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HIGH VELOCITY CONTINUOUS-FLOW REACTOR FOR THE PRODUCTION OF SOLAR GRADE SILICON

FIRST QUARTERLY REPORT

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DECEMBER, 1977

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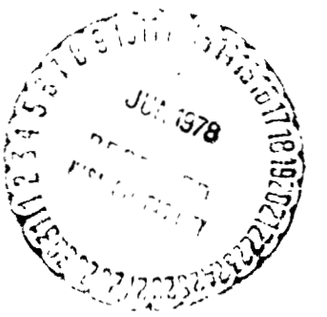

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FORWARD AND ACKNOWLEDGEMENTS

This is the first Quarterly Progress Report of the contract. However, in order to comply with JPL's report schedule, it covers only the period of October 24, 1977 to December 24, 1977.

During this period the following individuals contributed to the program:

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ABSTRACT

This program is designed to test the feasibility of a high volume, high velocity continuous reduction reactor as an economical means of producing solar grade silicon. Bromosilanes and hydrogen are used as the feedstocks for the reactor along with preheated silicon particles which function both as nucleation and deposition sites.

During this first reporting period which covers the period of October 24, 1977 to December 24, 1977, efforts have been devoted to the investigation of system design and system materials of construction. A complete reactor system has been designed and fabricated. Initial preheating studies have shown the stability of tetrabromosilane to being heated as well as the ability to preheat hydrogen to the desired temperature range. Several test runs have been made and some silicon was obtained from runs carried out at temperatures in excess of 1180°K.

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I. SUMMARY

The goal of this contract is to demonstrate the feasibility of a high velocity, high volume continuous reduction reactor into which heated silicon particles are continuously introduced to act as deposition substrates. Bromosilanes and hydrogen, which are separately preheated to reaction temperature, are independently introduced into the reactor. Mixing between the two preheated streams and the heated silicon particles takes place in the reactor with the resulting silicon being deposited on the substrate particles.

This report, the first of the contract program, concerns itself mainly with the design aspects and materials of construction for the continuous reactor. The current reactor design is discussed as well as factors which lead to the selection of the design and the materials of construction. Heat transfer studies described in the report have indicated that a four pass heat exchanger is sufficient for preheating the reactant streams. Quartz was selected as the material for the heat exchangers.

Preheating studies carried out on tetrabromosilane have demonstrated that it is stable to at least 1463°K. Establishment of this fact was very important as the process depends on energy input to the gas streams.

Initial test runs using only tetrabromosilane and hydrogen indicated that silicon could be produced at temperatures in excess of 1182°K and at a molar ratio of hydrogen to tetrabromosilane of about 15. The initial runs pointed up several problems in the original design concept which have been rectified.

II. - INTRODUCTION

The volume and economic requirements for solar grade silicon projected for the 1980's precludes the use of the existing batch based technology which is costly from both production and investment points of view. Capital investment and production costs can be reduced by removing the batch reduction aspect from existing technology and replacing it with a continuous high volume reduction step.

Continuous high temperature tubular reactor processes are used extensively throughout the materials and chemical process industries. For example, continuous pyrogenic processes are used for the production of carbon pigments and fillers, silica fillers, and titanium dioxide for pigment usage. Each of these processes produce thousands of tons of material per year per reactor.

The approach being taken in this program is to apply and extend existing technology applicable to pyrogenic processes to the development of a high volume continuous reduction reactor for halosilanes to produce solar grade silicon. The J. C. Schumacher Company research program, which began under this contract on October, 24, 1977, has been designed to investigate the feasibility of this approach. More specifically, the program objective is to determine the feasibility of a high velocity, gaseous-reaction process for the hydrogen reduction of bromosilanes utilizing a continuous-flow reactor having

continuously introduced particles which act as silicon deposition substrates.

Briefly, the concept being utilized in this program involves the high temperature hydrogen reduction of bromosilanes according to the following idealized reaction.

$$SiH_xBr_{(4-x)\ (g)} + \frac{(4-x)}{2} H_2(g) = Si(s) + \frac{(4-x)}{} HBr\ (g) \quad (1)$$

The complete process which is being considered for the production of solar grade silicon can be described by the following reactions.

$$Si_{(s)}\ (impure) + (4-x)\ HBr = SiH_xBr_{4-x} + \frac{X}{2} H_2 \quad (2)$$

where $0 < x \leq 4$

$$SiH_xBr_{4-x\ (g)} + \frac{4-x}{2} H_{2(g)} = Si_{(s)_{(pure)}} + (4-x)\ HBr_{(g)} \quad (1)$$

Both existing chemical vapor decomposition technology, and the proposed concept requires a heated substrate upon which or in the vacinity of which the reduction reaction takes place. However, in contrast to CVD techniques, the latter approach utilizes reactants preheated above the reaction temperature, and greatly increses the heated substrate "deposition surface to heated volume" ratios. Each reactant is separately heated to the desired temperature and then mixed with the other and allowed to react in the gas phase. Preheated silicon particles are continuously injected into the gas phase to act as nucleation and deposition sites for the reaction product.

The bromosilane/hydrogen system has been selected as it is energetically more favorable than the chlorosilane/hydrogen system. It has been reported that the reduction of bromosilanes to silicon takes place at a lower temperature and with a more favorable conversion ratio than the analogous chlorosilane reduction [2,3]. The reduced energy consideration makes the overall process more attractive from both an economic and engineering materials point of view.

As the duration of the contract is rather short, a limitation has been placed on the number of areas to be investigated. Only two (2) bromosilanes, $SiBr_4$ and $SiHBr_3$, will be investigated and the program is limited to the design and development of the continuous reactor system.

As currently defined, the program consists of three (3) main tasks. These are: 1) Inital design and material selection, 2) Preheating and heat transfer studies, and 3) Reaction chemistry studies. This Quarterly Report will discuss mainly the activities associated with Task 1 and 2 and will briefly touch on Task 3.

III. TECHNICAL DISCUSSION

III. 1.0 TASK-1, REACTION SYSTEM DESIGN

The primary goal of this task is the design and selection of materials for the complete continuous flow reaction system. An analysis of the total system required for this program indicated that the system could be considered to be composed of four (4) distinct subsystems or functional units. The four (4) subsystems have been defined as: 1) Delivery and metering system for all streams being used, 2) Preheating system for the reactants, 3) Mixer and reactor system, and 4) Reaction product collection system. Figure 1 is a schematic flow diagram which denotes the respective subsystems. The approach that has been utilized is to apply as much existing technology to the system design as possible so as to minimize the problems that are associated with the introduction of new technology. A description of the design and materials of construction for each subsystem follows.

