AN ELECTRIC ARC HEATER PROCESS TO PRODUCE SOLAR GRADE SILICON

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Keywords: silicon, photovoltaics

Compounds: Liquid sodium and silicon tetrachloride will be reacted at high temperature to produce solar grade silicon.

ABSTRACT

The objective of this program is to develop a process to produce solar grade silicon in large quantities based on the high temperature sodium reduction of silicon tetrachloride ($SiCl_4$) via an ac electric arc heater to yield molten silicon and the coproduct salt vapor (NaCl). Analyses and designs are presented that support the test system which is currently under development.

1. INTRODUCTION

A program has been initiated by the United States Department of Energy (DOE) to develop technology for the generation of cost effective electrical power from direct sunlight (i.e., photovoltaics).[1] As part of the DOE program, the Jet Propulsion Laboratory (JPL) is currently sponsoring the Westinghouse Electric Corporation to develop the arc heater process for the production of high capacity, low cost "solar grade" silicon (a basic material for solar cells).[2] Process and economic analyses indicate that the Westinghouse process can satisfy the high production requirements (3000 MT) predicted for 1986 at a $9.42/kg product cost (1975 dollars) which satisfies the DOE cost objective for polycrystalline silicon.

2. PROCESS DESCRIPTION

The process development is based on the high temperature sodium reduction of $SiCl_4$ utilizing electric arc heaters to produce the required high temperature environment for liquid silicon collection.[3] A reaction temperature on the order of above 3000°K is planned for the process. Commercial ac electric arc heaters will be utilized to provide a hyper-heated H_2-Ar mixture which supplies the energy necessary for the elevated product temperature and the reactor heat losses.

A flowsheet for the process in the totally integrated mode with coproduct recycle is presented in Figure 1. In this configuration,

the overall process is centered around the arc heater reduction of $SiCl_4$ by sodium with additional unit operations for recycling the NaCl coproduct and producing the reactant materials. The $SiCl_4$ reactant is formed by the chlorination of purchased silicon carbide with the resultant $SiCl_4$ purified via distillation prior to injection into the reactor.[4,5] The coproduct, NaCl, is recycled to electrolysis cells that yield the elemental constituents of Na and Cl_2. The Na is returned to the reactor while the Cl_2 is used for chlorination of the silicon carbide. Likewise, the argon-hydrogen mixture is cooled, scrubbed, compressed, and recycled to the arc heaters.

Although the process has been analyzed in the recycle mode, the experimental program underway is directed toward verification of the reduction and final product separation. The remaining process requirements fall within state of the art technology and actual verification is not necessary. During the experimental testing the reactants (Na and $SiCl_4$) will be purchased and piped to the reactor from tank storage systems. In addition, the Ar-H_2 mixture for the arc heaters is supplied from tank storage. Following the reaction, the silicon is collected on a batch basis in a quartz-lined crucible with the NaCl treated for disposal and the effluent gases (Ar-H_2) treated and subsequently combusted in a burnoff stack.

3. REACTION CHEMISTRY-ANALYTICAL

Analyses were conducted to a) select the optimum reductant for the $SiCl_4$, b) determine the sodium vaporization distance as a function of reactor length, and c) determine the silicon reactor wall design requirements and the expected silicon product separation performance.

Reductant selection was accomplished via a computerized complex equilibria analysis utilizing both the equilibrium constant and free energy minimization techniques. Results of these analyses predicted the conditions for maximum yield of silicon as a function of temperature, pressure, and molar feed rates of reactants.[2] Based upon the results of the equilibria analyses and considerations for material cost, reductant purity, and state of the art technology, sodium was selected as the reductant.[6]

Since the liquid sodium will be sprayed axially into the reactor through a nozzle, a heat, mass, and momentum transfer model was developed to determine sodium droplet vaporization as a function of reactor length.[7] The sodium is sprayed into the reactor as small droplets ($\sim$ 100μm diameter), entrained in the arc heater H_2-Ar mixture, and vaporized by the hot stream. The results of this analysis indicate that the sodium droplets are vaporized within the first 25 cm of reactor length.

Downstream of the arc heater plenum section, the $SiCl_4$ is injected as a liquid into the reactor and the reaction with sodium occurs rapidly. The silicon that is produced is separated from the gas stream and collected onto the walls by condensation. A numerical analysis was conducted to determine the silicon reactor wall design requirements and expected silicon product separation performance based on the condensation

reaction mode.[8,9] The results of this analysis are shown in Figure 2 for the nominal case having an initial product stream temperature of 3500°K, a constant reactor tube diameter of 15 cm, a silicon wetted wall temperature of 1685°K, a silicon flow of 0.0126 kg/s for an input composition of 6.62 H_2: 1.66 Ar: 4.0 Na: 1.0 $SiCl_4$. The curve indicates that an axial reactor length of 6 meters will separate 80% of the silicon product (i.e., $\beta = 0.2$). The wall heat flux results were used as a guide to establish the proper thermal resistance of the reactor internal skull diameter used in the model.

