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NOVEL DUPLEX VAPOR-ELECTROCHEMICAL METHOD FOR
SILICON SOLAR CELLS

Quarterly Progress Report No. 9, February 1—April 30, 1978

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April 1978

Work Performed Under Contract No. NAS-7-100-954471

SRI International
Menlo Park, California

U.S. Department of Energy

MASTER

Solar Energy

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April 1978

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PREFACE

The JPL Low-Cost Silicon Solar Array Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, by agreement between NASA and DOE.

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SUMMARY

Economic analyses of the SRI process for the production of silicon show that silicon can be produced at a cost of \$6.20/kg with a total fixed capital of \$9,006,985 (1975 dollars) for a 1000 MT/yr operation. The cost per kilogram of silicon varies with the annual tonnage produced. On increasing the annual production to 3000 MT/yr, the cost was calculated to be \$5.30/kg, while for a 5000 MT/yr operation, the cost of silicon production dropped to \$5.00/kg. The yield of acceptable product silicon from the silicon produced was assumed to be 80 percent. By-product credit was obtained by converting the fluorides of sodium and hydrofluoric acid to marketable cryolite (Na_3AlF_6). These calculations also include the cost of environmental treatment and disposal for the waste effluents.

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INTRODUCTION

During the last quarter, economic studies of the SRI process for the production of silicon were performed. These studies cover the recovery of SiF_4 gas from fluosilicic acid (H_2SiF_6), sodium reduction of SiF_4 gas, separation of silicon from the reaction products by leaching the sodium fluorides, conversion of residual fluorides to cryolite, and the environmental treatment of the waste effluents. Since the sodium reduction of SiF_4 gas is highly exothermic, an attempt was made to understand the problems of heat transfer in the system and possibly predict their effect on the annual rate of silicon production. This report discusses the details of the process economics and describes the heat transfer studies.

SILICON PROCESS ECONOMICS

A study of materials costs begun in the previous quarter was extended to include process engineering and preliminary process economics. The process has been modified to produce cryolite (Na_3AlF_6) as a by-product rather than NaF and HF or NaHF_2 . Detailed flow sheets were devised based on currently available experimental results and published literature. Materials and energy balances were made from the flow sheets using reasonable assumptions about material losses and product yields. The flow sheets and materials balances were used to size all equipment for a plant producing 1000 MT/yr of acceptable silicon product. Equipment costs were determined or estimated. Capital costs were then estimated by two separate methods, but both were factored from equipment costs.

Operating costs for the plant were also estimated by using two separate methods. However, these estimates were based on the same set of determining parameters, namely, annual utilities and process material requirements (based on the materials and energy balances), current prices for these materials, and a manning table. Capital cost dependent contributions to the operating costs were based on the capital cost estimates.

All capital and operating cost estimates are for conversion of a solution of H_2SiF_6 (21%) to leached and washed silicon powder and a dry salable cryolite co-product powder.

Cryolite By-Product

Closer examination of the markets for NaF and NaHF_2 indicates that the markets are small. The principal uses seem to be as modifiers in

detergents and water conditioning agents, but use of sodium fluoride chemicals in these products is not essential. Demand for these chemicals is variable and prices are volatile. Most important, the market is insignificant compared with the long term potential demand for solar cell grade silicon. Nevertheless, because SRI's silicon process uses H_2SiF_6 and sodium as feedstocks, solutions containing large amounts of sodium and fluorine must either be disposed of as a waste, with potential environmental problems, or converted to a large tonnage salable product.

By far the largest consumption of fluorine among all chemicals is in the form of synthetic cryolite (Na_3AlF_6), which is the molten salt electrolyte used for electroreduction of aluminum from alumina (refined bauxite) in the Hall-Heroult process, accounting for 99% of all aluminum production in the world. Annual U.S. cryolite consumption is about 90,000 tons. Fortunately, cryolite is also a sodium salt of fluorine, and it is relatively simple to convert the silicon process waste liquor streams to cryolite by precipitation with alumina hydrate. The alumina hydrate also neutralizes the acid (HF) contained in these liquors and originating from the H_2SiF_6 used as the source of silicon. In the United States, Kaiser Aluminum Company is already producing cryolite from H_2SiF_6 .

Process Chemistry

Net Process Chemistry

Without taking into account process losses and less than stoichiometric yields, the overall process chemistry for SRI's silicon process in its present modification can be summarized by the following chemical reactions:

Acid

Fluosilicic acid provides only two-thirds of the acid (H^+) required to neutralize the amount of alumina hydrate necessary to convert all the fluorine in the fluorosilicic acid to synthetic cryolite. We have made up the additional acid as H_2SO_4 , because it is relatively inexpensive. However, any inorganic acid of adequate purity would suffice, and the selection of the additional acid is going to be dependent upon purity, price, availability, and environmental discard considerations.

Reduction of one equivalent of silicon requires four equivalents of sodium in the actual $\text{SiF}_4(\text{g})$ reduction step. Consequently, one extra equivalent of sodium is available over that required to produce synthetic cryolite and this results in the formation of the sodium salt of the additional acid used in the process.

Process Module Chemistry

The overall chemical reaction (equation 5) is the sum of four process modules each described by the sets of chemical reactions shown as equations 1, 2, 3 and 4; hence the modules are:

- Conversion of H_2SiF_6 to SiF_4 (equation 1)
- Reduction of SiF_4 by sodium (equation 2)
- Leaching to separate NaF from Si (equation 3)
- Precipitation of cryolite (equation 4)

A fifth plant module would be the environmental control section of the plant. This may involve rejection to evaporation ponds, deep well injection, or discard to a sewer. In our capital and operating plant calculations, we have assumed that aqueous effluents from the plant would be treated with excess lime which would convert sodium sulfate to gypsum and would precipitate residual soluble fluoride ion as calcium fluoride.

All but the second of these process modules involve primarily wet chemical processes requiring standard chemical engineering process equipment. The exothermic reduction of gaseous SiF_4 with sodium is module 2 and the critical step in the process, which is being extensively researched. Precipitation of cryolite and environmental treatment are entirely wet processes but conversion of H_2SiF_6 to $\text{SiF}_4(\text{g})$ involves first the precipitation of Na_2SiF_6 with recycled NaF, and subsequently, the drying and thermal decomposition of Na_2SiF_6 to produce $\text{SiF}_4(\text{g})$ and NaF(s).

A simplified block flow diagram for the process is shown in Figure 1. Fluosilicic acid enters agitated precipitation vessels with recycled NaF(s) and some makeup caustic solution (NaOH). The caustic makeup is

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FIGURE 1 SRI SILICON PROCESS BLOCK FLOW SHEET

required to replace sodium ions contained in NaF purged from the $\text{SiF}_4(\text{g})$ conversion system to remove impurities. The sodium is needed to precipitate Na_2SiF_6 . To the extent that NaOH replaces NaF in this cycle, less HF is produced in the Na_2SiF_6 precipitator, and consequently, more H_2SO_4 must be used to neutralize alumina hydrate in the cryolite precipitator. In fact, each hydroxyl ion added to the Na_2SiF_6 precipitator must be compensated by additional acid added to the cryolite precipitator. Both purged NaF and HF produced in the conversion of H_2SiF_6 to SiF_4 are sent to the cryolite precipitator. The plant must be designed so that the Na_2SiF_6 decomposition step, essentially a retort, provides SiF_4 gas as demanded by the reduction plant. This retort will operate at about 650°C .

The net products of the reduction plant are silicon powder and NaF. It is assumed that any residual Na_2SiF_6 formed in the reduction step is converted to NaF and SiF_4 by a postreduction heat treatment of the reaction products, as required. This gas is removed to a scrubber and eventually passes to the cryolite precipitator. Unreacted sodium is oxidized by water and leached by acid in the leaching and washing step. The resulting leach liquor, containing mostly dissolved NaF, passes to the cryolite precipitator.