III. 1.1 REACTANTS DELIVERY AND METERING SYSTEM

The function of this subsystem is to meter and deliver the reactant streams to the preheater subsystem. Figure 2 is a diagram of this subsystem.

Hydrogen and inert gases are transferred from high pressure cylinders to the reaction system gas header via type 304

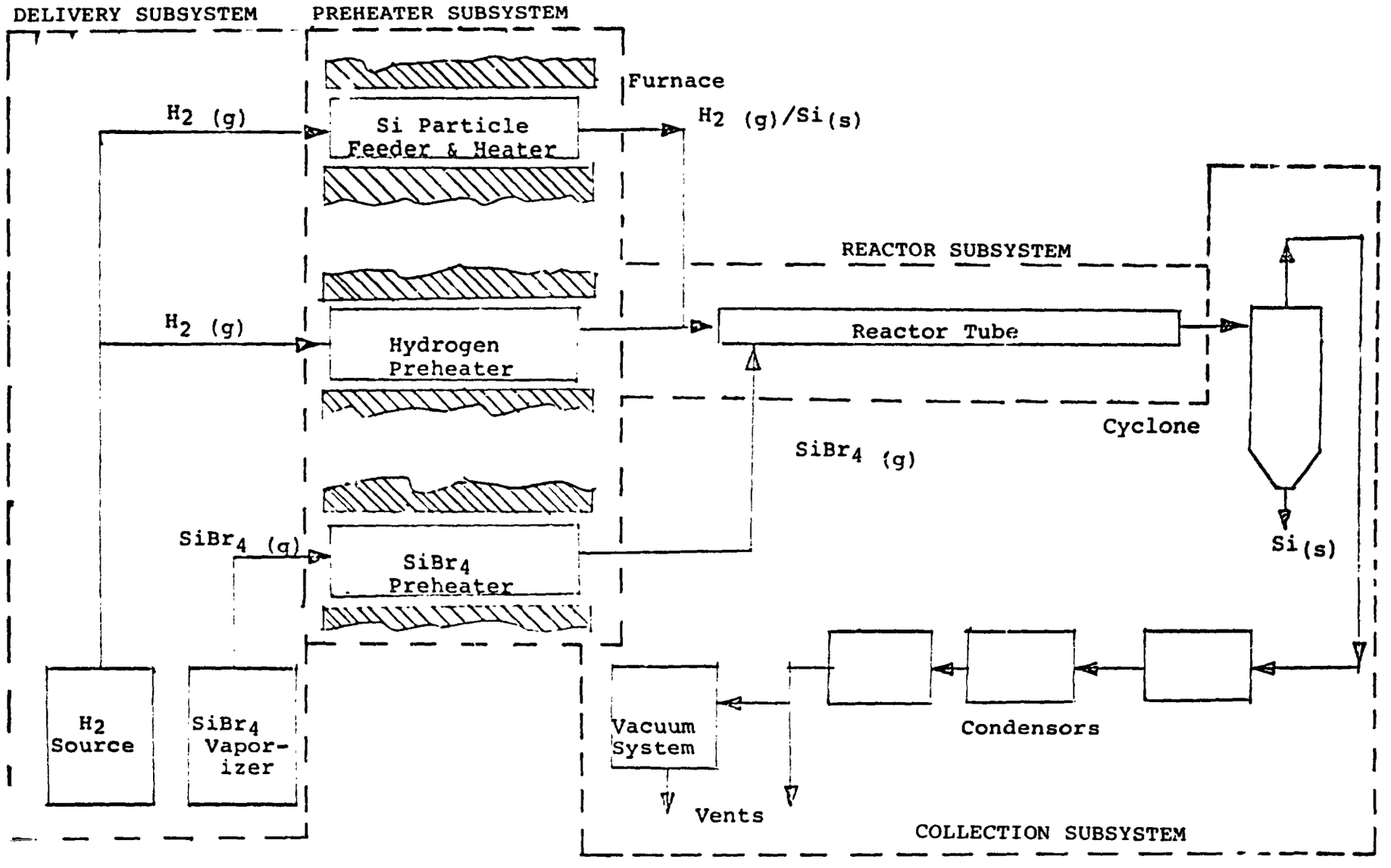


FIGURE I. REACTION SYSTEM SCHEMATIC

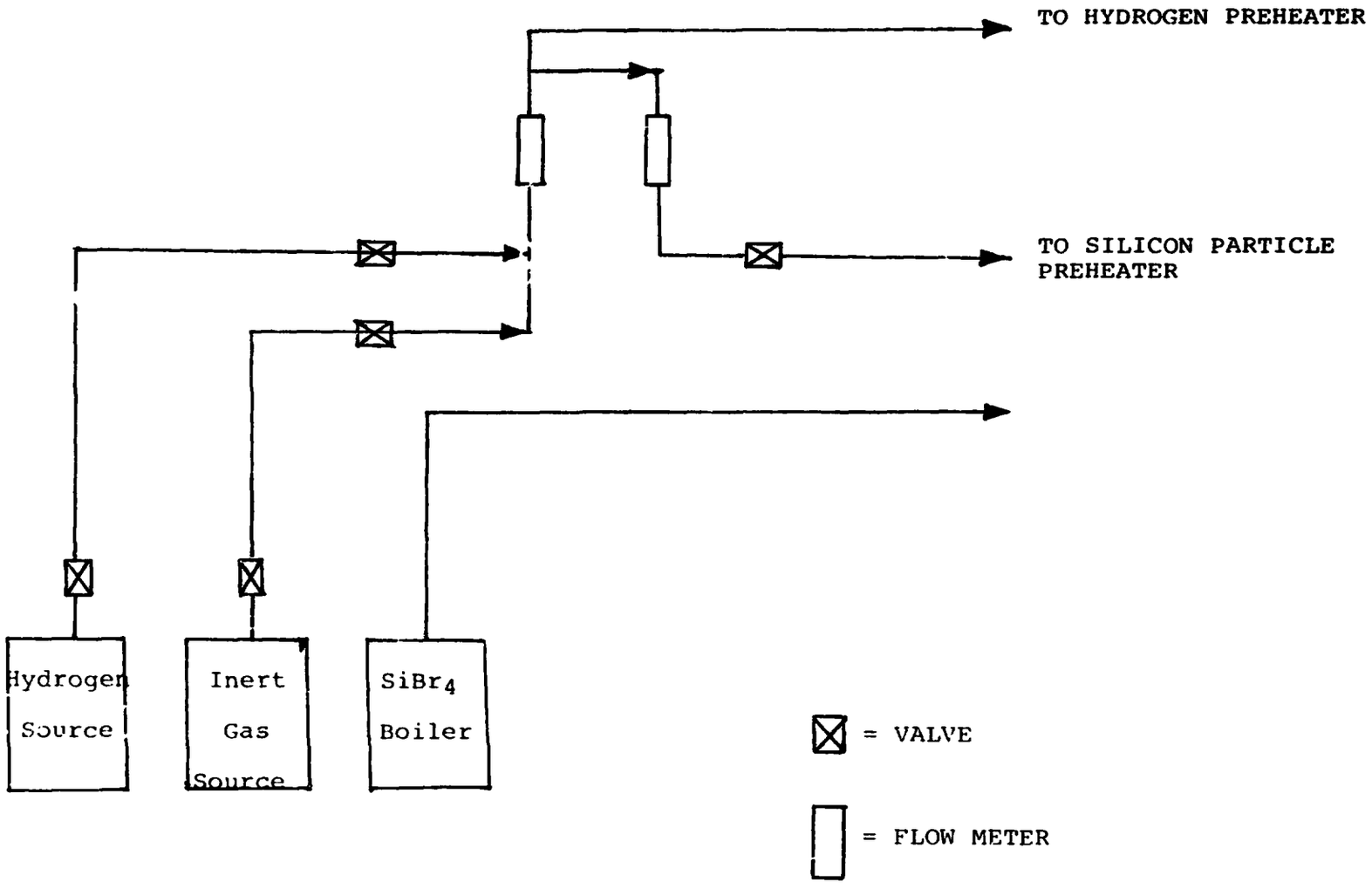


FIGURE 2. REACTANT DELIVERY AND METERING SYSTEM

stainless steel tubing. The remainder of the delivery system from the gas header to the preheaters has been constructed from 10 mm o.d. pyrex tubing. Teflon fittings have been used to join the pyrex tubing as required. Both the hydrogen and inert gas streams are metered with commercially available flow meters. The meters provide an accuracy of a $\pm$ 5% for a full scale reading.

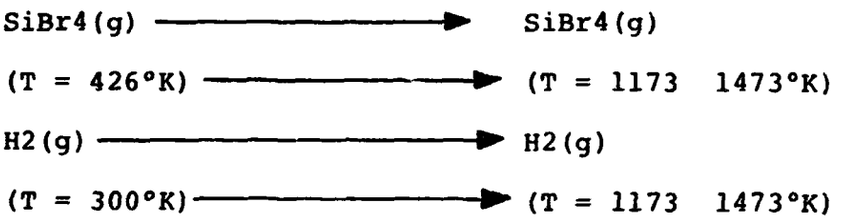
The bromosilanes are currently being vaporized in a boiler constructed of pyrex which is partially immersed in an oil bath. Heat to the oil bath is supplied by a resistively heated coil fabricated from 16 gauge Kanthal type A-1 wire which is immersed in the oil. This current design is a prototype and is being used to determine the best method for having a constant and predictable vaporization rate for the bromosilanes.

Metering the bromosilanes has proven to be quite difficult due to their corrosive nature. Stainless steels are pitted and etched after long exposure to either liquid or gaseous tetrabromosilane. Likewise, passage of the bromosilanes through a commercial flow meter is not feasible as the bromosilanes react with the valve packing materials as well as becoming contaminated with boron from the pyrex flow tube. As stated previously, the current metering system for the bromosilanes is a prototype to determine the feasibility of the design. When the prototype has been deemed to be

feasible, all pyrex components will be replaced with quartz to reduce possible contamination by boron from the pyrex. (2)

III. 1.2 PREHEATING SYSTEM FOR THE REACTANTS

This subsystem has the functional requirement to impart the necessary energy to the reactant streams. The specifications require that this subsystem increase the temperature of the two reactant streams from approximately room temperature or slightly above to a temperature range of 1173° to 1473°K. This must be accomplished separately and without contaiminating the two streams. The process can be readily described by the following diagram:



