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Low Cost Solar Array Project
Task I - Silicon Material

Gaseous Melt Replenishment System

Fifth Quarterly Progress Report
17 April 1980 - 17 July 1980

JPL Contract 955269

by

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The JPL Low-Cost Silicon 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.

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I. ABSTRACT

1.1 Intent

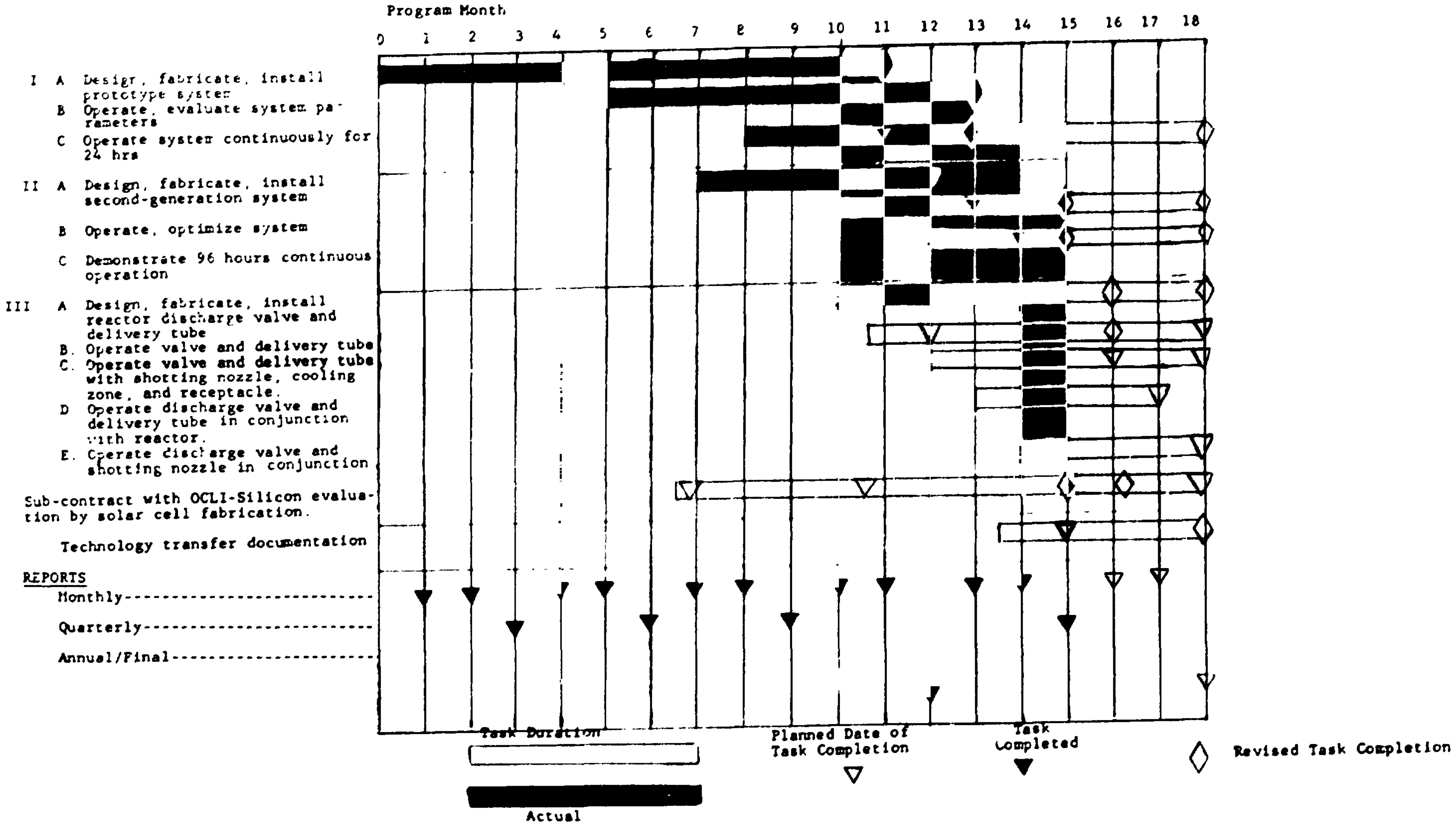
This 18 month contract is intended to research and develop an innovative method of low cost silicon production from known technology: deposition of silicon from a hydrogen-chlorosilane mixture.