Process Flow Sheets

The entire SRI silicon process plant has been divided into two departments, the "wet" plant and the "reduction" plant. Detailed flow sheets for each are shown in Figures 2 and 3.

Wet Plant

The wet plant consists of conversion of H_2SiF_6 to SiF_4 , leaching of reaction products and cryolite precipitation. Process materials required for the wet plant are deionized water produced from an on-site battery limits deionized water plant, process water (also used for cooling),

FIGURE 2 WET PLANT FLOW SHEET

H_2SiF_6 , caustic solution, and H_2SO_4 . It was assumed that water would be received from a utility and that liquid chemicals would be received by tank car and stored in receiving tanks. In addition to the concentrated sulfuric acid storage tank, there is a high purity dilute acid storage tank used as a feed source for leaching the silicon sponge.

The large volume in tonnage of H_2SiF_6 (21% solution) required by this process makes it likely that the silicon process plant would be located adjacent to a phosphate fertilizer plant providing the H_2SiF_6 by an across-the-fence pipeline.

Two solid process materials are required by the wet plant, alumina hydrate and lime. These are received as pulverized materials and transferred from hopper cars to their respective storage silos by a common discharge hopper and elevator.

The plant module for conversion of H_2SiF_6 to SiF_4 gas consists of four unit operations: (1) batch precipitation of Na_2SiF_6 , (2) solid-liquid separation on a belt filter, (3) drying of the filter cake (wet Na_2SiF_6), and (4) thermal decomposition (retorting) of the dry Na_2SiF_6 to produce $\text{SiF}_4(\text{g})$. Since three Na_2SiF_6 batch precipitators in parallel are employed, one is always available as a surge tank to continuously feed the belt filter. No storage capacity is provided between the belt filter and cake dryer. However, a dry Na_2SiF_6 silo is provided for material surge between the dryer and Na_2SiF_6 retort.

Decomposition of Na_2SiF_6 occurs on demand from the reduction plant by controlling the rate at which Na_2SiF_6 is fed to the externally fired retort and controlling the temperature within the retort. Retort temperature is selected so that some Na_2SiF_6 , approximately 10%, remains in the sodium fluoride retort residue, which is recycled to a hopper above the Na_2SiF_6 batch precipitators.

Gases purged from both the dryer and the reduction plant are sent to a scrubber where they are scrubbed with the lime solution from the environmental control section to solubilize SiF_4 and neutralize the resulting H_2SiF_6 .

Some of the sodium fluoride discharged from the Na_2SiF_6 rotary retort is periodically purged to a sump and pumped to the sodium fluoride lagoon. This lagoon also receives filtrate and wash water from the Na_2SiF_6 belt filter and the leach and wash liquor from the silicon leaching section, which constitutes the largest liquor flow.

The silicon leaching section contains a small ball mill to break up lumpy silicon sponge from the reduction plant. The silicon powder is agitation leached briefly and then pumped to filter presses where it is thoroughly leached and washed prior to discard of the silicon cake. Wet, but clean silicon powder is discharged to a vacuum dryer. All leach liquors and wash waters are discharged to a common sump and pumped to the sodium fluoride lagoon.

The cryolite precipitation section consists of a series of CSTR reactors receiving liquor from the sodium fluoride lagoon. Part of this liquor is used to slurry alumina hydrate which is pumped to the first tank of the bank of cryolite precipitators. The resulting dilute cryolite slurry is pumped to a thickener. The clear thickener overflow is then pumped to the environmental treatment section and the thickener underflow is pumped to a disk filter, with recycle of filtrate and wash water to the thickener. In effect, the thickener is a surge tank before the filter, while the sodium fluoride lagoon is the surge tank and blender for feed to the cryolite precipitators.

The wet cryolite cake goes to a direct fired dryer and cooler followed by discharge to a cryolite storage silo. The cryolite is marketed in covered hopper cars loaded from the cryolite silo.

Although the effluent liquor overflowing the thickener has already been neutralized with alumina hydrate, environmental constraints would probably require lime treatment to control the concentration of soluble fluoride ion. The lime treatment would also reduce the concentration of sulfate ion by precipitating gypsum.

Reduction Plant

Silicon tetrafluoride gas produced by thermal decomposition of Na_2SiF_6 passes through a tube and shell cooling heat exchanger and gas filter and directly to batch operated reduction pots. These pots are closed chambers that are vacuum pumped prior to each batch run. Each reduction pot is made of stainless steel lined with a nickel inner cladding and contains a detachable sodium canister over the reduction pot. The canister is valved off, filled with liquid sodium, and connected by a bolted seal ring to the reduction pot. After assembly, the reduction pot is conveyed by a 10 ton overhead bridge crane to the fluid bed reduction pit.

Because the sodium reduction of silicon tetrafluoride is extremely exothermic, it is necessary to rapidly transfer heat through the reduction pot walls to prevent an excessive temperature excursion. The highest rate of heat transfer can be accomplished by a fluidized sand bed operated at the reduction pot temperature. The fluid bed reduction pit has sufficient volume to hold four reduction pots. The external fluid sand bed heats the reduction pot walls to the reaction initiation temperature, 200°C . After evacuation, $\text{SiF}_4(\text{g})$ and liquid sodium are brought together and react in the reduction pot. Reaction is continued by feeding both reactants until the reduction pot is essentially full, at which time the sodium and SiF_4 valves are closed and the reduction pot is transferred from the fluid bed pit to a soaking pit to finish the conversion of any residual Na_2SiF_6 to SiF_4 , which either reacts with residual sodium or is evacuated from the reduction pot. Temperatures are maintained in the soaking pit by a fuel burner.

The reduction pit consists of a sand bed fluidized by air recirculating at a high volumetric flow rate. Gradual attrition of the sand slowly produces dust and a purge treatment of this recirculating air is required to control dust levels in the bed. This purge stream treatment is essentially wet scrubbing to remove dust. The sand is never in contact with any of the chemical reactions and is completely inert. Control of the fluid bed temperature is obtained by direct injection of water in the bed. The resulting steam will add to the fluidizing gas load and controls the rate at which air and steam are bled from the recirculating system to the dust scrubber. Details on heat transfer calculations and production rate calculations for the reduction pots are contained in Appendix A.

After removal from the soaking pit, the reduction pots are aircooled and transferred to an unload/reload station where the emptied sodium canister is uncoupled from the silicon pot. Sodium canisters are transferred to a sodium loading station while the silicon bearing pots are sent to a discharge station where they are inverted, reamed if necessary to remove the silicon/NaF sponge, and dumped into transfer drums for conveyance to the ball mill in the wet plant. The sodium canisters are evacuated and refilled with molten sodium from an electric heated sodium receiver tank. Sodium is pumped from special 40-ton sodium tank cars, using hot oil to melt the sodium in the tank car, and gaseous nitrogen from a liquid nitrogen reservoir to pump sodium to the electric sodium receiver tank. Sodium filled canisters and empty reduction pots are recoupled and the reduction cycle is repeated.

Materials and Energy Balance

Materials and energy balances were done for a plant to produce 1000 metric tons per year of acceptable silicon, that is, silicon powder meeting product specifications.

It was assumed that the plant would operate on a three shift basis, and that 7000 hours per year of operating (on-line time) would be obtained. Using 3-foot diameter x 12-foot tall pots requires an average number of pots on line during the 7000 hours of operating time to be 2.4. The number of pots actually on line at any time would be from 0 to 4.

It was assumed that only 80% of the reduced silicon powder would be acceptable. This recovery estimate is based on bench scale work and is, therefore, highly uncertain. Operating and capital costs are extremely sensitive to the yield of acceptable product.

