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DEVELOPMENT OF A PROCESS FOR HIGH CAPACITY ARC HEATER
PRODUCTION OF SILICON FOR SOLAR ARRAYS

Low-Cost Solar Array Project, Silicon Materials Task; Quarterly Technical
Report, January—March 1978

By
William H. Reed

Work Performed Under Contract No. NAS-7-100-954589

Westinghouse Electric Corporation
Power Circuit Breaker Division
Trafford, Pennsylvania

MASTER

U.S. Department of Energy

Solar Energy

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LOW COST SOLAR ARRAY PROJECT

SILICON MATERIALS TASK

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DEVELOPMENT OF A PROCESS FOR HIGH CAPACITY
ARC HEATER PRODUCTION OF SILICON FOR SOLAR ARRAYS

Contract No. 954589

Quarterly Technical Report: January - March, 1978

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1. INTRODUCTION

1.1 Program Description

A program has been established at Westinghouse to develop a high temperature silicon production process using existing electric arc heater technology. Silicon tetrachloride and a reductant will be injected into an arc heated mixture of hydrogen and argon. Under these high temperature conditions, a very rapid reaction is expected to occur and proceed essentially to completion, yielding silicon and gaseous sodium chloride. Techniques for high temperature separation and collection of the molten silicon will be developed using standard engineering approaches, and the salt vapor will later be electrolytically separated into its elemental constituents for recycle. Preliminary technical evaluations and economic projections indicate not only that this process appears to be feasible, but that it also has the advantages of rapid, high capacity production of good quality molten silicon at a nominal cost.^{1, 2}

As currently envisioned, the Westinghouse program consists of a four-phase effort directed to the development and implementation of this technology. The initial phase of the program, Phase I, was an eleven-month study funded by JPL which was completed in September, 1977. While the overall program objective is to produce 1000 metric tons of high quality silicon per year on a continuous basis, Phase I was defined as a comprehensive feasibility and engineering review of the reaction process, and a formulation of the design for a test system to experimentally verify the high temperature reaction.

Phase II, currently underway, involves a multi-task approach including (1) a detailed engineering analysis of the entire process (2) design, fabrication, and assembly of the experimental system (3) experimental testing of the reduction reaction to produce silicon and (4) complementary research programs to augment the experimental

system design. The Phase II effort was initiated in October, 1977, and work is progressing on the various stages of this effort.

2. PROJECT SUMMARY

During the quarter, the System Purity Analysis which utilizes the CHEMEQ computer program to predict impurity concentrations at equilibrium in the liquid silicon product based on initial amounts in the feedstocks was completed. The impurities that were analyzed include molybdenum, zirconium, copper, and titanium. For all four metals, the entire amount of the initial impurity is present in the liquid silicon product for the sodium reduction case, while 100% of the Mo, 92% of the Cu, ~ 35% of the Ti, and ~ 14% of the Zr is contained in the molten silicon product for the hydrogen reduction case.

The process economic analysis was reevaluated in order to determine the silicon product cost based on a homogeneous reaction mode. Results of this analysis are presented for both heterogeneous and homogeneous reaction modes.

During the reporting period, detailed design effort continued for the test system preparation. The test system has been divided into two main categories: 1) system components and 2) test system-laboratory integration. Included in the system components are the following systems: a) instrumentation and control (I&C), b) plasma reactor-separator, c) SiCl_4 storage and injection, d) sodium storage and injection, e) silicon collection, and f) effluent disposal. The test system-laboratory integration category includes: a) electrical distribution system, b) arc heater gas system, c) cooling water system, and d) the gas burnoff system.

Development of unit requirements, component specifications, and a system schematic was undertaken for the I&C system. Design and drawing effort continued for the arc heaters, plasma reactor and cyclonic separator. In addition, analyses were initiated to evaluate shell materials for the reactor components based on the physical and chemical properties of the candidate materials. The final design configuration for the SiCl_4 system was completed based

on the preliminary design developed during Phase I of the project. Specifications for safety requirements, storage tanks, and SiCl_4 monitors were initiated for the SiCl_4 storage and injection system. Detailed designs for both the sodium storage-injection system and the NaK cooling circuit were completed, components specified and procurement initiated. Initial operating sequences for the sodium system were also identified. Analyses continued for the silicon collector and the effluent system to provide design information for the drawing effort which is in progress in addition to vendor interface for these systems. For the test system-laboratory integration, activity continued on detailed design, component specification and selection in preparation for procurement of components.

Fabrication and assembly of the sodium injection chamber for the Injection Techniques continued throughout the reporting period. Nozzles have been procured for sodium and silicon tetrachloride injection, and preliminary testing with water has been initiated. Methods of particle size measurement have been estimated; sieving and inertial impaction have been identified as the most appropriate techniques for this task.

The design of the entire Kinetics test apparatus, including the injection nozzle, three test sections, scrubber and the SiCl_4 injection subsystem, have been finalized. Fabrication of all system components is currently in progress. Initial tests with a tunable dye laser indicate that the laser absorption technique is capable of detecting the presence of silicon vapor. A zirconium oxide filter will be used for particle size determination during initial experiments.

The design of the test system for Reaction Demonstration has been completed and the majority of the equipment and system materials of construction have been procured. Fabrication of the sodium and silicon tetrachloride generation subsystems is in progress. Based on a detailed comparison of internal and external generation

of sodium vapor, the external approach was selected because of the very large sodium containment crucible required for internal generation. The overall system design was discussed in detail by staff from both the R&D Center and PCB at a task design review.

During the quarter, analyses have continued for the purpose of defining a design which provides effective silicon product separation. Two approaches to product separation have been pursued. The first separation mode examines silicon separation via condensation following a high temperature reaction producing superheated silicon vapor. The condensation model results indicate that 80% of the silicon can be removed via condensed silicon collecting at the reactor wall. The design has been modified to accomodate the higher temperature process (e.g., initial product gas stream temperature of 3500°K).

The second approach depends upon a heterogeneous reaction mode which permits effective product separation. An analysis examined a partial low temperature reaction followed by a high temperature thermal treatment process step.

From the results of the product separation study, it was concluded that the Phase II design will be based upon the condensation mode. Even though high product separation efficiency is indicated for a reactor operated in this manner, considerations of both power requirement and reactor product flow rate may justify a slight modification of the reactor to examine heterogeneous mechanisms for the actual process. Fortunately, the basic reactor is readily adaptable to the various heterogeneous operating modes.

3. PROCESS ENGINEERING ANALYSIS

Task Investigators: F. J. Harvey, W. H. Reed

3.1 Summary

During the quarter, the System Purity Analysis which utilizes the CHEMEQ computer program to predict impurity concentrations in the liquid silicon product based on initial amounts in the feedstocks was completed. The impurities that were analyzed include molybdenum, zirconium, copper, and titanium. For all four metals, the entire amount of the initial impurity is present in the liquid silicon product for the sodium reduction case, while 100% of the Mo, 92% of the Cu, ~ 35% of the Ti, and ~ 14% of the Zr is contained in the molten silicon product for the hydrogen reduction case.

The process economic analysis was reevaluated in order to determine the silicon product cost based on a homogeneous reaction mode. Results of this analysis are presented for both heterogeneous and homogeneous reaction modes.

With the completion of the System Purity Analysis, this task is now complete; thus, all aspects of the Process Engineering Analysis are fulfilled.

3.2 System Purity Analysis

The control of metallic impurities is critical to the processes that are currently being developed for the low cost, high capacity production of solar grade silicon. The two principal sources of impurities in all metallurgical and chemical processes are the feedstocks and materials of construction. In the present analysis, thermochemical calculations have been carried out to determine the maximum impurity levels that could result in the liquid silicon produced by the arc heater process as a result of impurities present in the Na and SiCl_4 feedstocks. The metallic impurities that have been considered during the present quarter include Mo, Zr, Cu and Ti; while Al, B, Cr, Fe, Mn, P and V have been previously

analyzed². Since the arc heater process involves a multicomponent system, i.e., Si-H-Cl-Ar (H₂ reduction) and Si-H-Cl-Na-Ar (Na reduction), the free minimization computer program CHEMEQ was used for the analysis. The calculations have been carried out for binary solutions of liquid silicon and the various impurities. Because the range of impurity concentrations is small, the results can also be used to approximate multicomponent solutions of liquid silicon. Activity coefficients, which are required for the calculations, are not available for Mo, Zr, Cu or Ti. The coefficients were estimated based on experimental data for Fe-Si and Cr-Si solutions where these coefficients range from 1×10^{-2} (1700°K) to 4.5×10^{-2} (2200°K).

The results for both hydrogen and sodium reduction are shown in Table 3.1 for initial conditions that are representative of projected process conditions. For all four metals, the entire amount of the initial impurity is present in the liquid silicon for sodium reduction, while 100% of the Mo, 92% of the Cu, ~35% of Ti and ~14% of the Zr is contained in the molten product for H₂ reduction. As previously discussed,¹ the behavior of the impurities is a result of the stability of the impurity chlorides relative to the reductant chlorides, i.e., NaCl and HCl, as well as the activity coefficient of the metals in liquid silicon. In the case of zirconium, for example, less impurity is present in the silicon for hydrogen reduction than for sodium reduction because HCl is less stable than NaCl.

A summary of representative results for all impurities analyzed is given in Table 3.2, in terms of the percent of feedstock impurity that is present in the liquid silicon. These values represent the maximum amount of impurity possible in the molten silicon since the analysis is based on the equilibrium condition. Under actual process condition, the amount of impurity that is present may be considerably less due to kinetic factors. For arc heater reduction by sodium, the results indicate that purity levels should substantially improve with respect to P and Al, moderately so for Mn, and not at all

TABLE 3.1
RESULTS OF SYSTEM PURITY ANALYSIS FOR Mo, Zr, Cu, Ti

Impurity	Reductant	Temp. (°K)	Impurity Content in Feedstocks (g-atm)	Impurity Content in Si(l) (g-atm)	Impurity Mole Fraction in Si(l)
Molybdenum	*Na	1900	1×10^{-4}	9.99×10^{-5}	1.01×10^{-4}
		1900	1×10^{-5}	1.00×10^{-5}	1.01×10^{-5}
		1900	1×10^{-6}	1.00×10^{-6}	1.02×10^{-5}
	**H ₂	2200	1×10^{-2}	1.00×10^{-2}	2.80×10^{-2}
		2200	1×10^{-3}	1.00×10^{-3}	2.94×10^{-3}
		2200	1×10^{-4}	9.99×10^{-5}	2.96×10^{-4}
Zirconium	*Na	1900	1×10^{-4}	1.00×10^{-4}	1.00×10^{-4}
		1900	1×10^{-5}	1.00×10^{-5}	1.01×10^{-5}
		1900	1×10^{-6}	1.00×10^{-6}	1.01×10^{-6}
	**H ₂	2200	1×10^{-2}	1.44×10^{-3}	4.15×10^{-3}
		2200	1×10^{-3}	1.39×10^{-4}	4.11×10^{-4}
		2200	1×10^{-4}	1.38×10^{-5}	4.10×10^{-5}
Copper	*Na	1900	1×10^{-4}	1.00×10^{-4}	1.01×10^{-4}
		1900	1×10^{-5}	1.00×10^{-5}	1.01×10^{-5}
		1900	1×10^{-6}	1.00×10^{-6}	1.01×10^{-6}
	**H ₂	2200	1×10^{-2}	9.25×10^{-3}	2.60×10^{-2}
		2200	1×10^{-3}	9.22×10^{-4}	2.72×10^{-3}
		2200	1×10^{-4}	9.22×10^{-5}	2.73×10^{-4}
Titanium	*Na	1900	1×10^{-4}	9.98×10^{-5}	1.01×10^{-4}
		2200	1×10^{-2}	3.57×10^{-3}	1.02×10^{-2}
	**H ₂	2200	1×10^{-3}	3.52×10^{-4}	1.04×10^{-3}
		2200	1×10^{-4}	3.50×10^{-5}	1.03×10^{-4}

*Initial conditions: 1900°K; 4.0 mols Na, 1 mol SiCl₄, 0.66 mol Ar,
2.65 mols H₂

**Initial conditions: 2200°K; 25 mols H₂, 1 mol SiCl₄

TABLE 3.2
SUMMARY OF TYPICAL RESULTS FOR ALL
IMPURITIES ANALYZED

Impurity*	Percent of Initial Impurity in Liquid Silicon	
	Na Reduction**	H ₂ Reduction***
Aluminum	19	0.2
Boron	100	52
Chromium	100	81
Copper	100	92
Iron	99	94
Manganese	71	0.7
Molybdenum	100	100
Phosphorus	1	0.3
Titanium	100	35
Vanadium	100	100
Zirconium	100	14

*Initial amount is 1×10^{-4} g-atm for all impurities.

**Initial conditions: 1900°K; 4.0 mols Na, 1 mol SiCl₄, 0.66 mol Ar, 2.65 mols H₂

***Initial conditions: 2200°K; 25 mols H₂, 1 mol SiCl₄

for B, Cr, Cu, Fe, Mo, Ti, V and Zr. In the case of hydrogen reduction, there is essentially complete impurity removal for Al, Mn, and P, significant removal for B, Ti and Zr and little or no removal for Cr, Fe, Mo and V.

3.3 Process Economics

As a result of the Product Separation Analysis which examined a homogeneous (condensation) reaction mode, the process economics as reported previously² have been revised to accomodate both the heterogeneous and homogeneous reaction modes. Table 3.3 presents the economic projections for both fixed capital and silicon product cost (without profit) based on a 500 MT/year batch process and a 3000 MT/year recycle process for the arc heater-silicon process. The respective DOE/JPL cost goals for silicon are as follows:

500 MT/yr; \$25/kg Si (1975 dollars)

3000 Mt/yr; \$10/kg Si (1975 dollars)

Thus, both reaction modes are projected to meet the DOE/JPL cost goals for the silicon product.