1.2 Task Specifics and Milestones

The contract is divided into four major Tasks and a subcontract for evaluation of silicon produced. Planned time frames are shown in the Milestone Chart on page 2. Month zero is April of 1979.

The goal of Task I is to produce 0.5kg/hr. silicon for 24 hours with at least 18% conversion of trichlorosilane to silicon. The Task II goal is to improve the reactor to produce 0.5kg/hr. at a minimum conversion of 18% for 96 hours. The goal of Task III is to deliver liquid silicon from the reactor in two different manners. 1) through a shotting nozzle into a cooling zone and receptacle or 2) through a delivery tube into a receptacle. Silicon produced in the innovative reactor will be evaluated by solar cell fabrication by Applied Solar Energy Corporation.

PROGRAM PLAN - Milestone Chart - (JPL Contract 955269)



1.3 Innovative Reactor

The innovative reactor is a resistively heated quartz vessel; the chlorosilane-hydrogen mixture will flow through the inside of the vessel where silicon will deposit. The deposit will be melted and then drained from the vessel.

1.4 Support Systems

Support equipment will: 1) deliver to the vessel and heat a known trichlorosilane/H_2 mixture, 2) effeciently insulate the hot vessel, therefore reducing power consumption, 3) recover and recirculate hydrogen gas, 4) melt the silicon deposit and allow it to flow from the vessel to a collection box or a delivery tube, 5) monitor gas composition at various points, 6) maintain a slight positive pressure inside the vessel to prevent collapse and 7) collect particles that do not deposit in the vessel.

II. INTRODUCTION

The objective of this program is to develop an improved silicon production reactor with periodic batch delivery of product to either a casting or shotting process or through a liquid silicon transfer system directly to a crystal growth system.

The processes and equipment are scaled such that a modest investment can make available to the Czochralski crystal grower a low cost source of silicon. In addition, the smaller scale of operation means that the systems can be put into operation without large capital investments, guarantees of markets, etc.

The chemical reactions are those in commercial usage now. The major innovation is in reactor design which allows a high productivity of silicon. The reactor has been conservatively sized on the basis of epitaxial deposition rates. The conclusion of this calculation is that a reasonably sized system can produce rapidly enough to keep pace with either 10cm or 12cm diameter Czochralski crystal growth operating in a semi-continuous mode.

The major factors, subsequent to the innovative reactor design, which will lower the cost of silicon production are: 1) the effective utilization of the energy involved with bringing the reactants to high temperature and 2) the separation of the by-products for recycle, sale, or disposal.

III. INNOVATIVE REACTOR

3.1 Basis for Design

The reactor is based upon 1) experiments showing silicon deposition in quartz tubes, 2) the Siemens process, and 3) data by Hunt, Sirtl, and Sawyer on Si-H-Cl equilibrium. Predicted benefits and improvements of the design will allow a production rate of 0.5kg/hr. silicon at 20% conversion, a dense silicon product, an energy efficient system, and an extended reactor life compared to quartz tube experiments.

