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

Low Cost Silicon Solar Array Project, Silicon Materials Task;
Quarterly Technical Report, October–December 1977

By
W. 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

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LOW COST SILICON SOLAR ARRAY PROJECT

SILICON MATERIALS TASK

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

Contract No. 954589

Quarterly Technical Report: October-December, 1977

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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

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, thus work on many of the tasks has just commenced during the last quarter of 1977.

2. PROGRAM SUMMARY

Since the initiation of Phase II of this program in October 1977, tasks were established for the purpose of: completing detailed system designs, procurement, fabrication, assembly and installation of the test system at the Arc Heater Laboratory. The preliminary subsystem designs were completed during Phase I while the actual detailed designs for total system implementation are being conducted during the early stages of Phase II. The systems that are undergoing detailed design have been divided into two main categories: 1) system components and 2) test system - laboratory integration. The system components include the detailed designs for the following systems: a) instrumentation and control, b) plasma reactor/separator, c) SiCl_4 storage and injection, d) sodium storage and injection, e) silicon product collection, and f) effluent disposal. Included in the test system - laboratory integration category are a) system electrical distribution, b) arc-heater gas system, c) cooling water system, and the d) gas burnoff stack.

During the quarter, the process economics for the process were completed and presented to Jet Propulsion Laboratory in the Design Review held at Westinghouse on November 11. The process economics were compiled for a 1000 MT/year plant to produce silicon continuously based on a recycle-type process. Equipment-system costs were assembled in addition to estimations of fixed capital and silicon product costs. For a 1000 MT/year of silicon, an estimated product cost of \$9.76/kg Si (1975 dollars) was calculated for the arc heater-sodium reduction of SiCl_4 process to produce silicon.

Effort on the System Purity Analysis continued via calculations of the equilibrium compositions of liquid silicon produced by the arc heater reduction of SiCl_4 with the separate impurities in the feedstocks (Na or H_2) as follows: iron, chromium, manganese, aluminum, vanadium, phosphorus, and boron were performed. Results are presented for these potential impurities as to the predicted concentrations in the silicon product.

The design of the experimental set-up was essentially completed for the Kinetics experiments. It offers flexibility with regard to the reactant injection system and gas temperature control. An experiment has been set up for testing of the silicon vapor detection technique. Two alternative methods will be tested, one involving optical absorption, the other fluorescence measurements. Three different diagnostic techniques for particle size determination are being investigated: Optical scattering, high temperature impactor in the gas stream, and extracting and diluting a gas sample for measurement under ambient conditions.

Design of the system for Injection Technique studies was initiated during the reporting period. An existing stainless steel chamber with an internal volume of 75 liters (2.65 ft^3) has been identified for use as the test chamber. This vessel is undergoing modification to meet the injection techniques test requirements.

The sodium supply tank for these studies has been designed and is being fabricated. The nozzle holder design is near completion. A schematic arrangement of the test system was completed and procurement of components is underway. Particle size measurement technique selection was initiated and is being integrated into the test system design.

The design of a laboratory-scale system to demonstrate the high temperature reaction between Na and SiCl_4 has been formulated. The principal components of the system are (1) a silicon carbide, Globar furnace with a maximum temperature capability of 1925°K , (2) a silicon tetrachloride generator with associated flow train, (3) a sodium vapor generator with associated flow train, and (4) a product collector. Heat transfer and residence time calculations have been carried out to determine the reaction chamber size and the range of reactant flow rates. On this basis, a Harper Globar Furnace has been ordered. Design of both the SiCl_4 and Na vapor generation systems has been initiated.

3. PROCESS ENGINEERING ANALYSIS

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

3.1 Summary

During the quarter, the process economics for this task were completed and presented to Jet Propulsion Laboratory in the Design Review held at Westinghouse on November 11. With the exception of the System Purity Analysis (0211), the Task 5 effort was completed. The process economics were compiled for a 1000 MT/year plant to produce silicon continuously based on a recycle-type process. Equipment-system costs were assembled in addition to estimations of fixed capital and silicon product costs. For a 1000 MT/year of silicon, an estimated product cost of \$9.76/kg Si (1975 dollars) was calculated for the arc heater-sodium reduction of SiCl_4 process to produce silicon. Therefore, the Westinghouse process is projected to meet the DOE/JPL cost goal for 1986 of \$10/kg Si.

Effort on the System Purity Analysis continued via calculations of the equilibrium compositions of liquid silicon produced by the arc heater reduction of SiCl_4 with the separate impurities in the feedstocks (Na or H_2) as follows: iron, chromium, manganese, aluminum, vanadium, phosphorus, and boron were preformed using the previously described complex equilibria analysis (computerized).² Results are presented for these potential impurities as to the predicted concentrations in the silicon product.

3.2 System Purity Analysis

Two of the potential sources of metallic impurities in the arc heater production of silicon are the SiCl_4 and Na feedstocks. The maximum impurity level attainable in the liquid silicon for a given feedstock impurity level will occur under equilibrium conditions. Consequently, the upper bound for any specific impurity was obtained by modifying the complex equilibria calculations that were carried out in Phase I of this contract.² These changes involve expanding the system considered from the Si-H-Cl-Na-Ar system to the

Si-H-Cl-Na-Ar-X (where X is Fe, Cr, Al, etc.) system and permitting a liquid silicon solution to form. Measured activity coefficients of the various impurities in dilute liquid silicon are also required for the calculations. Because the range of impurity concentrations are small, the calculations which were carried out on a binary basis for liquid silicon solution, also apply to the multi-component situation.

The free energy minimization computer program CHEMEQ, which was previously used in Phase I, has been appropriately modified so that complex equilibria involving condensed phase solutions can be solved.

The appropriate activity coefficients for the selected impurities were obtained from either the literature or calculated as discussed previously.³ The specific impurities that were analyzed during the quarter include: a) iron, b) chromium, c) manganese, d) aluminum, e) vanadium, f) phosphorus, and g) boron. Results of the complex equilibrium analysis which predicts the maximum concentration of a specific impurity in the silicon product is presented in Table 3.1. In addition, the initial conditions for both the Na and H₂ reductant cases are listed in the table. Also presented are the ranges of the initial amount of the impurity in the feedstock, the resultant impurity content in the liquid silicon, and the impurity mole fraction in the silicon liquid.

Based on the data presented in Table 3.1, for the sodium reductant case essentially all of the iron, chromium, vanadium, and boron is dissolved into the silicon product; while for manganese, aluminum and phosphorus the final concentrations are reduced to approximately 74%, 15% and by an order of magnitude respectively as compared to the initial amount. In the case of the H₂ reduction of SiCl₄, the initial impurity content is essentially equal to the final content for the following impurities: vanadium (~ 100%), iron (~ 95%), chromium (~ 82%). However, for the H₂ reduction when considering the

TABLE 3.1 - Results Of System Purity Analysis

<u>Impurity</u>	<u>Reductant</u>	<u>Temp.</u> (°K)	<u>Impurity</u> <u>Content</u> <u>in Feedstock</u> (g-atm)	<u>Impurity</u> <u>Content</u> <u>in Si(l)</u> (g-atms)	<u>Impurity</u> <u>Mole</u> <u>Fraction</u> <u>in Si(l)</u>
<u>Iron</u>	Na*	1900	1.0×10^{-4}	9.9×10^{-5}	1.0×10^{-4}
			1.0×10^{-5}	9.9×10^{-6}	1.0×10^{-5}
			1.0×10^{-6}	9.9×10^{-7}	1.0×10^{-6}
	H ₂ **	2200	1.0×10^{-2}	9.43×10^{-3}	2.6×10^{-2}
			1.0×10^{-3}	9.41×10^{-4}	2.8×10^{-3}
			1.0×10^{-4}	9.61×10^{-5}	3.4×10^{-4}
<u>Chromium</u>	Na*	1900	1.0×10^{-4}	9.99×10^{-5}	1.0×10^{-4}
			1.0×10^{-5}	9.99×10^{-6}	1.0×10^{-5}
			1.0×10^{-6}	9.99×10^{-7}	1.0×10^{-6}
	H ₂ **	2200	1×10^{-2}	8.81×10^{-3}	2.29×10^{-2}
			1×10^{-3}	8.13×10^{-4}	2.38×10^{-3}
			1×10^{-4}	8.11×10^{-5}	2.40×10^{-4}
<u>Manganese</u>	Na*	1900	1×10^{-4}	7.46×10^{-5}	7.52×10^{-5}
			1×10^{-5}	7.14×10^{-6}	7.23×10^{-6}
			1×10^{-6}	7.56×10^{-7}	7.62×10^{-7}
	H ₂ **	2200	1×10^{-2}	7.45×10^{-5}	2.18×10^{-4}
			1×10^{-3}	7.31×10^{-6}	2.16×10^{-5}
			1×10^{-4}	7.30×10^{-7}	2.16×10^{-6}
<u>Aluminum</u>	Na*	1900	1×10^{-4}	1.31×10^{-5}	1.31×10^{-5}
			1×10^{-5}	1.85×10^{-6}	1.86×10^{-6}
			1×10^{-6}	1.32×10^{-7}	1.33×10^{-7}
	H ₂ **	2200	1×10^{-2}	1.61×10^{-5}	4.71×10^{-5}
			1×10^{-3}	1.59×10^{-6}	4.70×10^{-6}
			1×10^{-4}	1.59×10^{-7}	4.70×10^{-7}

TABLE 3.1 (Continued)

<u>Impurity</u>	<u>Reductant</u>	<u>Temp.</u> (°K)	<u>Impurity</u> <u>Content</u> <u>in Feedstock</u> (g-atm)	<u>Impurity</u> <u>Content</u> <u>in Si(l)</u> (g-atms)	<u>Impurity</u> <u>Mole</u> <u>Fraction</u> <u>in Si(l)</u>
<u>Vanadium</u>	Na*	1900	1×10^{-4}	1.00×10^{-4}	1.01×10^{-4}
			1×10^{-5}	1.00×10^{-5}	1.01×10^{-5}
			1×10^{-6}	1.00×10^{-6}	1.02×10^{-6}
	H ₂ **	2200	1×10^{-2}	9.99×10^{-3}	2.79×10^{-2}
			1×10^{-3}	9.99×10^{-4}	2.94×10^{-3}
			1×10^{-4}	9.99×10^{-5}	2.96×10^{-4}
<u>Phosphorus</u>	Na*	1900	1×10^{-4}	4.41×10^{-7}	4.46×10^{-7}
			1×10^{-5}	1.11×10^{-7}	1.13×10^{-7}
			1×10^{-6}	1.99×10^{-8}	2.02×10^{-8}
	H ₂ **	2200	1×10^{-2}	6.73×10^{-6}	1.99×10^{-5}
			1×10^{-3}	1.73×10^{-6}	5.13×10^{-6}
			1×10^{-4}	3.13×10^{-7}	9.27×10^{-7}
<u>Boron</u>	Na*	1900	1×10^{-4}	9.97×10^{-5}	1.01×10^{-4}
			1×10^{-5}	9.97×10^{-6}	1.01×10^{-5}
			1×10^{-6}	1.00×10^{-6}	1.02×10^{-6}
	H ₂ **	2200	1×10^{-2}	5.13×10^{-3}	1.52×10^{-2}
			1×10^{-3}	5.24×10^{-4}	1.55×10^{-3}
			1×10^{-4}	5.23×10^{-5}	1.55×10^{-4}

*Initial Conditions: 4 mols Na, 1 mol SiCl₄, 2.67 mols H₂, 0.67 mol Ar

**Initial Conditions: 25 mols H₂, 1 mol SiCl₄

remaining four impurities that were analyzed, a decrease was noted comparing initial impurity concentration versus the resulting silicon impurity content (i.e., both manganese and aluminum are reduced to only about 1% of the initial amounts, boron is reduced to approximately 53% of the initial content, and phosphorus is reduced by an order of magnitude).