Likewise, the choice of the material used for the bromosilane preheater must not promote or catalyse the decomposition of these materials.

The design that was selected for the preheaters is a multi-pass heat exchanger. Quartz was initially selected as the material of construction. The initial selection of quartz was based on the fact that it is used in the pyrogenic process for producing pigmentary titanium dioxide. (4,5) Although the titanium dioxide process operates at the lower

end of the temperature range specified for the process, the work did indicate that sufficient heat could be transferred through quartz in this temperature region. Experimental investigations described in detail in Section III. 2.1 confirmed this.

Idealized heat transfer calculations based on a model utilizing quartz tubes 1.1 meters in length having an outside diameter of 10 mm and a wall thickness of 1 mm indicated that four passes would be sufficient to attain the specified temperature range of 1173°K to 1473°K. Preliminary experimental investigations, (See Section III. 2.1), confirmed these calculations.

Physically, the heat exchangers have been fabricated by placing the tubes in parallel so as to form bundles. Each tube is approximately 2.5 cm. from any adjacent tube. Connections on each end between adjacent tubes are made by fusing quartz U-bends to each tube. Reinforcement and mechanical stability of the tube bundle is achieved by fusing 2 mm diameter solid quartz rods between adjacent tubes. The complete bundle is tied together in this manner.

Energy for preheating the reactant streams is supplied by a resistively heated Omega tube furnace. The furnace is capable of operating up to temperatures of 1623°K. It is capable of supplying 11 kilowatts of energy continuously.

Heat balances have shown that this is more than sufficient for the experimental system. Both heat exchangers are placed in a single furnace tube. Connections to the delivery subsystem (low temperature side) have been made through teflon fittings, whereas the connections to the reactor-mixer subsystem have been made by fusion of the quartz tubes into a solid joint.