In support of the process development, a laboratory scale experiment was conducted by Heberlein, et al.[10] Using the same reactant composition and heat input from a dc plasma torch, the results of this study confirmed the formation and separation of silicon.

4. HARDWARE SUBSYSTEMS

The main subsystems required for operation of the experimental test unit include: a) Na storage and injection system, b) the arc heater-reactor assembly, c) $SiCl_4$ storage and injection system, and d) the effluent disposal system. Figure 3 presents a photograph of the arc heater-reactor assembly for silicon production. The experimental reactor is designed for a nominal silicon flow rate of 45 kg/hr. The three arc heaters (3Ø system) are shown at the left foreground, with the inclined reactor sections connected to the right, and the silicon cyclone-collector with effluent disposal shown at the top right.

The liquid sodium reductant (m.p. $\sim$ 98°C) is pumped from a heated tank storage system to the sodium injection nozzle situated upstream of the arc heaters. The sodium is injected axially into the reactor at flow rates over the operating range of 15 to 150 kg/hr of sodium. The system design utilizes a stainless steel, all welded construction as prescribed by liquid metal handling technology.

Three electric arc heaters provide gases of high purity and controlled composition at an extremely high temperature (e.g., 4500°K) for the process. The arc heaters are coupled to the reactor in a 3Ø arrangement. Each arc heater consists of a closely spaced, water-cooled pair of tubular copper electrodes within which an electric arc discharge is magnetically rotated at high velocity (300 m/s) via a dc field. The Ar-H_2 gas mixture in injected at high velocity through the gap between the electrodes while sparkover in the electrode gap initiates the arc discharge following current zeros of the ac power supply (e.g., 4 kV, 60Hz). Thus, the combination of high arc rotation frequencies and large feedstock throughput velocities yields a high operating efficiency (70-80%) with minimum electrode erosion.

The liquid $SiCl_4$ reactant is pumped from tank storage via a positive displacement pump to the hydraulic injection nozzles at the reactor. Injection is accomplished downstream of the arc heater plenum section. Due to reactivity of $SiCl_4$ with moisture, the $SiCl_4$ supply loop was designed as a hermetically sealed supply loop with a dry inert cover gas system. The $SiCl_4$ system incorporates design practices compatible with the safe handling of the reactant.

During the experimental testing phase, the silicon product is collected on a batch basis in a quartz-lined crucible which is located beneath the silicon separator cyclone. This cyclone permits separation of the silicon from the effluent gases (NaCl, Ar, and H_2). The effluent gases exit from the top of this cyclone and are piped to a scrubber-demister system which cools the gases, quenches the NaCl vapors to solids, while the NaCl is treated for disposal, and the Ar-H_2 is piped to a burnoff stack. Sampling of both the liquid and gaseous effluents will provide information on system chemistry and environmental quality.

5. PROCESS ECONOMICS

In order to evaluate the process economics based on a 3000 MT/year production capacity, the purchased equipment costs for the recycle system and the associated subsystems were required. A total cost for the purchased equipment was assembled and adjusted to the reference year (January, 1975 dollars).[3]

Following the completion of equipment costs, an estimation of the fixed capital was determined. Table 1 presents the results of the fixed capital determination for 3000 MT/year production of silicon. The format and percentages used in the table were standardized throughout all of the JPL programs.[11] A total fixed capital for the plant was established to be $24.9 million (1975 dollars).

Finally, a determination was made to estimate the silicon product cost (without profit) in 1975 dollars. Table 2 presents a summary of the product cost data. The format and values (labor, electricity, etc.) used in the table represent values standardized throughout the JPL programs.[11] An estimated silicon product cost (without profit) of $9.42/kg silicon (1975 dollars) was determined which meets the 1986 DOE cost goal of $10/kg silicon.

In addition, a sensitivity analysis was performed to assess the effect of changes in certain cost items upon the resultant product cost. The items of labor, raw materials, arc heater utilities, and fixed capital contingency were varied by $\pm$ 10% of the nominal value. The results indicate that for the 10% variations in any one factor causes less than a 2% variation in the estimated product cost.