The relative behaviour of the various impurities is a result of the stability of the impurity chlorides as well as the activity coefficient of the metals in liquid silicon. The gaseous chlorides of aluminum (for example) are more stable (per gram-atom of chlorine) than that of manganese which, in turn, is more stable than those of chromium. In addition, the activity coefficient in liquid silicon at infinite dilution is greatest for aluminum and least for chromium. For a given element, less impurity is present in the silicon for hydrogen reduction because HCl is much less stable than NaCl thus permitting more of the gaseous impurity chloride to form. The effect of temperature is due to the larger decrease in the free energy of formation of the sodium chloride with increasing temperature.

The results for phosphorus show that the impurity concentrations in the liquid silicon are orders of magnitude less than those in the feedstocks. On the other hand, essentially all the boron present in the feedstocks ends up in the liquid silicon for Na reduction, while approximately 53% of the initial boron is present in the liquid silicon for H_2 reduction. On this basis, boron feedstock impurity levels will have to be strictly controlled while much more phosphorus can be tolerated in the feedstocks.

It must be emphasized that these results represent only the maximum amount of impurity possible in the liquid since the analysis is based on the assumption of equilibrium. Under actual conditions, the amount of impurity may be much less depending on kinetic factors. These results will be used as general guidelines in specifying feedstock impurities.

During the upcoming quarter, impurity analyses will be performed for molybdenum, zirconium, copper, and titanium.

3.3 Recycle Process For Silicon Production

A flowsheet for the Westinghouse process for continuous silicon production is presented in Figure 3.1. This process is based on the arc heater - sodium reduction of SiCl_4 to produce liquid silicon and the co-product (NaCl) vapor. Additional unit operations for SiCl_4 production (chlorination), SiCl_4 purification (distillation), NaCl electrolysis to produce Na and Cl_2 for reuse in the process, and a gas recycle system for the arc heater gases are presented in the flowsheet. This is the preliminary system design that was evaluated and costed for the process economic analysis based on producing 1000 MT/year of silicon.

The subsystems that are interfaced with the plasma reactor/separator (see Figure 3.2) for silicon production (i.e., sodium feed system, SiCl_4 feed system, arc heaters, arc heater gas system, and the effluent handling system) were designed and costed previously as part of Phase I of the project. These subsystems have been discussed and pictorially depicted in previous reports.¹⁻⁴

3.4 SiCl_4 Production

Individual flowsheets were prepared for each of the unit operations. Figure 3.3 presents the system proposed for SiCl_4 production. This process is based on information received from Van DeMark Chemical Company. In this process, purchased silicon carbide (SiC) is reacted with gaseous chlorine (obtained from the NaCl electrolysis cells) to produce the raw SiCl_4 . Descriptions of reactant feed rates, process equipment and vessels were obtained from Van DeMark. This information was used to determine equipment and vessel sizes required for the Westinghouse process. In addition, vendors were contacted to obtain price information for the SiCl_4 production equipment. In order to produce 1000 MT/year of silicon, the SiCl_4 requirement is approximately 6000 MT/year. The Van DeMark

Figure 3.1 - Process Flow Sheet Of Westinghouse Process For Continuous Silicon Production

Figure 3.2 - Preliminary Layout Of The SiCl_4 Reduction System For Silicon Production

equipment was scaled to provide ~7000 MT/year production capacity for SiCl_4 . The purchased equipment costs and piping for SiCl_4 production were estimated at \$324.3K (1977 dollars).

3.5 SiCl_4 Purification

The SiCl_4 that is produced in the chlorinator will require purification to remove undesirable impurities. An analysis was conducted by CYM Engineering to develop a preliminary design for SiCl_4 purification via distillation. A flowsheet based on the CYM study is shown in Figure 3.4. The purification unit consists basically of two distillation columns plus auxiliary equipment (e.g. pumps, condensers, accumulators, reboilers, and holding tanks). This flowsheet is based on Case B of the CYM study which enables the removal of both p- and n-type impurities from the SiCl_4 in addition to the undesirable metals (Ti, V, Fe), thus yielding a very versatile system design. A calculated analysis by CYM for the purified SiCl_4 product (SiCl_4 storage) yielded the following impurity levels:

	<u>ppb</u>
Boron	1
SiCl_4	remainder
Phosphorous	2
Titanium	neg.
Vanadium	neg.
Iron	neg.

The CYM analysis provided design information on utility requirements and purchased equipment costs that were factored into the 1000 MT/year economic analysis. For the SiCl_4 purification unit (Case B) depicted in Figure 3.4, the purchased equipment costs and piping were estimated by CYM to be \$219.4K (1977 dollars).

3.6 NaCl Electrolysis System

Since the reaction co-product, NaCl, can be separated into its elemental constituents, Na and Cl_2 , via the electrolysis of NaCl, the unit operation of NaCl electrolysis is beneficial to

the system design. By producing Na and Cl_2 within the overall silicon production process, the need to purchase raw materials or reactant is minimized. The Na that is produced is recycled back to the arc heater-reactor for the SiCl_4 reduction and the Cl_2 is compressed and stored for subsequent use in the chlorination of SiC to produce the SiCl_4 reactant. A process flowsheet for NaCl electrolysis is presented in Figure 3.5. The information for NaCl electrolysis was obtained from RMI Corporation primarily. However, additional sources of information were Ethyl Corp., DuPont, and available technical literature.

Each of the above sodium producers have provided a typical analysis of their commercial grade sodium. These analyses are shown in Table 3.2. In addition, typical trace elements found in commercial sodium are reported in Kirk-Othmer "Encyclopedia of Chemical Technology"⁵ and are reproduced in Table 3.3. It is the consensus of the three sodium producers that the majority of the impurities in the sodium come from the feed salt used in the production of sodium. After initial start-up of the Westinghouse process, very pure sodium chloride will be produced as a by-product which will be recycled to produce sodium. In addition, a high purity salt (see Table 3.4) can be purchased for use as the make-up salt for the sodium production unit. For these reasons it can be assumed that state-of-the-art electrolysis for NaCl can be used to produce sodium for the reduction of silicon tetrachloride to silicon and sodium chloride.

Actual equipment costs for the components of the electrolysis system were not available from the above sources. However, the fixed capital for an NaCl electrolysis plant that was actually built was obtained from the literature.⁶⁻¹⁰ Since this fixed capital included the various cost items as listed in Table 3.7, the capital was added to the fixed capital subtotal for the remaining systems of the plant. The capacity of the Na plant that was costed into the fixed capital was approximately equal to the 3300 MT/year

Figure 3.3 - Chlorination Unit (Based On Information From Van DeMark Co.)

Figure 3.4 - SiCl_4 Purification Unit (Based On Analysis By CYM Engineering Co.)

Figure 3.5 - NaCl Electrolysis Unit (Based On RMI Information)

TABLE 3.2

Typical Analysis Of Commercial Grade Sodium

	<u>E.I. DuPont</u>	<u>Ethyl Corp.</u>	<u>RMI</u>
Impurity			
Oxygen		26 ppm	
Calcium	300 ppm	400	400 ppm
Chlorides	30	<15	50
Boron	1		
Iron		3	
Nitrogen		<3	
Phosphate		<5	
Sulfate		<20	
Heavy Metals (Bi,Cu,Pb,Sn)		<5	
Aluminum		<10	
Barium		10	
Lithium		<10	
Magnesium		20	
Manganese		<10	
Nickel		<10	
Potassium	350	600	
Strontium		30	

TABLE 3.3

Trace Elements in Commercial Sodium

Impurity	Parts per million	
	KAPL ^a	DP ^b
aluminum	8	1-4
barium	2	
beryllium	1 ^c	
bismuth	10 ^c	
boron	4	0.1-0.17
cadmium	1	<0.05
calcium, in regular-grade sodium	190	200
in reactor-grade sodium	2	2-8
cerium	2	
cesium	5	5
chlorides	30	30
cobalt	2	0.11-0.21
copper	2	
gold		<2
indium	2	7-13
iron	2	
lead	1	≤1
lithium	17	<0.06-0.36
magnesium	5	
manganese	2	
mercury	4 ^c	
molybdenum	2 ^c	
nickel	2	
nitrogen		<3 ^d
palladium	5 ^c	
phosphorus	10	<1
potassium	100 ^c	86-180
rare earths		4
silicon	5	
silver	1	<2
strontium	5	
sulfur	14	1-6
tin	10 ^c	≤1
titanium	10 ^c	
tungsten		3-7
uranium	5	
vanadium	4	
zinc	1	2-5
zirconium and hafnium		2

NOTE: This table has been adapted from reference 83.

^a Analyses by Knowles Atomic Power Laboratory, General Electric Co., Schenectady, N.Y.

^b Analyses by Research Laboratory, E. I. du Pont de Nemours & Co., Inc., Niagara Falls, New York.

^c Analyses made, but no impurity detected. Values given are the sensitivity limits of the method used.

^d Total nitrogen, ie, dissolved gas plus nitrogen compounds in reactor-grade sodium.

Note: This Table Has Been Taken From Reference 5.

TABLE 3.4

The following information was reported by Diamond Crystal Salt Company.

NaCl	99.95%
Na_2SO_4	<.05%
Calcium	< 20 ppm
Copper	< 1 ppm
Iron	< 1 ppm

of sodium that is required for the Westinghouse process.¹⁰ The total fixed capital for the NaCl electrolysis system factored into the economic analysis was \$3,429K (1975 dollars).

3.7 Process Economics

The energy requirement for producing 1000 MT/year of silicon is presented in Table 3.5. This data was also used to compile the estimated product cost for the economic analysis.

In order to assemble the process economics for 1000 MT/year of silicon, the purchased equipment costs for the various subsystems and unit operations were required. Each of the subsystems was costed as reported in Table 3.6. The total of the purchased equipment costs was adjusted to January, 1975 dollars via the Marshall and Steven's cost index.¹¹ January, 1975, is the reference year for cost data according to Jet Propulsion Laboratory requirements.

After the purchased equipment costs were totalized, an estimation of fixed capital was determined. Table 3.7 presents estimation of fixed capital (1975 dollars) for the 1000 MT/year case based on the recycle process. The format and percentages of purchased equipment costs (PE) presented in Table 3.7 are taken from previous Lamar University Quarterly Reports prepared for Jet Propulsion Laboratory.^{11, 12} The fixed capital for the Westinghouse process to produce 1000 MT Si/year is \$9,865,700 (1975 dollars).