Details of the stoichiometric equations that were used to obtain materials balances for the various process steps are summarized in Table 1. A summary of product recovery and major reagent utilization assumptions is given in Table 2. Some excess sodium is required because sodium is incompletely reacted in the reduction pot. The ratio of acceptable product silicon to silicon contained in the H_2SiF_6 is only 68%. Losses occur because of Na_2SiF_6 purge in the SiF_4 conversion module.

Because of the large volume of water in the cryolite precipitator, the purged silicon should remain soluble as Na_2SiF_6 and pass to the environmental section where precipitation of fluoride as calcium fluoride will cause the precipitation of SiO_2 (silica gel). Although not shown, some CaSiF_6 will also precipitate. Although the solubility of Na_2SiF_6 is limited, it should be sufficient to prevent any significant silicon contamination of the cryolite by-product. Hence, we have assumed that all the cryolite produced would be an acceptable product. A 1% wind loss was assumed, and with the level of soluble fluorides in the cryolite

Table 1

SUMMARY OF CHEMICAL REACTION STOICHIOMETRY (MATERIALS BALANCE)
for the SRI SILICON PROCESS

A. Reduction, Leaching and Qualification of Silicon

I. Quality Control (Estimate 80% yield)

II. Net Reduction Plant Reaction

III. Net Silicon Leaching Chemistry

B. Conversion of H_2SiF_6 to $\text{SiF}_4(\text{g})$

IV. Thermal Decomposition of Na_2SiF_6 to Produce $\text{SiF}_4(\text{g})$

V. Precipitation of Na_2SiF_6

Table 1
(Continued)

C. By-Product Recovery and Environmental

VI. Cryolite Precipitation

1. Feed (reactants)

Sources

(Silicon Leach Liquor)

(SiF_4 (g) Conversion Purge)

(Na_2SiF_6 ppt+ Filtrate)

Alumina hydrate

Make-up

2. Net Reactions

3. Cryolite Product

VII. Scrubber Chemistry

VIII. Environmental Lime Treatment

1. CaF_2 Precipitation

2. Gypsum Precipitation (Partial)

Table 2

PRODUCT RECOVERY AND REAGENT UTILIZATION ASSUMPTIONS (YIELD)

Acceptable Product Silicon/Reduced Silicon Powder	80 %
Acceptable Product Silicon/Silicon Feed (H_2SiF_6)	68.4%
Reduced Silicon/Sodium	88.9%
Acceptable Cryolite/Cryolite Produced	100 %
Conversion of Available Fluorine to Cryolite	85.4%

precipitator effluent, it is possible to calculate the anticipated conversion of fluoride in the feedstock to cryolite. A yield of fluoride feed to cryolite of about 85% is projected. Other significant losses of fluoride are in the scrubber effluent from gas scrubbing operations at both the production plant and in the Na_2SiF_6 dryer.

The materials balances for a plant producing 1000 metric tons per year of acceptable silicon product, shown in Table 3 for the Wet Plant and Table 4 for the Reduction Plant, were calculated for 95% yield. Annual materials and utilities requirements were calculated and later when the recovery was downgraded to 80%, proportional increases in materials and utilities were made as shown in subsequent tables (Tables 5 through 9).

Process Materials and Utilities: Requirements and Costs

Materials and utilities requirements were determined from the energy balance for one year's production. Electricity requirements were determined from the energy balance, including direct electrical heating of the sodium melter, and from the installed horsepower, which was calculated after a determination of the size of all of the equipment.

Listed prices (January 1978) were used for minor process materials which are 50% caustic soda (liq) and 100% H_2SO_4 . Lime was priced on the assumption that it is available within reasonably close distance of the silicon plant. A price increment for delivery of all materials to the plant was assumed based on railroad transportation of carload lots.

It was assumed that the silicon plant would be located on a site adjacent to a phosphate fertilizer plant supplying the H_2SiF_6 . This was done because of the large tonnage involved in H_2SiF_6 which constitutes approximately 40,000 tons per year of 71% by weight of all process materials. The price for 21% H_2SiF_6 was taken as SRI's estimate of the cost of producing fluosilicic acid at a phosphate fertilizer plant.

Table 3

WET PLANT MATERIALS BALANCE

Stream		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Component	Units	Water	Di Water	Dilute H ₂ SO ₄ to Leach	Di Water	NaF Liquor	H ₂ SiF ₆ Feed	NaOH Feed	Na ₂ SiF ₆ Slurry	Na ₂ SiF ₆ Wash	Belt Filtr.	Na ₂ SiF ₆ Wet Cake	Sulfuric Acid	Alumina Slurry	NaF Liquor	NaF Liquor	Thickener O' Flow	Filtrate Return	Thickener U' Flow	Cryolite Wash Water	Cryolite Wet Cake
Solution Flow	Avg GPM	175	160	65	65	130	1.9	0.6	19.9	20	32.8		tr	13		146.8	166.3	20.6	17.1	10	
	Max GPM			125	125									20.68							
Solids Flow	Avg lb/Min								58.9			58.2							48.54		48.5
	Max lb/Min																				
Slurry Flow	Avg GPM								19.9					14.5					19.7		
	Max GPM																				
Pot Solids (Approx)									26%			49%		~14%					25%		47%
Gas Flow	Avg ACFM																				
	Max ACFM																				
Temperature	°C																				
Water	Avg GPM	175										7.1					166.3			10	6.5
Water	Avg lb/Min		160	65	65							60									54.7
Deionized Water	Avg GPM									20											
H ₂ SiF ₆ (100%)	Avg GPM						39.5														
(21% Soln)	Avg GPM																				
NaOH 50%	Avg lb/Min							6.38													
	Avg GPM							0.6													
H ₂ SO ₄ (100%)	Avg lb/Min		17.2										1.15								
Al ₂ O ₃ ·3H ₂ O	Avg lb/Min																				48.0
Na ₃ AlF ₆	Avg lb/Min																0.8	48.0			
CaO (95%)	Avg lb/Min																				
NaF(dissolved)	Avg lb/Min					29.53								2.5		28.4					
Fluorine in acid	Avg lb/Min										10.58										
Silicon in Solution																					
Na ₂ SiF ₆ (solid)	Avg lb/Min								58.9			58.2									
(dissolved)	Avg lb/Min								1.45		2.19						5.29				
Na ₂ SO ₄ (dissolved)	lb/Min																5.17				

Table 3 (Concluded)

Component	Stream		Units	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41
Solution Flow	Avg	GPM	100	166.3		100	115							3.0										
	Max	GPM																						
Solids Flow	Avg	lb/Min		12.3					18.8	8.4	58.15	19.1	1.91	1.91		47.0	5.25	4.77						
	Max	lb/Min																						
Slurry Flow	Avg	GPM		167										3.0										
	Max	GPM																						
Percent Solids																								
Gas Flow	Avg	ACFM													92.6				3200	1600	4200	100	100	173
	Max	ACFM													128.0									
	Avg	lb/Min													26.8									
Temperature		C						25							41				140	140	100			
Water	Avg	GPM																						
Deionized Water	Avg	GPM																						
H ₂ SiF ₆ (100%)	Avg	lb/Min																						
(21% Soln)	Avg	GPM																						
NaOH (50%)	Avg	lb/Min																						
	Avg	GPM																						
HF (70%)	Avg	lb/Min																						
	Avg	lb/Min																						
H ₂ SO ₄ (100%)	Avg	lb/Min			6.0																			
	GPM				0.4																			
Al ₂ O ₃ 3H ₂ O	Avg	lb/Min							18.8															
Na ₃ AlF ₆	Avg	lb/Min																47.6						
CaO (95%)	Avg	lb/Min								8.4														
NaF (dissolv.)	Avg	lb/Min												0.6										
(solid)	Avg	lb/Min										10.3	1.03	1.033										
Fluorine in acid	Avg	lb/Min																						
silicon (dis)	Avg	lb/Min																						
silicon solid	Avg	lb/Min														5.56	5.25							
Na ₂ SiF ₆ solid	Avg	lb/Min							58.15				0.88	0.88										