Included in the preheating subsystem is the heating of the silicon seed particles that are continuously introduced into the reactor. This system consists of a small tube furnace capable of operating to a temperature of 1473°K. A small diameter quartz tube (2.5 cm by 30 cm) containing the silicon particles is placed in the furnace. Transport of the particles to the reactor is accomplished by utilizing a metered stream of hydrogen which causes the particles to be fluidized and entrained in the gas stream. This gas stream, which is small in mass flow rate when compared to the mass flow rate of hydrogen in the preheater, is added to the last pass of the preheater prior to entry to the reactor/mixer subsystems. The current system design does not allow a precise measurement of the particle mass flow rate, rather, only an average value per unit time can be obtained. Connection of this unit to the heat exchanger is by fusion of the quartz tubes. Figure 3 is a diagram of this subsystem.

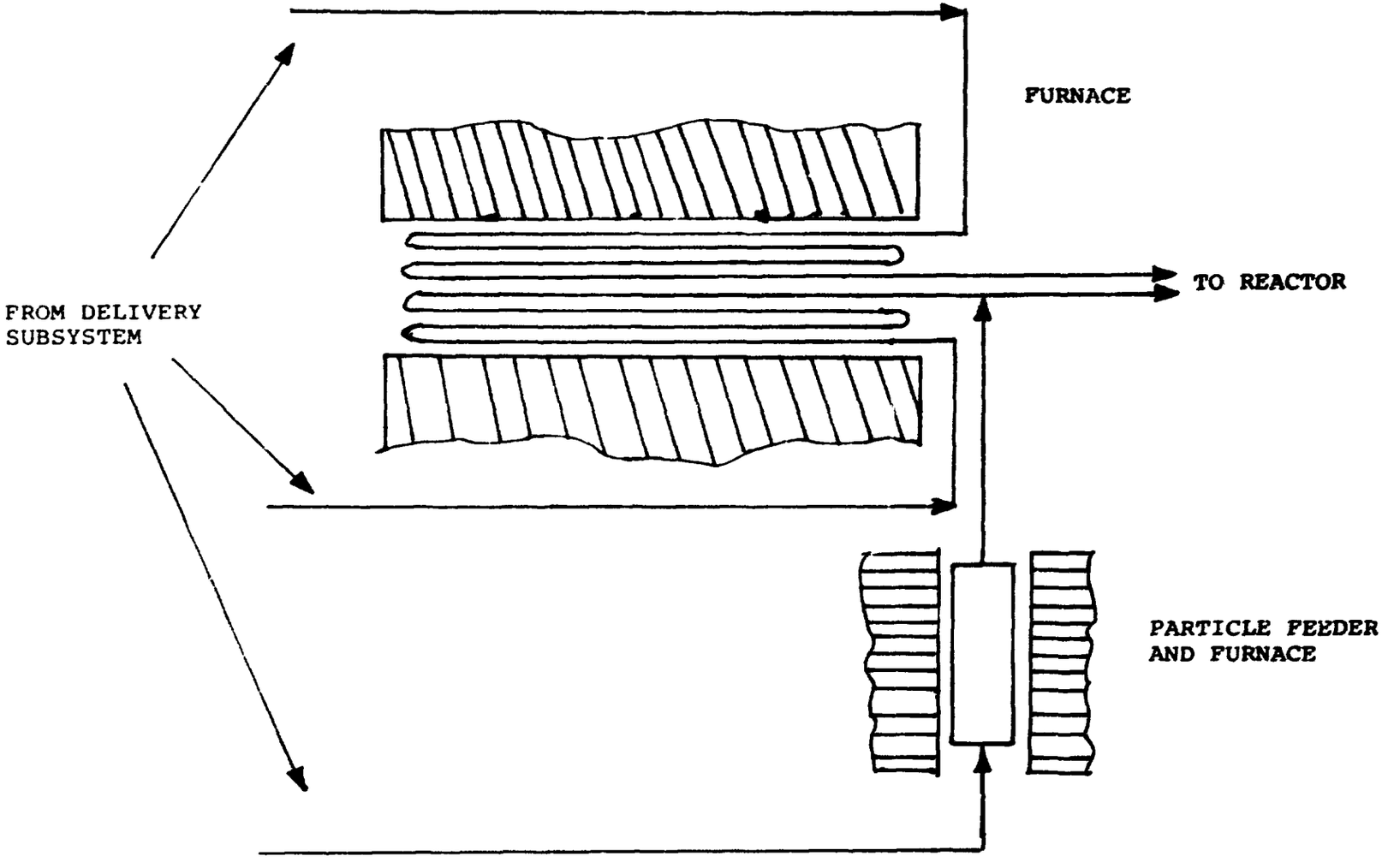


FIGURE 3. PREHEATING SUBSYSTEM

III. 1.3 REACTOR/MIXER SUBSYSTEM

The design of the reactor/mixer subsystem is by far the most important design area of the total system. It is within this area that reaction (1) must take place along with deposition on the substrate particles. This area must also provide conditions which maintain the equilibrium in reaction (1) as far to the right as possible.

This simple analysis indicates that the major factors that must be considered in design are: 1) Merging of the two preheated gas streams with a minimum amount of energy loss, 2) Thorough mixing of the gas streams to promote rapid and more complete reaction, 3) Removal of excess heat so as to inhibit the reverse of reaction (1); that is, the redesolution of the silicon formed, and 4) The removal of both the injected and formed particulate matter from the reaction zone along with any other reaction products so as to maintain the equilibrium as far to the right as possible, and 5) Mixing chamber pressure levels. A secondary design factor that must also be considered is limitations imposed by materials of construction.

Pressure considerations are important since the mixer design should not inhibit a smooth flow of the bromosilane stream. As cited in Section III. 1.1, the bromosilane delivery system operates at atmospheric pressure or slightly above because of the boiler design and materials limitations. Thus, the

reactor/mixer should be of a design that will promote the smooth flow of the bromosilane stream rather than being of a design which would cause irregular pulses or flashes in the stream.

As quartz is the only acceptable material for handling bromosilanes in the temperature range under consideration the design must be of such a nature that it can be fabricated without the introduction of new problems associated with machining quartz, etc. Likewise, the design should be simple and easily repairable if failure should occur.