Table 3.3

ESTIMATION OF SILICON PRODUCT COST (\$/kgSi)

COST ITEM	PRODUCTION CAPACITY (MT/YR)			
	500 MT ¹	500 MT ²	3000 MT ³	3000 MT ²
	BATCH	BATCH	RECYCLE	RECYCLE
DIRECT MANUF.	\$13.84	\$10.19	\$5.67	\$4.41
INDIRECT MANUF.	1.51	1.09	1.54	1.31
PLANT OVERHEAD	<u>0.64</u>	<u>0.53</u>	<u>0.59</u>	<u>0.53</u>
TOTAL MANUF. COST	15.99	11.81	7.80	6.25
GENERAL EXPENSE	<u>2.40</u>	<u>1.78</u>	<u>1.18</u>	<u>0.95</u>
TOTAL PRODUCT COST ⁴ (\$/kgSi) WITHOUT PROFIT	18.39	13.59	8.98	7.20
FIXED CAPITAL ⁴ (K\$)	3,582	2,720	22,035	19,073

NOTES:

1. HOMOGENEOUS REACTION (CONDENSATION), ASSUMES 80% YIELD ON BATCH
2. HETEROGENEOUS REACTION, ASSUMES 100% YIELD ON BATCH AND RECYCLE
3. HOMOGENEOUS REACTION (CONDENSATION), ASSUMES 100% YIELD ON RECYCLE
4. 1975 DOLLARS

4. TEST SYSTEM PREPARATION

4.1 Summary

During the quarter detailed design effort continued for the test system preparation. The test system has been divided into two main categories: 1) system components and 2) test system-laboratory integration. Included in the system components are the following systems: a) instrumentation and control (I&C), b) plasma reactor-separator, c) SiCl_4 storage and injection, d) sodium storage and injection, e) silicon collection, and f) effluent disposal. The test system-laboratory integration category includes: a) electrical distribution system, b) arc heater gas system, c) cooling water system, and d) the gas burnoff system.

Development of unit requirements, component specifications, and a system schematic was undertaken for the I&C system. Design and drawing effort continued for the arc heaters, plasma reactor and cyclonic separator. In addition, analyses were initiated to evaluate shell materials for the reactor components based on the physical and chemical properties of the candidate materials. The final design configuration for the SiCl_4 system was completed based on the preliminary design developed during Phase I of the project. Specifications for safety requirements, storage tanks, and SiCl_4 monitors were initiated for the SiCl_4 storage and injection system. Detailed designs for both the sodium storage-injection system and the NaK cooling circuit were completed, components specified and procurement initiated. Initial operating sequences for the sodium system were also identified. Analyses continued for the silicon collector and the effluent system to provide design information for the drawing effort which is in progress in addition to vendor interface for these systems. For the test system-laboratory integration, activity continued on detailed design, component specification and selection in preparation for procurement of components.

Specific activities and status of both categories which comprise the test system preparation are presented in Sections 4.2 and 4.3.

During the next report period, component procurement and fabrication will begin for the test system in addition to completing the various detailed drawings and design.

4.2 System Components

4.2.1 Control & Instrumentation (J. W. George, I. N. Bova)

During the quarter, the determination of individual unit requirements was completed for the current design of each subsystem. Any subsequent design changes that may be made to the subsystems will necessitate only slight revisions to the unit requirements.

A preliminary instrumentation and control schematic has been completed for the overall test system (see Figure 4.1). The schematic was reviewed with the task investigators of the various subsystems. Comments and suggested revisions are currently being resolved and the diagram is being revised accordingly. The schematic may also be used for designing a graphic type control panel which is being considered.

The instrumentation and control component specifications for the cooling water system were completed and submitted for comments and approval to the task investigators of both the cooling water and electrical systems. Following the review, the document will be finalized and released to prospective suppliers for quotations and delivery dates.

Specifications for the gas (H_2 and Ar) manifold and mixing chamber were completed and released to a vendor for a proposed design and quotation. As specified, the manifold package will include all required instrumentation and controls.

Quotations for hydrogen and oxygen level detectors which will monitor the quality of air in the test cell were received.

Figure 5.1 - Preliminary Instrumentation And Control Schematic

An engineering evaluation of the vendors proposal concluded that the oxygen level detector was much more sophisticated than necessary for the intended application. The vendor was requested to submit a revised proposal for a less complex detector system.

The specifications for instrumentation and control components for the other subsystems are in various stages of completion.

During the upcoming quarter, it is planned to complete the specifications for instrumentation and control for all subsystems. As the specifications are completed, the procurement phase for instrumentation and control equipment will be initiated.

4.2.2 Plasma Reactor-Separator (C. B. Wolf, T. N. Meyer, J. R. Meyer)

During the quarter, design and layout drawings for the reactor components were initiated based on the results of the Product Separation Analysis (see Section 9). Initial results of the analysis indicated that the reactor length of 5 meters will be adequate for silicon collection by condensation. The reactor bore diameter will be approximately 15 centimeters.

For silicon separation via condensation within the tubular reactor, the cyclone is not depended upon for product separation. The internal cyclone surface will provide additional condensation area. However, to maximize the particulate or droplet collection efficiency, the cyclone design has been modified. The cyclone design analysis shows that higher inlet velocities and reduced body diameters will collect higher percentages of small diameter particles, but will have a higher overall pressure drop. The design chosen will be approximately 45 cm inside diameter of liner, and the inlet velocity will be greater than 100 m/s. Collection

efficiency will be nearly 100% for all particles exceeding 4 μ m diameter. The pressure drop will be less than 0.1 atm.

Preliminary heat transfer analysis of the reactor liner combination of graphite and refractory insulation indicate that by varying the thickness of these components, the inside diameter of the water-cooled shells of the reactor sections can remain constant at approximately 30 cm.

With the results of the separation analysis indicating reactor diameter and length, and having sized the cyclone upon a collection efficiency basis, layout and detailed design are progressing. Figure 4.2 is a preliminary layout of the overall reactor assembly mounted on a frame structure. The arc heater plenum and reactor sections are inclined at a 10° angle. The liquid silicon being continuously collected onto the inner walls will flow into the collector. The arc heater connections are inclined at a 30° angle to provide for improved mixing of the hot gases. Figure 4.3 is a cross-section layout of the sodium injector mounting. This design provides for axial adjustment of the sodium nozzle by the addition (or subtraction) of refractory liner sections and corresponding adjustment of the retaining studs. Figure 4.4 is a cross-section layout of a portion of the cyclone outlet piping and refractories. The cyclone cover is included as part of this piping. Figure 4.5 presents the assembly drawing of the arc heater design which will be used for the test system. The downstream portion (shown on left of Figure 4.5) is designed to extend into the plenum inlet to minimize inlet heat losses and reduce insulation requirements at this location. Figure 4.6 and 4.7 are preliminary sketches with dimensioning of the arc heater plenum and the cyclone body. Final manufacturing drawings of these and all other reactor components will begin, pending the completion of a material and stress analysis now in progress.

FIGURE 4.2- SILICON PROCESS REACTOR ASSEMBLY

Figure 4.3 - Layout Drawing Of Sodium Injector

Figure 4.4 - Layout Drawing Of The Outlet Piping For The Silicon Cyclone

Figure 4.5 - Assembly Drawing For The Arc Heater

Figure 4.7 - Drawing Of Silicon Cyclone Body

Heat transfer rates and, therefore, material temperature gradients are higher for the presently proposed vapor condensation method of collecting silicon. Prior stress analysis of materials for the heterogeneous (liquid silicon particles) collection indicated that Type 316 stainless steel is a suitable material. Higher thermal stresses for the condensation collection mode may rule out the use of stainless steel. A complete stress and compatibility analysis of all candidate materials is in progress. Materials to be included are stainless steel, Inconel 625, Incoloy 825, Monel 400, carbon steel, copper, aluminum, and nickel 200. Primary factors which will affect selection are; chemical compatibility, thermal stress, yield strength, buckling stress, availability, and fabricating constraints such as joining and vendor limitations. For improved chemical compatibility of materials, protective platings such as copper or nickel will be considered. For example, if aluminum or carbon steel are found to be superior in other respects, then plating may become a necessity. Chamber material stress calculations include the following list:

1. Radial and axial stresses of outer and inner shells due to internal water pressure.
2. Radial and axial internal stress of inner shell due to temperature gradient thru the wall.
3. Axial stress of inner and outer shells due to differential thermal expansion.
4. Buckling of inner shell due to water pressure.

As mentioned earlier, preliminary calculations of refractory thickness requirements were conducted to determine metal chamber diameters. Early in the next reporting period, detailed analysis of all graphite and refractory components will be completed. Final component design will depend on

heat transfer properties, thermal stress, thermal expansion, material compatibility, availability, and formability. Material interface designs are being considered for alignment, containment, and sealing purposes.

4.2.3 SiCl₄ System (R. E. Witkowski, G. C. Burrow)

The activities for this quarter, as summarized below, were primarily concerned with finalizing the design of the SiCl₄ storage and injection system.

- The specifications and engineering drawings for the SiCl₄ storage tanks were sent to vendors for cost quotations and delivery dates.
- The details of the SiCl₄ transfer lines were received from the vendor.
- The final design of the SiCl₄ storage and injection loop was completed.
- OSHA and NIOSA safety requirements for the safe handling of SiCl₄ were established.
- Three suppliers of room HCl monitors were located and contacted.
- The specifications for the infrared on-line process analyzer were prepared for the vendor.

The specifications and engineering drawings, see Figures 4.8 and 4.9, for the main (4016 gal. capacity) and loop (264 gal. capacity) SiCl₄ storage tanks were prepared and delivered to vendors for costing and delivery date information. Quotations were requested for fabrication of 304 or 316 stainless steel or carbon steel with a rubber lining (or other lining compatible with SiCl₄ as discussed in the MCA-102 Chlorosilanes Data Sheet).³ The Van De Mark Chemical Co., Inc. provided the information necessary to interface the storage tank facility with their SiCl₄ delivery

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Figure 4.8 - Details Of 4000 Gallon SiCl_4 Storage Tank

Figure 4.9 - Details Of 200 Gallon SiCl_4 Day Tank

tank truck. The truck is equipped with a 2 inch-cast iron companion flange and the dry air (inert gas) padding line is equipped with a 1/2 inch Air-King hose coupling. The maximum pressure required to unload the SiCl_4 is 25 psig; dry air (at a minimum -40°F dewpoint) or dry nitrogen may be used.

An updated flow diagram was prepared of the SiCl_4 injection loop (see Figure 4.10) and details of its operation were provided to the Instrumentation and Control (I&C) Task.

Discussions were held with the Westinghouse Industrial Hygiene Group concerning the OSHA and NIOSA requirements for establishing and maintaining a safe working environment and appropriate personnel protection. Three potential suppliers for a room air HCl monitor were located and contacted for information.

The SiCl_4 on-line monitoring specifications were detailed for the supplier of the IR process analyzer for the purpose of finalizing instrument operation parameters.

A suitable working area for the storage of components and assembly of the SiCl_4 loop was evaluated and acquired.

The selection and specification of all SiCl_4 loop components has been completed, purchase requisitions will be issued in the second quarter. Upon receipt of costing and delivery dates from the storage tank vendors, procurement details for fabrication will be initiated. Efforts will continue in preparing SiCl_4 loop operational specifications including details regarding shutdown procedures; considering both normal and emergency conditions. Work will also continue on the SiCl_4 system user's manual.

Figure 4.10 - SiCl_4 Flow System Schematic

4.2.4 Sodium System (A. R. Keeton)

Detailed design of the sodium system and the NaK thermal control loop was completed. Component arrangement and piping layout in the sodium room was finalized. Procurement of long lead components and raw materials for parts fabrication was initiated. Fabrication of the sodium base tank and drum heating jackets was started.

The sodium system schematic drawing was revised and is presented in Figure 4.11. This drawing shows the features of the gravity drain system for emptying the sodium transport drums into the base tank. Operation of the system is described as follows:

A flow path from one of the sodium drums (B) is established to the base tank (A) by opening the proper manual and automatic valves. Sodium is drained from the drum as necessary to maintain the desired sodium level in the base tank. This is accomplished automatically by a level control system (I) in the base tank. Gas pressure is independently controlled in the drums and in the base tank to facilitate draining.

When the active sodium drum is empty a full drum is automatically switched on line. The empty drum is then replaced and the sodium melting sequence is started so that, the replacement drum will be ready for draining when it is required. Thus each drum is drained and replaced individually allowing continuous operation over an extended period of time.

Sodium is pumped from the base tank by electromagnetic (EM) pump (C) through one of the filters (E) and into the plasma reactor. Flow rate is sensed by electromagnetic (EM) flow meter (J) which is part of an automatic sodium flow control system that controls power to the EM pump. Remotely actuated valves provide the capability of recirculating the

Figure 4.11 - Sodium Supply System Schematic

sodium back to the base tank instead of into the plasma reactor. This mode is desirable for startup, shutdown and checkout of the system.

4.2.5 Silicon Collection System (I. E. Kanter)

A substitute insulation material of alumina ceramic fiber is proposed for use to cushion the quartz crucible and along sealing surfaces. A set of preliminary system dimensions have been used to estimate the system weight at 2265 lbs. The preliminary dimensions were also used to perform a steady state heat transfer calculation assuming free convection at the external surface. This surface is not expected to rise appreciably over 700°F while molten silicon is in the crucible. A detailed layout drawing of the assembly is under preparation.

A substitute material was evaluated to replace the graphite felt previously planned for use to cushion the fused quartz crucible and along sealing surfaces of the silicon collection system. The reason for the change was due to the fragile nature of graphite felt which could transport impurities throughout the system.

The candidate substitute material is a vacuum formed high-alumina ceramic fiber with an inorganic binder. It is available as a moist felt which can be manipulated into irregular shapes and air dried to a rigid configuration. Type WRP-X material is usable to 2300°F (1650°C). The analytical analysis of the alumina ceramic fiber felts WRP-X-AW, sample "I", and WRP-XA-AW, sample "II", is given in Table 4.1. Although the results indicate high Fe (~ 300-500 ppm) content similar to the purified graphite, it is expected that this material will not be subject to widespread dispersal and should, therefore, be acceptable for use. The material will be investigated for use as an insulator elsewhere in the test system.

Table 4.1 - Spectroscopic Analysis Of The Alumina Ceramic-Fiber Felts

(Percentage, w/o)											
Sample	Al	Ag	B	Bi	Ca	Cd	Co	Cr	Cu	Fe	
I	>10	<.0001	.1	<.001	.04	<.001	<.001	<.001	.001	.05	
II	>10	<.0001	.05	<.001	.02	<.001	<.001	<.001	.005	.03	
Sample	K	Mg	Mn	Mo	Ni	Pb	Sb	Si	Sn	Ti	V
I	.001	.01	<.001	<.001	.001	<.001	<.01	>10	<.001	.008	<.001
II	.001	.01	<.001	<.001	.001	<.001	<.01	>10	<.001	.008	<.001
Sample	Zn	Zr	Na								
I	<.01	.005	.55								
II	<.01	.005	.22								

Estimates have been made of the weight of the silicon collection system components. Using the preliminary dimensions, a total system weight of 2,265 pounds was calculated and broken down as follows:

<u>Component</u>	<u>Weight</u>
Steel housing and support ring	1,155 lbs.
Insulating brick	415 lbs.
Graphite crucible	345 lbs.
Felt insulation	~ 50 lbs.
Quartz crucible	~ 50 lbs.
Silicon (full charge)	<u>250 lbs.</u>
Total	2,265 lbs.