Based on a fixed capital of \$9,865.7K, a determination was made to estimate the product cost (without profit) in 1975 dollars. Table 3.8 presents a summary of the product cost estimation for a 1000 MT/year plant. As stated before, the format and percentages used to compile product costs were taken from previous Lamar University Quarterly Reports. The cost data used for utility costs (i.e. electricity, gas, steam, cooling water, etc.) were also based on Lamar University figures. The result of the product

TABLE 3.5

ENERGY REQUIREMENT: 1000 MT SI/YR (RECYCLE)

ELECTRICITY

- ARC HEATER/REACTOR @ 12	$\frac{\text{KW HR}}{\text{KG SI}}$	1508 kW
- NaCl ELECTROLYSIS @ 42.8	$\frac{\text{KW HR}}{\text{KG SI}}$	5354
- SiCl ₄ PURIFICATION		1.5
- PUMPS		200
- OTHER		<u>80</u>
TOTAL ELECTRICITY		7143.5 kW

STEAM

- SiCl ₄ PRODUCTION	253.9 MBTU
- SiCl ₄ PURIFICATION	539.6
- NaCl DRYING	<u>5553.9</u>
TOTAL STEAM	6347.4 MBTU

TABLE 3.6

PURCHASED EQUIPMENT COST -- 1000 MT Si/YR (RECYCLE)

<u>ITEM</u>	<u>COST, \$K</u>
CHLORINATION SYSTEM AND PIPING	324.3
SiCL ₄ PURIFICATION SYSTEM AND PIPING	219.4
ARC HEATER/REACTOR SYSTEM	339.4
REACTANT INJECTION SYSTEMS	100.7
GAS/SALT SEPARATOR AND PIPING	16.9
GAS RECYCLE, MAKE-UP AND BURNOFF	59.2
SILICON COLLECTION	145.3
COOLING WATER SYSTEM	40.2
ELECTRICAL SYSTEMS	<u>199.6</u>
TOTAL	1445.0

ADJUSTED TO 1975 \$1218.1

TABLE 3.7

ESTIMATION OF FIXED CAPITAL* 1000 MT Si/YR (RECYCLE)

<u>ITEM</u>		<u>\$K</u>
PURCHASED EQUIPMENT (PE)	100%	1218.1
INSTALL PURCH. EQUIP.	43%	523.8
INSTRUMENTATION & CONTROL	13.5%	164.4
BUILDING WITH SERVICES	23.5%	286.3
YARD IMPROVEMENTS	11.5%	140.1
SERVICE FACILITIES, INSTALLED	55%	670.0
LAND	6%	73.1
ENGR. AND SUPERVISION	32.5%	395.9
CONSTRUCTION EXPENSE	37.5%	456.8
CONTRACTOR'S FEE	19%	231.4
	SUBTOTAL	4160.0
ELECTROLYSIS PLANT (TOTAL FIXED CAPITAL)*		3429.0
		7589.0
	CONTINGENCY (30%)	2276.7
	FIXED CAPITAL*	9865.7

* 1975 DOLLARS

TABLE 3.8

ESTIMATION OF PRODUCT COSTS 1000 MT Si/YR (RECYCLE)

FIXED CAPITAL: \$9,865,700 (1975 DOLLARS)

	<u>\$/KG Si</u>
1. DIRECT MANUF. COST	
A. RAW MATERIALS	1.33
B. DIRECT OPERAT. LABOR (10 AT \$5.90 M-HR)	0.59
C. UTILITIES (\$.03/KW-HR)	1.81
D. SUPERVISION & CLERICAL (15% OF 1B)	0.09
E. MAINT. & REPAIR (10% OF FIXED CAPITAL)	0.99
F. OPERATING SUPPLIES (20% OF 1E)	0.20
G. LAB CHARGES (15% OF 1B)	0.09
H. PATENTS & ROYALTIES (3% OF PRODUCT COST)	<u>0.29</u>
	5.39
2. INDIRECT MANUF. COSTS	
A. DEPRECIATION (10% OF FIXED CAPITAL)	0.99
B. LOCAL TAXES (2% OF FIXED CAPITAL)	0.20
C. INSURANCE (1% OF FIXED CAPITAL)	0.10
D. INTEREST (8% OF FIXED CAPITAL)	<u>0.80</u>
	2.09
3. PLANT OVERHEAD (60% OF 1B + 1D + 1E)	1.00
4. TOTAL MANUF. COST (1 + 2 + 3)	8.48
5. GENERAL EXPENSES	
A. ADMINISTRATION (6% MANUF. COST)	0.51
B. DISTRIBUTION & SALES (6% MANUF.COST)	0.51
C. RESEARCH & DEVEL. (3% MANUF.COST)	<u>0.26</u>
	1.28
6. TOTAL COST OF PRODUCT, 4 + 5 (WITHOUT PROFIT)	\$9.76/KG Si

cost analysis yielded a silicon product cost (without profit) of \$9.76/kg Si (1975 dollars) which meets the 1986 DOE/JPL cost goal of \$10/kg Si. For comparison purposes, the fixed capital was calculated as a function of silicon production capacity and the results are listed in Table 3.9. In addition, an estimation of silicon product cost (without profit) in 1975 dollars was calculated as a function of production capacity. The results are presented in Table 3.10. The DOE/JPL cost goal for a 500 MT/year silicon plant is \$25/kg Si and the cost goal for the other capacities presented (1000, 1500, and 3000 MT) is \$10/kg Si. In all cases analyzed, the Westinghouse - arc heater process for silicon production meets the cost goals developed by DOE/JPL.

TABLE 3.9

COMPARISON OF SILICON PRODUCTION CAPACITY

VS.

TOTAL FIXED CAPITAL

<u>CAPACITY - MT/YR Si</u>	<u>TOTAL FIXED CAPITAL - K\$</u>	
	<u>1975 \$</u>	<u>1977 \$</u>
500 MT (BATCH)	2,720	3,227
1000 MT (RECYCLE)	9,866	11,703
1500 MT (RECYCLE)	12,583	14,926
3000 MT (RECYCLE)	19,073	22,625

TABLE 3.10

ESTIMATION OF SILICON PRODUCT COST * (\$/kgSi)

COST ITEM	PRODUCTION CAPACITY (MT/YR)			
	500 MT	1000 MT	1500 MT	3000 MT
	BATCH	RECYCLE	RECYCLE	RECYCLE
DIRECT MANUF.	\$10.19	\$5.39	\$4.81	\$4.41
INDIRECT MANUF.	1.09	2.09	1.73	1.31
PLANT OVERHEAD	<u>0.53</u>	<u>1.00</u>	<u>0.72</u>	<u>0.53</u>
TOTAL MANUF. COST	11.81	8.48	7.26	6.25
GENERAL EXPENSE	<u>1.78</u>	<u>1.28</u>	<u>1.10</u>	<u>0.95</u>
TOTAL PRODUCT COST (\$/kgSi) WITHOUT PROFIT	13.59	9.76	8.36	7.20

* 1975 DOLLARS

4. TEST SYSTEM PREPARATION

4.1 Task Description and Summary

Since the initiation of Phase II of this program in October 1977, tasks were established for the purpose of: completing detailed system designs, procurement, fabrication, assembly and installation of the test system at the Arc Heater Laboratory. The preliminary subsystem designs were completed during Phase I while the actual detailed designs for total system implementation are being conducted during the early stages of Phase II. Following the detailed design effort, component procurement, fabrication, etc. will commence. The systems that are undergoing detailed design have been divided into two main categories: 1) system components and 2) test system - laboratory integration. The system components include the detailed designs for the following systems:

a) instrumentation and control, b) plasma reactor/separator, c) SiCl_4 storage and injection, d) sodium storage and injection, e) silicon product collection, and f) effluent disposal. Included in the test system - laboratory integration category are a) system electrical distribution, b) arc-heater gas system, c) cooling water system, and d) the gas burnoff stack.

A preliminary layout of the test system areas within the Arc Heater Laboratory are shown in Figure 4.1. The current status for both categories of test system components and test system - laboratory integration are presented in Sections 4.2 and 4.3, respectively.

4.2 System Components

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

Time objectives were established and milestone charts for this subtask were prepared and integrated into the detailed milestone chart for the project.

Information on control and instrumentation requirements was gathered from project personnel responsible for the

Figure 4.1 - Test System Layout At The Arc Heater Laboratory - Building MX-10

design and operation of the various subsystems. A master listing was begun detailing descriptions of sensors/monitors including data readout at both local and control room locations, visual and recorded data, need for interlocks and alarms, description of devices, signal types, quantity and ranges required.

To insure complete coverage of the project, as far as control and instrumentation is concerned, the C&I system has been subdivided into seven separate subsystems.

1. Reactant Storage and Feed (Na and SiCl_4)
2. Gas Storage and Feed
3. NaK Heating and Cooling
4. Cooling Water
5. Plasma Reactor including arc heaters
6. Product Separation and Collection
7. Effluent Separation including Gas Burnoff
Stack and Sodium Chloride Disposal

As each of the subsystem (Plasma Reactor, Sodium Storage and Feed, etc.) detailed designs are finalized, the Control and Instrumentation requirements will be finalized and integrated into the subsystem. In the interim, component specification has been initiated and the writing of these specifications will be assisted by the Manufacturing Electronics Group located at the Westinghouse Research Center.

A preliminary control logic diagram has been developed for the operation of the sodium storage system. This diagram will be used to define and specify a programmable process controller. This device will be used to control the melting of sodium contained in drums and to sequentially drain the drums of molten sodium into a base storage tank.

During the upcoming quarter, emphasis will be placed on completing the individual unit requirements and component specifications. In addition, panel layouts for locating components will be made and panel size requirements will be specified.

4.2.2 Plasma Reactor - Separator (C. B. Wolf)

Early in this reporting period a milestone schedule was prepared for planning, fabricating, and installation of the complete reactor system. Included in the reactor system are the Arc Heaters, plenum, reactant injection sections, reaction chambers, cyclone, and all the associated refractory liners. The drafting effort necessary for interfacing the existing Arc Heater design with the plenum and reaction chambers for this process have been completed. A preliminary sketch of the test laboratory as shown in Figure 4.1 includes the reactor - separator assembly as presently designed.

Final drafting work required for manufacturing drawings of reactor - separator components is being deferred to allow for possible design changes which could result from the product separation analysis being carried out in Task 11 (see Section 9). Parameters which could be affected are reaction chamber diameters and lengths, the reactant materials injection locations, and refractory lining design.

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

During this quarter, a number of activities were initiated which will lead to the complete SiCl₄ subsystem assembly within the time framework as detailed in the program milestone schedule. Efforts which were completed and/or initiated include:

- Preliminary specification of SiCl₄ system refinements, to be compatible with and to

interface directly with the sodium injection subsystem, were initiated.

- Preliminary specification of the requirements for the integration of the SiCl_4 control and instrumentation subsystem with the entire test facility.
- Identification of long-lead components and detailing of procurement specifications.
- Detailed laboratory modification design specifications for housing the SiCl_4 feed system were identified.
- The specification and identification of safety and emergency clean-up equipment and the location of these items within the test laboratory.
- A comprehensive literature survey has been completed which has further identified additional information related to SiCl_4 impurity analysis, reactions of SiCl_4 with water, oxygen, containment materials and large SiCl_4 systems.
- The identification of vendors and a preliminary detailing of specifications of the SiCl_4 injection loop storage tanks.

SiCl_4 System Refinements and Control Integration. With the basic design of the SiCl_4 feed sytem completed,⁴ overall refinement of the design continued. Discussions were held with investigators of the sodium system task, thus leading to a more thorough understanding of the needs for control and interfacing of these reactant facilities. It has been especially noted that in order to permit maximum control of the feed material composition precise flow adjustment of each reactant through appropriate control

instrumentation will be required. Specifications for the integration of control instrumentation has been initiated and will continue through the next report period.

Long-Lead Component Specifications. Detailed specifications of the SiCl_4 loop components have been prepared and long-lead items have been identified; procurement will be initiated pending approval by JPL to release purchase orders. This is expected in late January or early February, 1978.