Table -1

REDUCTION PLANT MATERIALS BALANCE

Stream		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Component	Units	Sir Feed	Sodium Feed	Sponge	Scrap	Fluid Bed Cooling Water	Fluidizing Blower	Fluid Bed Vent Fan	Soaking Pit Vent Blower	Soaking Pit Fuel Gas	Na Melter Power	Reduction Pot Vacuum	Sodium Flask Vacuum	Start up Fuel Gas	Dust Discard	Make-up Sand	Scrubber Make-up Water	Scrubber Vent	Purging Nitrogen
Solids Flow	Avg lb/Min		19.24	40.4	2.126										0.02	0.02			
	Max lb/Min		40.0																
Gas Flow	Avg ACFM	78					10,000	1,500	2,000	20				5.0				2,400	250
	Max ACFM	128					10,000	2,700	2,500	60				60				2,000	1,000
	Avg lb/Min	22.58																	
	Max lb/Min	37																	
Temperature	°C	25					200	200	225									85	
Water	Avg GPM					4		4							5		7	6	
	Max GPM					8		8							50		50	10	
Silicon	Avg lb/Min			5.25	0.276														
	Max lb/Min																		
Electric Pow.	Avg kW										10								
	Max kW										20								
Methane (Nat. Gas)	Avg SCFM									20				5.0					
	Max SCFM									60				60					
Sodium	Avg lb/Min		19.24																
	Max		40.0																
Gas Evacu.	Avg SCFM											2.2	0.8						
	Max SCFM											22	8						
Blower Press.	Avg. PSIG						8.0	1.5	0.5										
	Max PSIG						12.0	2.0	1.0										
High Purity N ₂	Avg. SCFM																		250
	Max																		1,000
	Avg																		19.5

This price includes direct operating costs, indirect operating costs, and capital amortization. This price does not take into account the environmental regulations requiring phosphate fertilizer plants to install production facilities for producing H_2SiF_6 to prevent atmospheric discharge of SiF_4 . In summary, although the H_2SiF_6 price is slightly lower than listed values for carload lots, we believe that the price used is conservative and that it should be possible to negotiate a lower price from a fertilizer plant that is currently producing H_2SiF_6 for which there are no sales.

The price used for synthetic cryolite is FOB the silicon plant, and the price used was discounted from quoted prices to reflect SRI's best judgment of current (January 1978) long term contract prices for sale of synthetic cryolite.

Plant direct operating costs for process materials and utilities are summarized in Table 5. The by-product credit for the sale of synthetic cryolite is included as a credit in the process materials at the plant. The result of the by-product credit is that the net process materials cost is reduced from \$5,725,020 to \$815,000. This is an extremely powerful economic factor in SRI's silicon process. We believe that it is realistic technologically, and that the economics have been conservatively estimated. Synthetic cryolite is normally produced from fluorspar (CaF_2) via HF.

Manpower Requirements

Maintenance labor production costs were determined as a percentage of fixed capital costs using the Lamar University formula. Consequently, a maintenance manning table was not required.

Operating labor requirements were estimated from consideration of the unit operations in the process; see flow sheets, Figures 2 and 3. Operating labor necessary to run a three shift, 7-day per week schedule was included. Our estimated manning requirement was 32 wet plant operators

Table 5

OPERATING COST COMPONENTS

<u>Products</u>	<u>Units</u>	<u>\$/Unit</u>	<u>Units/Yr</u> [*]	<u>\$/Yr</u>
Silicon Powder	short tons (metric tons)		1,102.5 (1,000)	
<u>Process Materials(Delivered)</u>				
Sodium	short tons	600	5,093	3,056,130
H ₂ SiF ₆ (21%)	short tons	45	39,487	1,776,920
50% caustic soda liquid	short tons	140	1,338	187,380
H ₂ SO ₄ (100%)	short tons	25	3,859	96,470
Alumina Hydrate	short tons	140	3,965	555,200
Lime (90% CaO)	short tons	30	1,764	52,920
Co-product credit				
Synthetic Cryolite	short tons	475	10,336	(4,909,600)
<u>Total</u>				<u>815,420</u>
<u>Utilities</u>				
Nitrogen	Mscf	0.50	80,000	40,000
Water	M gal	0.25	165,000	41,250
Natural gas	M ft ³	2.0	200,000	400,000
Electricity	M kWh	30.0	7,775	<u>233,250</u>
<u>Total</u>				<u>714,500</u>

Notes:

1. On line time = 7000 hr/yr
2. Installed HP = 1000 at 1 kW/HP x (1/0.90)

* Rounded off more than \$/yr

and helpers and 24 reduction plant operators and helpers. We believe this number would not increase appreciably with a larger increase in scale from 1000 MT/yr since the unit operators and numbers of units would not increase. Rather, equipment size would increase. With plant experience, it may be possible to reduce the number of operators.

Capital Cost Estimates

The materials balances and flow sheets were used to obtain a complete list of equipment for a plant to produce 1000 metric tons per year of silicon. This equipment list is given as Appendix B. Pieces of equipment are categorized, numbers of units are given, and capacities are specified in terms of volume, size and appropriate dimensions. Capacities of all reactor vessels and storage units also includes stream residence times. A two to four week residence time has been provided for storage of incoming process materials. Construction material specifications are given, but these are limited to present available information on corrosion and, more important, the contamination from corrosion that might result in the silicon product. Unfortunately, the extent of this knowledge at the present time is quite limited.

Laboratory data were not available for sizing solid-liquid separation equipment, but in determining equipment costs, assumptions for thickener and filter sizes were made.

An important part of the equipment list is the design and sizing of the silicon reduction pots. Sizing is based on present laboratory experience with the reduction of silicon in the SRI process and by a heat transfer analysis. The design and sizing calculations are presented in Appendix A, along with production rate calculations for reduction pots. The production capacity that can be achieved and the yield of acceptable purity specification product that can be produced in the reduction pots are the greatest uncertainties in the SRI silicon process and the areas where scaled up experimental work is required.

The cost of purchased equipment was determined using log-cost versus log-capacity charts and exponential formula available in handbook sources. Most of the data were determined at a Marshall and Stevens Index of 300 from Parkinson and Mular.¹ These costs were then converted to 1975 costs (M&S = 430).

A fixed capital cost estimate for 1975 was then determined from the equipment costs using the method of Professor Yaws² of Lamar University. This fixed capital cost is summarized in Table 6. Because the required 20 reduction pots are not installed equipment, their purchase price was excluded and computed on the basis of the amount of stainless steel and nickel used in the pot. All of the remaining equipment was multiplied by an equipment cost factor of 4.1 for a solids/liquids plant. Then, the 30% contingency was added, and the total fixed capital cost in 1975 dollars for the 1000 metric tons plant was \$9,006,985.

As a check on our purchased equipment cost estimating, we isolated those items of equipment for which SRI's chemical process economics cost estimating computer program has on-line cost data. In general, this involved all of the tanks and pumps. These costs were estimated for January 1978 and compared with the same items of equipment estimated by the Handbook data elevated to 1978 (M&S = 530). Good agreement was achieved.

¹ E. A. Parkinson and A. L. Mular, "Mineral Processing Equipment Costs and Preliminary Capital Cost Estimations", Special Volume 13, Canadian Institute of Mining and Metallurgy, 1972.

² Carl L. Yaws, private communication, January 1978.

Table 6

FIXED CAPITAL COST SUMMARY
(Lamar University Method)

Purchased equipment to be installed (M and S = 430)		\$1,616,840
Cumulative factor for solids/liquids plant*		<u>X 4.1</u>
		\$6,629,450
20 reduction pots	\$ 230,000	
Cumulative factor	1.3 [†]	<u>299,000</u>
		\$6,928,450
Contingency at 30%		<u>2,078,535</u>
TOTAL FIXED CAPITAL COST (1975 Dollars)		\$9,006,985

*Includes materials and labor, engineering, construction, instrumentation, offsites and buildings

†Engineering only, not installed equipment.