The criteria cited above has led to the selection of a design for the reactor/mixer which is based on that of a common steam ejector. [7] As is well known, steam ejectors are used extensively throughout the chemcial process industry for vacuum applications due to their design simplicity and efficiency. Design selection was based on the following analysis.

Steam ejector physics can be described as follows:
A high-volume, high-velocity, gas stream referred to as the "motive-gas", is forced through a small diameter nozzle into a chamber or second stage. The dynamics of the motive gas cause a reduction in pressure in the chamber thus exerting a pulling effect on a second gas stream which enters the chamber. The second gas is referred to as the "suction

gas". The two combined gas streams enter a second stage of constant area where mixing takes place. A diffuser is the third stage of the ejector where the gases emerging from the mixing stage are allowed to expand. The critical design parameters in the selection of a steam ejector are: 1) ratio of constant mixing area to the motive gas nozzle area, 2) desired suction pressure, and 3) the pressure in the exhaust area.

The selection of a steam ejector as a model for the mixer/ reactor which satisfies the intial requirements, becomes readily apparent if one considers the following. Hydrogen is considered to be the motive gas and the bromosilane stream is the suction gas. The reduction in pressure caused by the motive gas will tend to pull on the bromosilane stream thus removing the possibility of pulses due to any pressure build-ups. The second stage of an ejector provides for an area where the two gas streams will be thoroughly mixed and allowed to react.

In the last stage or diffuser stage, the gaseous stream is allowed to expand. This expansion has a cooling effect on the stream as it can be considered to be an adiabatic or approximate an adiabatic expansion. This, of course, meets the criteria of quenching or cooling the gas stream. The design provides for high gas velocities within the mixing area and at the start of the diffusor area which meets another of the initial requirements.

The design of the mixer/reactor was carried out using the methods outlined in reference 7. An initial set of operating conditions was selected and then a trial and error method applied until realistic parameters were obtained for area ratios, compression ratios, and expected performance. The design parameters were verified by selecting a set of initial conditions that included exhausting into a reduced pressure environment. The final design parameters, which are indicated on Figure 4, are a hybrid of the initial two sets of conditions. Although the design parameters have been arrived at by utilizing charts based on idealized conditions, the design does meet the requirements that were set forth earilier.

The remainder of the reactor/mixer subsystem consists of a quartz tube 1.2 meters in length having an internal diameter of 1.3 cm. This section is used to dissipate some of the thermal energy remaining in the gas stream prior to entering the collection subsystem. It also provides an area for agglomeration of any fine particles produced in the reaction. Connection of the tube to the mixer/nozzle portion is by a quartz socket joint.

III. 1.4 PRODUCT COLLECTION SYSTEM

The product collection subsystem is quite simple. It consists of a cyclone separator shown in Figure 5, several condensers or cold traps, and a vacuum pump. The cyclone separator

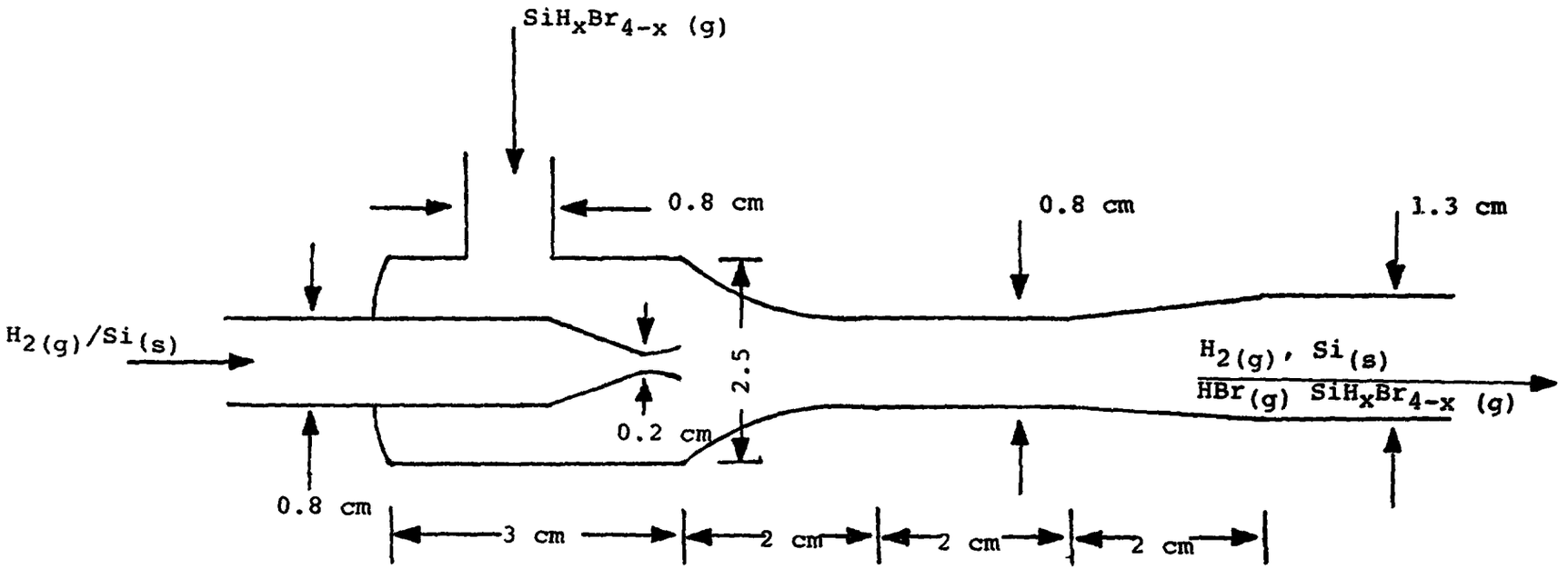


FIGURE 4 MIXER NOZZLE

shown in Figure 5 has been designed according to the relationships given in reference 8. It has been constructed of pyrex with a two liter round bottom flask being utilized to hold solids removed from the gas stream.

Basically, the collection system operates in the following manner. The product stream emerging from the reactor is passed through the cyclone separator where the solids are removed. It then passes through two cold traps maintained at a -78°C where any unreacted bromosilanes or bromosilanes formed in the reactor are removed. The stream is then passed through cold traps maintained at liquid nitrogen temperature which removes any hydrogen bromide and then through an oil baffle and on to a flare where the hydrogen is burned. By diverting the stream from the last cold trap to a vacuum pump, it is possible to operate the complete reaction system at reduced pressure. In this case, the exhaust from the vacuum pump is conducted to the flare and burned.