3.2 Basic Design and Operation

A schematic cross-section of the reactor system is shown in Figure 1. Polycrystalline silicon is deposited on the inside walls of a resistively heated, multi-walled fused silica reaction chamber by H_2 reduction of $SiHCl_3$. After sufficient silicon has been produced, the reactor is flushed with argon and the silicon melted out of the reactor into a receptacle such as a Czochralski crystal growth crucible or any other desired container. The reactor is then returned to the deposition stage. The reaction chamber and the crystal growth system are separated by a heated delivery tube. The "U-tube" acts as a valve, when the temperature is adjusted above or below the melting point of silicon. A more detailed

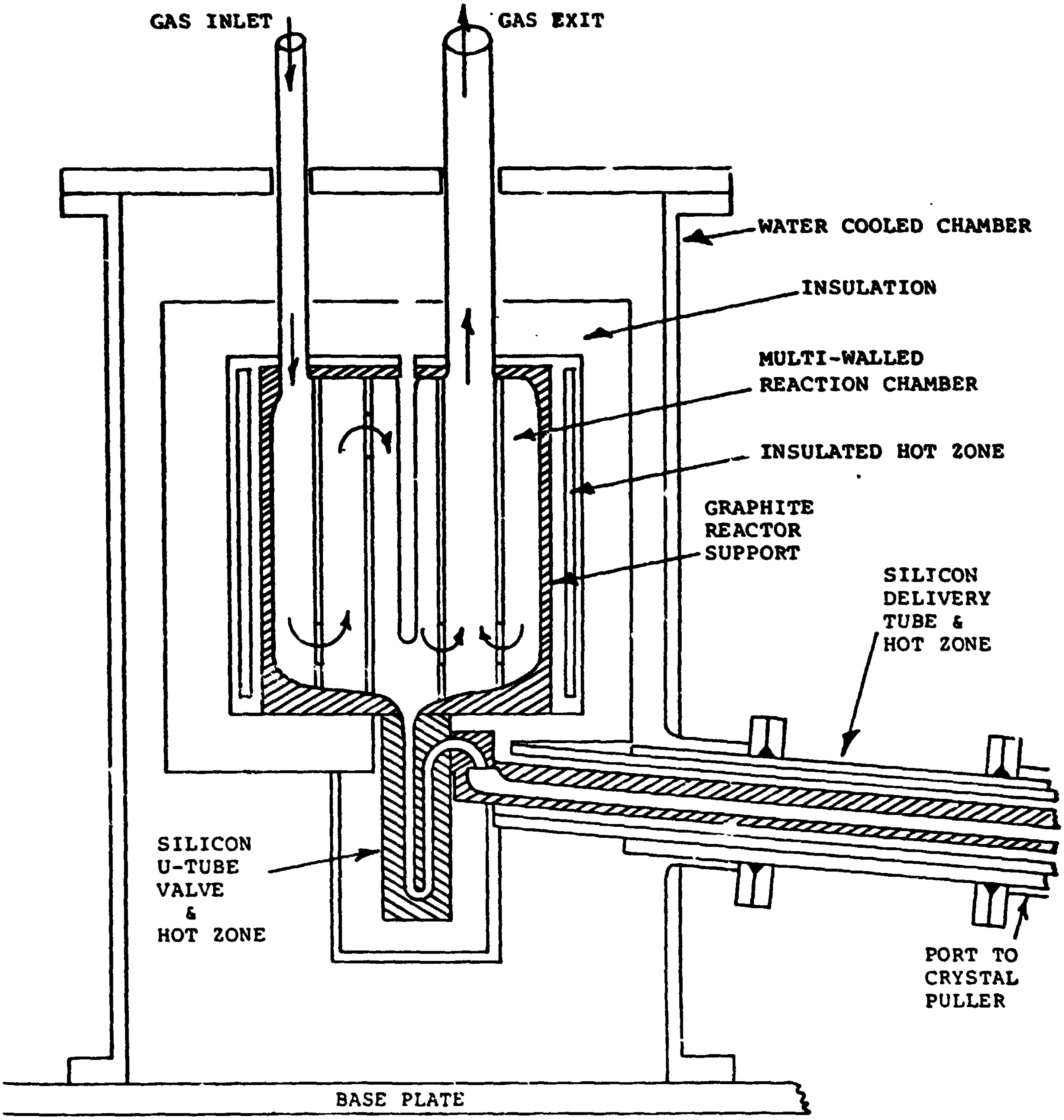


Figure 1.