We also used the SRI computer program to generate a January 1978 capital cost. This is also a purchased equipment cost factored method of estimating capital costs, but the factors are entirely different from the Lamar University method. The "battery-limits" investment for the plant was \$8,817,000. With the off-site investment added on, the total fixed capital was \$10,639,000. This figure compares well with the total fixed capital costs from the Lamar University method, which also includes off-sites, when inflation from 1975 to 1978 is considered. The 1978 dollar estimate (SRI computer method) is 18.1% higher than the earlier 1975 dollar estimate using the Lamar University method. In our judgement, this is excellent agreement between two completely separate capital cost estimating methods. The capital costs calculated in both cases do not include start-up costs or working capital.

Estimation of Product (Silicon) Cost

The operating costs for producing marketable silicon (80% yield) were calculated using the method of Professor Yaws of Lamar University. The results are summarized in Table 7. The direct manufacturing costs for raw materials (1.1) and utilities (1.3), and the by-product credits (4) are as previously shown in Table 5. Note that although the production costs are being estimated for 1975 dollars and involve 1975 labor and capital costs, we are actually using January 1978 raw materials and utilities costs in making this estimate.

The cost of direct operating labor (1.2) was computed from the manning requirements and at an equal split of labor rate of \$6.90/hour and \$5.90/hour. All other items of direct cost, all indirect costs, and general expenses were then determined using Professor Yaws percentage factors derived from materials, labor and utilities costs, and the fixed capital costs of \$9,006,985, shown in Table 7. Total manufacturing cost before general expenses was \$5.39 per kilogram.

Table 7

ESTIMATION OF PRODUCT COST
(Lamar University Factors)

	<u>\$/yr</u>	<u>\$/kg Si</u>
1. Direct Manufacturing Cost (Direct Cost)		
1. Raw materials	5,721,540	5.725
2. Direct operating labor	674,000	.674
3. Utilities	714,500	.714
4. Supervision and clerical	101,100	.101
5. Maintenance and repairs	900,698	.901
6. Operating supplies	180,140	.180
7. Laboratory charge	101,100	.101
2. Indirect Manufacturing Cost (Fixed Cost)		
1. Depreciation	900,698	.901
2. Local taxes	180,140	.180
3. Insurance	90,070	.090
3. Plant Overhead	735,270	.735
4. By-Product Credit	(4,909,600)	(4.910)
4a. Total Manufacturing Cost, 1 + 2 + 3 + 4	5,392,656	5.393
5. General Expenses		
1. Administration	323,588	.324
2. Distribution and Sales	323,588	.324
3. Research and Development	161,794	.162
6. Product Cost Without Profit, 4a + 5	6,201,626	6.202
7. 25% ROI (Profit)	2,251,745	2.251
8. Cost + 25% ROI (Profit), 6 + 7	8,453,371	8.454

The resulting net cost of producing acceptable (saleable) silicon without profit is \$6.20 per kilogram. This cost involves a very important cryolite by-product credit of \$4.91 per kilogram of silicon. Raw materials were by far the largest cost component involving \$5.72 per kilogram of silicon.

Although previous silicon production cost comparisons for the Task 1 of the LSSA Program have involved silicon cost without profit, we have, as a matter of interest, also shown cost plus 25% return on investment for profit in Table 7. The 25% ROI adds another \$2.25 per kilogram of silicon for a total product cost, plus profit, of \$8.45 per kilogram of silicon, which is under the \$10.00 per kilogram goal for production of solar grade polycrystalline silicon in 1986.

Although the process did not include capital or operating costs for silicon powder melting, ingot casting, or unidirectional solidification, it is believed that the addition of these costs will be within the \$10.00 per kilogram goal.

Production costs would be reduced substantially by increasing plant capacity above 1000 MT/yr. With the use of the 0.6 factor rule on capital cost scaling,

$$C_1/C_2 = (P_1/P_2)^{0.6},$$

the resulting effects of increased plant size on silicon production costs have been calculated and are shown in Table 8. The result is a reduction in the silicon cost, without profit, to the range of \$5.00 per kg and lower for a modest increase in size relative to the ultimate solar cell production goals. An expected increase in labor productivity by using larger equipment in a scaled up plant also reduces costs.

The SRI computer method was used for estimating capital and production costs for a hypothetical "green field" Gulf Coast site. Comparison of both capital investment and production costs of the two methods are

Table 8

ESTIMATE OF FIXED CAPITAL AND PRODUCTION COSTS WITH PLANT SIZE

<u>Silicon Capacity</u>	<u>Total Fixed Capital</u>	<u>Silicon Cost</u> ¹	<u>Silicon Cost</u> ²
1000 MT/yr	\$ 9,006,985	\$ 6.20/Kg	\$ 6.20/Kg
3000	\$ 17,412,141	\$ 5.30	\$ 4.29
5000	\$ 23,657,096	\$ 5.00	\$ 3.79

1

Does not include any increase in operating labor productivity with scale.

2

Assumes no increase in total operating labor with increased scale or in the indirect costs factored from the operating labor.

summarized in Table 9. Note that the Lamar University method is for capital costs in 1975 dollars whereas the SRI method is for capital costs in 1978 dollars, but both methods estimate operating costs from the same basis. A big difference between the two estimates is that the SRI method includes \$4,521,000 for start-up and working capital which was not included in the Lamar University method capital cost. The result is a larger total capital investment, and this requires a higher net silicon cost because of the capital dependent operating cost factors. Both operating costs would benefit from economies of scale above 1000 MT/yr.

We believe these production costs have been realistically estimated based on the available knowledge of the SRI silicon process, and we believe they are reasonably conservative. The \$10.00 per kilogram goal for silicon production cost was never considered at any time in making these estimates.

Production Cost Sensitivity

A sensitivity analysis was made on the net silicon cost estimated using the Lamar University method, which was \$6.20/kg for our nominal case producing 1000 MT/yr of saleable silicon. The results of this cost sensitivity analysis are presented in Figure 4. The net silicon cost is plotted against percent deviation from the value of the nominal case summarized in Table 7. The deviation represents increases or decreases in prices or required quantities of process materials, utilities, labor, capital, etc. All cost contributing components which had a significant effect on the net silicon cost are shown in Figure 4.

The net silicon cost is not particularly dependent on costs of labor, utilities, or capital. By far the most important cost parameter, as with most extractive processes, is the silicon recovery or yield. In our nominal case we assumed 80% yield of saleable silicon from the production of reduced silicon. Although unlikely, it is theoretically

Table 9

COMPARISON OF RESULTS--1000 MT/YR

	<u>Lamar University Method</u>	<u>SRI Computer</u>
Date	1975	Jan. 1978
Equipment	\$1,846,000	\$ 2,004,800
Battery Limits Investment	-	8,817,000
Offsites	-	1,822,000
Contingency	2,028,535	-
 TOTAL FIXED CAPITAL	 9,006,985	 10,639,000
Start-up and Working Capital	Not included	4,521,000
 TOTAL CAPITAL INVESTMENT	 \$9,006,985	 \$15,160,000

PRODUCTION COSTS IN \$/kg Si

Total production cost	\$11.112	\$11.977
Cryolite Credit	(4.910)	(4.909)
<u>Net Silicon Cost</u>	6.202	7.068
25%/Yr ROI (Profit)	2.251	2.653
Product Price	8.454	9.722

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FIGURE 4 COST SENSIVITY ANALYSIS (LAMAR METHOD)

*Does not include ROI (Profit)

possible to increase this yield to 100% which would lower the net silicon cost to slightly under \$5.00/kg. Conversely, if only 50% of the reduced silicon meets product quality specifications, the net silicon cost would rise to nearly \$10.00/kg. Hence, it is extremely important to obtain a high yield of silicon meeting specifications. The next most important cost sensitivity factor is all materials taken in aggregate. However, the price and yield of cryolite have a greater impact on the net silicon cost than any single process material or any of the other cost factors except silicon yield. Since sodium and H_2SiF_6 are the major reactants, they have the greatest effect of individual process materials.