Building Modification/Specifications. In cooperation with the investigators specified to detail the laboratory which will house the test facilities, recommendations were made regarding the SiCl_4 system room. These specifications, which include facility requirements (electrical, drains, ventilation) and emergency systems were finalized and, are presently being incorporated in the laboratory modification plans. Information regarding the exact detailing of the building specifications was derived from the revised MCA data sheet for chlorosilanes.¹³

Literature Survey. In an effort to continue to build on the available knowledge of SiCl_4 handling and chemistry, which is being continually released in the open literature, a comprehensive computer data search was made to supplement the already existing material on hand. This search has identified 30 items from the ERDA data base, 21 items from NTIS files, 28 items from Engineering Index and 165 abstracts from a search of Chem. Abstracts. From these, pertinent papers, patents, and reports have been identified which address such topics as SiCl_4 impurity analysis, SiCl_4 material interactions and large SiCl_4 system design details.

SiCl_4 System Storage Tanks. The original system design specified that SiCl_4 would be stored and injected directly from the tank trailer in which the material would be delivered.

In refining the feed system design, it was found that an intermediate storage facility with a capacity of 200 gal. would be required and, because of vendor requirements, a large main storage tank of 4000 gal. capacity would be preferred as opposed to utilizing a tank trailer for storage of SiCl_4 . Because of the stringent specifications placed on such storage facilities by the MCA data sheet,¹³ a number of tank vendors were approached; three potential tank suppliers have been identified. At the present time, detailed SiCl_4 storage tank specifications are being prepared and will be submitted to each vendor for appropriate review.

4.2.4 Sodium System (A. R. Keeton, E. D. Berczik)

Detailed design of the sodium system continued throughout the reporting period. Several important conceptual changes were made. These include:

- Draining the transport sodium drums by gravity into the base supply tank instead of by differential gas pressure.
- Developing the logistics of sodium drum management so that all sodium drum handling is accomplished with the sodium in the solid state.
- Providing two additional drum heating and draining stations (total of five) so that sodium can be supplied to the chemical reactor continuously for an extended period of time at a Si production rate of 200 lb/hr.

The location and arrangement (within the sodium room) of the sodium melting and drain stations is shown in Figure 4.1 and 4.2. These stations are elevated 3-1/2 ft above the floor to allow space for the base tank underneath. The

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Figure 4.2 - Preliminary Layout Of The Sodium System Room

sodium is drained by gravity from one drum at a time into the base tank. A level control system in the base tank automatically controls the sodium flow from the on-line drum.

Sodium drum heating is accomplished by a specially designed jacket, containing heaters, thermal insulation and temperature sensors. The heating jacket is split and hinged for rapid installation and removal. Each heating jacket is rated at 30 kW with the heaters arranged in 3 zones of 10 kW each. Each of those heating zones is controlled separately.

The sodium base tank, is designed to provide a reservoir of sodium so that an uninterrupted flow can be supplied to the chemical reactor during drum changes. The base tank also acts as a prefilter to prevent large particles of oxide or other matter from entering the EM Pump.

Filtering of the sodium is also accomplished at each drum. This 20 mesh wire filter prevents large particulates from entering and accumulating in the base tank. This filter is necessary because complete draining of each drum is desired to minimize sodium decontamination requirements.

Control and instrumentation requirements for the sodium system have been defined as follows:

- Heat energy must be applied to each sodium drum, beginning at the sodium-gas interface and progressing away from this point.
- Each drum heating zone must also be independently temperature controlled.
- When all the sodium in a drum is liquid, the top 2 heater zones should be deenergized.
- The temperature of each drum heating zone should

be displayed upon command to the sodium system operator.

- All sodium system piping and components must be trace heated above the melting point of sodium and the temperature of each zone displayed upon command.
- Emptying of a sodium drum must be detected and cause automatic switching to a full drum.
- Sodium level in the base tank must be automatically controlled to a predetermined level.
- Sodium flow to the chemical reactor must be automatically controlled to a variable preset level.
- Sodium flow rate must be displayed and recorded on command.
- Atomizing gas flow must be ratioed to the sodium flow.
- The clean sodium filter must be automatically switched into service if the on-line filter plugs.
- An emergency shutdown circuit must be provided to de-energize all sodium system electrical circuits and close all automatic valves.

The handling and storage of the sodium drums has been analyzed and finalized. The following are the steps to be followed: (Refer to Figure 4.1.)

- 1 - Move drums into storage area using fork lift.
- 2 - Manipulate full drum onto metal pallet located on transfer cart.

- 3 - Transport drum to sodium room and assemble heating jacket.
- 4 - Disconnect piping from empty drum on rack then lift empty drum from rack and place onto transfer cart.
- 5 - Place full drum onto rack and connect associated piping.

Major handling equipment such as fork lifts are available in-house while minor devices such as a simple drum manipulator will be procured.

4.2.5 Silicon Collection (I. E. Kanter)

The final analysis and design of the silicon collection system is continuing. Thermal analysis for the majority of the system components has been completed and machining dimensions are being specified. Vendors are being contacted for alternative insulation for the graphite felt previously specified under the quartz crucible. Purity of a moldable alumina-silica felt is being determined via chemical analysis. Final contours of the crucible will be determined during the upcoming quarter.

Slight delays are expected with final description of the crucible due to the uncertainty in the bottom contour of the fused quartz crucible and the thickness of felt to be used for expansion and release purposes. It is not expected that this will delay the procurement phase.

4.2.6 Effluent Disposal System (J. McDonald)

During the quarter, the engineering analysis was completed on the solid-salt injection system for cooling and removing the NaCl(v) from the effluent gas stream.³ In this system, particulate NaCl at ambient temperature is injected into the high temperature product stream as it

exits the silicon cyclone. This injected NaCl(s) lowers the gas stream temperature from 1750⁰K to below the dew point of the NaCl. For equilibrium, the gas stream temperature would be reduced to 1372⁰K. A rough thermal calculation was made to verify that the injected salt particles can cool the gas stream and condense the NaCl(v) within a reasonable distance. It was found that the NaCl(v) can be condensed in a duct length less than 3 meters. This approach will not be pursued further at this time with the planned effluent separation system to be described in the following paragraphs.

However, an alternative scheme for effluent separation and disposal is being evaluated for the test system during the experimental verification effort (testing). This alternative scheme makes use of a water-cooled scrubber unit which is simpler to operate and should be less expensive than the salt injection scheme. In the water-cooled unit, the gases exiting the silicon cyclone are conducted through a refractory lined pipe to a venturi scrubber and quencher unit. The venturi scrubber generates a mist which occludes the submicron particles of condensed salt. The gas containing the water mist is conducted to a wire mesh separator. At the separator, by impingement, the water is collected on wires and falls as droplets to the bottom of the separator where it flows to subsequent treatment and drainage. The Ar-H₂ gas is conducted to the stack where it is burned.

During the next quarter, the detailed design and operation specifications for the effluent gas scrubber will be compiled. In addition, the insulated pipe which connects the silicon cyclone to the water-cooled gas scrubber will be designed. Layout drawings for the effluent system will be initiated.

4.3 Test System-Laboratory Integration

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

The initial design and layout of the major arc heater power system components were completed. This included selection of a power transformer, layout of the motor control center, layout of the three new distribution panels, layout of the sodium drum heater supplies and preliminary heating and ventilation requirements.

Descriptive information has been prepared for each of these major components. This information included the component description, supplier, quantity, catalog number and the location of where the components are used.

This information has been reviewed with Westinghouse Plant Engineering and copies of all sketches and information have been given to Plant Services which will proceed in making final detailed and layout drawings for review and approval.

Power requirements for the transformers and motor control center have been finalized. Power will be available at the following conditions.

- (a) 480 V - 3 $\emptyset$ Δ @ 750 KVA; water pumps-DC power supply, sodium barrel heaters, etc.
- (b) 208Y/120 V - 3 $\emptyset$ @ 150 KVA; lighting, receptacles, trace heating.
- (c) 240 V - 3 $\emptyset$ Δ @ 30 KVA; sodium & NaK pumps and specialized voltage sensitive equipment.
- (d) 120 V - 1 $\emptyset$ @ 5 KVA; isolated & regulated instrument power, for digital instruments, data logger, etc.

(e) 250 V DC @ 25 KVA; special test equipment.

The power supply requirements for the DC field coils have been set at approximately 1000 Amps @ 72 volts. This will be accomplished by connecting 4 DC power supplies in a series and parallel combination. The arc power reactor requirements have been set at approximately 400 to 700 amps.

Sketches for the cable tray system have been started, but have not yet been discussed with Plant Engineering and similarly for the building ground system. Initial work has just begun on the communication and power equipment interlock system.

4.3.2 Gas System (C. B. Wolf, J. Meyer, J. McDonald)

During the early part of this reporting period, milestone charts were prepared for the planning and installation of the gas system. Expected usage rates were determined to establish storage requirements. Trailer size and parking space requirements were established so that, the outdoor storage planning by Plant Service Engineering could begin. In accordance with insurance company safety recommendations, all high pressure regulation and flow control equipment for hydrogen will be located outside of the main test cell area. For convenience the argon controls will be at the same location. Other safety features of the gas system are: automatic shut off of normally closed solenoid valves when power fails; test cell ventilation electrically interlocked with gas shut off valving so that gas cannot be admitted when ventilating fan is not operating; automatic purging of the entire reactor for both normal and emergency shut downs.

A schematic drawing of the Arc Heater gas supply system was prepared and reviewed by the other task investigators involved. Gas flow measurement and controls consist of

sonic orifices, pressure and temperature measurement, local dome loaded pressure regulators with remote (control room) dome loaders, and solenoid operated valving.

Final gas system design will include the requirements of both the silicon-tetrachloride system and the sodium system. An overall schematic drawing will be made as an overlay of the laboratory, and will include piping size and material information. This information will then be incorporated into Plant Service Engineering drawings for the laboratory piping system. Piping to the storage area and control station which are located external to the laboratory will be included in these drawings.

4.3.3 Cooling Water System (C. B. Wolf, J. R. Meyer)

During the reporting period, the overall flow requirements of the cooling water system were finalized so that, laboratory planning by Plant Service Engineering could progress. Size and location of inlet and drain water requirements were determined. Overall flow rate requirements for the system as presently planned are 250 gpm, but for a safety margin, it was decided to plan for a maximum flow of 350 gpm. Pump room design includes a fully-sized water inlet and drain. There will be a trench around three walls of this room which is sized to contain any possible spill. The drain line will extend around the outside of the building to the base of the exhaust stack.

A schematic of the overall cooling water system was prepared and circulated to appropriate task investigators for review and additions, if necessary. The arc heaters are cooled by high pressure-recirculating water with a flow of about 210 gpm, with heat being removed by a low pressure heat exchanger with a flow of 100 gpm. The reactors sections, silicon cyclone, and piping are cooled by low pressure-

recirculating water with a flow of about 150 gpm, with heat being removed by a low pressure heat exchanger with a flow of 100 gpm. The gas burnoff stack will be cooled with ~ 50 gpm of raw cooling water.

The 200 gpm coming from the two heat exchangers will be routed to the effluent scrubber for exhaust cooling and for by-product salt removal. This water and the gas burnoff stack cooling water are routed to the catch basin at the base of the stack where mixing will be completed before piping to the sanitary drain by means of an overflow pipe. The salt concentration in this drain water will be considerably below sea water levels and within the maximum levels permitted by Allegheny County Sanitation Authority.

The pump room equipment layout is near completion. Included in this layout are the two pumps, two heat exchangers, surge tank, deionizer, and interconnecting piping and valving.

