Estimated power required for furnace heating elements (with 50% heat loss to ambient) will be 1.46 kW.

A comparison of the heat required for transfer to the bed in the rotating drum with that in a fluidized bed can be made. For reactors of equivalent silicon deposition rate, e.g., 500 gms per hour, we estimate the reactor wall surface area for the RDR to be $\approx 1000 \text{ cm}^2$ and for the fluid bed 240 cm^2 and the heat required for the reaction (to be transferred through the reactor wall) to be 2100 kcal and 1400 kcal per hour. The different heat requirements are because the fluidized bed reactor has a separate preheater. The relationship of reactor wall surfaces can be seen in the diagram of Figure 9. Hence, the necessary heat input will be significantly greater in the case of the fluid bed, $\approx 5.8 \text{ kcal/cm}^2$, than that required for the RDR, i.e., $\approx 2.1 \text{ kcal/cm}^2$. Furthermore, the wall surface area radiating to the bed in the rotary system is much larger than the interior area of a fluid bed, providing more effective heat transfer.

The RDR reactor which was constructed is sketched in Figure 10 and shown in the photographs of Figure 11 and 12. Reactant inlet, by-product exhaust, seed particle input and product withdrawal were accomplished by concentric tubes on the rotation axis. Provision for reactant flow and rotation control were located beneath the RDR. Furnace power supply and control was provided in a separate power cabinet (right side of Figure 12). Investigation of bed agitation disclosed that an internal reactant tube design containing a series of 10 curved flights (lifters) provided good bed agitation at low rotation rates. The flights can be seen in Figure 12.

No experimental runs were made with this equipment.

E. PRELIMINARY ECONOMIC ESTIMATE

A first-pass economic analysis of the manufacturing cost of polysilicon was made using the JPL/Lamar University costing model.⁴ The result is given in Table VIII. The similarity of much of the process to known costed processes allows some credibility to be assigned to conventional process

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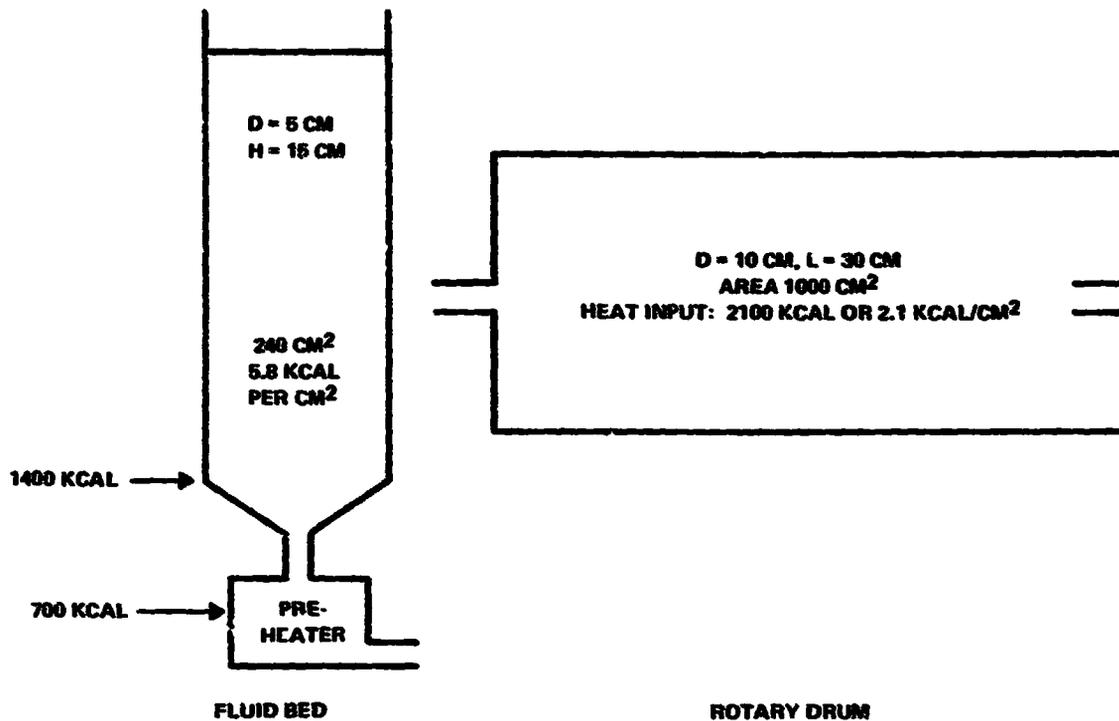


Figure 9. Comparison of Fluidized Bed and Rotating Bed Reactor Designs for 500 Grams per Hour Silicon Deposition Rate

steps, e.g., separation of silicon halides, and hydrogen and hydrogen chloride. Major unknowns exist in the areas of deposition and by-product regeneration reactor costs and operating expenses.