Stress analysis of the graphite crucible which holds the quartz crucible has been performed to determine the adequacy of the design to hold the 200 lb. charge of silicon at temperature. Maximum stresses due to the bending moment at the bottom corner of the cylindrical wall were determined to be ~ 2 psi if the bottom surface is fully supported. This negligible stress implies that only thermal stresses will control the design configuration in this case. Changes will be made in the design to insure that the bottom surface is fully supported and that the load is not transferred to the upper lip. Adequate clearances will be provided in the present design and an additional felt layer will be added between the bottom of the graphite crucible and the top layer of insulating bricks.

A dimensional sketch of the collection system assembly has been submitted for preparation of a detailed layout drawing. Cold assembly gaps have been included to prevent interference while at temperature. The elliptical bottom contour for the quartz crucible has been verified by the vendor and incorporated in the preliminary drawing.

A steady state heat transfer calculation has been made on the collector assembly using the preliminary dimensions. Radial heat flow was assumed with free convection at the collector outer diameter and hot molten silicon (1649°C) in the crucible. For this case the steel housing will attain a steady state temperature of approximately 700°F. Residual gaps may drop this value by $\sim 100^\circ\text{F}$. An external insulation layer may be applied to prevent a personnel hazard during cooldown.

4.2.6 Effluent Disposal System (J. W. George, J. McDonald)

During the quarter, a preliminary design drawing was made of the lined pipe which extends from the silicon cyclone to the effluent scrubber unit. The lining consists of three separate-layered materials. The inside layer is a 2" thick, 10" (ID) tube of SiC-infused graphite; surrounding the graphite is a 2" thick 75% Saffil, 25% Kaowool sleeve. This combination is wrapped in a Fiberfrax blanket and inserted into the water-jacketed pipe. The pipe will consist of two mitered ells, forming a "U" configuration.

A design review meeting was held during February to review the venturi scrubber design. It was noted that the effluent design must be capable of handling full flow of unreacted Na or SiCl_4 for a minimum time to be determined. The liner interface between the cyclone and the effluent pipe must not permit contamination of the product via contaminated material returning to the silicon collector.

The design specification and the information requested with the quotation is given as follows:

Design Specification For The Scrubber

1. General Description Of Process

The scrubber will be used in a process in which SiCl_4 and Na are reacted to form Si and NaCl. The products

of the reaction are passed from the reactor to a cyclone in which the Si is separated out as a liquid. The NaCl, as a vapor, and the carrier gas, H_2 and Ar, flow from the cyclone to the scrubber at a temperature of 2300°K (3680°F). The gas composition is as described in 3 below. The gas must be cooled to below 355°K (180°F), and scrubbed to remove the NaCl. An entrainment separator will be used to remove the bulk of the water from the gas.

This scrubber-separator unit should be designed for use with brine as well as water.

2. Reason For Cleaning The Gas

To eliminate atmospheric pollution and recover the salt (NaCl) for subsequent use or disposal.

3. Composition And Flow Rate Of Gas To The Scrubber

<u>Gas</u>	<u>Flow Rate</u> <u>SCFM</u>
NaCl (v)	187.5
H_2	150
Ar	37.5

4. Total - 375 SCFM @ 32°F & 30" Hg

5. Approximate Temperature - 1750°K (2690°F)

6. Actual volume/min - 2890 cu ft/min as of 1750°K or (3680°F) and atmospheric pressure.

7. The gas upstream of the scrubber can have a pressure of from 0 to 2 psig.

8. State Of Contaminate

NaCl is the contaminate; it enters the scrubber as vapor and is condensed to a solid. The solid must be dissolved in the scrubbing liquid (water or brine).

9. Particle Size

Submicron to granular, condensed from the vapor.

10. Amount Of Scrubbing Liquid Available

Water - 200 gpm
Pressure - 75 psig
Temperature - 120°F max

11. Material Of Construction Requested

Incoloy 825... Incoloy 825 is used because of its corrosion resistance in the presence of chloride ion.

12. An entrainment separator should be supplied with the scrubber.

Information Requested With The Quotation

1. Sketches indicating (1) the location of connecting pipes, (2) pipe size and (3) overall dimensions of the individual units and their separations.
2. The materials of construction of any items not of Incoloy 825 such as a wire mesh or tower packing.
3. A description of how the hot gas will be introduced into the scrubber without build up on cold surfaces such as water pipes or water-cooled walls; also at wet-dry boundaries.
4. The water flow and water pressure required for each unit of the scrubber.
5. The pressure drops in the gas flow through the scrubber system.

The above design specifications for the effluent scrubber were sent to four vendors; Koch Engineering, Ametek, Croll-Reynolds and Sly Manufacturing. Quotations have been received from three of the vendors with the fourth

quotation promised for delivery during the first week of April. However, Sly Manufacturing was requested to review their proposal because the cooling water requirement of their scrubber appears to be insufficient to cool the incoming gases (NaCl, H₂ & Ar) from 2300°K to 355°K.

During the next quarter, work will continue on designing a neutralization system for the scrubber water. The design of the pipe liner-joint interface between the pipe from the silicon collection cyclone and the gas scrubber will be completed. A design review will be conducted to evaluate the interface design and the scrubber system including the neutralization system. Suppliers for the scrubber system and the neutralization system will be selected and the equipment ordered.

4.3 Test System-Laboratory Integration

4.3.1 Electrical System (P. E. Martin, W. J. Melilli)

Based on the initial design and layout information provided in the fourth quarter of 1977, Plant Engineering has completed most of the electrical power system drawings during the past quarter. As refinements were made in each of the subsystems this initial information was updated during periodic meetings with Plant Engineering.

In general, these drawings include electrical equipment layout, distribution panel layouts, cable size and routing, and schematic diagrams.

Figure 4.12 depicts the general electrical equipment arrangement in the Arc Heater facility as per the layout drawings. As shown in this figure, the master control room will house two main system control panels; 1) the silicon test cell and 2) the existing test cell. Power equipment for the silicon process apparatus DC arc heater power supply,

Figure 4.12 - Electrical Equipment Layout For The MX-10 Facility (Arc Heater Test Laboratory)

distribution equipment and panels are located in the electrical distribution room. The sodium room contains a local control panel and a rack with heaters for the sodium drums. The pump room houses both cooling water pumps and the compressor for instrument air. Various disconnect switches and bus work have been added for distribution of the arc heater power system.

Due to the redistribution of the D.C. arc heater field coils, the original scheme of series/parallel combination of the D.C. power supplies has been changed. The present configuration will use the four supplies in parallel to provide a maximum field coil current of 4000 amps @ 45V D.C. The power cables for the field current, as well as the A.C. arc heater power, will be routed through enclosed cable trays with ventilation fans in each duct to prohibit gas from collecting around the cables during testing.

A control and interlock scheme has been developed for the heating and ventilation system. This scheme assures the emergency vent system has power available and locks out the normal heating and venting system when the emergency system is manually or automatically energized.

The disassembly of the present control system has been started and the remaining useful circuits have been traced and tagged. These circuits will be consolidated into the existing panels to accomodate the silicon test cell controls. The layout consolidating these controls has been completed with the schematic and connection diagram scheduled to start shortly.

During the upcoming quarter, design and layout work will continue on the electrical control system. In addition, review of component specifications for the control system

and procurement of long lead electrical items will be initiated.

4.3.2 Gas System: (C. B. Wolf, J. W. George, W. J. Melilli)

Plant Engineering prepared a laboratory gas piping drawing based on a schematic and layout piping sketch prepared in the previous quarter. This drawing is shown in Figure 4.13. It includes an outline of the building with the routing of the argon and hydrogen lines overlaid on the building plan. Also shown is the location of the argon-hydrogen mixing panel, valve sizes and the air piping.

Several meetings were held during the quarter with representatives of Air Products, a gas system supplier, to discuss the argon-hydrogen system. One of the sessions was held at the Arc Heater Laboratory. At this meeting, a member of their technical staff examined the site and made several suggestions on equipment and storage areas. A sketch and schematic of the gas system was provided to Air Products for further comment. At present Air Products is reviewing this information and preparing design recommendations for the gas storage and mixing equipment.

A meeting is scheduled for the early part of the quarter with Air Products to review their recommendations and finalize the facility requirements. Based on these meetings and Air Products design recommendations, the gas system drawings will be revised to include any changes.

After reviewing the requirements for compressed air, it was decided to eliminate the added expense of a compressor with its large volume capability and replace it with a bottled nitrogen system. Most of the pneumatically operated equipment require little gas volume to operate so that, the dry nitrogen system will be adequate and especially

1. ALL HYDROGEN (H₂) AND ARGON (Ar) LINES ARE TO BE 1" WELDED
MAX H₂ PRESS = 3000 PSI
MAX Ar PRESS = 300 PSI
2. MANIFOLD AIR LINES ARE TO BE .25" SST TUBE
MAX AIR PRESS = 150 PSI
3. PLANT ENGRG TO FURNISH BALL VALVES (1) H₂ + (10) AIR
+ (6) Ar + (2) He & Ar
4. MANIFOLD ASSY WITH CABINET TO BE SUPPLIED BY ARC HEATER ENGRG.
5. COMPRESSOR AIR LINES ARE TO BE .5" STL TUBE.

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Figure 4.13 - Plan View Of Gas Systems

suited for pneumatic valve use.

4.3.3 Cooling Water System (C. B. Wolf)

The engineering phase of this task is nearly complete. The preliminary water system schematic was distributed to task investigators for review. This information was then transferred to a plan view of the silicon test facility (Arc Heater Laboratory) with all water system components schematically shown and located. Included are pipe sizing and flow rate information. A preliminary plan view layout of the pump room components was prepared. With these inputs, Plant Service Engineering began, and have nearly finalized complete installation drawings for the pump room and the test cell manifolding.

The Control and Instrumentation task investigators have reviewed the plan view schematic, and are preparing detailed procurement specifications for all the control and instrumentation components. Included are temperature sensing elements, flow measuring devices, pressure sensors and switches, and liquid level controllers.

Similar detailed specifications for the mechanical components such as pumps and heat exchangers will be finalized during the next reporting period. Procurement for the longer lead-time items will begin. In addition, piping materials, valves, and installation materials will be procured which include the surge tank and heat exchanger support frame.

4.3.4 Gas Burnoff Stack (C. B. Wolf)

As described in the previous Quarterly Report, the gas burnoff stack is a water-cooled vertical-exhaust pipe supported by an iron structure over a waste water reservoir at the base.² The bore diameter required was determined by estimating the area required at the inlet for natural

convection admission of combustion air to be admitted at a rate of at least 200% excess. The reservoir at the base of the stack serves as a holding tank for both effluent system water and stack cooling water. Drawings of the stack are complete. Plant Service Engineering drawings of the stack base are near completion but, approval is delayed pending the requirements of the waste water treatment system. For example, the holding capacity may have to be increased to provide longer residence time of waste water.

Plans for the required stack igniter system are in progress; considerations include type (gas torch or electrical spark), flame detection, and safety circuitry.

5. TESTING

5.1 Task Description

As a task of the Phase II program, a series of tests will be conducted to establish and verify the process reaction for the arc heater-sodium reduction of SiCl_4 to produce liquid silicon. The verification test system that is designed, fabricated, assembled and installed at the Arc Heater Laboratory located at the Westinghouse East Pittsburgh Site will be operated to produce silicon on an experimental basis. This test system has been described in the previous section (Section 4).

Prior to system operation each subsystem (i.e., arc heater-reactor, SiCl_4 system, Na system, gas system, etc.) will undergo shakedown operations. The initial series of tests to produce silicon are entitled shakedown tests which will develop operating data, procedures optimization, and produce silicon for preliminary purity evaluation. The final series of verification tests are defined as demonstration tests which are intended to produce silicon and test data for evaluation of the process. This test series for verification of the process are scheduled to be conducted in the November, 1978 through February, 1979, time frame with appropriate data reduction, system evaluation, and results being compiled during and after the test phase.

6. INJECTION TECHNIQUES

Task Investigators: M. G. Down, J. Bauerle, A. R. Keeton,
F. J. Harvey

6.1 Summary

Fabrication and assembly of the sodium injection chamber continued throughout the reporting period. Nozzles have been procured for sodium and silicon tetrachloride injection, and preliminary testing with water has been initiated. Methods of particle size measurement have been estimated; sieving and inertial impaction have been identified as the most appropriate techniques for this task.

A detailed test plan (see Appendix A) for the task has been compiled and approved by a review meeting of Westinghouse staff both from the R&D Center and PCB.

During the next quarter the final stages of assembly will be completed and sodium injection phase of the nozzle testing commence. In parallel with this, water testing will be continued using high speed video recordings and strobe photography to determine measurement parameters for the analytical equipment. Work will continue on the design and assembly of the silicon tetrachloride and coinjection systems for use with the test chamber.

6.2 Work Description

Fabrication of the stainless steel test chamber for sodium and silicon tetrachloride injection studies is almost complete. Several aspects of the system design have been given detailed attention since the previous quarterly report. These include the design and construction of a heater for preheating the nozzle gas and thereby preventing premature freezing of the sodium. Also the flow of both argon and liquid sodium will be controlled by fast acting-electrically operated valves linked to a programmable controller to enable the accurate control of short injection bursts. The output potential from the sodium flow meter will be

recorded on a high speed (160 inches per second) chart recorder to provide a detailed flow profile for short duration (1 second) injections. The sodium storage tank, Figure 6.1, has been fabricated and leak tested. The tank is constructed from type 304 schedule 10 stainless steel (24" x 6") and is designed to provide a minimum liquid sodium pressure of 14 psi plus line losses at a flow rate of 100 gallons per hour. It has a capacity of 3 gallons and incorporates 2 level-probes for detecting when the tank is completely full or empty.

Control consoles are being constructed for the monitoring and adjustment of the sodium and argon heaters, flow meter outputs and thermocouple voltages (11 in all).

Stainless steel test nozzles have been procured for both silicon tetrachloride and liquid sodium injection tests. The former is a hydraulic atomizing nozzle (Spraying Systems Co. 1/4 LN-D6) with a capacity of 13.4 gph at 200 psi and 16.5 gph at 300 psi. For liquid sodium injection a sonic atomizing nozzle has been chosen for testing which is shown in Figure 6.2. This nozzle utilizes a field of sonic energy to accomplish liquid atomization. Advantages over conventional air atomization are large orifice diameter which will reduce the likelihood of blockage, and a high liquid flow capacity while maintaining small spray particle size. The selected nozzle (Type 312T, Sonic Development Corporation) can operate at 100 gph liquid and 36 SCFM gas, a liquid to gas mass ratio considerably higher than that of more conventional air atomizing nozzles. ^{4, 5}

While the manufacturers claim that this nozzle produces an extremely fine spray, they are unable to provide detailed particle size data. It is, therefore, the chief aim of this task to fully characterize nozzle performance and to this end, preliminary testing has been initiated using water as the spraying fluid.