Another schematic will be prepared in which the plumbing lines will be shown as an overlay of the laboratory floor plan. This will assist Plant Service Engineering in preparing plumbing drawings for the laboratory.

Other drawings which will be required to finalize water system design include working drawings of the surge tank and the heat exchanger support structure.

Equipment specifications will be reviewed during the next quarter in preparation for anticipated procurement cycle.

4.3.4 Gas Burnoff Stack (C. B. Wolf, J. R. Meyer)

Work on this subtask has been of a preliminary nature during the quarter. Drawings of the existing water-cooled stack at the laboratory are being reviewed for design guidance. As presently envisioned, the stack will be internally water-cooled with about 50 gpm of water and will be double walled steel construction about 3 ft. dia. by 24 ft. high. It will

be supported by a structural iron and gridwork base located above a concrete catch basin. This catch basin will hold about 1200 gallons of process cooling water during testing, and will have provision for overflow, draining, and sampling. At the base of the stack, provisions will be made for a flame-type igniter, and also equipment for monitoring and treating the waste water, if necessary, to comply with sanitary sewer regulations.

Rough sizing calculations will be made early in January so that drawing work may proceed. It is expected that by the end of January, the drawings should be near completion, and planning for waste water treatment will be in progress.

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. KINETICS STUDY

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

6.1 Task Description

In this task, the reaction kinetics for the reduction of SiCl_4 by Na, as well as Si droplet growth are being investigated. The results of these experiments will provide input for the optimum operating conditions of the verification test system.

6.2 Summary

The design of the experimental set-up is essentially completed. It offers flexibility with regard to the reactant injection system and gas temperature control. An experiment has been set up for testing of the silicon vapor detection technique. Two alternative methods will be tested, one involving optical absorption, the other fluorescence measurements. Three different diagnostic techniques for particle size determination are being investigated: Optical scattering, high temperature impactor in the gas stream, and extracting and diluting a gas sample for measurement under ambient conditions.

The design is being finalized and construction will begin during the next quarter. A selection of the most suitable vapor detection techniques will be made.

6.3 Work Accomplished

The experimental system for studying the reaction kinetics of the silicon tetrachloride reduction process has been designed. A schematic of the system layout is shown in Fig. 6.1. A commercial plasma torch heats a mixture of hydrogen and argon to temperatures around 8000°K [(1) in Fig. 6.1]. This mixture as well as the total flowrate depends on the torch capabilities and the desired downstream conditions. In the mixing chamber section, cold gas is added to reduce the temperature of the plasma jet. Energy balances for the

FIGURE 6.1 - SYSTEM LAYOUT SCHEMATIC OF KINETICS EXPERIMENT

mixing chamber section indicate that 25% to 50% of the total gas will be injected as cold gas, depending on the selected downstream conditions. The reactants are injected into the downstream portion of the mixing chamber. Several injection ports are located at different axial locations along the mixing chamber for this purpose.

The ratio of flow rates of hot flow to cold flow are selected to give an average gas temperature at the exit of the mixing chamber, [(2) in Fig. 6.1] between 2000°K and 4000°K . A computer program has been set up based on an equilibrium energy balance of the mixing section. This program calculates the flowrates required for a preselected temperature at the mixing section exit.

The gas vapor mixture enters a water-cooled test section where there are several viewing ports for optical diagnostics. The vapor concentrations of Na and Si will be determined at several axial locations along this section. In addition, measurements of particle size distributions can be made at several locations along the downstream portion of the test section.

The test section is followed by a heat exchanger, scrubber for NaCl removal from the gas, and finally by a hydrogen burn-off stack.

6.3.1 Laser Vapor Detection

The in situ detection and density measurement of silicon vapor requires either an absorption or resonance fluorescence measurement. Absorption can be measured either from the $3p^2\ ^3P$ ground multiplet to the $4s^3P^0$ multiplet at $\sim 40000\text{ cm}^{-1}$, e.g. the strong absorption at $2516\text{\AA}$, or from the $3p^2\ ^1D$ level at 6299 cm^{-1} to the $4s^1P^0$ level at 40992 cm^{-1} ($2882\text{\AA}$). Alternatively, if the $2882\text{\AA}$ transition is pumped, fluorescence should be observable from the excited state to the $3p^2\ ^1S$ level at 15394 cm^{-1} . This fluorescence would be centered at $3905\text{\AA}$. Any of these absorptions, and the fluorescence, should be quite strong at the vapor densities and temperatures

contemplated in the test system design.

There are advantages and disadvantages associated with each of the two measuring techniques. In an ideal optical medium, an absorption measurement is more straightforward in interpretation than fluorescence, because in the latter, experimental or theoretical knowledge of the quantum efficiency of the fluorescent transition is required. However, in a turbulent medium involving scattering by both optical inhomogeneities and by particles, changes in transmission may become difficult to interpret. The absorption or fluorescence measurement from the $2882\text{\AA}$ transition is attractive because this wavelength is accessible with the tunable dye laser. A laser offers many advantages as an optical source. The spatial coherence of the laser minimizes the problem of optical access and spatial definition. The laser produces a spectral brightness and energy density which is much higher than that available from alternate sources such as a hollow cathode lamp. The pulsed nature of the flashlamp-pumped dye laser makes it possible to use gated detection systems which use time as well as frequency discrimination to reject background signals. The disadvantage of the dye laser is that the $2516\text{\AA}$ transition from the ground multiplet is not accessible to tunable dye lasers. Consequently, absorption and fluorescence measurements will be made, using the $2882\text{\AA}$ transition. Since this transition starts from an excited state, interpretation of the data requires a knowledge of the temperature. Because of the various unknowns involved, experiments are being carried out to determine which optical technique is best suited for the kinetic experiments.

Two cells are being constructed in order to test the sensitivity of various optical detection techniques. The first cell, which is illustrated in Fig. 6.2 consists of a section of single crystal sapphire tubing with sapphire windows sealed to

- a Al₂O₃
- b Nb
- c Si
- d SiC Heater
- e Thermal Insulation
- f Viewing Port

FIGURE 6.2 - ALL SAPPHIRE CELL

the ends with high temperature frits. A section of small niobium tubing is used as a pumpout tube. This construction is very similar to that used in high pressure sodium lamps. The cell is currently being fabricated. During a typical experiment the cell will be filled with elemental silicon, sealed off, and then heated to $\sim 1650^{\circ}\text{C}$ in a hollow silicon carbide heater. The heater will be continuously flushed with nitrogen to prevent oxidation of the niobium. Because of size limitations on available sapphire tubing, an aperture of several millimeters diameter will be used. This arrangement will be quite suitable for the laser probe, but a rather restrictive geometry for an incoherent source such as a hollow cathode lamp or flashlamp. There will be a side viewing port; thus either transmission or fluorescence can be measured.

At the maximum operating temperature of silicon carbide ($\sim 1650^{\circ}\text{C}$) the density of silicon vapor is $3.8 \times 10^{13} \text{ cm}^{-3}$. The calculated absorption coefficient for the $2516\text{\AA}$ line is 50/cm while that of the $2882\text{\AA}$ line is 3/cm. This calculation takes into account the temperature activated population of the initial state for the $2882\text{\AA}$ transition. The actual measured absorption coefficient will depend on the frequency spectrum of the source, but appreciable absorption and fluorescence should occur in this cell. As a backup to the test cell described above, another system is being constructed which is illustrated in Figure 6.3. This cell consists of a quartz tube with two molybdenum electrodes and filled with SiI_4 . The main body of the tube will be maintained at a temperature of $\sim 500^{\circ}\text{C}$. The cold-finger temperature will be regulated by a separate heater at $\sim 150^{\circ}\text{C}$. The vapor pressure of SiI_4 in the main tube will be fixed at the desired pressure, by controlling the temperature of the cold-finger. A rapid electrical discharge between the two electrodes will dissociate the SiI_4 to produce free silicon. The temperature of the

- a Quartz Cell
- b Electrodes
- c SiI₄ in Cold Finger
- d Oven
- e Auxiliary Oven
- f Viewing Port

FIGURE 6.3 - SiI₄ DISCHARGE CELL

gas can be estimated from the energy input to the discharge. Based on a number of previous experiments with other metal halide systems, silicon vapor densities of $\sim 10^{16} \text{ cm}^{-3}$ should be obtainable for $\sim 50 \mu\text{s}$ in the afterglow of the discharge before recombination occurs. Since the tube has a reasonably large aperture ($\sim 12 \text{ mm}$), optical access is quite good. The quartz tube has been constructed and is ready to be filled and sealed. The heater and a pulser to produce the electrical discharge are available.

Although the discharge tube has a number of advantages in terms of optical access and high number density, it has deficiencies as a test and calibration device. Both the ground state population of silicon and the temperature must be determined separately because the system is not in thermal equilibrium. These values can be determined through auxiliary measurements and calculations, but the difficulties are such that the halide dissociation test system will be used only if the all sapphire cell proves infeasible in practice.

Figure 6.4 schematically represents the experimental arrangement for proposed calibration measurements. The light source will be the tunable dye laser, a hollow cathode lamp or a flashlamp plus monochromator. The test cell will be either of the two described above. Both transmission and fluorescence can be observed. The filter shown will be initially a small monochromator, which may be replaced with a suitable interference filter, if possible. For the case of the dye laser as the light source, the boxcar integrator can be gated by synchronization pulses from the laser.

6.3.2 Particle Diagnostics

Three different techniques are being considered for determination of the particle size distribution. There are two alternative methods involving commercial impactors. First, an

- a Light Source
- b Test Cell
- c Filter
- d Detector
- e Box Car
- f Lens

FIGURE 6.4 - EXPERIMENTAL ARRANGEMENT FOR LASER TESTS

impactor designed for use in high temperature gases would be used directly in the test chamber. The second possibility would involve extracting a sample of the gas stream with a rapid quenching probe. The particles in the diluted gas sample will then be sized with an impactor at normal ambient temperatures. Optical techniques can also be used to measure the size of particles in high temperature gas streams. Several commercial systems obtain the required information by measuring the angular dependence of laser light scattered from the particles. Several systems are currently being evaluated.

6.3.3 Injection System

Because of the low flow rates ($\sim .05$ moles/sec) and the relatively short running times (< 30 min.), the Na and SiCl_4 injection systems will be relatively simple. The supply tanks will have volumes between 2 and 3 liters. High pressure gas will be used to drive the reactants into the mixing section. The injection will be through several small nozzles on the circumference of the inside mixing chamber wall.

7. INJECTION TECHNIQUES

Task Investigators: A. R. Keeton and F. J. Harvey

7.1 Task Description

The purpose of this task is to evaluate and characterize reactant injection techniques. Both sodium and silicon tetrachloride will be tested with their selected injection nozzle under conditions as near prototypic as possible. In addition, co-injection tests will be conducted to determine the feasibility of co-injecting both reactants through the same nozzle.

7.2 Summary

Design of the system for injection technique studies was initiated during the reporting period. An existing stainless steel chamber with an internal volume of 75 liters (2.65 ft³) has been identified for use as the test chamber. This vessel is undergoing modification to meet the injection techniques test requirements.

The sodium supply tank for these studies has been designed and is being fabricated. The nozzle holder design is near completion. A schematic arrangement of the test system was completed and procurement of components is underway. Particle size measurement technique selection was initiated and is being integrated into the test system design.

During the next quarter, design and fabrication of test system components will be completed and the system will be assembled. Particle size measurement technique selection will be made and sodium tests initiated.