Schematic Diagram of "Poly" Reaction Chamber (Scale ≈5:1) description of a process cycle is given below:

1. The reactor is brought up to temperature under inert gas flow.

2. A small amount of silicon is melted in the "U-tube" to form a positive gas seal. The "U-tube" temperature is dropped to about 1200^0C.

3. At the selected reaction temperature $SiHCl_3$ and H_2 are introduced into the chamber and their flow rates set to optimize the maximum mass deposition of silicon.

4. The reaction is allowed to run for several hours until the desired amount of silicon has been deposited. This is determined by the desired cycle time and the reactor vessel size.

5. At this point the reactant gases are flushed out of the reactor with Ar.

6. Keeping the "U-tube" at 1200^0C, the reactor is raised to about 1450^0C to melt down the silicon produced.

7. The gas pressure between the reactor and the delivery tube is equilibrated.

8. The "U-tube" and delivery tube are raised to about 1415^0C. When the silicon is melted in the "U-tube", the reactor will empty due to gravity, causing liquid silicon to flow out through the delivery tube to either the Czochralski

crucible or an intermediate replenishment crucible. Due to the equilibrated pressures and a vent to prevent siphoning, the "U-tube" will remain full after the reactor has been emptied.

9. The reactor is returned to reaction temperature and the "U-tube" and delivery tube are returned to 1200°C.

10. The reactant gas flow is then re-admitted to the chamber to start the cycle again.

3.3 Specific Vessel Designs

A square quartz reaction vessel was designed and manufactured. It is a 10 inch square box of 0.135" thick quartz plates. The bottom is sloped five degrees toward the centered silicon drain tube.

The internal walls are 0.135" thick vertical plates. There are fourteen internal walls; each is 10" high. Some of the internal walls have notches at the bottom for silicon drainage to the bottom center tube. The total internal surface area is 15.28 ft.^{2}; 3.6 ft.^{2} comprise heat exchange surface between the incoming gas and the outgoing gas. The four central walls that comprise most of the heat exchange surface are shown in Figures 5a to 5b, on page 17 of the First Quarterly Report.

The silicon drainage tube is 10mm I.D. quartz tube with a 6mm I.D. "anti-siphon" vent tube located at the top of the spill-over side of the "U-tube".

The innovative design feature of this reaction chamber is large surface area per volume of reactor (26.4 ft.^{2} surface area per cubic foot) with internal heat exchange capabilities. The reactor is described in the Equipment section of the First Quarterly Report on page 16.

The internal path of the square vessel is a long or "serpentine" path. A short path with parallel walls and an impaction oriented path were also considered. Due to the expense of the first serpentine vessel that was made, alternatives were considered. A six-inch cylindrical tube, 10 in. long with a single baffle down the center was made at considerably lower cost. This is representative of a parallel flow path. Problems occurred securing the center baffle and therefore a similar 6" diameter tube was used with baffles perpendicular to the tube axis. These were simple to make and represent the serpentine or long flow path as well as showing areas of impaction.

IV. NECESSARY SUPPORT SYSTEMS

4.1 Description

The five necessary support systems are: 1) the materials handling system, 2) the vessel pressure equalization system, 3) the vessel support system, 4) the material sampling system and 5) the waste treatment system. All of these systems are directly or indirectly connected.

The materials handling system 1) supplies a known pressure and volume of trichlorosilane and hydrogen to the reactor vessel, 2) heats the inlet gases by heat transfer from the hot outlet gases, 3) removes particles from and cools the by-product gases, 4) condenses the chlorosilane by-products from the gas stream and pumps them to storage, 5) removes by-product HCl from the hydrogen gas by means of activated charcoal adsorbtion and 6) recycles the clean hydrogen back to the reactor as a reactant.

The pressure equalization system continually adjusts the pressure outside of the quartz reaction vessel to about 2" H_2O less than the pressure inside the vessel, therefore preventing the vessel from sagging or collapsing.