Figure 6.1 - Photograph Of The Sodium Storage Tank

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Fig. 6.2- Schematic of sonicore 312 nozzle

6.2.1 Particle Sizing Of Sodium Droplets Collected From The Injection Tests

It is important that the droplets generated by the sodium injection system be quite small, i.e., less than 100 microns in diameter.

Four techniques for size distribution determination were considered and were discussed with Westinghouse R&D personnel having actual experience with the techniques:

- Microscopy (plus T.V. image analysis)
- X-ray sedimentation
- Cascade impactor separation
- Sieving

Figure 6.3 gives an indication of the particle size ranges appropriate for these methods. Brief discussions of the essential characteristics for each technique follow:

Microscopy

In this technique the sodium particles are dispersed in a liquid, and a sample placed on a slide under a microscope. The particle size distribution is then determined automatically by a T.V. camera (coupled to the microscope) plus a processor which analyzes the pulses in the T.V. scans.

Commercial instrument: Leitz-Classimat

Advantages: Wide range of measurable sizes (~1-1000 microns). Amount of material required is small (~0.5g).

Disadvantages: Difficulty of dispersing particles on microscope slide (clusters are counted as large particles). Reaction of sodium particles with air and moisture when dispersing fluid evaporates.

Fig. 6.3— Particle size analysis ranges

X-Ray Sedimentation

In this technique, the sodium particles are dispersed in a liquid of appropriate density and viscosity and placed in a flat vertical cell. A beam of soft x-rays traversing the cell is used to monitor the mass of particles in the cell at a given position, as a function of time. The rate of settling of the particles is used to determine the particle size distribution; this is automatically calculated by the instrument and recorded graphically.

Commercial instrument: Micromeritics Sedigraph 5000D
Particle Size Analyzer

Advantages: Automated operation and recording of results.

Disadvantages: Agglomeration of particles can produce erroneous results. Large amount of particle material is needed (5-10g). Peristaltic pump used in instrument may deform clusters of soft metal particles. Upper size measurement limit is low (50-100 microns).

Cascade Impactor

This technique differs from the previous ones in that it would employ direct sampling of the sodium aerosol generated in the sodium injection test chamber. The cascade impactor is a multi-stage, inertial separation device. Each stage contains orifices and a collection plate toward which aerosol flow from the orifices is directed. The size of the particles which impact on the collection plate of a particular stage depends on its aerosol flow velocity (determined by orifice sizing). Weighing the individual collection plates enables one to obtain the size distribution of material collected.

Commercial Instrument: Sierra 226 Source Cascade
Impactor.

Advantages: Direct collection and sizing from sodium
aerosol generated in the injection test.

Disadvantages: Upper size limit of particles collected
is too low (15-30 microns). Time-
consuming procedure.

Sieving

Sieving is a well-known technique which employs a series of wire-screen separators of decreasing size plus some type of mechanical agitation to effect the particle separation. The size distribution is then obtained by weighing the separated fractions. For sodium droplet sizing the entire procedure, of course, would be carried out in the inert atmosphere of a glove box. Refinements in sieving technique which may be useful for this work are: sonic, or ultrasonic agitation; wet sieving methods employing a carrier liquid; and the use of special ultra-fine sieves (5-50 microns).

Commercial apparatus: Fisher Scientific Co., stainless
steel sieves (37-1000 microns),
nickel mesh sieves (5-50 microns),
various types of agitation
equipment.

Advantages: Flexibility in choice of size range
(5-1000 microns). Particle size in terms
of mass percent obtained directly. Small
amount of material required (~1g).

Disadvantages: Possible problem of particle clustering
or adherence to sieves (alleviated by
wet sieving). Time-consuming procedure.

From the four techniques discussed above, sieving has been chosen as the primary method for determining sodium droplet sizes. The features which make it attractive are directness, reliability, and flexibility for covering different ranges of size. At this time it appears that the distribution of particle sizes in the range of 50 to 200 microns will be critical in determining whether the subsequent evaporation and reaction processes take place efficiently. Sieving methods should be nearly ideal for this range. If it becomes essential to obtain detailed information on the particle distribution for sizes less than 30 microns, the cascade impactor technique would be added.

6.2.2 Sodium Droplet Freezing In The Sodium Injection Tests

In order to collect the droplets generated in the sodium injection tests for size analysis, they must be frozen before contact with any test chamber surface. The particles will then settle to the bottom of the chamber where the collection system, Figures 6.4 and 6.5 is located.

A minimum condition for freezing the sodium droplets is that a suitable overall heat balance be achieved. The injection conditions assumed are that 1.5 gpm of sodium at 150°C and 35 SCFM of nitrogen at 150°C. A calculation shows that 24.6 kW of cooling power would be required to achieve this final condition.

Continuous operation of the injector under these conditions might be achieved by continuously flowing precooled gas through the injection chamber to supply the necessary cooling; however, this would require 263 SCFM of nitrogen at -100°C or 160 SCFM of nitrogen at -196°C. Cooling on a continuous basis thus appears impractical, not only because of the large volumes of precooled nitrogen required, but also because essentially all of the sodium aerosol generated

Figure 6.4 - Schematic Of The Sodium Particle Collection System

Figure 6.5 - Photograph Of The Sodium Chamber Base Flange

would be swept from the injection chamber by the high velocity cooling gas.

Intermittent operation of the injector appears possible if the test chamber is filled with precooled nitrogen gas just prior to the injection. There is then sufficient cooling capacity stored in the chamber to handle the heat load provided the injection period is short. With the chamber gas cooled to -100°C the maximum injection period is 1 second; for gas at -196°C the allowable period becomes 3.4 seconds. A final aerosol temperature of 50°C is assumed here, as in the earlier estimates. As described above, these short injection times will be achievable by solenoid valve control of the nozzle fluids.

6.2.3 Sodium Testing

As outlined in the test plan (Appendix A), general nozzle characteristics are being evaluated using water and nitrogen gas prior to the actual sodium injection tests. While these experiments will be only partially applicable to liquid sodium injection, these serve to shakedown some of the experimental aspects of nozzle performance. In addition, the water tests provide a means of evaluating the suitability of monitoring sodium tests with photographic and video techniques. Not only is water a convenient fluid for use in preliminary tests, it will also provide background data on nozzle performance that can be correlated with the sodium test data throughout the study.

Water tests have been performed with the Sonicore nozzle mounted in an adjustable cylindrical shroud, Figure 6.6. The distance, L , can be varied to enable either simple spraying directly into the atmosphere or alternatively a simulation of actual reactor conditions where injection occurs within a closed-end cylinder. In the former mode,

Dwg. 6428A39

Figure 6.6 - Water Testing Shroud

visual observations indicated that the nozzle operated satisfactorily producing a voluminous mist of water at a flow rate of 1.5 gpm. It was apparent, though, that the spray angle was large ($\sim 60^\circ$) and that a considerable quantity of high velocity droplets were being projected at high angles. This observation was confirmed by using the water collection shroud with L varying between 0 and 12". With the flow rate held at 1.5 gpm, water which hit the inner wall of the shroud was collected over a period of 60 seconds. The results are presented in Figure 6.7 as a plot of percentage water recovered versus L. With the nozzle 12" from the edge of the shroud only $\sim 1\%$ of the injected water emerged from the shroud as a mist. At 8" the figure was 50%. It was apparent that the high percentage of water collected from the walls was not due to the formation of particularly large droplets but was caused by the wide spray angle. In addition, the stationary atmosphere within the shroud caused the spray angle to increase compared with that in the open atmosphere. For a value of $L = 10"$ the angle between nozzle and shroud exit is 60° yet only $\sim 20\%$ of the water emerges. In an attempt to facilitate the forward motion of water droplets, the shroud has been adapted to produce a flow of air along the walls. It was hoped that a sufficiently high velocity of gas would turn the water particles away from the wall. Preliminary results from the use of a gentle gas flow (~ 0.25 cm/s) are included in Figure 6.7 but no appreciable effect can be discerned.

Figure 6.7 - Sonicore Nozzle Performance For Water Spray Tests

7. KINETICS STUDY

Task Investigators: J. V. R. Heberlein, D. F. Ciliberti,
D. W. Feldman, J. F. Lowry, and
E. J. Harvey

7.1 Summary

The design of the entire test apparatus, including the injection nozzle, three test sections, scrubber and the SiCl_4 injection sub-system, have been finalized. Fabrication of all system components is currently in progress. Initial tests with a tunable dye laser indicate that the laser absorption technique is capable of detecting the presence of silicon vapor. A zirconium oxide filter will be used for particle size determination during initial experiments.

During the next quarter, the Plasmadyne SG 1B 40 kW plasma torch will be procured and acceptance tests carried out. Fabrication and assemblage of the entire test apparatus will be completed. The laser vapor detection experiments will be finalized and shake-down testing with the test system will be initiated.

7.2 Task Description

In this task, the overall kinetics of reaction between SiCl_4 and Na is being investigated in a laboratory scale plasma reactor. The results of these experiments will provide input for the optimum operating conditions of the commercial scale experiments on the arc heater production of solar grade silicon.

The task consists of the following subtasks:

1. Test system design and fabrication;
2. Laser vapor detection;
3. Particle diagnostics;
4. Injection system;
5. Data acquisition.

7.3 Work Accomplished

Test System Design and Fabrication

An overview sketch of the test apparatus is shown in Figure 7.1. The plasma torch is located at the left end of the system. Immediately adjacent to the torch are the reactant injection nozzles. The two test sections to be used for monitoring the progress of the homogeneous reaction are adjacent to the nozzle section. These sections consist of an axial ceramic reaction tube with perpendicular side tubes both of which are enclosed in an outer cylindrical (stainless steel) chamber. Either one or both of these sections can be used as required since a flange arrangement is used for assembly. The product separation test section is located next to the homogeneous reaction segments. A straight tube condenser, which is not shown, can be inserted into the product separation test section to study the overall reaction in a condensation mode. Provisions for sampling the gas stream at the condenser exit for particle size analyses have been made at the right end of the reactor.

A drawing of the injection nozzle is shown in Fig. 7.2. There are three circular plenum chambers for liquid Na, SiCl_4 -vapor and high pressure cooling water, respectively. Several small channels extend from the Na and SiCl_4 chambers to the nozzle. The material of construction of the nozzle is 316 stainless steel.

Design drawings of the test sections are shown in Figs. 7.3 and 7.4. Inlets for introducing a tangential flow of gas are located in the side wall of the main cylinder of the test section. This gas will provide both additional temperature control of the inside ceramic tube, as well as a cover gas for the test section. At two axial locations, there is an arrangement of three viewing ports around the chamber periphery. These ports permit access for gas diagnostic measurements using both absorption and scattering techniques. The identical second and third test sections

Fig. 7.1—Assembly drawing of test apparatus

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Fig. 7.2—Reactant injection nozzle

Fig. 7.4—Product separation test section

(Figure 7.4) differ from the first section in that, the two opposing viewing ports are at slightly different axial locations. The larger scattering angle required for laser scattering techniques can be accommodated in this design. The viewing ports are shown in Fig. 7.5. The quartz window is protected from condensation of reaction products by a shutter. When the shutter is open, its U-shaped flapper provides maximum viewing access. A small amount of gas flow entering close to the window counteracts the diffusion flow of reaction products from the main stream. The outer chamber of the test section is constructed of stainless steel, while the inner ceramic tube is silicon carbide. Copper tubing will be affixed around the outer chamber for cooling purposes. The end section of the test apparatus is closed with a water-cooled plate with the scrubber connected to a flange at the bottom of the section.

A heat transfer analysis indicates that a considerable portion of the energy from the gas is transferred to the wall by Na radiation stemming from dissociated NaCl molecules. Consequently, the gas will cool faster than anticipated, and heating of the downstream portions of the inner ceramic tube may be required to avoid condensation of NaCl. The heat transfer analysis based on a laminar flow Nusselt number of 2.1 also indicates that radiation cooling of the ceramic wall will be sufficient if the wall temperature is about 2000°K, and the mean gas temperature is below 4000°K.

Scrubber Design

The actual flow conditions will vary greatly throughout the test plan thus, the scrubber has been designed to accommodate the largest gas flow envisioned, which is:

$$H_2 = 0.05 \text{ moles/sec}$$

$$Ar = 0.05 \text{ moles/sec}$$

Equilibrium calculations indicate that the mole fractions of HCl and SiCl₄ in the gas leaving the reactor will be as follows:

Fig. 7.5—Viewing port assembly

$$Y_{\text{HCl}} = 0.04$$

$$Y_{\text{SiCl}_4} = 0.012$$

It has been assumed that all of the SiCl_4 will be converted to HCl when the gas is spray cooled from 600°C to $<100^\circ\text{C}$ prior to entry into the scrubber. This assumption leads to the following expression for the expected maximum HCl mole fraction into the scrubber:

$$Y_{\text{HCl}} = \frac{4Y_{\text{SiCl}_4}^{\text{out}} + Y_{\text{HCl}}^{\text{out}}}{1 + 3Y_{\text{SiCl}_4}^{\text{out}}} = \frac{(4)(0.012) + (0.04)}{1 + 3(0.012)} = 0.085$$

It has been assumed that the mole fraction of HCl in the gas leaving the scrubber is to be reduced to 0.001; representing a 99% removal factor.

Equilibrium Data

The equilibrium data relating the mole fraction of HCl in the vapor above water containing dissolved HCl at 30°C and 1 atm is presented in Fig. 7.6. From this graph, it can be seen that the equilibrium partial pressure of HCl is very small for liquid mole fractions below 0.10.

Liquid to Gas Ratio

Ordinarily the minimum molar liquid to gas ratio is determined by an operating line drawn from the desired outlet concentration to the inlet concentration at the point of intersection with the equilibrium curve. In this example, this occurs at an $\bar{L}/\bar{G}$ {moles $\text{H}_2\text{O}/(\text{hr}\cdot\text{ft}^2)/\text{moles gas}/(\text{hr}\cdot\text{ft}^2)$ } of 0.391 or a liquid rate of 5.6 lb/hr. For this particular application, however, one must determine if this is enough liquid to dissolve the NaCl entrained in the flow. The mass flow of NaCl for the assumed conditions is calculated to be 27.8 lb/hr. Using the solubility of NaCl in water

Curve 695412-A

7-10

Fig.7.6—HCL - H_2O mole fractions

at 30°C, the water requirement is calculated to be 77 lb/hr or 0.15 gpm. For a conservative design, 100 lb/hr or about 0.2 gpm has been assumed.

Column Diameter

Using standard techniques, one can calculate the gas mass flow rate at flooding. For 0.25 in. Raschig ring packing, the flooding value of G is 336 lb/hr-ft². For a very conservative design it is assumed that the column will be operated at 1/2 flooding velocity or 168 lb/hr-ft². From this the cross-sectional area of the column can be calculated to be 0.099 ft² which corresponds to a diameter of 4.26 in. Using these same correlations, the pressure drop per unit length of packing can be calculated as 0.009 lb/in²/ft.