CONCLUSIONS

Based on the models developed and analyses conducted, the following conclusions are drawn: a) sodium droplet vaporization occurs rapidly within a short flight distance inside the reactor, b) the reactor is suited to separate the silicon product by condensation, c) a product separation efficiency of 80% is predicted, and d) the projected silicon product cost ($9.42 kg/Si) meets the 1986 Department of Energy goal. The laboratory experiments of the $SiCl_4$-Na reaction have shown: a) the reaction proceeds rapidly as thermodynamically predicted and b) silicon can be separated and collected as predicted by the condensation model.[10]

ACKNOWLEDGEMENTS

This project is sponsored by the United States Department of Energy (DOE)

under Jet Propulsion Laboratory (JPL) Contract No. 954589. The authors gratefully acknowledge the guidance of R. Lutwack and A. Briglio from JPL. In addition, the authors would like to thank the following Westinghouse personnel for their capable assistance (equipment design and analyses): Power Circuit Breaker Division--J. W. George, C. B. Wolf, W. J. Melilli, P. E. Martin, J. J. Brado; Research Laboratories--D. F. Ciliberti, J. Cyphers, J. V. R. Heberlein, I. E. Kanter, A. R. Keeton, R. E. Kothmann, J. F. Lowry, and R. E. Witkowski.

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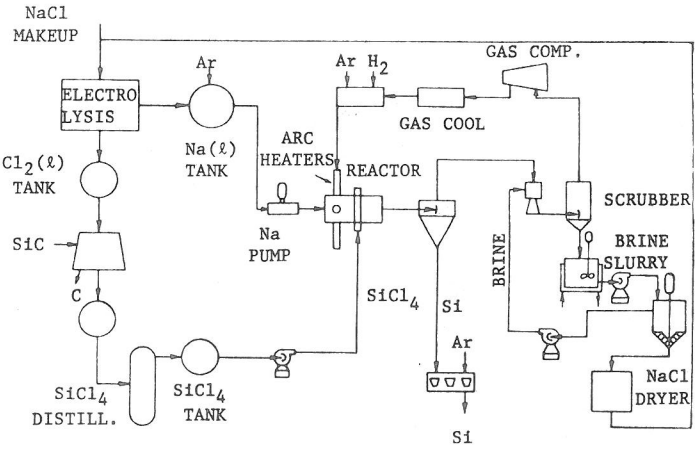
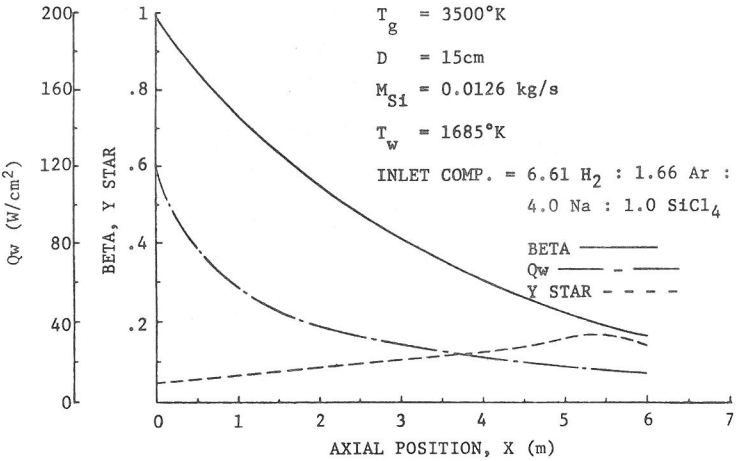


FIG. 1 - RECYCLE PROCESS FOR SILICON PRODUCTION



BETA: RATIO OF TOTAL SILICON FLOW (X) TO INITIAL TOTAL FLUX (X = 0)

FIG. 2 - DEPENDENCE OF PRODUCT SEPARATION (BETA), NON-DIMENSIONAL RADIAL LOCATION OF CONDENSATION (Y STAR), AND WALL HEAT FLUX (Qw) UPON AXIAL LOCATION (X).