Discussion of Process Economics Implications for Future Research

The preliminary capital and operating costs for producing silicon shown in this analysis indicate that if the SRI silicon process can be scaled up with technological success, the process should produce silicon at a very satisfactory price. The cost sensitivity analysis indicates the primary importance of a high recovery of specification silicon, and economic credit for the co-product, cryolite.

Since the technology of producing cryolite is known and it is a commodity chemical sold in large tonnage quantities, most of the future research effort should be devoted to ensuring high recovery of adequate quality silicon by the SRI silicon process. Because the major process uncertainties of production throughput and product purity are centered around the sodium reduction step, it is most important that this step be scaled up. These tests should be aimed at demonstrating a high batch silicon production rate with very high heat removal rates and thus produce sufficient quantity of silicon for further impurity determinations and actual characterization of solar cells produced from the material.

The problem of high heat transfer has not really been encountered in the present experimental program, and it will become of increasing importance with scale-up. As large amounts of silicon are produced, the very exothermic sodium reduction reaction will produce large amounts of heat that must be removed from the reduction pot.

FUTURE WORK

A large batch (1 kg) of product silicon is currently being prepared by the SiF_4 -Na reaction. Silicon thus produced will be characterized by multiple chemical impurity analyses and by measuring the electrical properties. Further purification of this silicon by the $\text{Si} + \text{SiF}_4 \rightleftharpoons 2\text{SiF}_2$ reaction will be examined.

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Appendix A

SILICON REDUCTION POT HEAT TRANSFER AND DESIGN

I. Reduction Chemistry and Heat Release

Chemical reaction between liquid sodium and SiF_4 is extremely exothermic:

With the incoming gas at room temperature and sodium slightly above its melting point, it is possible to calculate the rate of heat release from the reduction pot that is required to maintain the product silicon and sodium fluoride at 1177 K, which is the boiling point of sodium. This amounts to 113 kcal/mole of reduced silicon, and it is necessary to dissipate 4036 kcal, or 16020 Btu from the reduction pot for each kilogram of silicon reduced. Sodium boiling will limit the temperature, and if the reaction is accelerated, reduction will spread through the pot as a vapor phase reaction.

II. Heat Transfer

A fluidized sand bed is used to maximize the rate of heat transfer away from the reduction pot, and thereby improve the production rate of silicon. The reduction pot is inserted in the fluidized sand bed in a pit for which the estimated heat transfer rate, h , is

$$\begin{aligned} h &= 400 \text{ kcal m}^{-2} \text{ hr}^{-1} \text{ } ^\circ\text{C}^{-1} \\ h &= 82 \text{ Btu ft}^{-2} \text{ hr}^{-1} \text{ } ^\circ\text{F}^{-1} \end{aligned} \quad (2)$$

¹ D. Kunii and O. Levenspiel Fluidization Engineering, J. Wiley, New York, 1969, chap. 9.

The fluidized bed is maintained at 482°F by water injected into the fluid bed. This temperature is high enough to initiate the reduction reaction for a newly inserted pot.

The external wall of the reduction pot is taken as 1000°F with a temperature difference in the fluid bed boundary layer of $\Delta T = 518^{\circ}\text{F}$ and a heat transfer flux according to the following equation,

$$\dot{q} = h\Delta T \quad (3)$$

which provides a fluid bed heat transfer flux,

$$\dot{q}_{\text{FBR}} = 42,500 \text{ Btu hr}^{-1} \text{ ft}^{-2} \quad (4)$$

$$\dot{q}_{\text{FBR}} = 11.8 \text{ Btu ft}^{-2} \text{ sec}^{-1}$$

The inner wall temperature of the reduction pot will exceed 1000°F by an amount depending on the wall thickness and alloy thermal conductivity. The estimated increase in inner wall temperature with thickness for a composite wall stainless steel and nickel reduction pot is shown in Figure A.1.

Heat transfer by radiation to a black body from a reduction pot with an external wall temperature of 1000°F was also calculated and is only about 20% of the fluid bed heat transfer rate. However, radiation would provide a greater rate of heat transfer than would natural convection without use of the fluid bed.

As reduction proceeds, silicon and sodium fluorides accumulate to form a more or less conical stalagmite rising from the bottom of the reduction pot. The reaction occurs primarily on and near the surface of the top of the stalagmite where injected sodium drips. Based on mass transfer calculations and experimental observations, for any reasonable drop height, most of the falling sodium droplet is unreacted and unvaporized when it strikes the top of the stalagmite, where it dribbles down the reacted mass while reacting with SiF_4 . The vaporization of sodium tends to limit the

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FIGURE A.1 APPROXIMATE REDUCTION POT WALL TEMPERATURE WITH THE OUTER WALL FIXED AT 1000°F IN A FLUIDIZED SAND BED

reaction temperature on the stalagmite surface to the sodium boiling point, 1177 K. Excess sodium boils off and reacts with SiF_4 in the vapor phase.

High reaction rates lead to high temperatures and quasi-solidification of the stalagmite mass. Laboratory growth of both thin and thick stalagmites has been demonstrated and the shape of the stalagmite cone is an important consideration for heat transfer and possibly burning of the reduction pot walls.

Heat is transferred from the reaction zone by radiation and conduction through the inner wall of the reduction pot. Order of magnitude calculations indicate that solid state thermal conduction down through the stock of the product stalagmite can account for only 5 to 10% of the required rate of heat release and is, therefore, relatively insignificant. Significant heat transfer from the hot stalagmite tip to the reduction pot wall is by radiation from the stalagmite and by convection from the homogeneous combustion by SiF_4 of boiling sodium. The reduction reaction can induce high localized temperatures, T_r , and high rates of radiative heat release by

$$\dot{q} = \epsilon \sigma (T_r^4 - T_w^4) \quad (5)$$

with $T_r = T_{BP}$ of sodium (1177 K)

As a matter of conservative design for thermal protection of reduction pot walls, we have considered a reduction pot consisting of a vertical cylinder of diameter, D . The taper section of the growing product stalagmite must be controlled so that there is a sufficiently long zone on the axis of the cylinder from which heat is radiating. This is necessary so that heat is not overly concentrated in a thin section of the cylinder wall causing a burn-out or high reactivity between the reaction products and reduction pot wall. However, it is also necessary to obtain a significantly large yield of reaction product in each batch run. Hence, the reaction product stalagmite must not be too thin, leaving an excessive volume of reduction pot vessel that is not filled with reaction product at the end of the run. The results of improper control of the stalagmite taper section are illustrated in Figure A.2.

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FIGURE A.2 GROWTH OF REACTION PRODUCT ($\text{Si} + 4\text{NaF}$) "STALAGMITE" IN THE REDUCTION POT

Design of the liquid sodium injector nozzles will be an important aspect of further development of a scaled-up SRI silicon process. We believe that the injector design and operator control of the reduction process can be such that the height of the hot zone section of the reduction pot, H , is at least equal to the diameter, D , of the reduction pot cylinder, $H \geq D$. Hence, we have calculated a silicon production rate that generates excess heat at a rate, $\dot{Q}$, equal to the rate of heat transfer through the reduction pot walls to the fluidized sand bed for a right circular section, whose height is equal to its diameter, $H = D$. An estimate of the production rate of silicon, $\dot{N}$, expressed in kilograms of silicon per hour, was obtained by the following calculation:

$$H = D \quad (6)$$

$$A = \pi DH = \pi D^2 \quad (7)$$

$$\begin{aligned} \dot{Q}(\text{Btu hr}^{-1}) &= 3500 \pi [D(\text{ft})]^2 \\ \dot{Q}(\text{Btu sec}^{-1}) &= 11.3 \pi [D(\text{ft})]^2 \end{aligned} \quad (8)$$

where $A(\text{ft}^2)$ is the reacting surface area.