III. 1.5 STATUS OF TASK-1

Task-1 has been essentially completed. The total reaction system has been assembled and tested for safety and environmental considerations. It is expected that several modifications will be required as the chemistry studies (See Section III. 3) are extended.

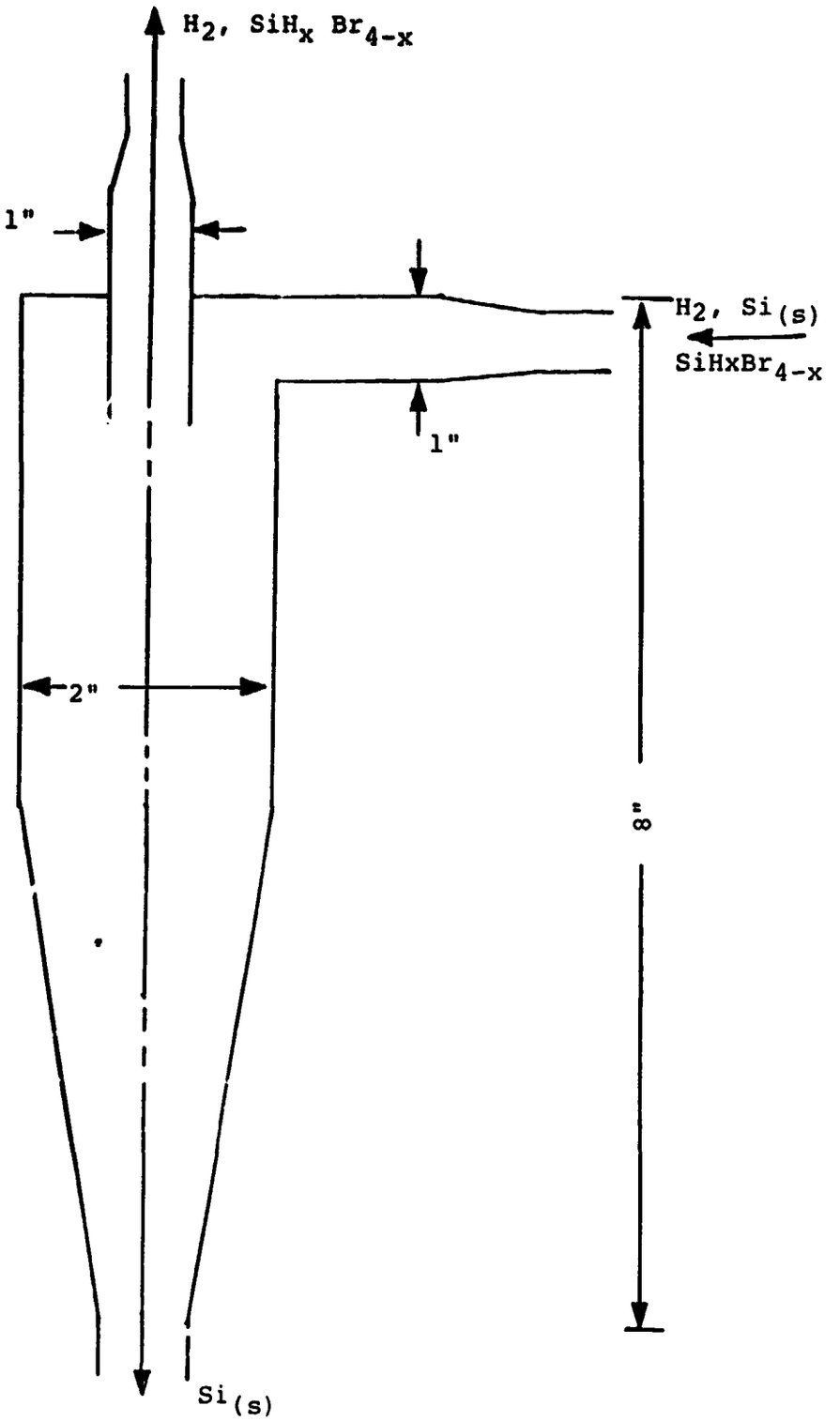


FIGURE 5 SILICON CYCLONE SEPARATOR

III. 2.0 TASK-2 PREHEATING/HEAT TRANSFER STUDIES

Two goals have been defined as the objectives of Task-2. The first goal included the design of the heat exchangers and the experimental verification of both the design and materials of construction. The second goal was to determine the thermal stability of bromosilanes. The latter goal is of utmost importance to the program as the total process is dependent on being able to heat the bromosilanes to high temperatures (1273°K to 1473°K) without causing their decomposition.

III. 2.1 INITIAL CONSIDERATIONS

Previously, it was indicated in an earlier part of this chapter that quartz had been selected as the material to be used for the heat exchangers. It was selected because of its resistance to corrosion and high temperature service, its extensive use throughout the semiconductor industry as well as in applications in other similar pyrogenic processes. [4,5] Table 1 summarizes some of the more relevent thermal properties known for quartz.

As a starting point for these studies a heat exchanger model using quartz tubes was assumed. The dimensions of the tubes were 1.1 meters in length, 1 cm. outside diameter, and 0.8 cm. inside diameter. Various mass flow rates for hydrogen, which would be representative of typical experimental

TABLE 1. THERMAL PROPERTIES OF QUARTZ [9]

Coefficient of Thermal Expansion	5.5×10^{-7} m/m °K
Thermal Conductivity	(293°K - 593°K) 3.3×10^{-3} cal·cm/cm^2·sec·c°
Specific Heat	0.18 cal/gm.
Fusion Point	2023°K
Softening Point	1943°K
Annealing Point	1413°K
Strain Point	1343°K

conditions, were then assumed. The thermal energy required to raise these mass flows to temperatures in the range of 1273°K to 1473°K was computed from heat capacity data. This data was then used in idealized heat transfer computations which assumed various inlet and outlet temperatures for each pass, average velocity of the gas in a pass based on the average of the entrance and exit temperature for the pass, and a varying number of passes. By this trial and error method, a value of four passes was arrived at as being sufficient to increase the temperature of hydrogen to the desired range. Four passes, as will be shown later, are actually an over-design feature; however, because of uncertainties in film coefficients, entrance and exit temperatures per pass, and other parameters, this number was selected even though the idealized calculations indicated a fewer number of passes could be used. This latter fact was confirmed by experimental results which are discussed in the following section.