The impact of the design criteria to eliminate costs from the documented Siemens process is seen to be substantial. Continuous closed-cycle processing and efficient material usage reduces direct material costs from \$15.34 per kg silicon product for the Siemens process to \$1.11 for the closed-cycle process. Plant investment costs for a 1000 T/y plant are reduced from \$92M to \$18M. Direct labor costs per kg silicon are reduced from \$3.65 to \$0.30 and indirect labor from \$2.71 to \$0.26. Utility costs are reduced from \$14.26 to \$0.90 due to improved heating methods for smaller amounts of material. The lower capital reduces depreciation, taxes, and insurance costs from \$8.05 to \$2.01.

The results of this initial cost estimate demonstrate “on paper” success of the approach and results from Phase I would have allowed refinement of the estimate with more intelligence. The present manufacturing cost estimate is certainly in line with JPL/LSA cost goals and the existence of a vast technical and manufacturing background enhances process success probability.

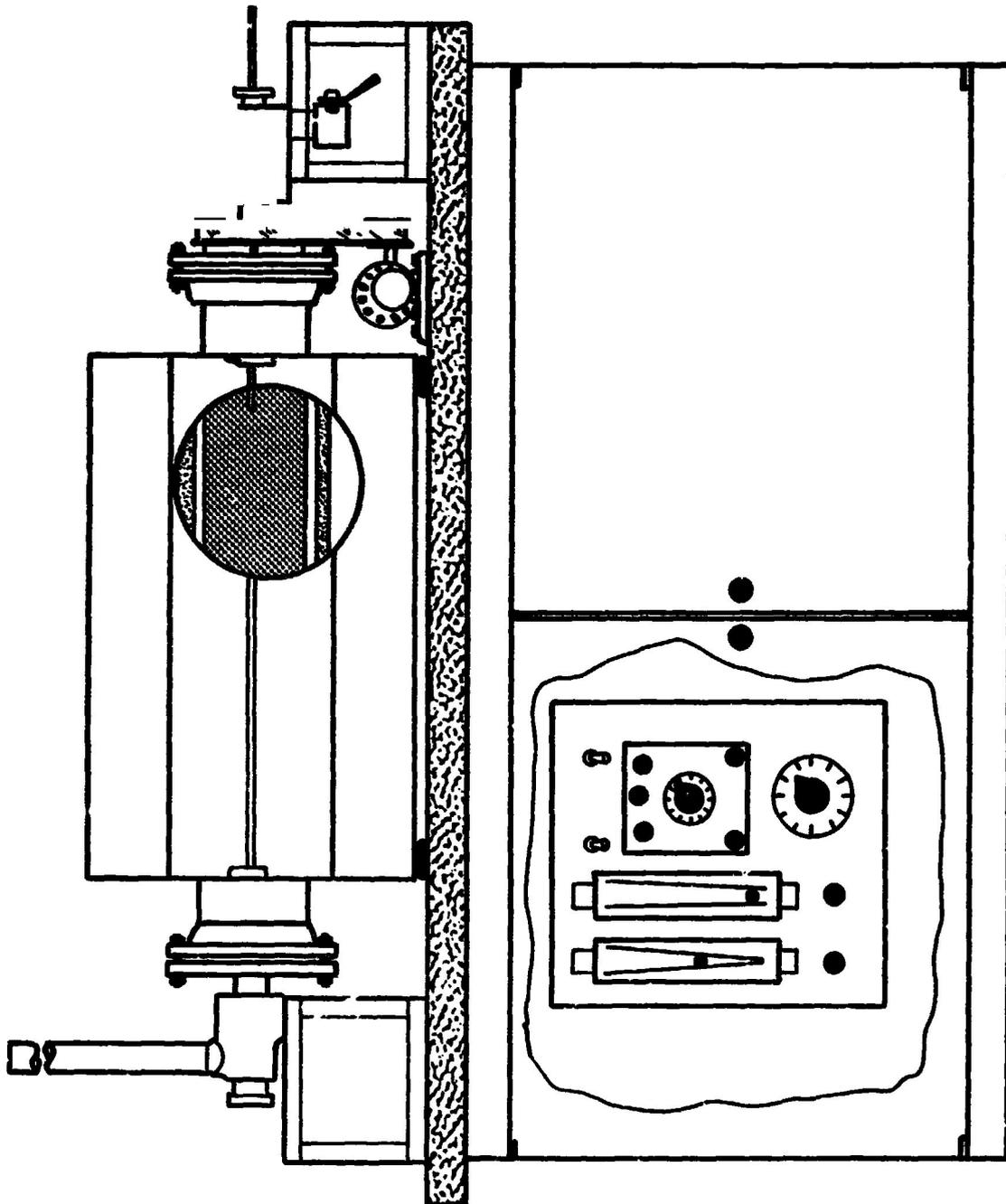


Figure 10. Laboratory Rotary Drum Reactor

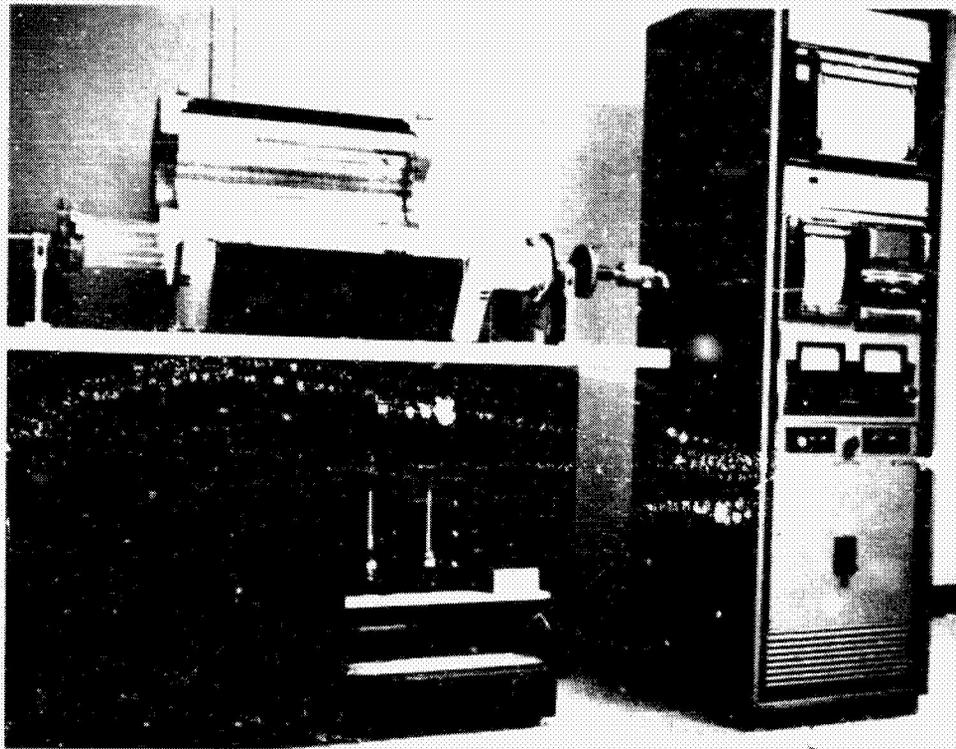


Figure 11. Rotary Drum Reactor Showing Rotating Tube
in Furnace and Temperature Control Cabinet