7.3 Work Accomplished

A stainless steel vessel (Fig. 7.1) with internal measurements of 34 cm (13-1/2 in) dia. x 81 cm (32 in) high is being modified for use as the test chamber for injection techniques studies. This cylindrical vessel is flanged at each end and is mounted on a 2 ft

Figure 7.1 - Injection Techniques Test Chamber

high support stand. Sight ports are located 180° apart and are angled 45° from the horizontal.

Figure 7.2 is a schematic representation of the test system set up for sodium injection testing. Sodium is fed from the supply tank (12) through the flow meter (19) to the test nozzle (2) where it is sprayed into the test chamber. The end of the spray nozzle is located in the center of the chamber where it can be viewed through the view ports. The nozzle inlet line, and supply tank are all heated above the sodium melting point (99°C).

Nozzle performance will be evaluated by several techniques. These include visual observations, photographic or electro-optical techniques, post-test analysis and particlesize analysis. The most crucial of these is the particle size analysis. An investigation has been initiated on the selection of particle size measurement techniques. Results of this investigation will be integrated into the design of the test system. The first part of this investigation is concentrated on sodium because sodium will be tested first and because sodium particle formation is more critical to the chemical reactor operation.

The test system in Fig. 7.2 shows one method that may be useful for particle size analysis. A counterflow of cold gas is circulated through the spray plume, freezing the sodium particles as they fall down the test chamber. A collection system at the bottom of the chamber collects the frozen particles prior to transport to a glove box for analysis. Some of the ultra fine particles may be exhausted with the gas stream but this will result in a conservative evaluation of the nozzle.

Dwg. 1693846

1. Injection Chamber
2. Test Nozzle
3. Nozzle Holder
4. Filter
5. Ball Valve
6. Gas Circulator
7. Gas Cooler
8. View Port
9. Support Stand
10. Gas Distribution Funnel
11. Particle Collector
12. Test Fluid Supply Tank
13. View Port Sweep Gas
14. Gas Supply
15. Pressure Con'l Solenoids
16. Emergency Pressure Relief
17. Elect. Heater
18. Gas Flowmeter
19. Liquid Flowmeter

Figure 7.2 - Injection Techniques Test System

8. REACTION DEMONSTRATION

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

8.1 Task Description

The objective of this task is to determine the nature and extent of the high temperature reaction between sodium vapor and silicon tetrachloride gas utilizing laboratory apparatus under conditions that are similar to the experimental verification testing. The laboratory experiments will, therefore, be conducted at the same temperature, pressure, reactant concentration, and residence time range as the verification testing. The ranges for these test variables are: (1) temperature, 1800-2000°K; (2) reactant concentrations, 40-45% sodium, 45-50% arc heater gas (80% H₂ - 20% Ar), 10-11% SiCl₄; (3) residence time, ~ 0.1 second.

8.2 Summary

The design of a laboratory-scale experimental system has been formulated. The principal components of the system are (1) a silicon carbide, glow bar furnace with a maximum temperature capability of 1925°K, (2) a silicon tetrachloride generator with associated flow train, (3) a sodium vapor generator with associated flow train, and (4) a product collector. Heat transfer and residence time calculations have been carried out to determine the reaction chamber size and the range of reactant flow rates. On this basis, a Harper Glow Bar Furnace has been ordered. Design of both the SiCl₄ and Na vapor generation system has been initiated.

The design of both the SiCl₄ and Na vapor generators and subsequent fabrication of the process vessels will be completed. The components of the three principal flow trains will be procured and the fabrication of these subsystems completed. Transpiration experiments will be initiated to determine the conditions of liquid sodium temperature and carrier gas flow rate in which, the required concentration of sodium vapor is achieved in the gas stream. Design

of the product collection system will be finalized and construction of the necessary components initiated.

8.3 Work Accomplished

An experimental design has been developed to simulate the conditions of the verification scale demonstration. A schematic drawing of the experimental design is shown in Figure 8.1. The required temperature range can be attained by enclosing the reaction tube within a glow bar furnace. The reactant concentrations can be generated in the gas phase by passing separate streams of a H_2 -Ar gas mixture over the $\text{SiCl}_4(\text{l})$ and $\text{Na}(\text{l})$ at controlled temperatures, i.e. at known vapor pressures. The silicon tetrachloride generation can be performed external to the furnace tube by submerging a sealed container of $\text{SiCl}_4(\text{l})$ in a constant temperature bath and consequently, piping the mixture into the furnace tube. Sodium vapor generation can be accomplished either within the hot zone of the furnace (in situ) or external to the furnace and transported to the hot zone. In the internal mode of generation, which is shown in Figure 8.1, a container of sodium is placed inside a separately heated tube which, in turn, is inside and concentric to the main furnace tube. The end of the inner tube extends into the hot zone of the furnace. By flowing the $\text{SiCl}_4(\text{g})$ - H_2 -Ar mixture down the annulus between the inner and outer furnace tubes, the reactants are mixed together when both are in the gaseous state which is similar to the large scale experiment.

The extent of reaction will be measured by two techniques. A cooled probe will be placed in the gas stream immediately downstream from the reaction zone in order to trap the condensable reaction products as well as any sodium that has not reacted. The deposit will be weighed and chemically analyzed after each experiment. On this basis, the fractional conversion can be determined by a mass balance. In addition, the exhaust gas will be sampled and the concentration of silicon chlorides determined from which the

Figure 8.1 - Schematic Of The Reaction Demonstration (Task 10) Apparatus

fractional conversion can also be calculated.

In order to determine the size of the furnace tube, as well as the magnitude of the gas flow rate, residence time and heat transfer calculations were carried out. The calculations were based on (1) a 1200kW(e) arc heater operating at 70% efficiency, (2) an arc heater gas containing 80% H_2 -20% Ar with an initial enthalpy of 5300 cal/g and (3) a reactor diameter of 30.48 cms. The corresponding residence time for these conditions is 0.1 sec. This residence time can be achieved on the laboratory scale with a furnace tube I.D. of 5.08 cms, a gas flow rate of ~ 5 liters/min at STP and a reaction length of from 1-10 cms. Heat transfer calculations carried out with the above parameters indicate that a hot zone length of 25 cms is sufficient to heat the hydrogen-argon gaseous mixture from an ambient temperature of $300^\circ K$ to $1850^\circ K$.

On the range basis of the above dimensions, as well as the required temperature, a model #GTW-2D4S-HT-30 Harper Global Furnace was ordered. The furnace is rated for a maximum use temperature of $1650^\circ C$. The heating element is made of silicon carbide and has an overall length of 122 cms. The heating chamber length is 91.4 cms of which ~ 66 cms in the center is the flat temperature zone. The furnace O.D. is 7.62 cms and its I.D. is 5.08 cms.

The flow meter range required for the H_2 -Ar- $SiCl_4$, H_2 -Ar-Na and purge gas streams have been determined. In addition, design of the $SiCl_4$ generation vessel and an internally and externally generated sodium vapor system have been initiated. The latter two designs will be compared and the superior mode of sodium vapor generation chosen.

9. PRODUCT SEPARATION ANALYSIS

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

9.1 Task Description

The objective of this task is to determine a reactor design which provides effective separation and collection of the silicon product. Product separation means are being analyzed based upon a 1) homogeneous reaction and 2) heterogeneous reaction. Results of both analyses will be evaluated and translated into a reactor design.

9.2 Summary

During the 4th Quarter, development began on both the condensation and the heterogeneous reaction product separation models. The basic computer program for the condensation model has been debugged and various cases have been run to test the operation of the program. In addition, the boundary layer analysis yielded relations determining the point of condensation and the effect of condensation upon the heat and mass transfer. The heterogeneous analysis has been subdivided into two analyses: One analysis examines the initial low temperature-diffusion limited reaction between $\text{SiCl}_4(\text{v})$ and the $\text{Na}(\text{l})$ droplets forming $\text{Si}(\text{s})$ and $\text{NaCl}(\text{s})$ on the same droplet. The degree to which the $\text{Na}(\text{l})$ reacts with the SiCl_4 is a controllable parameter of the analysis. The second analysis examines the subsequent particle heating (i.e., $\text{Na}(\text{l})$ vaporization, $\text{Si}(\text{s})$, $\text{NaCl}(\text{s})$ melting and $\text{NaCl}(\text{l})$ vaporization) by the high temperature arc heater gases. The equations governing the diffusion controlled heterogeneous chemical reaction were formulated and the development of the computer code is underway. In addition, the equations have been formulated with the initial computer program written for the particle/droplet heating following the heterogeneous chemical reaction. The computer program is presently being debugged and modified accordingly.

9.3 Condensation Reaction

The condensation analysis examines the rate of silicon removal onto the reactor wall as a result of condensation. Unlike the first condensation analysis¹⁶, the present analysis is to account for the variation in the properties, condensation within the boundary layer, and the effect of developing boundary layer upon the mass and energy transport. The model is described with the aid of Figure 9.1. The reacted products enter the condenser tube axially, tangentially or via a combination. The silicon vapor diffuses to the wall with no condensation in the boundary layer. This point will be addressed in more detail later. In addition, reaction in the boundary layer is also neglected and this will be considered as a further modification. The manner of entrance and the corresponding transfer correlations must be introduced. The gas composition $\{X_i\}$, the gas temperature, and the mass flow rate are specified. The tube diameter is preselected, and the wall is molten silicon at the melting point. Over an axial section of thickness Δz , the governing energy equation is:

$$\frac{d(\dot{m}h)}{dz} = - Q_w - \Gamma_{si} h_{si} T_w \quad (1)$$

But the total heat flux absorbed by the wall includes that due to condensation.

$$Q_{wt} = Q_w + \Gamma_{si} \left(h_{si} - h_{si(l)} \right) T_w \quad (2)$$

The mass transfer can similarly be written as:

$$\frac{d\dot{m}}{dz} = - \Gamma_{si} \quad (3)$$

Figure 9.1 - Basic Condensation Model

Condensation in the boundary layer will be accounted via a modification. For now, it is assumed that condensation only occurs at the wall.

Combining the energy and mass equation the axial gradient of enthalpy is written:

$$\frac{dh}{dz} = \frac{1}{\dot{m}} \left[-Q_w + \Gamma_{Si} (h_{Ts} - h_{SiTw}) \right] \quad (4)$$

The gas conducted wall heat flux can be written as:

$$Q_w = Nu_k \pi (T_s - T_w) + Q_r \quad (5)$$

With the mass flux similarly written as:

$$\Gamma_{Si} = NuD_{Si-m} \pi C (X_{Si} - X_{SiW}) \quad (6)$$

"Qr" represents the energy exchange due to radiation. For the present analysis, this term will be neglected with convective exchange taken to dominate the energy processes. Since the vapor diffusing has a mole fraction less than 0.1, the mass transfer correction, θ is 1.05.¹⁴ Therefore, the high mass transfer coefficient correction is neglected. It can similarly be shown that the high mass transfer correction in the energy equation can also be neglected. To numerically solve this problem, properties of the free stream and the film must be obtained. Using a nominal elemental composition of:

4.0	Na
1.0	Si
6.62	H
0.83	Ar

the equilibrium composition and transport properties¹⁷ can be determined for a range of temperatures at a pressure of 1 atm. Since the silicon is being lost from the stream with distance Z,

the same calculation is performed for 0.5 Si instead of 1.0 Si and repeated again for 0.25 Si. This variation was incorporated to establish a correlation between total silicon remaining in the mix and the composition/properties. Figures 9.2 through 9.7 give the properties of density, thermal conductivity, dynamic viscosity, diffusion coefficient for monatomic silicon in the mixture, Schmidt number and kinematic viscosity as a function of temperature. Two curves are shown for thermal conductivity. The curve labeled K_m represents the energy transferred per unit temperature gradient for complete equilibrium (i.e., it includes reaction energy). The curve labeled K_f is the energy transferred per unit temperature gradient where the composition is that corresponding to equilibrium and composition gradients do not exist. Thus, K_m is the mixture equilibrium thermal conductivity and K_f is the mixture frozen thermal conductivity. Consequently, K_f is much smaller than K_m at temperatures where significant change in chemical composition occurs. With respect to Figures 9.2 through 9.7, these properties were calculated for all three levels of silicon and differences within the accuracy of the graphs were not observed. However, Figures 9.8 through 9.10 indicate property differences for the three cases. The letter "C" denotes the gas properties when the condensed silicon phase is permitted to exist and "NC" denotes the gas properties when the condensed phase is not permitted to exist in the equilibrium calculation. Figure 9.8 indicates the gas enthalpy increases with added fraction of silicon for the higher temperature range. Figure 9.9 indicates the effect upon Prandtl number as a result of the silicon content. It should be noted that this Prandtl number includes the equilibrium thermal conductivity (K). Since the Prandtl number is raised to the $1/3$ power, the differences for the three fractions of silicon content are not significant and a mean value can be used with negligible error.