Scrubber Length

To calculate the scrubber length the height of a transfer unit for both the liquid phase, $H(\ell)$, and the gas phase, $H(g)$, must be calculated. These quantities have been correlated by empirical equations of the form:^{15, 16}

$$H(g) = \alpha G^\rho L^\gamma (Sc_g)^{0.5}$$

$$H(\ell) = \phi (L/\mu)^\eta (Sc_\ell)^{0.5}$$

For the system under consideration, the following values were used:

$$\alpha = 2.32 \quad \phi = 0.0018$$

$$\rho = 0.45 \quad \eta = 0.46$$

$$\gamma = -0.47$$

and Sc is the Schmidt number defined as $Sc = \mu/\rho D$.

For the gas phase, the Schmidt number has been estimated as:

$$(Sc_g) = 0.72$$

and for the liquid phase:

$$(Sc_l) = 335$$

Combining these results leads to the values of $H(g)$ and $H(l)$ of:

$$H(g) = 0.76 \text{ ft}$$

$$H(l) = 0.58 \text{ ft}$$

The tower length is the product of $N(g)$ and $H(g)$ where $N(g)$ is the number of transfer units and is defined by the equation:

$$N(g) = \int_{Y_{out}}^{Y_{in}} \frac{dY}{Y - Y_i} + \frac{1}{2} \ln \frac{1 - Y_{out}}{1 - Y_{in}}$$

where Y_i is the gas phase mole fraction of HCl at the interface of the liquid and water. The value of Y_i is usually evaluated graphically by extending a line of slope:

$$C = - \frac{H(g) \tilde{L} (1-Y)_{lm}}{H(l) \tilde{G} (1-X)_{lm}}$$

from various points on the operating line to the equilibrium curve where Y_i is read. For the system being designed, the value of C is about -9.15. This has the consequence that virtually all the Y_i 's of interest are essentially equal to 0 as can be seen from Fig. 7.1. This allows the integral to be evaluated explicitly and results in the following:

$$N(g) = \ln \left[\frac{Y_{in}}{Y_{out}} \right] + \frac{1}{2} \ln \left[\frac{1 - Y_{out}}{1 - Y_{in}} \right] = 4.48$$

Therefore, the overall tower height is calculated as:

$$Z = 4.48 \times 0.76 = 3.4 \text{ ft}$$

Scrubber Description

The embodiment of these calculations in hardware is shown in Fig. 7.7 which is a schematic of the scrubber system. From the reactor, the gas enters a 2 ft section of 4.0 in. pipe where it is spray cooled from about 600°C to less than 100°C. The cooled gas then flows through a 0.75 in. tube to the scrubber inlet. The gas flows up through a distributor plate into the packed column. The liquid level in the bottom is maintained by a trap arrangement and prevents the gas from escaping out through the drain. This section is fitted with a liquid level detector and sight glass to prevent back up in the column. The scrubbing water is admitted at the top of the packed section through a spray nozzle to insure uniform water distribution over the packing. The region above the spray nozzle is packed with glass wool to eliminate the possibility of HCl carry over in the form of fume. The cleaned gas then exits the scrubber and goes through a burnoff stack into the exhaust system. The actual system will be fitted with a bypass of the entire scrubber system so that it will not be necessary to shut down the reactor immediately should a problem arise in the scrubber system. This bypass system will only spray cool the gas and is intended for short term emergency use. With completion of the scrubber, the design of the test system is essentially complete.

Laser Vapor Detection

Optical absorption measurements on silicon vapor were performed using a tunable dye laser and a gated signal averager. The generation of silicon vapor was to be accomplished by placing silicon in an evacuated sapphire test cell which, in turn, is placed into the hot zone of a silicon carbide-resistance furnace.

Dwg. 6435A36

Figure 7.7 - HCl Scrubber System

However, sealing problems have been encountered with the sapphire cell. For this reason the initial tests were carried out with an alumina cell with small apertures at either end. The principal drawback associated with this latter cell is that oxygen in the furnace environment can react with the silicon forming a layer of silica. Although there still is silicon vapor in the atmosphere above silica, its value is much lower than the equilibrium vapor pressure. In order to minimize oxidation of the silicon the test cell atmosphere was flushed with argon. However, no attempt was made to achieve a tight cell so that some oxygen contamination of the cell environment was probable. On this basis, the initial test results given in the present report are intended to establish the basic feasibility of the laser technique for detecting the presence of silicon vapor in a gas phase rather than provide quantitative information. Pending the outcome of the sealing problem, future measurement will be performed with the sapphire cell or in an inert environment.

With the alumina cell, absorption was noted at several oven temperatures above $\sim 1500^{\circ}\text{C}$ at the atomic silicon absorption line of 288.1 nm. As an example, a temperature of 1616°C and an 8.6 cm absorption distance produced a transmission of 9.7%, or an optical density of 0.3 cm^{-1} . This temperature corresponds to a total silicon density of $7.5 \times 10^{14}\text{ cm}^{-3}$ and a density in the excited state from which absorption occurs of $6.2 \times 10^{12}\text{ cm}^{-3}$. The observed line width of the absorption was $\sim 0.3\text{ cm}^{-1}$ which is consistent with the measured line width of the laser source. The observed change in absorption with temperature was found to be consistent with the change in equilibrium pressure. It appears that atomic densities in the excited state of $\sim 10^{12}\text{ cm}^{-3}$ can easily be measured. The total densities corresponding to this excited state density will depend on the temperature, but at the temperatures expected in the test system, a total silicon density of $\sim 10^{14}\text{ cm}^{-3}$ should be readily measurable.

The alumina cell tests have demonstrated that measurements of silicon vapor can be achieved by laser absorption techniques. In addition, absorption in sodium vapor at comparable densities has been observed and it appears that the same laser and detector system will be capable of measuring sodium densities at the anticipated values.

Particle Diagnostics

Particle size determinations in the initial experiments will be performed with a zirconium oxide filter. In a typical test, the filter will be placed into the gas stream at a location where the NaCl is still in the gas phase. A microscopic examination of the filter will be carried out after the test to obtain an indication of the particle size range in the reacted gas phase.

After positive identification of particles in the micron size range, a final decision will be made regarding the particle size distribution measuring system. Titanium particle impactors which are placed in the hot gas stream, probes which extract and rapidly quench a sample of the gas stream, and laser scattering techniques are the methods under consideration.

SiCl₄ Injection System

A schematic of the SiCl₄ supply system is shown in Fig. 7.8. Liquid SiCl₄ is loaded into the reservoir which is then attached to the system at the Swagelok union. The reservoir is then pressurized with argon to about 100 lb/in². The argon pressure is used to deliver SiCl₄ through the system to the injection nozzle. The reservoir capacity is approximately 1.5 gal, which should permit at least 55 min of operation. The reservoir has an in-line pressure relief valve, which can be vented to an exhaust hood or some other suitable vent. A flat bottom facilitates placement of the reservoir in a dry box for reloading. A removable top cover plate, sealed with a teflon O-ring, is provided for cleaning and/or inspection of the interior of the reservoir. All parts are to be fabricated from type 304 stainless steel.

Figure 7.8 - Schematic Of The SiCl_4 Supply System

In the boiling vessel, SiCl_4 is heated to its boiling point and vaporized. The calculated power requirement is 466 W for a liquid flow rate of 2.55 gm/sec and a reservoir (vessel A in Fig. 7.8) temperature of 20°C, neglecting all heat losses from the boiling vessel. This vessel consists of two cylindrical, coaxial, stainless steel tubes welded to stainless steel end plates. A 1.0 kW immersion heater is sealed inside the smaller tube, with a suitable heat transfer fluid (for example, Dowtherm A) at atmospheric pressure, used to transfer heat to the SiCl_4 . A 500-1000 W heating tape is wound around the outside of the larger tube. Both heating units can be controlled from variacs, or through automatic solid state control units if desired. Liquid SiCl_4 enters the bottom of the boiling vessel and passes out as a gas at the top. The tube from the boiling vessel to the injection nozzle is also heated to prevent condensation of SiCl_4 vapor.

Two electrically-operated valves are provided for safety purposes: one to quickly stop the flow of SiCl_4 by removal of electrical power, and the other to purge the boiling vessel and nozzle system with argon when desired.

8. REACTION DEMONSTRATION

Task Investigators: A. Y. Ranadive, D. F. Ciliberti, and
F. J. Harvey

8.1 Summary

The design of the test system has been completed and the majority of the equipment and system materials of construction have been procured. Fabrication of the sodium and silicon tetrachloride generation subsystems is in progress. Based on a detailed comparison of internal and external generation of sodium vapor, the external approach was selected because of the very large sodium containment crucible required for internal generation. As part of the design of the sodium generation system, set up tests were carried out to determine optimum materials and the basic configuration of the sodium conveying flowtrain and various methods were considered for controlling the sodium flow. The overall system design was discussed in detail by staff from both the R&D Center and PCB at a task design review.

During the upcoming quarter, fabrication of all system components will be finalized and assembly and installation of the entire apparatus will be completed. A test plan and schedule will be developed and shakedown testing initiated.

8.2 Work Accomplished

A schematic of the overall system is shown in Fig. 8.1. Sodium and silicon tetrachloride vapors will be generated externally and each separately introduced into the reaction tube along with an Ar-H₂ carrier gas. The reaction tube will be heated by a tubular globar furnace. Temperatures of up to 1920°K can be produced in a constant temperature hot zone which is 26 in. long and 2 in. in internal diameter. Upon entering the furnace, the reactant vapors will be brought up to temperature and then allowed to mix and react in the isothermal reaction zone. The products of the reaction will

Figure 8.1 - Schematic Of The Test System For The Reaction Demonstration Studies

be condensed out on the surface of a cold finger type condenser while the uncondensed gases will exit from the side tube to a scrubber. The extent of the reaction will be determined by chemically analyzing and weighing the deposit on the condenser and also by determining the concentration of silicon chlorides in the scrubber.

The system is conveniently broken down into three subsystems, (1) The Reaction Tube and Condenser, (2) The SiCl_4 System, and (3) The Na System.

As shown in Fig. 8.2, the reaction tube is a high alumina ceramic tube inserted concentrically into the heating tube of the furnace. The annular region between the reaction tube and the heating element will be continuously swept with Ar. Stainless steel end plates with clamp attachments seal the reaction tube at either end. Sodium vapor from the vaporizer is piped into the reaction tube through an alumina tube wrapped with heating wire and jacketed in an outer tube of Inconel 600 which is connected to the stainless steel end plate by a conax packing gland. The SiCl_4 vapor is introduced into the reaction tube through a stainless steel tube welded onto the end plate. The condenser is comprised of a sealed alumina tube which projects to the edge of the reaction zone and through which a cool gas will rapidly flow. The length of the reaction zone can be varied by appropriately varying the position of the condenser. The uncondensed gases will exit through a side tube cemented to the reaction tube at the far end.

The SiCl_4 generator is shown in Fig. 8.3. The system consists of the reservoir, a flowmeter, a vaporizer and attendant tubing. Silicon tetrachloride is charged to the reservoir through the filling port. The liquid SiCl_4 is transported to the vaporizer by means of the positive pressure of argon maintained over the reservoir. The required SiCl_4 flow rate is established by means of the rotameter. The liquid SiCl_4 enters the vaporizer where it is gasified and, subsequently, transported from the system by a H_2 -Ar carrier gas.

Figure 8.2 - Sketch Of The Reaction Tube That Is Inserted In The Glow Bar Furnace

Figure 8.3 - Schematic Of The SiCl_4 System

The sodium system shown in Fig. 8.4 is similar to the SiCl_4 system with some exceptions which arise because of the higher melting and boiling points of Na. For example, the Na reservoir and tubing are wrapped with heating tape and the Na vaporizer is enclosed in a furnace to achieve the high vaporization temperatures and heat requirements. Various methods have been considered for controlling the low Na flow (i.e., 5 ml/min of liquid Na). While this low flow can be achieved using a positive displacement bellows pump, the pulsating output from this pump may be a problem. At the present time, it is planned to use a low flow metering valve to control the flow. A calibration experiment will be carried out to confirm the feasibility of this technique.

A number of set up tests were conducted in order to determine the optimum materials and configuration of the flowtrain between the sodium vaporizer and the reaction. Since vapor will be transported through this line, the temperature in the flowing gas stream must be on the order of 900°C . Based on the results of these experiments, the flowtrain will consist of an inner alumina tube wrapped with Kanthal wire (11 turns/in.) and an outer Inconel tube. The annular space between the tubes will be filled with a high purity alumina based cement.

The required equipment and materials that have been procured include a Harper model GTW-2D48-HT30-SP globar furnace (the instrumentation and control system have not yet been obtained), flowmeters for controlling the H_2 -Ar-gas and liquid SiCl_4 flows, and ceramic tubes for the reactor. Fabrication of all subsystem components is currently in progress.

Figure 8.4 - Schematic Of The Sodium System

9. PRODUCT SEPARATION ANALYSIS

Task Investigators: F. J. Harvey, T. N. Meyer, D. F. Ciliberti,
R. E. Kothmann and J. A. Cyphers

9.1 Summary

During the quarter, analyses have continued for the purpose of defining a design which provides effective silicon product separation. Two approaches to product separation have been pursued. The first separation mode examines silicon separation via condensation following a high temperature reaction producing superheated silicon vapor. The condensation model results indicate that 80% of the silicon can be removed via condensed silicon collecting at the reactor wall. The design has been modified (see section 4.2.2) to accomodate the higher temperature process, (e.g., initial product gas stream temperature of 3500°K.) The basic design configuration has not changed from that previously presented.

The second approach depends upon a heterogeneous reaction mode which permits effective product separation. An analysis examined a partial low temperature reaction followed by a high temperature thermal treatment process step. The success of this approach depended upon:

- a) an initial partial reaction with Na droplets forming large particulate* comprised of Na, NaCl, and Si (i.e., 50µm in size),
- b) a high temperature arc heater gas treatment with the remaining reaction proceeding homogeneously and forming ultrafine submicron silicon particulate, and
- c) the final collection of the silicon submicron particles onto the particles formed in step (a).

*The word particulate used in this writing does refer to both the solid and liquid phases.

The collection mechanisms (i.e., coagulation by Brownian motion and turbulence) known to exist for this mode of reactor flow are not believed adequate for effective collection. If the actual process does in fact proceed as described in step (b) and is not dominated by some heterogeneous process, the following two alternate heterogeneous modes may be capable of effective product separation:

- I) Complete the Na, SiCl_4 reaction at low temperatures followed by a thermal treatment with arc heater gas to vaporize off Na and NaCl leaving behind the large molten silicon particles to be separated inertially.
- II) Perform an initial reaction as described in step (a) above and then provide a high temperature reaction with the remaining product silicon existing in the vapor state to be condensed onto the initially form seed material.