The vessel support system is broken into three subsystems:

1. The physical support of the vessel.

2. The power control and heaters.

3. The temperature monitoring instruments.

The outside physical support system is a steel double walled water cooled chamber. Inside, the quartz vessel is surrounded by a graphite box, the main heating elements, another graphite box, 2" of insulation, and a thin stainless steel box which holds the insulation in place. In addition, a removable silicon trap extends below the support chamber. Silicon which is melted from the reaction vessel will drop from the "U-tube" into the trap.

Two power supplies, 24kva and 6kva, supply power to the Grafoil® main heating elements and the Grafoil® "U-tube" heating elements, respectively. Automatic controllers increase or decrease power according to thermocouple feedback.

Other thermocouple junctions are placed at various places in the support system. Thermocouples approximate the inlet gas, the vessel gas and the outlet gas temperatures.

A Varian 921 gas chromatograph is used to monitor the reactant, the by-product, the post condenser and the recycle gas streams. The sample lines are heated to prevent internal condensation. Percent conversion can be determined by comparing chromatograph analysis of the reactant and by-product gases.

The waste treatment system is gas-liquid adsorption of any vented chlorosilanes or hydrochloric acid gases into a 10% sodium-hydroxide solution. The HCl from the materials handling system's activated charcoal scrubber is the major source of HCl gas. The purge gas from the chlorosilane storage drum is the major source of chlorosilanes that are scrubbed.

4.2 Operation Results

The vessel pressure equalization system, the vessel support system and the waste treatment system have worked as designed. The materials handling system has functioned as designed with the exception of the charcoal scrubbing tanks and the primary heat exchange. The gas chromatograph and its sampling lines were completed after the sixth run; adequate data was produced during run number eight.

The charcoal absorption tanks were undersized; therefore after a period of time HCl is present in the hydrogen recycle stream. Regeneration of these tanks has proved to be a lengthy procedure.

The primary heat exchanger, which was designed to heat the inlet gas by heat exchange from the outlet gas, has only been slightly effective because the exiting gas has not reached the high temperatures expected. This is partly due to the smaller test vessels used which resulted in less heat transfer to the gas passing through the hot vessel. A preheater was added to the heat exchanger before test number eight which added 100^{0}C effective temperature to the gas.

V. TECHNICAL PROGRESS

During the past three months, four silicon deposition reactors were tested at various trichlorosilane composition percentages. Tables I and II show each test's data and consequential derived data. The length of test runs was limited by silicon oxides/silicon polymer plugging of the gas outlet tube which is depicted in Figure 2. Derived data explanations follow the tables. The actual Cl/H ratios were determined from gas chromatograph peak ratios. The difference between the intended and actual Cl/H ratio is caused by HCl in the recycled hydrogen gas. This decreases the actual percent conversion from the expected percent conversion for the effective temperatures and trichlorosilane concentrations. Recycled HCl slows the desired decomposition of trichlorosilane and enhances the reverse, etching reaction.

Quartz etching is limited during deposition by keeping the wall temperatures below 1250°C, although during the "melt down" step, SiO_2 is formed, as evidenced by the residue in the reactor gas outlet tube.

Table Ia

Reactor Test Data

Run No.	Grams Silicon Produced	Hours of Deposition	Total Gas Flow (SCFH)	Mole. % TCS	Actual Cl/H Ratio
5	150	5	225	1.5	
6	293	8.75	170	5.0	
7	467	8.5	255	6.25	0.11
8	1050	4.49	170, 216 270	17.5	0.303

Table Ib

Run No.	Total Surface Area (in.^{2})	Deposition Surface Area (in.^{2})	Total Volume (in.^{3})	Deposition Volume (in.^{3})	% of Surface Area Used
5	355	177	280	92	33
6	355	220	280	175	62
7	355	341	280	269	96
8	428	428	280	280	100