Up to this point, the boundary layer has been considered nonreacting and the superheated silicon vapor is leaving the free

Figure 9.2 - Density (ρ) vs. Temperature (T)

Figure 9.3 - Thermal Conductivity (k) vs Temperature (T)

Figure 9.4 - Viscosity (μ) vs Temperature (T)

Figure 9.5 - Average Si-Mixture Diffusion Coefficient ($\bar{D}_{Si-m}$) vs Temperature (T)

Figure 9.6 - Schmidt Number (Sc) vs Temperature (T)

Figure 9.7 - Kinematic Viscosity (ν) vs Temperature (T)

Figure 9.8 - Enthalpy (H) vs Temperature (T)

Figure 9.9 - Prandtl Number (Pr) vs Temperature (T)

Figure 9.10 - Specific Heat (c_p) vs Temperature (T)

stream and condensing upon the wall. At the elevated temperature, the silicon is in the form of Si, Si₂, Si₃, SiCl₂ and SiCl vapor. The majority is silicon vapor which diffuses toward the wall due to concentration gradients established as a result of condensation at or near the wall. At temperatures approaching the wall temperature (i.e., the wall temperature is equal to the melting temperature, 1685°K, species of SiCl₂ and SiCl are converted to pure silicon by reaction with free Na(v); thus, concentration of SiCl₂ and SiCl are low at a temperature where equilibrium indicates conversion to take place. The removal of silicon by reaction near the wall of SiCl₂ and SiCl will be considered but it is not reported in this quarterly. This quarterly will report on the analysis associated with the removal of silicon which is initially silicon vapor in the free stream.

9.3.1 Review of Transfer Correlations

Over twenty papers were selected from a literature survey made on the general subject of heat transfer and pressure drop for turbulent swirl flow in a pipe. Although the separation study is particularly interested in papers treating heat transfer and pressure drop for turbulent swirl flow in a hollow tube, most presentations that included heat transfer dealt with conditions for a tube having either an axial core or axial swirl promoters, which are not appropriate. Only three papers treated heat transfer and swirl flow in a hollow tube. Blum and Oliver¹⁸ presents raw heat transfer data but no friction data. The crucial variable, swirl angle, is not mentioned. It can be inferred from this paper that a heat transfer coefficient augmentation relative to pure axial flow of 9 times occurs at the inlet with significant swirl decay occurring in approximately 40 diameters. Mijay and Golubev¹⁹ present a theoretical analysis of the local effects of swirl flow on heat transfer, pressure drop and swirl angle. The analysis essentially replaces

the swirl flow by an equivalent rectilinear segment with equivalent velocity and length. Figures 2 and 3 from reference 20 are reproduced here as Figures 9.11 and 9.12. Figure 9.11 shows the augmentation in friction factor (λ) vs. distance from inlet in tube diameters for various inlet conditions. Figure 9.12 similarly shows the augmentation in Nusselt number, Nu. Alimov²⁰ presents an experimental investigation of flow friction and heat transfer inside a cylindrical tube with various degrees of swirl flow. Augmentation curves are presented. Further study of these and other papers is in progress and an assessment of these papers will follow.

9.3.2 Boundary Layer Analysis

With regard to condensation in the turbulent boundary layer, the following analysis was employed. The condensable silicon vapor is diffusing through a carrier gas toward the wall. The silicon is superheated in the free stream but reaches saturated condition in the boundary layer and remains saturated from this point to the wall. The condensate is assumed to form droplets which are continuously removed by vortex motion such that no significant buildup or reverse motion occurs.

The heat transfer for turbulent flow is represented as:

$$q = \rho c_p \left(\frac{v}{Pr} + \epsilon \right) \frac{dT}{dy} \quad (7)$$

with the mass transfer represented as:

$$j = \left(\frac{v}{Sc} + \epsilon \right) C \frac{dx}{dy} M \quad (8)$$

Figure 9.11*

Fig. 2. Hydraulic resistance in damped swirling flow.

1) $z_0 = 1$; 2) 0.8; 3) 0.7; 4) 0.6; 5) 0.5; 6) 0.4;
7) 0.3; 8) 0.9; 9) 0.444.

Figure 9.12*

Fig. 3. Heat transfer in damped swirling flow.

1) $z_0 = 1.0$; 2) 0.6; 3) 1; 4) 0.57; 5) 0.67; 6) from data of [8].

*Figures 9.11 and 9.12 were reproduced from Reference 19.

The rate of vapor condensation is given by:

$$\dot{m}' = \frac{dj}{dy} \quad (9)$$

with the heat release per unit volume represented as:

$$\dot{q} = \lambda \dot{m}' = \lambda \frac{dj}{dy} \quad (10)$$

An energy balance gives:

$$\frac{dq}{dy} = \dot{q} = \lambda \dot{m}' \quad (11)$$

For a relatively constant heat of vaporization, equation 11 can be integrated to yield:

$$q = q_w - \lambda (j - j_w) \quad (12)$$

The energy flux due to the ultimate motion of the condensate is neglected. Substitution of equation (12) into (7) yields:

$$\rho C_p \left(\frac{v}{Pr} + \epsilon \right) \frac{dT}{dy} = (q_w + \lambda j_w) - \lambda j \quad (13)$$

It is assumed that the universal turbulent velocity profile is applicable to define the turbulent eddy diffusivity. The velocity profile is:²¹

$$\begin{aligned} U^+ &= y^+; & 0 \leq y^+ \leq 5 = y_1^+ \\ U^+ &= 5 \left(1 + \ln \left(\frac{y^+}{5} \right) \right); & 5 \leq y^+ \leq 30 = y_2^+ \\ U^+ &= 5 + 2.5 \ln 1.2 + 2.5 \ln y^+; & y^+ \geq 30 \end{aligned} \quad (14)$$

where $U^+ = \frac{U}{\sqrt{\frac{\tau_w}{\rho}}}$

and $y^+ = \frac{y}{\nu} \sqrt{\frac{\tau_w}{\rho}}$

(15)

The regions of y^+ denoted above represent the laminar sublayer, the buffer layer and the turbulent core respectively. The corresponding relations for the eddy diffusivity are:

$$\frac{\varepsilon}{\nu} = 0 ; \quad 0 \leq y^+ \leq 5$$

$$\frac{\varepsilon}{\nu} = \frac{y^+ - 1}{5} ; \quad 5 \leq y^+ \leq 30$$

$$\frac{\varepsilon}{\nu} = \frac{y^+}{2.5} - 1 \quad y^+ \geq 30$$

(16)

It is convenient to define:

$$q_w^+ = \frac{q_w}{\rho c_p \sqrt{\frac{\tau_w}{\rho}}}$$

$$j^+ = \frac{j}{\rho \sqrt{\frac{\tau_w}{\rho}}}$$

(17)

Then, relation (13) can be written:

$$\left(\frac{1}{Pr} + \frac{\varepsilon}{\nu} \right) \frac{dT}{dy^+} = \left(q_w^+ + \frac{\lambda}{C_p} j_w^+ \right) - \frac{\lambda}{C_p} j^+ \quad (18)$$

and relation (8) becomes:

$$j^+ = \left(\frac{1}{Sc} + \frac{\varepsilon}{\nu} \right) \frac{dX}{dy^+} \frac{M}{M_T} = \left(\frac{1}{Sc} + \frac{\varepsilon}{\nu} \right) \frac{dw}{dy} + \quad (19)$$

In the saturated zone, the silicon vapor concentration and mass fractions are functions of temperature and written:

$$C_{Si} = C_{sat}(T) \quad (20)$$

$$W = \frac{M}{M_T} \frac{P_{sat}}{P}$$

For the saturated zone extending from the wall into the turbulent core, and the Schmidt number being approximately equal to the Prandtl number, the above can be used to obtain the wall heat flux:

$$q_w^+ (1 + A_w) = \frac{T_s - T_w + \frac{\lambda}{C_p} w_s}{F(y_s^+)} \quad (21)$$

where

$$F(y_s^+) = 5Pr + 5 \ln(1 + 5Pr) + 2.5 \ln \left[1 + \frac{Pr y_s^+ - Pr}{2.5} \right] \quad (22)$$

9.3.3 Mass Transfer

At the transition point the mass and heat fluxes are continuous and this requirement leads to:

$$\frac{w_s - w_*}{T_s - T_*} = \left(\frac{dw}{dT} \right)_* \quad (23)$$

Thus, the free stream conditions and relation (23)

determine the transition conditions i.e., w_* , T_* , $\frac{dw}{dT}_*$

Similarly, it can be shown that the silicon flux toward the wall is:

$$j_{*}^{+} = \frac{T_s - T_w + \frac{\lambda}{C_p} w_s}{F(y_s^{+}) \left[\left(\frac{dT}{dw} \right)_{*} + \frac{\lambda}{C_p} \right]} \quad (24)$$

and the location of transition from superheat to saturated conditions is:

$$y_{*}^{+} \doteq y_s^{+} \exp - \left[\frac{(T_s - T^{*}) \left(1 + \frac{\lambda}{C_p} \left(\frac{dw}{dT} \right)_{*} \right) F(y_s^{+})}{2.5 \left(T_s - T_w + \frac{\lambda}{C_p} w_s \right)} \right] \quad (25)$$

The above relations will be integrated into the model to include the effect of the boundary layer condensation. The method will be reported in the March Quarterly. The results from the integrated model will predict product separation effectiveness for the silicon reactor.

9.4 Heterogeneous Reaction

The basic chemical reaction in the arc heater reduction of silicon tetrachloride by sodium can occur in a heterogeneous manner. Two heterogeneous paths are possible in which product separation appears experimentally feasible. First, gaseous SiCl_4 and sodium vapor, which have been produced by injecting liquid sodium droplets into an arc heated gas stream, react on the surface of seed particles to produce liquid silicon and gaseous sodium chloride. The relatively large molten droplets of silicon are then separated by inertial means. Second, gaseous SiCl_4 reacts at low temperatures on the surface of liquid sodium droplets to produce solid silicon and sodium chloride. The product particles are then entrained into an arc heated gas stream where (1) any unreacted sodium is vaporized; (2) sodium chloride is melted and vaporized; and (3) silicon is melted. The result of this thermal treatment results in relatively large droplets of silicon which can be collected inertially.