From the results of the product separation study, it was concluded that the Phase II design (see section 4.2.2) will be based upon the condensation mode. Even though high product separation efficiency is indicated for a reactor operated in this manner, considerations of both power requirement and reactor product flow rate may justify a slight modification of the reactor to examine heterogeneous mechanisms for the actual process. Fortunately, the basic reactor is readily adaptable to the various heterogeneous operating modes.

9.2 Product Separation By Condensation

The previously Quarterly Report² described the condensation model development in progress. This quarterly will report:

- a) the means by which the one dimensional mass and energy conservation equations are integrated with the fully developed, constant property, turbulent boundary layer analysis,
- b) the relations utilized for mass, momentum, and energy

transport for developing turbulent pipe flow,

- c) the additional transport property set required due to a change in the reactant gas stream fraction, and
- d) the results of the condensation analysis.

Relations were developed², to assess the influence of boundary layer condensation upon the mass and energy transport to the wall. Due to the complexity of the physical mechanisms controlling this process, the following assumptions have been made:

- a) a constant property universal velocity profile⁶ can be used to assess condensation effects upon heat and mass transfer,
- b) silicon condensate forming in the boundary layer is collected by the wall,
- c) the energy transported to the wall as a result of the molten droplets exceeding the wall temperature is neglected,
- d) the Schmidt number is approximately equal to the Prandtl number,
- e) the wall temperature is equal to the silicon melt temperature,
- f) as a result of (e) the mass fraction of silicon vapor at the wall is essentially negligible for assumed equilibrium conditions, and
- g) the turbulent heat and mass transfer analogy is valid.

From the results developed in the previous quarterly², the ratio, R_m , of silicon mass transferred with condensation occurring in the boundary layer to that transferred without condensation occurring in the boundary layer is represented as:*

$$R_m = \frac{T_s - T_w + \frac{\lambda}{C_p} W_s}{\left[\left(\frac{dT}{dW} \right)_* + \frac{\lambda}{C_p} \right] (W_s - W_w)} \quad (1)$$

*A nomenclature table is given at the end of the section.

Similarly it can be shown that the ratio, R_Q , of heat transferred at the wall with condensation occurring in the boundary layer to the condition where no condensation occurs is represented as:

$$R_Q = \frac{T_s - T_w + \frac{\lambda}{C_p} W_s}{T_s - T_w} \quad (2)$$

The one dimensional relation accounting for axial variations resulting from radial mass and heat transport are reviewed with respect to the transport modifiers (see equations 1 and 2). The conservation of silicon flow is given as:

$$\frac{d\dot{m}}{dZ} = - Nu' D_{Si-M} \pi C \left(X_{Si} - X_{Si_w} \right) R_m \quad (3)$$

The conservation of energy equation can be written as:

$$\frac{dT_s}{dZ} = \frac{1}{\dot{m} C_p} \left[- Nu K \pi (T_s - T_w) R_Q - \frac{d\dot{m}}{dZ} \left(h_{Si(v), T_s} - h_{Si(l), T_w} \right) \right] \quad (4)$$

As a consequence of assumptions (e) and (f), all silicon reaches the wall in the liquid state. The diffusion coefficient and thermal conductivity are evaluated at the film temperature.

The consequence of combining these relations reduces to a one dimensional analysis accounting for axial stream property variations while correcting the transport relations based upon a constant property turbulent boundary layer having a universal velocity profile.

The relations above expressing the conservation of mass and energy must include the representation for mass and heat transfer coefficients. In ordinary turbulent, straight flow in a tube the

heat transfer coefficient⁷ may be expressed in terms of the friction factor, λ , as:

$$Nu = \frac{Re_D Pr \sqrt{\lambda/8}}{.833[5Pr + 5\ln(5Pr + 1) + 2.5\ln(\frac{Re_D \sqrt{\lambda/8}}{60})]} \quad (5)$$

This may be approximated as:

$$Nu = Nu_\infty \sqrt{\lambda/\lambda_\infty} \quad (6)$$

where:

$$Nu_\infty = 0.023 Re_D^{.8} Pr^{1/3} \quad (7)$$

Reference 8 provides a conservative representation of λ/λ_∞ given as:

$$\frac{\lambda}{\lambda_\infty} = 1 + 1.5 \exp \left(-0.25 \frac{X}{D} \right) \quad (8)$$

Boelter and coworkers⁹ experimentally determined local heat transfer coefficients for turbulent flow entering via a right angle bend and their results are shown in Figure 9.1. It can be seen that the use of relations (6) and (8) will yield lower values of Nu than shown in Figure 9.1. Thus, these relations will predict conservatively and longer reactor lengths required. It should be noted that the reactor Reynolds numbers are nominally 50,000

Curve 693981-A

Figure 9.1 - Local Nusselt Number Ratio vs. Distance Ratio Obtained From Boelter & Coworkers' Measurements On A Circular Tube With Right Angle Bend Entrance

and are comparable to the experimental results shown.

As a result of an analysis using the composition described in the previous quarterly² (i.e., 4.0 Na, 1.0 SiCl₄, 3.31 H₂, 0.83 Ar), the arc heater characteristics are not compatible with an initially high product temperature (e.g., 3500°K) required to maintain silicon in the superheated state. To obtain a high temperature product gas stream, it became necessary to change to a gas mix having one half the amount of reactants (i.e., 2.0 Na, 0.5 SiCl₄, 3.31 H₂, 0.83 Ar). For a silicon flow of 100 lb_m/hr, an arc heater power input of 1.54 MW is required for the 3500°K initial temperature.

The power facility at the East Pittsburgh site and the arc heater are compatible with this new composition and the 100 lb_m/hr flow of silicon. As a result of this change, new property data was determined and this data is displayed in Table 9.1. After the reaction is complete, silicon vapor begins leaving the flowing stream and condensing onto the reactor wall. Thus, the properties must be a function of temperature and the total content of silicon. The equilibrium properties are determined for:

a) $\beta^* = 1.0$	b) $\beta = 0.5$	c) $\beta = 0.00$
2.0 Na	2.0 Na	2.0 Na
2.0 Cl	2.0 Cl	2.0 Cl
0.5 Si	0.25 Si	0.00 Si
3.31 H ₂	3.31 H ₂	3.31 H ₂
0.83 Ar	0.83 Ar	0.83 Ar

For calculation purposes, all properties except enthalpy and silicon mole fraction were not found to be significantly affected by the relative fraction of silicon remaining in the stream. Thus, this two dimensional numerical interpolation need be performed only for the mole fraction and gas enthalpy during actual calculations.

* $\beta = 1.0$ corresponds to the initial fraction of elemental silicon, $\beta = 0.5$ corresponds to the mixture containing 0.5 of the initial fraction of elemental silicon.

PROPERTY DATA
BETA VALUES
1.00 .50 .00

TEMPERATURES (°K)		1700.0	1800.0	1900.0	2000.0	2100.0	2200.0	2300.0	2400.0
		2500.0	2600.0	2700.0	2800.0	2900.0	3000.0	3100.0	3200.0
		3300.0	3400.0	3500.0	3600.0	3700.0	3800.0	3900.0	4000.0
ENTHALPY (J/kg)									
B = 1.0		-.751+06	-.495+06	-.274+06	-.642+05	.148+06	.375+06	.628+06	.922+06
		.128+07	.172+07	.231+07	.310+07	.375+07	.430+07	.494+07	.566+07
		.649+07	.741+07	.843+07	.952+07	.106+08	.118+08	.129+08	.139+08
B = 0.5		-.751+06	-.495+06	-.274+06	-.642+05	.148+06	.375+06	.628+06	.922+06
		.128+07	.173+07	.231+07	.273+07	.321+07	.377+07	.441+07	.515+07
		.599+07	.694+07	.798+07	.910+07	.103+08	.114+08	.126+08	.137+08
B = 0.0		-.754+06	-.501+06	-.283+06	-.802+05	.122+06	.333+06	.559+06	.806+06
		.108+07	.139+07	.175+07	.216+07	.264+07	.319+07	.384+07	.459+07
		.545+07	.642+07	.749+07	.865+07	.986+07	.111+08	.123+08	.134+08
MOLE FRACTIONS									
B = 1.0		.0000	.0000	.0000	.0000	.0001	.0003	.0009	.0021
		.0046	.0094	.0000	.0182	.0339	.0430	.0459	.0477
		.0490	.0497	.0498	.0495	.0489	.0481	.0471	.0462
B = 0.5		.0000	.0000	.0000	.0000	.0001	.0004	.0009	.0021
		.0046	.0094	.0182	.0203	.0220	.0234	.0244	.0251
		.0255	.0254	.0255	.0251	.0247	.0242	.0237	.0232
B = 0.0		.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
		.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
		.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
THERMAL CONDUCTIVITIES, EQUILIBRIUM AND FROZEN (W/m-K°)									
Equil		.3285	.3214	.3115	.3583	.4018	.4460	.5528	.6712
		.8258	1.0200	1.2560	1.5490	1.8900	2.2740	2.6870	3.1070
		.5040	3.8400	4.0780	4.1850	4.1450	3.9620	3.6580	3.2660
Frozen		.2470	.2550	.2640	.2740	.2840	.2930	.3020	.3100
		.3180	.3240	.3280	.3360	.3450	.3540	.3640	.3750
		.3860	.3980	.4110	.4240	.4370	.4510	.4640	.4780
VISCOSITY (Pa-s)									
		.510-04	.525-04	.544-04	.567-04	.588-04	.609-04	.628-04	.650-04
		.671-04	.690-04	.706-04	.726-04	.746-04	.764-04	.780-04	.799-04
		.813-04	.822-04	.833-04	.839-04	.846-04	.852-04	.858-04	.861-04
MIXTURE DIFFUSION COEFFICIENT OF SILICON(II) (m²/s)									
Equil		.400-03	.440-03	.480-03	.530-03	.580-03	.630-03	.690-03	.750-03
		.810-03	.880-03	.955-03	.102-02	.111-02	.121-02	.132-02	.141-02
		.152-02	.164-02	.176-02	.189-02	.205-02	.223-02	.240-02	.252-02
PRANDTL NUMBER, EQUILIBRIUM AND FROZEN									
Equil		.4318	.3709	.3410	.3181	.3014	.2864	.2703	.2559
		.2417	.2293	.2189	.2099	.2039	.2007	.2003	.2032
		.2077	.2136	.2218	.2309	.2410	.2516	.2623	.2731
Frozen		.5743	.4776	.4282	.4160	.4264	.4545	.4948	.5541
		.6277	.7219	.8382	.9677	1.1170	1.2892	1.4786	1.6636
		1.8854	2.0609	2.2007	2.2740	2.2859	2.2103	2.0679	1.8671
SPECIFIC HEAT (J/kg-K°)									
		.278+04	.232+04	.208+04	.201+04	.206+04	.218+04	.238+04	.264+04
		.298+04	.339+04	.390+04	.447+04	.517+04	.597+04	.690+04	.791+04
		.896+04	.998+04	.109+05	.115+05	.118+05	.117+05	.112+05	.104+05
SCHMIDT NUMBER									
		.6775	.6822	.6902	.6889	.6899	.6925	.6843	.6837
		.6847	.6785	.6895	.6795	.6767	.6725	.6678	.6607
		.6850	.6871	.6946	.6942	.6963	.6891	.6863	.6959
DENSITY (kg/m³)									
		.188+00	.175+00	.164+00	.155+00	.147+00	.140+00	.133+00	.127+00
		.121+00	.116+00	.110+00	.105+00	.993+01	.939+01	.885+01	.832+01
		.780+01	.730+01	.681+01	.635+01	.593+01	.555+01	.521+01	.491+01
SILICON MONATOMIC VAPOR ENTHALPY (J/kg)									
		.171+08	.172+08	.173+08	.173+08	.174+08	.175+08	.176+08	.177+08
		.177+08	.178+08	.179+08	.180+08	.181+08	.181+08	.182+08	.183+08
		.184+08	.185+08	.185+08	.186+08	.187+08	.188+08	.189+08	.189+08

NOMINAL COMPOSITION OF 2.0 NA, 0.5 SI, 2.0 CL, 3.31 H, 2.0.

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Table 9.1 - Equilibrium Properties

Table 9.1 lists properties as functions of temperature for a range of 1700°K to 4000°K (i.e., at a pressure of 1 atm). For example, the mixture enthalpy for $T = 2800^{\circ}\text{K}$ and $\beta = 0.5$ is $0.273 \times 10^7 \text{ J/kg}$.

The condensation results are calculated by use of a forward step numerical integration. The calculations included the following assumptions:

- a) transition from superheat to saturated conditions occur at a vapor pressure equal to the saturation pressure,
- b) the minor fraction of the silicon diffusing from the stream in the form of other species (e.g., SiCl , SiCl_2 , Si_2 , Si_3 , and SiH) is taken into account by using an effective silicon mole fraction,
- c) radiant energy exchange has been neglected, and
- d) the inner reactor wall is constant in diameter having a temperature equal to the melting point of silicon (i.e., 1685°K).

Results indicating a reasonable silicon product separation are shown in Figure 9.2. The results shown in Figure 9.2, indicate a product separation of 80% can be achieved. It is also shown that the saturation point occurs within 1 cm of the wall for the majority of the product separation. For the case shown in Figure 9.2, a pressure drop of 0.03 atm occurred over a 8.0 meter axial length. Thus, pressure drop is not significant for the 15 cm internal diameter reactor. It should also be noted that the constant diameter can be approximately realized by simply adjusting the effective wall thermal resistance. Such a wall configuration is now being determined for the nominal operating flow rate for silicon of $100 \text{ lb}_m/\text{hr}$.