III. 2.2 EXPERIMENTAL HEAT TRANSFER STUDIES

The experiments were carried out using quartz tubing which had the same dimensions as assumed for the model. Two tubes connected by a U-bend were used. The total length of tubing exposed to the hot zone of the furnace excluding the U-bend which was also in the furnace hot zone, was 2.2 meters. Refractory blocks were used at each end of the

furnace to support and center the tubes in the furnace. The tubes were purposely not supported in the center as it was desired to ascertain the degree of sagging of the tubes and under what conditions this would occur. Temperature measurements on the fluid were made by inserting a chromal-alumel thermocouple in the exit or outlet end of the second pass. It was not, however, within the hot zone of the furnace. The thermocouple was connected to a direct readout digital temperature display unit.

Initially, nitrogen was selected as the fluid to be passed through the tubes and heated. It was selected because the heat capacity of nitrogen is quite similar to hydrogen in the temperature range of interest. The thermal conductivity of nitrogen is appreciably lower than for hydrogen. It was reasoned that if nitrogen could be easily heated, little difficulty would be encountered in switching to hydrogen. The nitrogen stream was metered with a flow meter and allowed to pass through the tubes at various furnace temperatures and for various time periods. Flow rates of 0.080 to 11 liters per minute were used.

The results of the preheating experiments indicated the following facts. With flow rates exceeding 2 liters per minute, it appeared that a temperature differential of 120-140°K existed between the temperature of the gas exiting the second pass and that measured for the furnace. At low flow rates for example,

0.08 liters per minute, the differential increased and ranged as high as 275°K. In part, this can be attributed to two factors, the position of the thermocouple in the tube, and to a possible stagnant gas film inside the tube. In the first case, the position of the thermocouple is outside the furnace, thus at low flow rates it is possible that a large amount of heat was dissipated to the cooler tube walls. The second case can be rationalized on the basis that at low flow rates streamline flow is obtained which allows a stagnant film to develop thus inhibiting heat transfer to the bulk of the stream. High flow rates allowed the attainment of a maximum gas temperature of 1496°K with a furnace temperature of 1623°K.

Following the experiments with nitrogen, a similar set of experiments were carried out with hydroge as the fluid. The purpose was to verify that similar results could be obtained. Similar results were obtained for hydrogen with one exception, that being that lower flow rates of hydrogen than those required for nitrogen could be used to obtain the same temperature. Proof that the temperature being measured was truly the gas stream rather than radiation from the furnace was easily demonstrated when the fluid flow was reduced to zero. Terminating the flow would result in the temperature decreasing rapidly by 300 to 350°K below that noted with flow.

III. 2.3 MATERIALS EVALUATION

During the course of the heating experiments, the effects of time, temperature, heating rate, and thermal cycling on the quartz tubes was investigated. It was found that exposure of the tubes to temperatures in excess of 1548°K for long periods of time, about 5.5 to 6 hours, caused extensive degradation of the structural integrity of the tubes. Excessive warpage and brittleness were noted for tubes subjected to these conditions. At temperatures below 1548°K the effect is not as pronounced. As cited earlier, the tubes were purposely not supported in the center, thus, at temperatures of 1323°K to 1373°K for extended time periods, some bending was noted as would be expected. However, the tubes did not display the same brittle nature as found for the higher temperature runs. A very important factor that must be noted is the fact that at no time did any of the tubes fail during any of the high temperature runs. The fragile nature of the tubes is evident only on handling. No tube failure was encountered on thermal cycling or in changes in heating rates.

The conclusions that can be drawn from these investigations are that quartz will function adequately as a material for the heat exchangers. Even temperatures in excess of 1573°K may be used; however, once subjected to this temperature for prolonged periods of time, physical disturbance or handling

of the system will lead to failure due to fracturing of the quartz. This fact dictates that once the heat exchangers have been placed in the furnace they should not be disturbed.

Several experiments were repeated using the four pass exchangers. Similar heating results were found as would be expected. The degree of warpage was reduced considerably since the four pass system was allowed to rest on the bottom of the furnace tube and had been reinforced throughout by tying the tubes together with solid quartz rod.

III. 2.4 BROMOSILANE STABILITY STUDIES

These studies were undertaken to determine the maximum temperature to which tetrabromosilane could be heated without undergoing reaction or decomposing. The process reaction conditions require that the bromosilanes be heated to a temperature of at least 1273°K and preferably be stable to at least 1473°K. However, in the event that they could not be heated to this range, an alternative or contingency plan was developed. The alternative plan concerned itslef with determining the exact temperature at which any decomposition or reaction began. A knowledge of this temperature would allow thermal energy input to the system to be balanced between the hydrogen and bromosilane streams so as to avoid premature decomposition of the latter. In addition, the effects of using an inert gas as a transport vehicle for the tetrabromosilane was also studied.

A set of experiments were undertaken to determine not only the temperature stability of tetrabromosilane but also to investigate the effects of reduced pressure and the use of an inert carrier gas. The initial experiments were carried out using a 10.1 cm diameter tube approximately 1.5 meters in length. Use of the large diameter tube rather than those specified for the heat exchanger was for the following reasons. The large diameter tube allowed for a very low gas velocity, thus allowing for a long residence period within the furnace hot zone. The large surface of the tube, approximately 40 times that specified for one pass of the heat exchanger, allows maximum contact of the tetrabromosilane with the hot wall. Thus, if a hot wall catalysed decomposition were to take place, the large tube would provide a high probability of occurence when compared to the smaller tubing.

Two experiments with the large diameter tube were carried out by allowing the tetrabromosilane vapors to flow into the tube at atmospheric and reduced pressure. The exit stream was conducted through two cold traps maintained at -78°C. In the first experiment, which utilized a crude fraction of tetrabromosilane, 50 mls. were allowed to pass through the tube during a five hour period. Throughout the run a pressure of about one torr and an exit temperature of 1178°K was maintained. During the run, a slight amount of reddish brown gas was noted in the exit tube. The gas was thought to

be elemental bromine. One examination of the tube on cooling a black film was noted on the tube walls. Further examination of the film indicated that it was elemental carbon. The origin of the carbon was traced to probable organobromides that were present in the crude fraction. These were probably thermally cracked to carbon and elemental bromine. Approximately 49 mls. of liquid was recovered from the cold traps which showed no variation from the starting material in color, etc.