With an outer pot wall temperature at 1000°F and an inner wall temperature at 1150°F (Fig. A.1), it is possible to estimate the heat transferred to the wall by radiation from the stalagmite cone on the assumption that the cone is sufficiently covered with boiling sodium to keep the surface at 1177 K (1660°F). The cone area, also with its height equal to the pot diameter, is 43% of the cylinder area. With an estimated emissivity of 0.60, the radiation heat transfer rate is

$$\begin{aligned} \dot{Q}_r &= (0.43 \pi D^2) (.174) 0.60 \left[\left(\frac{T_r}{100} \right)^4 - \left(\frac{T_w}{100} \right)^4 \right] \\ \dot{Q}_r &= 5230 \pi D^2 \text{ BTU Hr}^{-1} \end{aligned} \quad (9)$$

Note that this is less than 10% of the heat dissipation rate with the outer wall at 1000°F ; see equation 8. Consequently, if the reaction is conducted

at a rate equal to the heat dissipation with the outer wall at 1000°F in a fluid bed, then about 80% of the sodium will vaporize on the hot stalagmite surface and react with the SiF_4 in the vapor phase surrounding the product stalagmite. The boiling sodium will produce a diffusion flame with the incoming SiF_4 . Radiation from the fine product particles of silicon and NaF (fume) and convection from the hot gas and fume will conduct most of the released heat to the pot wall.

The silicon production rate with heat release at an average temperature equal to the sodium boiling point would appear to be a safe operating condition. Using the heat dissipation rate from equation 8 yields

$$\left. \begin{aligned} \dot{N} &\approx \frac{42500 \pi D^2 \text{ Btu hr}^{-1}}{16020 \text{ Btu (kg-Si)}^{-1}} \\ \dot{N} &\approx 8.3 [D(\text{ft})]^2 \text{ kg-Si hr}^{-1} \end{aligned} \right\} \quad (10)$$

Constraining the system to minimize sodium boiling and silicon fume production would limit the production rate to about 20% of this value.

A high flow SiF_4 injection orifice should be used to prevent back flow of fume from the reduction pot. A high background pressure of SiF_4 is desirable at all times. This will limit the amount of unreacted sodium and confine the reaction flame front to a region near the product where sodium is vaporized after sodium droplets impact the previous reaction product. In summary, excess SiF_4 should always be present with the production rate controlled by the rate of injection of sodium.

III. Production Rate, Run Time, and Batch Size

With Equation 10, it is possible to compute annual production rates as a function of reduction pot diameter (ft) under the assumption that a reduction pot is on line 7000 hours per year. This is actually a calculation of the annual production from each reduction pot station that is on line since any individual reduction pot spends a large fraction of its time

being processed out of the fluidized bed reduction pit. A large number of reduction pots will be required.

From the annual production rate per reduction pot station, it is possible to compute the average number of units that must be on line during the 7000 hours per year of plant operating time. This calculation can also be augmented to take into account various assumptions about the yield of reduced silicon which is useable as a product. Results of these types of calculations for selected values are summarized in Table A.1.

The production rate is independent of the height of the pot because the hot zone in this conservative design is effectively limited to a distance equal to the pot diameter. For any right circular cylinder design, the effective heat transfer height will be proportional to the cylinder diameter. Hence, in scaling up any system, total height of the reduction pot will not affect the production rate when the pot is on line and running. However, the run time and total accumulation of product is proportional to the total reduction pot height. Hence, it will be necessary to design reduction pots with sufficient height to allow a reasonable cycle period so that excessive labor and time are not devoted to inserting and removing pots from the fluid bed for a reduction run of only a few minutes.

In calculating production cycle periods, it is necessary to take into account the effective density, ρ , of powdered silicon in the very porous reaction product. Also, silicon is a minor solid constituent compared with sodium fluoride. Laboratory measurements of reaction product indicate a very low apparent density of silicon, 1.7 kilograms per cubic foot. For any size pot that is operated optimally to fill the pot with reaction product, except for a final taper cone, the run time is proportional to the fill height of the reduction pot and independent of its diameter. A plot of run time, which is the period during which the silicon reduction reaction is occurring at the optimal rate based on heat transfer considerations and the reduction pot diameter, is plotted against the reduction pot fill

Table A.1

SUMMARY OF PRODUCTION RATES WITH REDUCTION POT SIZE

Reduction Pot Diameter D (ft)	Silicon Production Rate (kg hr)	Annual ¹ Production Rate (MT/yr)	Average Number of Pots Running ² for 1000 MT/yr	
			(100% Yield)	(80% Yield)
1	8.3	58	17.2	21.5
2	33	233	4.3	5.4
2.5	52	364	2.75	3.4
3	75	525	1.9	2.4

1. 7000 hr/yr

2. Needed to provide 1000 MT/yr plant output

height in Figure A.3. The initial induction period in this curve accounts for the fact that some open volume must be left for the final taper section in the reaction product stalagmite. A pot fill height of 9 to 10 feet is required for a run time of about 1 hour.

Additional freeboard would be required to prevent overheating the sodium injection nozzles. Without specific experimental data, we would recommend a freeboard at least equal to the reduction pot diameter.

If reduction pots become too large, there may be structural and total weight difficulties in handling the pots and transporting them between various plant stations. The approximate weights for different reduction pot sizes are shown in Table A.2. The total weight will involve the reduction pot, its contents, and the liquid sodium canister attached above the reduction pot. The volume required for liquid sodium is a chamber with the same diameter as the reduction pot and a working height about equal to the reduction pot diameter if a run time of one hour is desired.

IV. Design Selection

Consideration of reduction pot size, average number of reduction pots required to be on line at any time, labor required for assembling, disassembling, and handling reduction pots, run time, and reduction pot weight led to a selected reduction pot design that employs a 3-ft-diameter pot with a fill height of approximately 9 feet and a total height of 12 feet. At the top of the 12-foot reduction pot will be a 5-foot superstructure containing a 2½- to 3-foot high sodium canister. The sodium canister will have provisions for electrical resistance heating to keep the sodium molten. The reduction pot and sodium canister are joined by a sealed, bolted flange. The essential dimensions of the reduction pot are shown in Figure A.4.

Each pot run will produce approximately 75 kilograms of silicon. This will require 277 kilograms of liquid sodium and 2,331 standard cubic feet of SiF_4 . The sodium feed rate is about 3.6 kilograms per minute and the

FIGURE A.3 POT RUN TIME DEPENDENCE ON POT FILL HEIGHT

Table A.2

APPROXIMATE WEIGHTS OF REDUCTION POTS AND BATCHES

Pot Diameter (ft)	Fill Height (ft)	Total Height (ft)	Pot and Sodium Canister (lb)	Max Product Weight (lb)	Gross Weight (lb)
1	9	12	1000	200	1200
2	9	12	2000	800	2800
2.5	9	12	2700	1250	3950
3	9	12	3250	1800	5050

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FIGURE A.4 SILICON REDUCTION POT

SiF_4 gas feed rate is about 4.2 kilograms per minute, which is a gas flow rate of 32 standard cubic feet per minute. Although an average of only 2.4 pots will be running, provisions must be made for delivering gas in variable amounts from one to as many as four pots at any one time. Consequently, the retort that thermally dissociates Na_2SiF_6 must be capable of producing from 0 to 120 standard cubic feet of SiF_4 gas per minute.