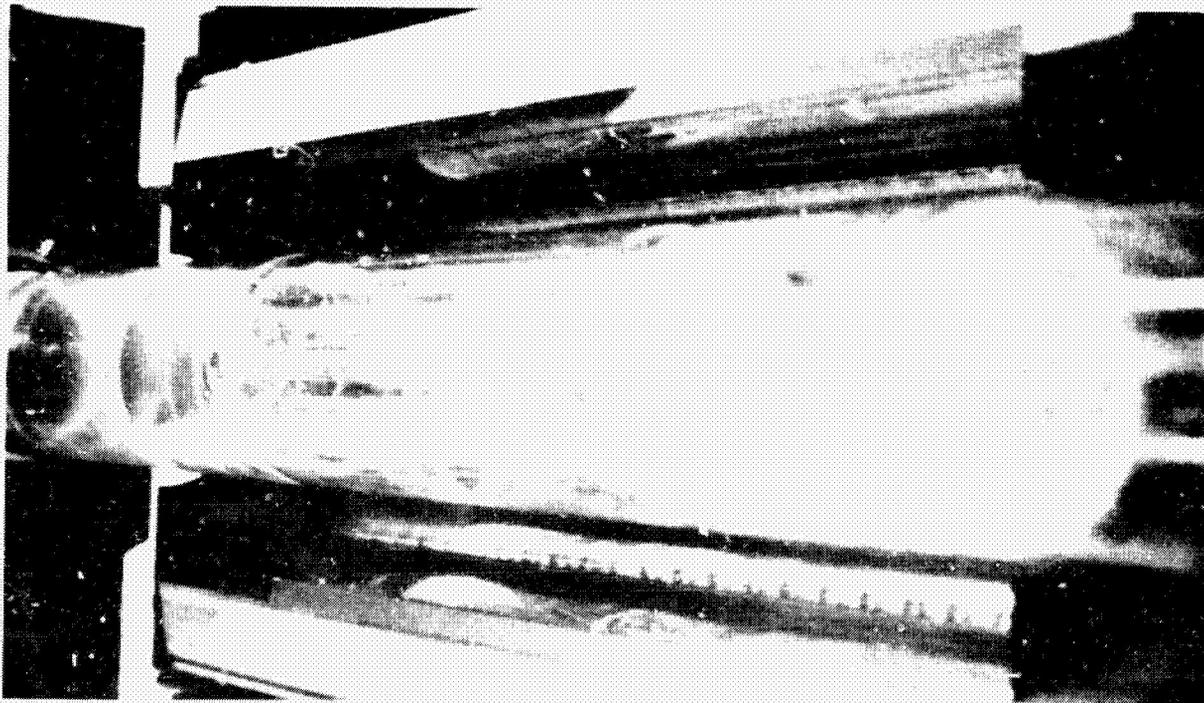


Figure 12. Rotary Drum Reactor Tube in Quartz Lamp Furnace

**Table VIII. Closed-Cycle Silicon Process Development
Manufacturing Cost Estimate¹**

	RJR
1) Plant Investment, \$M	18.5
2) Direct Manufacturing Costs, \$/kg Si	
Raw Materials	1.11
Utilities	.90
Labor & Supervision	.35
Other (QA, Supplies, R&M)	.36
	<hr/>
	2.72
3) Indirect Manufacturing Costs, \$/kg	
Depreciation, Taxes, Insurance	2.61
Plant Overhead	.32
By-product Credit	-
General Expenses	1.26
	<hr/>
4) Product Cost \$/kg Si	6.91

¹Lamar Univ. model⁴

SECTION III CONCLUSIONS

All results from the limited effort on this program tended to confirm the high potential of this approach to achieve a high-volume, low-cost production capability within the LSA Project Goals.

The extensive thermodynamic analysis identified optimum conditions for operation of a closed-cycle system for trichlorosilane decomposition and by-product silicon tetrachloride conversion. The analysis confirmed that a balanced system could be obtained which did not require additions, or create excess amounts, of the chemicals involved. Some make-up chemicals would be required in actual operation to replenish losses associated with impurity removal.

The analysis also concluded that the major operating trade-offs involved temperature and feed stream composition in the trichlorosilane regeneration unit.

The experimental work done on conversion of silicon tetrachloride to trichlorosilane in a liquid spray quenched unit indicated a conversion efficiency of $\approx 98\%$ of the theoretical conversion. The fluid bed quench conversion yielded a substantially lower conversion efficiency and had several difficult operational problems.

The direct, high temperature silicon tetrachloride conversion route investigated on this program appears to be far superior to a high-pressure, copper-catalyzed route in terms of better conversion yield, more production-worthy equipment and reduced potential for impurity (especially copper) introduction which could exacerbate the purification requirements.

The preliminary economic estimate used a highly conservative capital cost estimate and yielded a cost of \$6.91 per kilogram of silicon, of which 38% (\$2.61) was capital related.

**SECTION IV
RECOMMENDATIONS**

This program should be given high priority to complete the Feasibility Demonstration, and the Experimental Process System Deveiopment Unit phases.

**SECTION V
NEW TECHNOLOGY**

The rotary deposition reactor design was reported as a New Technology item from this program.

**SECTION VI
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