Table IIa

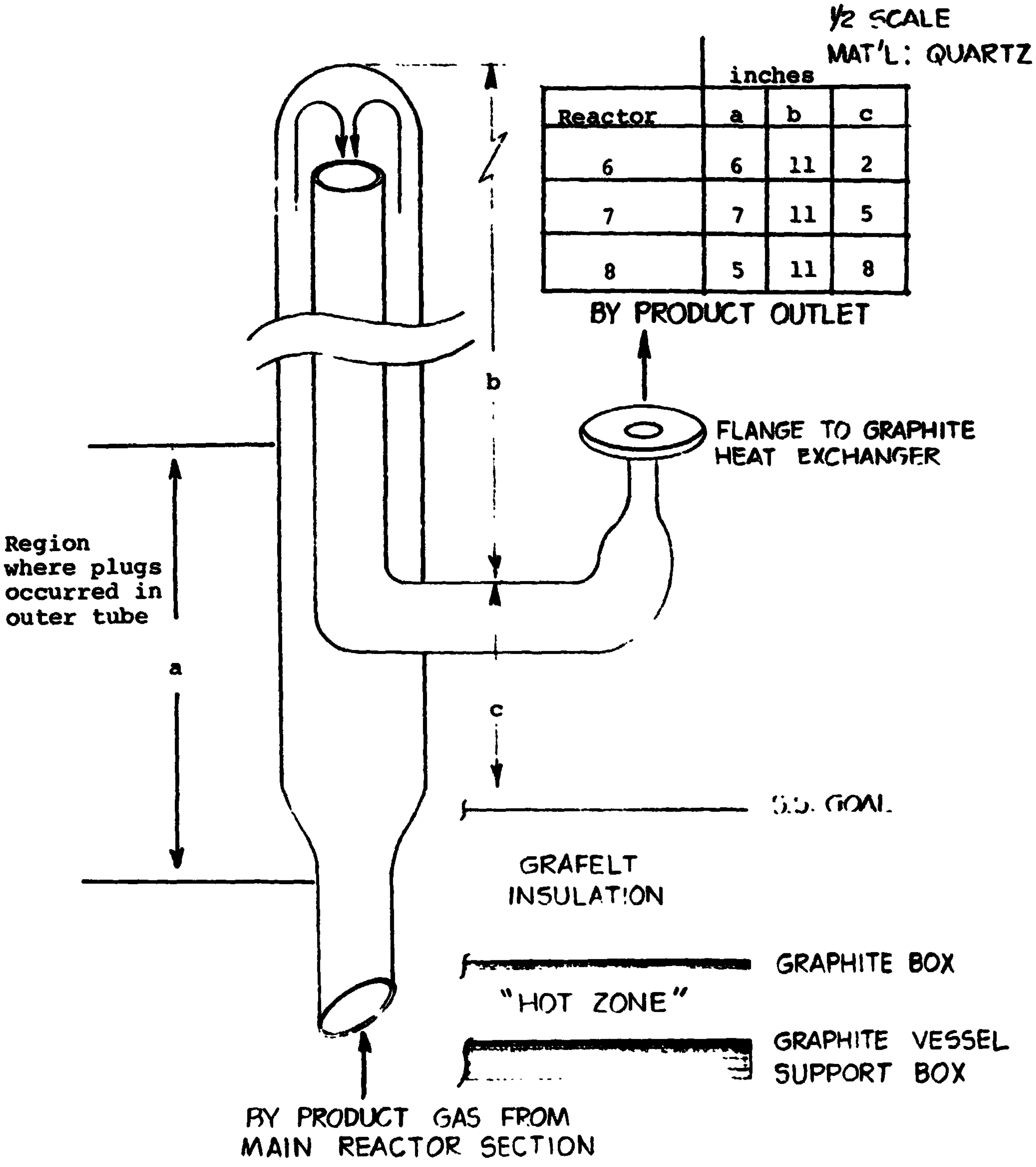
Derived Statistics from Reactor Test Data