A comparison of these two modes indicates that the latter route is superior because seed particles do not have to be added to the gas stream, and, consequently, an auxiliary seed particle production and injection system is not required experimentally. On this basis, the present analysis will be concerned with the reaction path in which SiCl_4 reacts on the surface of the liquid sodium droplets followed by the thermal treatment in the arc heater gas stream.

In both cases, some part of the total reaction may occur in a homogeneous manner. For example, in the case of the reaction on the sodium droplets, the sodium may not be completely converted to sodium chloride because of the formation of a solid product skin which would slow down the overall reaction rate. On subsequent injection of the multicomponent droplet into the arc heater gas stream, the unreacted sodium will vaporize and react homogeneous with the remaining SiCl_4 producing fine droplets of silicon. However, these fine droplets will be collected by collision with the large multicomponent droplets. Consequently, even if a portion of the reaction proceeds in a homogeneous manner, collection may still be realized.

In order to determine the feasibility of experimentally carrying out the reaction in a heterogeneous manner, an estimate of the reactor size is required. This estimate can be obtained by constructing a model of simultaneous heat and mass transfer of the reduction process. For purposes of convenience, two models will be constructed. The first model will describe the reaction between SiCl_4 and Na on the droplet's surface, while the second analysis will be concerned with the fusion and vaporization of a multicomponent droplet in a multicomponent gas stream. The results of the first model will serve as the initial boundary conditions for the second model.

9.4.1 Theoretical

A schematic representation of a cylindrical reactor for carrying out the arc heater reduction of SiCl_4 by Na in a

heterogeneous manner is shown in Figure 9.13. At the left end of the reactor, liquid sodium droplets are injected into a $\text{H}_2\text{-Ar-SiCl}_4$ gas stream. The sodium in the droplets react with SiCl_4 changing the composition and temperature of both the droplets and the gas phase. The prime objective of the model describing this reaction, i.e., the reaction model, is to determine the extent of reaction as a function of the axial distance. This multicomponent product droplet is then entrained into the arc heater gas stream where it is accelerated, heated and the volatile components vaporized. Simultaneously, the gas stream is decelerated, cooled and changed in composition. The principal objective of the model describing the arc heater thermal treatment, i.e., the thermal treatment model, is to determine the degree of vaporization of sodium and sodium chloride and the extent of fusion of the silicon as a function of axial distance. Based on the results of these two models, the length of the cylindrical reaction and thermal treatment sections can be obtained and, consequently, the experimental feasibility of promoting the reduction in this manner can be determined.

The major assumptions of the reaction model are as follows:

1. Plug flow.
2. Negligible axial transport.
3. Negligible pressure drop.
4. No droplet-droplet interaction.
5. Droplet velocity equal to gas velocity.
6. Droplet components are immiscible, i.e., activity of all components is unity.
7. Rate controlling step in the overall reaction is diffusion of SiCl_4 across the boundary layer.

The major assumptions of the thermal treatment model include numbers 1 through 6 above and in addition:

1. The gas phase is at equilibrium.

Figure 9.13 - Schematic Representation Of Silicon Reactor System

2. No chemical reaction on the surface of the droplets.

The two key assumptions are number 7 in the reaction model and number 2 in the thermal treatment model. The implication of the former assumption is that the possible formation of a solid product skin does not impede the progress of the reaction.* It is not known in the present case whether an impervious product barrier can form on the liquid sodium or whether a solid-liquid mixture will exist in which case the liquid would be accessible to the gas. On this basis, the results of the current model would predict the maximum extent of reaction for a given reactor length. In regards to the latter assumption, the implications are two-fold. First, any silicon containing components in the gaseous phase such as SiCl_4 , SiCl_3 , SiCl_2 , SiCl and SiH_xCl_y do not react with liquid sodium on the droplet surface in the thermal treatment section. This is reasonable since the concentration of such species will normally be small. On the basis of this assumption, the diffusion of these species across the mass transfer boundary layer will not be considered in the model. Second, monatomic hydrogen reacts homogeneously in the boundary layer to form diatomic hydrogen. Furthermore, because of the very steep temperature gradient between the gas phase and the droplet, the reaction goes essentially to completion very close to the edge of the boundary layer. On this basis, the gas mixture in the boundary layer will consist of H_2 , Ar, Na, Na_2 , NaCl and Na_2Cl_2 . This assumption is essentially correct when the gas phase temperature drops below 2500°K and is reasonable up to a temperature of 3500°K . When the concentration of monatomic is appreciable the bulk mole fractions used in the various mass transfer equations will be based on the equilibrium gas phase composition without the monatomic hydrogen present.

*This assumption also implies that the rate of the basic chemical reaction is also fast. However, this is reasonable in light of existing experimental evidence.

The formulations for both the reaction and thermal treatment models along with the respective computer programs are currently in progress. Details of both analysis models, calculated results, and reactor design implications will be presented in the next quarterly report.

NOMENCLATURE (For Condensation Analysis)

- C, C_{Si} = total molar concentration, silicon molar concentration
 D_{Si-m} = diffusion coefficient for Si, in the mixture
 h = enthalpy of the gas in the stream
 h_{Si} = enthalpy of the silicon vapor
 $h_{Si(l)}$ = enthalpy of the silicon liquid
 j = denotes the mass flux
 j_w = mass flux to the wall
 K = the thermal conductivity of the gas evaluated at the film temperature
 $\dot{m}'$ = vapor condensation per unit volume and time
 $\dot{m}$ = mass flow of the gas
 M = molecular weight of diffusing silicon
 M_T = molecular weight of mixture
 Nu, Nu' = the Nusselt number for heat and mass transfer respectively
 Pr = Prandtl number
 q = denotes heat flux toward the wall
 q_w = heat flux to the wall
 Q_r = is the radiative exchange between the wall and the stream
 Q_w = conductive heat flow to the wall per unit axial length
 Sc = Schmidt number
 w = mass fraction of silicon
 w_{sat} = mass fraction of silicon for saturated condition
 x = mole fraction of silicon in the boundary layer
 x_{Si}, x_{Si} = mole fraction of Si, in the stream and the wall respectively
 Γ_{Si} = mass flow of monatomic silicon vapor to the wall per unit length
 ϵ = denotes the eddy diffusivity
 λ = heat of vaporization of silicon
 ν = kinematic viscosity
 $*$ = denotes the values at the transition point from saturated to superheated conditions

During the Quarter, development began on both the condensation and the heterogeneous reaction models for silicon product separation. The basic computer program for the condensation model has been debugged and various cases have been run to test the operation of the program. In addition, the boundary layer analysis yielded relations determining the point of condensation and the effect of condensation upon the mass transfer. The heterogeneous analysis has been subdivided into two analyses: One analysis examines the initial low temperature-diffusion limited reaction between SiCl_4 and the $\text{Na}(\ell)$ droplets forming $\text{Si}(\text{s})$ and $\text{NaCl}(\text{s})$ on the same droplet. The second analysis examines the subsequent particle heating (i.e., $\text{Na}(\ell)$ vaporization, $\text{Si}(\text{s})$, $\text{NaCl}(\text{s})$ melting and $\text{NaCl}(\ell)$ vaporization) by the high temperature arc heater gases. The equations governing the diffusion controlled heterogeneous chemical reaction were formulated and the development of the computer code is underway. In addition, the equations have been formulated with the initial computer program written for the particle/droplet heating following the heterogeneous chemical reaction.

10. CONCLUSIONS

- Based on the preliminary process economics analysis, the arc heater process for silicon production can meet the 1985 DOE/JPL cost goal of \$10/kg of silicon.
- System Purity Analyses have indicated that only the phosphorus and aluminum concentrations in the Na feedstock are reduced during the arc heater-silicon process; while the impurity concentrations of Fe, Cr, Mn, V, and B are approximately the same for the feedstock impurity content versus the silicon product level.
- The basic designs for the subsystems developed during Phase I of the project are acceptable for the verification test system (Phase II) and are presently proceeding into the detailed design effort.

11. PROGRAM STATUS

11.1 Present Status

The Process Engineering Analysis was completed during the quarter with the exception of the System Purity Analysis subtask. This subtask will be completed during the next quarter. Since Phase II of the program was initiated in October, 1977, the activities of detailed design and laboratory preparation for the verification test system were just begun during the quarter. The complementary research programs (i.e., Kinetics, Injection Techniques, Reaction Demonstration, and Product Separation Analysis) were also initiated during the quarter with experimental system design begun.

11.2 Future Activity - During Next Quarter

- Complete the System Purity Analysis.
- Continue detailed design for the experimental verification system and laboratory preparation.
- Initiate procurement for the verification system components.
- Continue design, fabrication, and assembly of apparatus for the complementary research programs.
- Complete the Product Separation Analysis and conduct design review with JPL.

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APPENDIX A

Errata for Quarterly Report #ERDA/JPL 954589-77/2 covering the period of April-June, 1977.

The attached corrections affect the following items which are in error as presented in the April-June, 1977 Quarterly Report:

- a) Equation (2), page 4-6
- b) Table 4.1, page 4-7
- c) 10th line from bottom of page 4-8, change "near 0.1 μ m" to "near 1.0 μ m"
- d) Reword sentence on 11th line from bottom of page 4-8 to read: ... indicate very long reactor lengths. in place of: ... indicate reactor lengths in the range of 10 to 50m.
- e) Change the word viscosity to dissipation on line 8 page 4-6, line 10 page 4-6 and line 15 page 4-9.

In the April-June 1977 Quarterly Report, equation (2) for the turbulent energy dissipation (page 4-6) was based upon equation 4.10 of Levich¹. This equation was later noted to be incorrect with a correct representation given by J. Lauffer² as:

$$\epsilon = \frac{4}{\ell} \left(\frac{f}{2} \right)^{3/2} U^3 \rho \quad (1)$$

where ℓ is the pipe diameter
f is the Fanning friction factor
U gas velocity
 ρ gas density
 ϵ is the turbulent energy dissipation rate per unit volume

The Fanning friction factor for turbulent pipe flow is often represented as:

$$f = \frac{0.0791}{Re^{1/4}} \quad (2)$$

From the relation (1) and (2), Table 4.1 is reconstructed. As a result of the numerical value change of ϵ , the tabular values (see Table 4.1) for X_1 (the point at which turbulent diffusion is comparable to Brownian particle diffusion) change by $\left(\frac{1}{\epsilon} \right)^{1/4}$ (See equation 3C of the quarterly.) In addition, the estimate of

TABLE 4.1 - Reactor Flow Parameters

z (m)	Re	λ_0 (μm)	$\epsilon \left(\frac{\text{kg}}{\text{ms}^3} \right)$	$\epsilon_0 = \frac{\epsilon}{\rho} \left(\frac{\text{m}^2}{\text{s}^3} \right)$	X_1 (μm)	τ (s)	U (m/s)
0.2	36200	76	43.7	1.82×10^2	1.3	10.8	39
0.1	72500	23	3834.	1.60×10^4	0.7	1.12	150

coagulation time constants (Table 4.1) vary by $\left(\frac{1}{\varepsilon}\right)^{1/2}$ and these corrections are also included. The corrected time constants imply very long reactor lengths.

The coagulation time constants associated with velocity gradients are basically unchanged. Thus, coagulation near the wall is approximately the same and much greater than that due to turbulent diffusion in the free stream as shown in the new table attached.

References:

- 1) Levich, V. G., Physiochemical Hydrodynamics Prentice Hall, Englewood Cliffs, N.J., 1962.
- 2) Laufer, J., NACA Report 1174, 1954.