9.3 Heterogeneous Reaction Analysis

A heterogeneous reaction path by which the arc heater reduction of SiCl_4 can be accomplished has been previously outlined² including the basis of two models of simultaneous heat and mass transfer. As

- BETA: IS THE RATIO OF TOTAL SILICON MASS FLOW TO THE INITIAL VALUE ($X = 0$)
 Y STAR: IS THE RATIO OF RADIAL DISTANCE FROM THE WALL WHERE TRANSITION FROM SATURATION TO SUPERHEAT OCCURS TO THE REACTOR RADIUS.
 Q_W : IS THE REACTOR WALL HEAT FLUX (W/CM^2)

Figure 9.2 - Dependence Of Product Separation (Beta), Condensation Location (T Star) And Heat Flux (Q_W) Upon Axial Position (Equilibrium)

TABLE 9.2

NOMENCLATURE (For Condensation Analysis)

T_s	= Stream temperature
T_w	= Wall temperature
W_s	= Silicon mass fraction in the stream
λ	= Heat of vaporization for silicon per unit mass
C_p	= Specific heat of the gas
*	= Indicates an evaluation at the silicon saturation point
$\dot{m}$	= Mass flow of stream
Nu', Nu	= Mass and heat transfer Nusselt numbers, respectively
D_{Si-m}	= The diffusion coefficient for monatomic silicon in the gas mixture
C	= Gas molar concentration
X_{Si}, X_{Si_w}	= Silicon mole fraction in the gas stream and at the wall, respectively
K	= Thermal conductivity
$h_{Si(v)}_{T_s}$	= Enthalpy of silicon vapor evaluated at the stream temperature
$h_{Si(l)}_{T_w}$	= Enthalpy of silicon liquid evaluated at the wall temperature
Pr	= The Prandtl number
Re_D	= The Reynolds number based upon the reactor diameter
λ_∞	= The friction factor
∞	= Subscript to define fully developed conditions
X and Z	= Refer to axial distance from the entrance
Q_w	= Wall heat flux

shown in Figure 9.3 this reaction sequence consists of (1) a low temperature reaction between gaseous silicon tetrachloride and liquid sodium producing a multicomponent droplet of Si, NaCl and unreacted Na (if present), and (2) a thermal treatment in which both the Na (if present) and NaCl are removed from the droplet by vaporization and the silicon is melted. The intended result of the overall process is to produce large droplets of molten silicon which can be collected by inertial means. In concert with the dual nature of this reaction sequence, two analytical models, i.e., a reaction model and a thermal treatment model, were constructed.

Depending on the composition of the droplet produced in the low temperature reactor, the thermal treatment can be carried out in two different manners. If complete conversion to NaCl and Si occurs during the low temperature reaction, then the thermal treatment involves no further chemical reactions* only a physical heat affectation involving vaporization and melting. As previously discussed,² the extent of the low temperature reaction may be slowed down by the formation of a solid product skin on the droplets. If the low temperature reaction is impeded then the remaining SiCl_4 will react with the unconverted Na during thermal treatment in a homogeneous manner producing fine droplets. If a scavenging type collection mechanism is effective, these latter droplets may be collected by collision with the partially converted larger droplets. In the case that the scavenging mechanism would require an unreasonably large reactor vessel, then the overall reaction can be carried out in a different manner. Only part of the SiCl_4 would be introduced into the low temperature reactor with the remainder injected at the exit of the thermal treatment section. In addition, the temperature of this exit gas stream would be above the dew point of liquid silicon. Under these conditions, the reaction between the Na vapor and gaseous SiCl_4 would produce silicon vapor which could be removed from the gas stream by condensation.

*Assuming the NaCl and Si products are immiscible.

Figure 9.3 - Schematic Representation Of Silicon Reactor System In Which The Reduction Of SiCl_4 Is Carried Out In A Heterogeneous Mode

The mathematical formulation of the low temperature reaction and thermal treatment models is given below along with some selected results. The latter model will initially be formulated under the assumption that the low temperature reaction is incomplete, i.e., the worst case, and all SiCl_4 is added to the gas stream in the reaction section. Consequently, the experimental viability of this thermal treatment approach is dependent on the effectiveness of the scavenging collection mechanism. The plasma reactor configuration in which some of the SiCl_4 is added at the exit of the thermal treatment section will be considered in the future.

A potential problem can arise in the formulation of the reaction model as a result of the exothermic nature of the Na-SiCl_4 reaction. A very rapid temperature rise of the droplets may occur depending on the relative rates of heat and mass transfer. If the temperature is high enough, sodium vaporization will commence. The formulation of the reaction model is much simpler if sodium vaporization does not occur during the low temperature reaction, but only during the thermal treatment. Consequently, if a rapid droplet temperature rise does occur, then only part of the SiCl_4 will be introduced into the gas stream at the reaction section entrance with the remaining added at the exit of the reaction section, i.e., the entrance to the thermal treatment section (see Figure 9.3). This dual addition of SiCl_4 in the reaction section is consistent with the heterogeneous model as presently formulated since only part of the overall reaction is assumed to occur in the reaction section because of solid product formation, while the remainder occurs during thermal treatment.

9.3.1 Low Temperature Reaction Model

Droplet Equations

The equation describing the extent of reaction as a function of time (or position) is simply given by:*

$$\frac{d\xi}{dt} = \frac{-1}{N_{Na}^0} \frac{dN_{Na}}{dt} = \frac{-4\omega \text{ SiCl}_4}{N_{Na}^0} \quad (1)$$

where

$$\xi(Z) = \frac{N_{Na}^0 - N_{Na}(t)}{N_{Na}^0} \quad (2)$$

The initial conditions can be used to replace N_{Na}^0 in this equation as follows where f is the fraction of stoichiometric feed ratio of SiCl_4 to Na, i.e., $f = 1$ implies a 1 SiCl_4 to 4 Na feed ratio, $f = 1/2$ implies only 1/2 the amount of SiCl_4 required by stoichiometry is fed.

$$4 \left(C_g V_g y_{\text{SiCl}_4} \right)_{Z=0} = f \left(N_{Na} \lambda V_D \right)_{Z=0} \quad (3)$$

or

$$N_{Na}^0 = \left[\frac{4 C_g y_{\text{SiCl}_4}}{f \lambda} \right]_{Z=0} \quad (4)$$

*A nomenclature table is given at the end of the section.

This leads to the following form of the extent equation:

$$\frac{d\xi}{dz} = \left(\frac{-f\lambda}{C_g y_{\text{SiCl}_4}} \right)_{z=0} \left(\frac{\omega_{\text{SiCl}_4}}{V_D} \right) \quad (5)$$

A heat balance on the droplet that includes convective transfer to the gas, radiative transfer to the walls and heat of reaction on the droplet surface leads to the following equation for the droplet temperature:

$$\frac{dT_D}{dz} = \frac{4 \omega_{\text{SiCl}_4}}{V_D N_T \bar{C}_P^D} \left[\frac{h \theta_T}{\omega_{\text{SiCl}_4}} (T_D - T_g) - \frac{\tau \epsilon A_D}{\omega_{\text{SiCl}_4}} (T_D^4 - T_w^4) + \Delta h_{\text{RXN}} \right] \quad (6)$$

where

$$\Delta h_{\text{RXN}} = \left(h_{\text{Si}(s)}^{T_D} + 4 h_{\text{NaCl}(s)}^{T_D} - 4 h_{\text{Na}(l)}^{T_D} - h_{\text{SiCl}_4(v)}^{T_D} \right) \quad (7)$$

In this expression the convective heat transfer coefficient has been corrected for high mass transfer rates. Appropriate expressions for h and θ_T are given in the discussion of the thermal treatment model.

Gas Equations

A general expression for the heat balance on the gas flow is stated as:

$$\nabla \cdot (\bar{C}_g V_g h_g) = -\dot{S} + \lambda \tau \epsilon (T_D^4 - T_w^4) \quad (8)$$

$$\text{where } \dot{S} = \lambda \left[h_{\theta_T} A_D (T_g - T_D) - \omega_{Na} h_{Na}^{T_D} - \omega_{Na_2} h_{Na_2}^{T_D} - \omega_{NaCl} h_{NaCl}^{T_D} - \omega_{Na_2Cl_2} h_{Na_2Cl_2}^{T_D} + \epsilon \tau A_D (T_D^4 - T_w^4) \right] \quad (9)$$

After manipulation, equation (8) can be rearranged in the following manner for the case at hand:

$$\frac{dT_g}{dZ} = \frac{-\lambda \omega_{SiCl_4}}{(C_g V_g) \dot{C}_P^g} \left[\frac{h_{\theta_T}}{\omega_{SiCl_4}} (T_D - T_g) + h_{SiCl_4}^{T_D} - h_{SiCl_4}^{T_g} \right] \quad (10)$$

The total molar gas flow and species mole fractions can be obtained by use of an overall balance and a species balance, respectively. This results in the following set of equations for the gas phase flow and composition:

$$\frac{d(C_g V_g)}{dZ} = \lambda \omega_{SiCl_4} \quad (11)$$

$$\frac{d y_{SiCl_4}}{dZ} = \frac{\lambda \omega_{SiCl_4}}{C_g V_g} (1 - y_{SiCl_4}) \quad (12)$$

$$\frac{d y_{H_2}}{dZ} = \frac{-\lambda \omega_{SiCl_4}}{C_g V_g} y_{H_2} \quad (13)$$

$$y_{Ar} = 1 - y_{SiCl_4} - y_{H_2} \quad (14)$$

A zero molar flow of H_2 and Ar to the droplet surface is implicit in these equations. The $SiCl_4$ flow to the droplet is the only non zero flow and is given by:

$$\omega_{SiCl_4} = k_{SiCl_4-m} A_D \ln \left[\frac{1 - y_{SiCl_4}}{1 - y_{SiCl_4}^s} \right] \quad (15)$$

The surface mole fraction, $y_{SiCl_4}^s$, can be obtained from the equilibrium constant for the $SiCl_4 - Na$ system.¹⁰

The mass transfer coefficient for $SiCl_4$ through the mixture, and corrected for high rates was obtained in the same fashion that was employed in the thermal treatment analysis presented below.

This analysis has resulted in six differential equations, 5, 6, 10, 11, 12 and 13, for ξ , T_D , T_g , $(C_g V_g)$, y_{SiCl_4} and y_{H_2} . It is apparent that only three of these equations are independent as the equations for ξ , $(C_g V_g)$ and y_{H_2} can be solved in terms of y_{SiCl_4} . The resulting system of three differential equations and the concomitant algebraic equations can be solved using standard numerical integration techniques.

9.3.2 Thermal Treatment Model

Droplet Equations

The equations describing the steady state exchange of heat and mass across the surface of a single spherical droplet under the previously discussed assumptions are:²

$$\frac{dN_{Na}^D}{dz} = \frac{1}{V_D} \left(\omega_{Na} + 2\omega_{Na_2} \right) \quad (16)$$

$$\frac{dN_{NaCl}^D}{dz} = \frac{1}{V_D} \left(\omega_{NaCl} + 2\omega_{Na_2Cl_2} \right) \quad (17)$$

$$\frac{dN_{Si}^D}{dz} = 0 \quad (18)$$

$$\frac{dr_D}{dz} = - \frac{1}{4\pi r_D^2 V_D} \left(\frac{\omega_{Na} + 2\omega_{Na_2}}{\rho_{Na}} + \frac{\omega_{NaCl} + 2\omega_{Na_2Cl_2}}{\rho_{NaCl}} \right) \quad (19)$$

$$\frac{dT_D}{dz} = \frac{3}{4\pi r_D^3 \rho_D C_P} \left(h\theta_{T_D} A_D (T_g - T_D) - \epsilon \tau_{A_D} (T_D^4 - T_w^4) + Q_{Na} + Q_{NaCl} \right) \quad (20)^*$$

where

$$Q_{Na} = \omega_{Na} \left(h_{Na(c)}^{T_D} - h_{Na}^{T_D} \right) + \omega_{Na_2} \left(2h_{Na(c)}^{T_D} - h_{Na_2}^{T_D} \right) \quad (21)$$

$$Q_{NaCl} = \omega_{NaCl} \left(h_{NaCl(c)}^{T_D} - h_{NaCl}^{T_D} \right) + \omega_{Na_2Cl_2} \left(2h_{NaCl(c)}^{T_D} - h_{Na_2Cl_2}^{T_D} \right) \quad (22)$$

*Wall losses are assumed negligible.

The heat transfer correction coefficient for mass transfer is given by the expression:¹¹

$$\theta_T = \frac{\phi_T}{e^{\phi_T} - 1} \quad (23)$$

where

$$\phi_T = \frac{\sum_j \omega_j / A_D \bar{C}_P^j}{h} \quad (24)$$

Under conditions that the melting point of the sodium chloride or silicon is reached, then the temperature derivative in equation (20) is zero. For the case of NaCl fusion, a droplet energy balance yields the following equations:

$$\begin{aligned} \frac{df_{\text{NaCl}}^M}{dz} = & \frac{1}{N_{\text{NaCl}}^{\text{Do}} V_D h_{\text{NaCl}}^M} \left[h \theta_T A_D (T_g - T_{\text{NaCl}}^M) + \right. \\ & \left. - \epsilon \tau A_D (T_{\text{NaCl}}^M{}^4 - T_w^4) + Q_{\text{Na}} + Q_{\text{NaCl}} \right] \end{aligned} \quad (25)$$

where f_{NaCl}^M , the fraction melted, can be represented as:

$$f_{\text{NaCl}}^M = \frac{N_{\text{NaCl}}^{\text{Do}} - N_{\text{NaCl}}^D}{N_{\text{NaCl}}^{\text{Do}}} \quad (26)$$

A similar formulation can be performed for silicon melting.

In order to solve the above sets of non-linear, coupled differential equations, a knowledge of the gas temperature, T_g , the gas velocity, V_g and the molar rates, ω 's are required. The molar flow of any species, i , is given by the equation:

$$\omega_i = k_{i-M} \theta_{i-M} A_D \left(x_i^s - x_i^g \right) + x_i^s \sum_j \omega_j \quad (27)$$

where the multicomponent mass transfer coefficient, k_{i-M} , is given by the expression:

$$k_{i-M} = \frac{C_f^{D_{i-M}}}{2\bar{r}_D} Nu_{i-M} \quad (28)$$

The effective binary diffusion coefficient is calculated in the usual manner.¹¹

The mass transfer correction factor, θ_{i-M} , is given by the equation:

$$\theta_{i-M} = \frac{\phi_{i-M}}{e^{\phi_{i-M}} - 1} \quad (29)$$

where

$$\phi_{i-M} = \frac{\sum_j \omega_j / A_D}{k_{i-M}} \quad (30)$$

Substitution of equation (29) through (30) into (27) yields:

$$\omega_i = \frac{(x_i^s - x_i^g) \sum_j \omega_j}{\left(\sum_j \omega_j / A_{D,i-M} \right) e^{-1}} + x_i^s \sum_j \omega_j \quad (31)$$

There are six relations of the form given in equation (31), i.e., one for each of the diffusing species (Na, Na₂, NaCl, Na₂Cl₂, H₂, Ar). Introduction of these six equations has resulted in an additional twelve unknowns, six x_i^s 's and six x_i^g 's. The gas phase compositions are obtained by solving the complex equilibria as outlined below. The surface concentrations of the four vaporizing species (Na, Na₂, NaCl, Na₂Cl₂) are given by four equations of the form:

$$x_i^s = \frac{e^{\left(-\Delta G_i^0 / RT_D \right) - 1}}{P_T} \quad (32)$$

Two other applicable equations are:

$$\omega_{H_2} = 0 \quad (33)$$

that is, the hydrogen is stagnant, and

$$\sum_i x_i^s = 1 \quad (34)$$

The twelve equations given in (31), (32), (33) and (34) in conjunction with the transport coefficient equations (28), (29) and (30) constitute a set of twelve equations and twelve unknowns (for known x_i^g) which can be solved numerically. This set of equations must, of course, be solved in

conjunction with the coupled set of droplet differential equations.