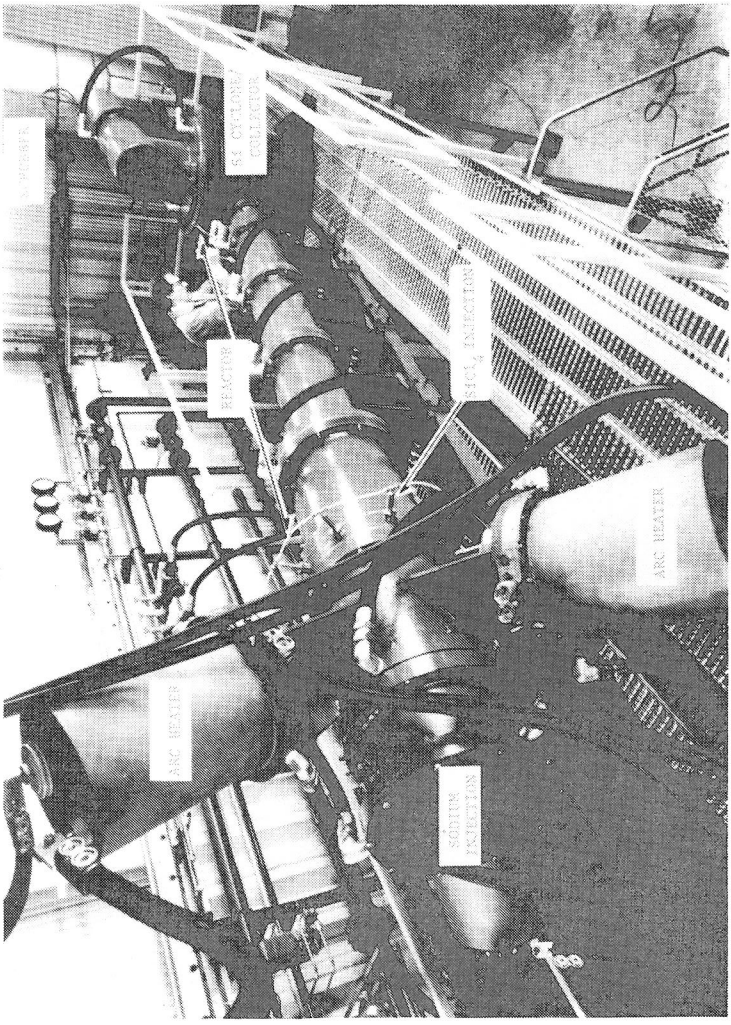


Fig. 3 - Photograph Of The Arc Heater-Reactor For Experimental Silicon Production.

TABLE 1 - ESTIMATION OF FIXED CAPITAL

PURCHASED EQUIPMENT (PE)	100%	$ 3660.0 K
INSTALL PURCH. EQUIP.	43%	1573.8
INSTRUMENTATION & CONTROL	13.5%	494.1
BUILDING WITH SERVICES	23.5%	860.1
YARD IMPROVEMENTS	11.5%	420.9
SERVICE FACILITIES, INSTALLED	55%	2013.0
LAND	6%	219.6
ENGR. AND SUPERVISION	32.5%	1189.5
CONSTRUCTION EXPENSE	37.5%	1372.5
CONTRACTOR'S FEE	19%	695.4
	SUBTOTAL	$12498.9 K
ELECTROLYSIS PLANT (TOTAL FIXED CAPITAL)*		6629.0
		19127.9
	CONTINGENCY (30%)	5738.4
*1975 DOLLARS	FIXED CAPITAL*	$24866.3 K

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TABLE 2 - ESTIMATION OF PRODUCT COST

		$/KG Si	
1.	DIRECT MANUF. COST		
	A. RAW MATERIALS	1.40	
	B. DIRECT OPERAT. LABOR (10 AT $5.90 M-HR)	.22	
	C. UTILITIES ($.03/kW-HR)	2.84	
	D. SUPERVISION & CLERICAL (15% OF 1B)	.03	
	E. MAINT. & REPAIR (10% OF FIXED CAPITAL)	.83	
	F. OPERATING SUPPLIES (20% OF 1E)	.17	
	G. LAB CHARGES (15% OF 1B)	.03	
	H. PATENTS & ROTALTIES (3% OF PRODUCT COST)	.28	
			5.80
2.	INDIRECT MANUF. COSTS		
	A. DEPRECIATION (10% OF FIXED CAPITAL)	.83	
	B. LOCAL TAXES (2% OF FIXED CAPITAL)	.17	
	C. INSURANCE (1% OF FIXED CAPITAL)	.08	
	D. INTEREST (8% OF FIXED CAPITAL)	.66	
			1.74
3.	PLANT OVERHEAD (60% OF 1B + 1D + 1E)	.65	
4.	TOTAL MANUF. COST (1 + 2 + 3)	8.19	
5.	GENERAL EXPENSES		
	A. ADMINISTRATION (6% MANUF. COST)	.49	
	B. DISTRIBUTION & SALES (6% MANUF. COST)	.49	
	C. RESEARCH & DEVEL. (3% MANUF. COST)	.25	
			1.23
6.	TOTAL COST OF PRODUCT, 4 + 5 (WITHOUT PROFIT)	$9.42/KG Si	