Run No.	1 Average Production Rate (gm/hr)	2 Deposition Rate (μ/hr)	3 Average Conversion %	4 Power $\frac{\text{kw-hr.}}{\text{kg}}$
5	30.0	170	20	410
6	33.5	100	13	352
7	85.0	166	18	145
8	234	364	20	56,45,35

Table IIb

Run No.	5 Total Residence Time (sec)	6 Deposition Residence Time (sec)	7 Effective Temperature (^{o}k)	8 Intended Cl/H Atomic Ratio
5	0.56	0.19	1100	0.02
6	1.04	0.63	900	0.08
7	0.64	0.61	975	0.10
8	0.88 0.69,0.55	0.88 0.69,0.55	1073	0.29

1. The average production rate is the total silicon produced divided by the hours of deposition.
2. The deposition rate is the average production rate divided by the deposition surface area.
3. The average % conversion is the total silicon produced divided by the silicon in TCS that was introduced to the reactor.
4. The power used is the steady state sum of the power through the main heater plus the power through the U-tube heater divided by the average production rate.
5. The total residence time is the total reactor volume divided by the total gas flow rate.
6. The deposition residence time is the deposition volume divided by the total gas flow rate.
7. The effective temperature is an estimate obtained by subtracting 200°K from the highest temperature measured in the reaction vessel.
8. The intended Cl/H ratio is based on the mole % trichlorosilane in a pure recycled hydrogen stream.



	inches		
Reactor	a	b	c
6	6	11	2
7	7	11	5
8	5	11	8

Figure 2

Cold Trap Design for Reactors #6, #7 and #8

VI. DISCUSSION OF TECHNICAL PROGRESS

The reactor test runs completed in this period showed successive increased production and deposition rates with a maximum of 234 gram silicon per hour produced at a rate of 364 microns/hr. in Run No. 8. The improvements up to Run No. 8 were caused by increased trichlorosilane concentration, increased surface area and increased effective temperature.

The mole percent trichlorosilane introduced to the reactor was increased from 1.5% to 17.5% from Run No. 5 to Run No. 8. This was done to allow comparison of percent conversion of trichlorosilane to silicon at various Cl/H ratios. The goal to convert more than 18% to TCS was reached. Unfortunately, the gas handling system could not remove all of the by-product gases from the hydrogen to be recycled; therefore, the average conversion rates were lower than predicted by data by Hunt and Sirtl, and the data comparison is weak evidence for optimization.

The internal surface area in reactors 5 through 7 was identical, 355 $in.^2$. Each reactor had three baffles. Reactor No. 8 had 5 baffles. The additional surface area was beneficial in two ways: there was more surface area available for silicon deposition and there is more surface area for heat transfer to the gas. Additional heat transfer increases gas temperature and effective temperature which is assumed to increase the rate of reaction; from data by Hunt and Sirtl this favorably changes the silicon to chlorine equilibrium ratio (up to 1350°K and up to a Cl/H ratio of 1). Because our effective temperatures were less than 1000°K for Runs No. 6 and 7, a preheater was also added which increased the effective temperature of Run No. 8 by 100 degrees. Run No. 5's effective temperature was 1100°K (higher than 6-8) because we did not limit the wall temperature to 1250°C to minimize quartz etching by HCl.

Based on data from Run No. 8, the square reactor with 15.3 ft.^{2} of deposition surface area available will easily produce 500 grams silicon per hour at greater than 18% conversion. The problem of HCl in the recycle hydrogen which lowers percent conversion can easily be "designed out" of the gas handling system. The problem of silicon oxide/silicon polymer plugging of the gas outlet tube can be eliminated by using an easily removable, large diameter outlet tube.

VII. SIXTH QUARTER PLANNED ACTIVITIES

During the next three months we plan to increase the surface area of a round reactor by two more baffles to 500 $in.^2$, and increase the mole percent trichlorosilane to 25%. Also, the gas outlet tube will be modified to maximize run time and minimize plugging. One or two large square reactors will be tested. An innovative silicon shotting technique and a silicon delivery tube will be tested.