Gas Equations

The remaining unknowns in the droplet differential equations are the gas temperature, velocity and composition. The gas temperature is obtained from the gas energy balance equation in conjunction with gas composition which, in turn, is calculated from the complex equilibrium analysis. However, the equilibrium calculation requires a knowledge of the temperature so that the solution must be carried out simultaneously. The gas energy balance is:

$$\frac{d}{dz} \left(C_g V_g \tilde{H}_g \right) = - \dot{S} + \lambda \left[\epsilon \tau A_D \left(T_D'' - T_w'' \right) \right] \quad (35)$$

where $\dot{S}$, the heat lost per unit volume to the droplets, is given by the equation:

$$\begin{aligned} \dot{S} = \lambda \left[h_{\theta_T} A_D \left(T_g - T_D \right) - \omega_{Na} h_{Na}^T - \omega_{Na_2} h_{Na_2}^{T_D} \right. \\ \left. - \omega_{NaCl} h_{NaCl}^{T_D} - \omega_{Na_2Cl_2} h_{Na_2Cl_2}^{T_D} + \epsilon \tau A_D \left(T_D^4 - T_w^4 \right) \right] \end{aligned} \quad (36)$$

and λ , the number of droplets per unit volume, is:

$$\lambda = G_{DI} / 4/3 \pi r_{DI}^3 \rho_{DI} V_D \quad (37)$$

The gas temperature can be obtained from the enthalpy flux, $C_g V_g \tilde{H}_g$, in conjunction with the gas composition calculation (as described below) since

$$\tilde{H}_g = \sum_i x_i^g h_i^g \quad (38)$$

and

$$C_g = P/R T_g \quad (39)$$

The gas velocity can be calculated directly from the argon continuity equation:

$$v_g = \frac{(x_{Ar}^g C_g v_g)_{initial}}{x_{Ar}^g C_g} \quad (40)$$

Under the assumptions of the model, the gas phase is always at equilibrium. Consequently, the composition can be obtained by solving the complex equilibria. For these calculations, silicon will be assumed to be in the gaseous state at all positions. During the thermal treatment, the gas phase can contain the following twenty three species: Si, Si₂, Si₃, SiCl₄, SiCl₃, SiCl₂, SiCl, SiHCl₃, SiH₂Cl₂, SiH₃Cl, H, H₂, SiH, SiH₄, HCl, Cl, Cl₂, Na, Na₂, NaH, NaCl, Na₂Cl₂ and Ar. The equilibrium constant method was used to solve the complex equilibria. This formulation is based on substitution of the equilibrium constant equations into the conservation equations and has been previously described in detail.¹²

The solution to the various equations requires expressions for the thermodynamic and transport properties. Appropriate expressions and values of the required enthalpies, heat capacities and equilibrium constant are available in thermochemical compilation.^{10,13}

The viscosity, thermal conductivities, and binary diffusivities can be calculated from the kinetic theory of gases.¹⁴ All properties are evaluated at the film temperature and concentration.

The simultaneous solution of the five droplet and two gas differential equations in conjunction with the twelve flux equations, the five gas phase equilibrium equations, the enthalpy flux equation and the various property equations will yield the temperature, composition and velocity of both the gas and droplet. A computer program based on standard numerical techniques was formulated to solve the above system of equations.

9.3.3 Results

Initial calculations with the low temperature reaction model showed that the temperature of the droplets rapidly rises to the boiling point of sodium. As previously discussed, the reaction model has been formulated on the basis that vaporization of sodium does not take place during the reaction. Acceptable droplet temperatures were achieved if a maximum of 10% of the SiCl_4 required, i.e., $f = 0.1$, was introduced into the gas stream at the entrance of the reaction section. The extent of reaction as a function of axial distance for the case in which $f = 0.1$ is shown in Figure 9.4. The various flowrates given in the figure correspond to a silicon production rate of 200 lb/hr. The results indicate that the maximum possible conversion is achieved in a very short distance, approximately 6 cm. The droplet temperature corresponding to this conversion is 950°K.

The results of a calculation using the thermal treatment model are shown in Figure 9.5. Based on the above reaction model results, the initial droplet is only 10% converted and 90% of the required SiCl_4 is introduced at the entrance of the thermal treatment section. These calculations indicate that the necessary fusion and vaporization which result in collectable liquid silicon droplets occurs in an acceptable reactor length. In parallel with the thermal treatment,

Curve 693968-A

Figure 9.4 - Extent Of Reaction, ξ , As A Function Of The Axial Distance For The Reaction Model

Figure 9.5 - Temperature And Radius Results For Droplets With An Initial Sodium Flowrate Of 3.6 Mols/s, An Initial Silicon Tetrachloride Flowrate Of 0.9 Mols/s And 10% Conversion

vaporized sodium reacted with SiCl_4 to form fine droplets of silicon. The fine droplets can be collected by the larger droplet provided that a scavenging mechanism is an effective means of collection. Calculations based on available information indicate that fine droplet collection by scavenging would require unreasonably long reactor length. For this reason the arc heater reduction of SiCl_4 carried out by partial low temperature reaction followed by a thermal treatment in which fine droplets are produced cannot be considered viable at the present time. This does not infer that fine droplets will indeed form in the actual process. It may be that reaction paths, in which either a majority of the conversion occurs during the low temperature reaction or unreacted SiCl_4 is added after the thermal treatment, can be considered as acceptable routes for the heterogeneous reduction of SiCl_4 by sodium.

9.4 Reactor Design

As a result of work accomplished under the Product Separation Task, it was concluded that the design will be based upon the condensation analysis. The associated design work is reported in Section 4.2.2. Since the reactor wall heat fluxes are considerably higher than the previous lower temperature process, additional considerations are made with respect to the shell configuration and final material selection. Similar considerations are being given to the refractory liner design. This design effort will be reported here and in the future quarterly reports under the section entitled Plasma Reactor Design.

TABLE 9.3

NOMENCLATURE (For Heterogeneous Reaction Analysis)

A_D	= Surface area of droplet
C_f	= Film molar density, i.e., P/RT_f
C_g	= Molar density of gas
$\bar{C}_{PD}^i$	= Molar heat capacity of species i in droplet
$\bar{C}_P^i$	= Molar heat capacity of species i in gas
$\bar{C}_P^D$	= Molar heat capacity of droplet
D_{ij}	= Binary diffusion coefficient
D_{i-M}	= Effective binary diffusivity
f	= Fraction of stoichiometric feed ratio of $SiCl_4$ to Na
f_i^M	= Fraction of i melted
G_D, G_{DI}	= Molar flux and initial molar flux of droplets, respectively
ΔG_i^0	= Standard Gibbs free energy of formation of species i at the droplet temperature
h	= Uncorrected heat transfer coefficient
$h_{i(c)}^{T_D}$	= Enthalpy of condensed species i at droplet temperature
$h_i^{T_D}$	= Enthalpy of gas phase species i at droplet temperature
h_i^T	= Enthalpy of gas phase species i at gas temperature
h_i^M	= Heat of fusion of species i
$\bar{H}_g$	= Molar enthalpy of gas
k_{i-M}	= Multicomponent uncorrected mass transfer coefficients

k_i	= Thermal conductivity of species i
K_i	= Equilibrium constant for species i
N_i^D	= Moles of species i in droplet
N_i^{Do}	= Initial moles of species i in droplet
N_i, N_j	= Molar flux of species i and j
N_{Na}^o	= Initial moles of Na in droplet
$N_{Na}(t)$	= Moles of Na in droplet at any time t
Nu_{i-M}	= Mass transfer Nusselt number (= 2)
P_T	= Total pressure
R	= Gas constant
r_d	= Droplet radius
r_{DI}	= Initial droplet radius
$\dot{S}_D$	= Heat lost per unit volume to the droplets
T_D	= Droplet temperature
T_g	= Gas temperature
T_i^M	= Melting temperature of species i
V_D	= Droplet velocity
V_g	= Gas velocity
ω_i	= Molar flow of species i and j
x_i^s	= Vapor mole fraction of species i at droplet surface
x_i^g	= Mole fraction of species i in gas
x_i^f	= Film mole fraction of species i
x_i^D	= Mole fraction of species i in droplet

y_i^s = Vapor mole fraction of species i at droplet surface
 y_i = Mole fraction of species i in gas
 Z = Axial position
 θ_{i-M}, θ_T = Mass and heat transfer correction factor
 ϕ_{i-M}, ϕ_T = Rate factors (equations 24 and 30)
 ρ_D = Molar density of droplets
 ρ_{DI} = Initial molar density of droplets
 ρ_i = Molar density of species i
 ϵ = Total emissivity of droplets
 τ = Stefan-Boltzman constant
 λ = Droplet number density (equation 37)
 ξ = Extent of reaction of droplet

10. CONCLUSIONS

- System Purity Analyses have indicated that only phosphorus, aluminum, and manganese concentrations are reduced during the arc heater-silicon process based on the sodium reduction scheme; while the impurity concentrations of boron, chromium, copper, iron, molybdenum, titanium, vanadium, and zirconium, are approximately the same for the feedstock impurity content versus the silicon product level.
- Based on the revised economic analysis for a homogeneous reaction mode, the arc heater process for silicon production can meet the 1985 DOE/JPL cost goal of \$10/kg of silicon.
- Preliminary silicon vapor measurements using the laser absorption technique indicates that silicon vapor can be measured accurately in the Kinetics experiment.
- Adequate methods (sieving and particle impactors) have been identified for sodium particle measurement during the Injection Techniques study.
- Based upon the Product Separation Analyses; a) Silicon can be effectively separated from the reactor gas stream via a condensation operating mode. b) The condensation mode was selected as the basis for the final reactor design. c) The basic reactor configuration has not changed from that previously described.

11. PROJECT STATUS

11.1 Present Status

The System Purity Analysis was completed during the quarter thus, all aspects of the Process Engineering Analysis have been accomplished. Detailed design of the system components for the experimental verification unit continued as well as initiating procurement of system components. The complimentary research programs (i.e., Kinetics, Injection Techniques, and Reaction Demonstration) continued with the completion of designs and initiating procurement and fabrication of the respective experimental hardware. The Product Separation Analysis was completed and results of this analysis were presented to JPL at a design review in February.

11.2 Future Activity

- Complete detailed design for the experimental verification unit and the associated subsystems.
- Continue procurement of the system components for the verification unit.
- Complete fabrication and assembly of the experimental hardware for the complimentary research programs.
- Initiate testing for the respective research programs.

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APPENDIX

TASK (09) INJECTION TECHNIQUES

Test Plan

1.0 This test plan is designed to provide a systematic approach to reach the task objective of evaluating and characterizing candidate injectors for the silicon production reactants.

2.0 Sodium Injection

A sonic atomizing nozzle, Sonicore Model 312 from Sonic Development Corporation, Upper Saddle, New Jersey, has been selected as the prime candidate for sodium injection. Two of these nozzles have been purchased for evaluation in this task.

2.1 Water Test (Video Monitor)

This test will consist of operating the Sonicore nozzle with water and nitrogen to investigate large droplet formation, angle of spray and general nozzle operating characteristics.

A television recording system Tm Instar will be used for this purpose as well as visual observations. Water and nitrogen flowrates will be varied to determine effective operating range. TV recordings will be played back in slow motion to study the nozzle performance.

2.2 Water Test (Collection Shroud)

This test will be conducted with the Sonicore nozzle again using water and nitrogen. A metal shroud will be positioned around the nozzle so that large droplets will be collected while the small droplets will not. A measurement of the collected water will be compared to the total water flow in order to quantify the mass of large droplet formation.

2.3 Sodium Test #1

This initial sodium test with the Sonicore nozzle will use argon as the atomizing gas. The purpose of this test is to shakedown the test system and determine gross effects of nozzle operation with sodium. The test procedure will be:

- Precool the test chamber and gas atmosphere in the chamber.
- Start hot argon flow to the nozzle then quickly inject a 1 sec burst of Na then immediately stop argon flow.
- Collect frozen Na particles, transfer to glove box and analyze.

2.4 Sodium Test #2

This test will be the same as sodium test #1 except more instrumentation will be used. Either high speed photography or the television Instar system will be used to record the test. A cascade impactor will be utilized for small particle analysis.

2.5 Sodium Test #3

This test will be the same as sodium test #2 except with a longer sodium flow time determined from above tests.

2.6 Sodium Test #4

This test will be the same as sodium test #3.

2.7 Sodium Test #5

This will be a long duration test (up to 1 minute) to determine if nozzle operating characteristics are uniform and consistent.

3.0 Silicon Tetrachloride Injection

Hydraulic atomizing nozzles, model 1/4 LNN6, from Spraying Systems Co., Wheaton, Illinois were selected as the prime candidate

for silicon tetrachloride (SiCl_4) injection. Ten of these nozzles will be required to supply the desired SiCl_4 flowrate into the chemical reactor. Two of these nozzles are being procured for injection techniques testing.

3.1 Water Test (Video Monitor)

This test will be the same as the test described in Section 2.1 except the model 1/4 LNN6 hydraulic nozzle will be used instead of the Sonicore nozzle.

3.2 Water Test (Collection Shroud)

This test will be the same as the test described in Section 2.2 except with the 1/4 LNN6 hydraulic nozzle.

3.3 SiCl_4 Test #1

SiCl_4 will be injected into the test chamber through the 1/4 LNN6 hydraulic atomizing nozzle at its normal operating pressure and flowrate. Either high speed photography or the television Instar system will be used to record the test.

3.4 SiCl_4 Test #2

SiCl_4 test #1 will be repeated with any required modifications for more complete analysis.

4.0 Na/ SiCl_4 Coinjection Testing

The Sonicore Model 312 nozzle utilizes a gas sonic shock wave to atomize the liquid. Because SiCl_4 has a low boiling point (57°C) it is possible to use the SiCl_4 in the gaseous state to produce the sonic shock wave. Thus coinjection of the Na and SiCl_4 through the same nozzle may be possible.

4.1 Coinjection Test #1

The purpose of this test is to investigate the feasibility of coinjecting Na and SiCl_4 . A mixture of argon, 90%, and SiCl_4 vapor, 10%, will be flowed through the nozzle, then a 1 sec.

burst of Na will be introduced. High speed photography will be used to study the reaction. Reaction products will be analyzed and buildup of reaction product on the nozzle will be investigated.

4.2 Coinjection Test #2

This test will be the same as coinjection test #1 except the fluid ratios will be adjusted after analysis of test #1.

4.3 Coinjection Test #3

This test will be the same as coinjection test #2 except that adjustments will be made after analysis of test #2.