A second run utilizing pure tetrabromosilane, which was carried out at atmospheric pressure at an exit temperature of 1225°K, showed no deposit of any sort present in the tube. No change was noted in the liquid collected in the cold traps and nearly a perfect material balance for the tetrabromosilane was achieved.

An additional two experimental runs were carried out at atmospheric pressure using a two pass heat exchanger constructed of tubes having an internal diameter of 0.8 cm. and a combined length of 2.2 meters. One run utilized nitrogen as the carrier gas. Both runs were carried out over a temperature range of 1323°K to 1363°K. Neither experiment showed any evidence indicating that the tetrabromosilane had undergone decomposition and in each case, the recovered material indicated nearly a perfect material balance for the tetra-bromosilane.

The experimental results indicate that tetrabromosilane is stable to temperatures of nearly 1373°K. Temperatures above 1373°K were not studied as it was felt that this temperature would be sufficient for all reaction studies.

III. 2.5 STATUS OF TASK-2

Task-2 has been totally completed. Heat exchangers which meet the requirements were designed, fabricated, and tested. Preheating of hydrogen and tetrabromosilane in a safe manner has been achieved. The thermal stability of tetrabromosilane was established under various conditions of temperature and pressure. No further activities will be carried out in this area.

III. 3.0 TASK-3 REACTION/CHEMISTRY STUDIES

The objective of this task is to study the chemistry of the reaction of bromosilanes with hydrogen in the continuous high velocity reduction reactor. The bromosilane currently being investigated is tetrabromosilane; however, future studies will be extended to include tribromosilane.

Reduction of tetrabromosilane with hydrogen has been known for a number of years. It has been reported that the free energy change for the reaction is zero at 1293°K and about a -8°K cal per mole at 1500°K.[2,10] Although the free energy value is not large, it is more negative than for the analogous

tetrachlorosilane reduction. The reduction reaction has been studied extensively and these works are reported in the literature. The bulk of the studies have been concerned with conventional C.V.D. reactors. No studies have been found that have utilized the continuous high velocity reactor.

This task has just begun. The results reported in a latter section are the results of test runs undertaken to determine the feasibility of early designs.

III. 3.1 PRELIMINARY EXPERIMENTAL STUDIES

These experiments were carried out with a reactor/mixer subsystem which differs from that described in Section III. 1.3. The reactor consisted of a 2.5 cm. o.d. quartz tube 2 meters in length. Hydrogen was brought into the end of the reactor tube and the tetrabromosilane was injected perpendicular to the hydrogen flow. The reactor tube was approximately 15 cm. from the two heat exchangers. Connection from the heat exchangers to the reactor tube was through small quartz tubes, which were joined by fusion of the quartz. Chromel-alumel thermocouples were mounted on the exterior of the reactor tube at the point where the two gas streams merged. Thermocouples were also mounted on each heat exchanger and in the furnace proper. The remainder of the system was the same as described earlier.

A total of five experimental runs have been carried out. These runs served two purposes, 1) a cursorary look at the reaction and 2) system testing. The conditions for each run are given in Table 2. Silicon particles were not injected into the system in any of the runs.

The results obtained from these runs proved to be very interesting and led to several modifications of the reactor/ mixer subsystem. None of the experiments produced any silicon particles that could be collected. Runs number two and five produced wall deposits in the reactor at the point where the two streams merged. Examination of the deposits showed that the material was silicon. The measured temperature for run number two was 1183°K and for number five 1182°K. In both cases the molar ratio of hydrogen to tetrabromosilane was nearly the same. No deposits were noted for any of the other runs.

One of the major problems noted during the runs was the inability to control the tetrabromosilane stream so that a uniform rate was introduced. Another problem which became obvious on observing the reaction in the reactor was the low velocities that were being obtained. It was possible to observe a fog or cloud in the reactor tube which appeared to move at a very slow rate down the reactor tube. The fog formation was probably due to adiabatic cooling of the gas during expansion from the small diameter quartz

TABLE 2. INITIAL TEST RUNS CONDITIONS

Run	H_2 Rate mole/min. x 10^{-1}	$SiBr_4$ Rate moles/min. x 10^{-3}	Reactor [a] Temp. °K	Moles H_2/moles $SiBr_4$
1	1.99	6.73	1143	29.6
2	1.33	8.5	1183	15.7
3	1.33	7.4	1138	18.0
4	1.33	11.9	1113	12.0
5	1.33	9.5	1182	14.0

transfer tubes to the large reactor tube. The low velocities obtained in the reactor allowed unreacted tetrabromosilane to condense on the wall of the reactor tube near the end of the reactor tube.

III. 3.2 SUMMARY OF RESULTS

The five test runs indicate that silicon can be expected to be formed at a temperature above 1182°K using a hydrogen to tetrabromosilane mole ratio of 15. Velocity problems and the tetrabromosilane transport problems led to the redesign of the mixer/reactor subsystem. The design given in III. 1.3 should remove or reduce the problems noted in this area. The remaining subsystems namely, the preheating and collection systems functioned adequately. Inspection of the tetrabromosilane heat exchanger after each run reconfirmed the stability of the material to preheating.

III. 3.3 STATUS OF TASK-3

This task is just beginning. Results obtained from the initial test runs indicated that some modifications of the system were required. The modifications have been completed and the task is continuing.

IV. CONCLUSIONS

A continuous high velocity reactor system has been designed and fabricated. Preheating of tetrabromosilane has been established as a viable concept. Quartz has been established as a suitable reactor material and material for the reactant heat exchangers. Test runs have demonstrated that the concept of merging two preheated gas streams to effect the reduction of tetrabromosilane to silicon is a viable concept.

V. PLANS

During the next quarter of the contract, effort will be devoted to a complete study of the chemistry taking place in the high velocity reduction reactor. Efforts will be aimed at establishing the optimum parameters associated with the reaction and reactor system. Tetrabromosilane will be the main reactant; however, the study will also be extended to include tribromosilane.

VI. NEW TECHNOLOGY

No reportable items have been identified as new technology.

VII. REFERENCES

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