The reduction pots should be fabricated of carbon stabilized stainless steels, SS321 or SS347, with an inner clad lining of commercially pure nickel. This material specification assumes that nickel is not a serious impurity in solar cell grade silicon.

Appendix B

Equipment Lists

WET PLANTEQUIPMENT LIST

DESIGNATION	NAME	NO. REQD.	CAPACITY	MATERIALS
<u>Tanks</u>				
T1	Deionized Water Storage	1	215,000 gal = 24 hr	FRP or rubber clad carbon steel (CS)
T2	Dilute H_2SO_4 Storage	1	18,000 gal = 4 hr	FRP
T3	H_2SiF_6 Storage	1	322,000 gal = 2 weeks	FRP or rubber lined CS
T4	Caustic Soda Liquor Storage	1	10,000 gal = 2 weeks	FRP or rubber lined CS
T6	H_2SO_4 Storage	1	40,000 gal = 4 weeks	CS
ST8	Na_2SiF_6 Precipitator Tanks	3	12 ft dia x 12 ft with 10 HP agitator 4-6 hr batches (10,000 gal)	304L stainless steel (SS) tank and impeller
T9	NaF Lagoon	1	864,000 gal = 4 days	Plastic lined bottom 20,000 ft ² x 6 ft deep
ST10	Cryolite Precipitation Tanks (series)	4	12 ft dia x 12 ft with 10 HP agitators each (2 hr residence for 4 tanks in series)	CS, SS impellers
ST11	Thickener	1	100 ft dia (2.5 in/hr settling rate)	CS

WET PLANTEQUIPMENT LIST

DESIGNATION	NAME	NO. REQD.	CAPACITY	MATERIALS
<u>Tanks</u>				
ST12	Alumina Hydrate Slurry Tank	1	7 ft dia x 7 ft with 2 HP agitator (2000 gal) (1 $\frac{1}{4}$ hr)	CS, SS impeller
ST13	Lime Hydrate and Water Treatment Tanks	2	8 ft dia x 8 ft with 3 HP agitators 3000 gal (5 min each)	CS, SS impeller
ST14	Silicon Sponge Reslurry Tank	2	8 ft dia x 8 ft with 5 HP agitator	Rubberlined CS with SS impellers
T15	Silicon Filter Sump	1	7 ft dia x 4 ft (7 min) 1000 gal	FRP or rubberlined CS
ST16	NaF Solids Purge Slurry Tank	2	7 ft dia x 7 ft with 2 HP motor (5 hr each)	FRP
ST17	Scrubber Sump	1	8 ft dia x 8 ft with 3 HP motor	CS

WET PLANTEQUIPMENT LIST

DESIGNATION	NAME	NO. REQD.	CAPACITY	MATERIALS
<u>Bins/Silos</u>				
S1	Alumina Monohydrate Storage Silo with discharge by 8 x 5 bucket elevator (continuous) to ST12 tank	1	4000 cu ft = 20 days 10 ft dia x 50 ft	Reinforced concrete
S2	Lime Storage Silo with continuous discharge 8 x 5 bucket elevator to ST13 Tank No. 1	1	2000 cu ft = 20 days 10 ft dia x 30 ft	Reinforced concrete
S3	Cryolite Storage Silo with 10 x 6 bucket elevator for loading ER cars	1	9000 cu ft = 14 days 15 ft dia x 50 ft	Reinforced concrete
S4	Na ₂ SiF ₆ Silo with screw conveyor	1	4000 cu ft = 6 days 10 ft dia x 50 ft	Reinforced concrete lined with 304L SS liner

WET PLANTEQUIPMENT LIST

DESIGNATION	NAME	NO. REQD.	CAPACITY	MATERIALS
<u>Pumps</u>				
P1	Deionized Water Pump Centrifugal	2	200 GPM, 60 ft head	All plastic or SS
P2	Dilute H_2SO_4 Pump Centrifugal	2	100 GPM, 60 ft head	All plastic or SS
P3	H_2SiF_6 Pump Centrifugal	1	50 GPM, 30 ft head	All plastic or SS
P4	Caustic Soda Solution Pump	1	10 GPM, 30 ft head	All plastic metering pump
P6	H_2SO_4 Pump	1	2 GPM, 75 ft head	All plastic metering pump
P7	Alumina Slurry Pump Centrifugal	2	50 GPM, 50 ft head	rubberlined
P8	Na_2SiF_6 Slurry Pump Centrifugal	2	50 GPM, 50 ft head	Rubberlined SS
P9	Filtrate Pump Centrifugal	1	50 GPM, 45 ft head	All plastic or SS
P10	Scrubber Feed Pump Centrifugal	1	100 GPM, 50 ft head	CI

WET PLANTEQUIPMENT LIST

DESIGNATION	NAME	NO. REQD.	CAPACITY	MATERIALS
<u>Pumps</u>				
P11	Cryolite Slurry Pump Centrifugal	1	200 GPM, 60 ft head	Rubberlined CS or CI
P12	Thickener U'flow Pump Diaphragm Pump (positive displacement)	1	25 GPM, 60 ft head 45 ft head, 25% solids	CS or CI Diaph.
P13	Silicon Slurry Pump Centrifugal	1	50 GPM, 45 ft head	All abrasion resistant plastic or rubberlined S.S.
P14	Silicon Leach Liquor Pump Centrifugal	1	200 GPM, 30 ft head	SS
P15	Silicon Leach Liquor Pump Centrifugal	1	200 GPM, 30 ft head	SS
P16	Thickener U'Flow Pump Centrifugal	1	200 GPM, 30 ft head	CI

WET PLANT

EQUIPMENT LIST

DESIGNATION	NAME	NO. REQD.	CAPACITY	MATERIALS
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Pumps

P17	Purge Pump Centrifugal	1	25 GPM, 30 ft head	SS
P18	Scrubber Recycle Pump Centrifugal	2	100 GPM, 60 ft head	CI

WET PLANTEQUIPMENT LIST

DESIGNATION	NAME	NO. REQD.	CAPACITY	MATERIALS
<u>Equipment</u>				
<u>Miscellaneous</u>				
M1	Battery Limits Deionized Water Plant, equipment only	1	200 GPM	
M2	Bulk Solids, RR Unloading System with Elevator to S1 and S2	1	75 T/hr Capacity	CS
M3	Weigh Belt Feeder for NaF with 10 Ton Covered Hopper	1	0-10 T/hr	SS
M4	Belt Extractor (Filter)	1	25 GPM feed 2.0 T/hr Solids	All plastic or SS (area to be calculated)
M5	Disc Filter	1	18 GPM Feed 2.0 T/hr Solids	Standard service (area to be cal- culated)
M6	Filter Press for Silicon Washing	3	130 GPM with 3000 lb/hr of solids when loading	All plastic (dilute acid duty, HF) (area to be calculated)

WET PLANTEQUIPMENT LIST

DESIGNATION	NAME	NO. REQD.	CAPACITY	MATERIALS
<u>Equipment</u>				
<u>Miscellaneous</u>				
M7	Conveyor Belt to Dryer with Drive	1	18-in. x 75 ft	CS
M8	Conveyor Belt to Dryer with Drive	1	18-in x 100 ft	CS
M9	Heat Exchanger, Tube/Shell	1	24000 Btu/min with 100 GPM water flow through tubes	All copper condenser tube & shell.
M10	Indirect Dryer for Na_2SiF_6 , Double Shell Rotary Dryer	1	Remove 50 lb/min water, avg, 100 lb. max 1.5-3.0 T/hr solids	Inner Shell is 316L SS
M11	Cryolite Dryer, Direct Fired Rotary	1	50 to 100 lb /min water 1.5 to 3.0 T/hr solids	Brick lined CS
M12	Cryolite Cooler Rotary	1	5 ft dia x 35 ft	CS
M13	Rotary Na_2SiF_6 retort Double walled indirect firing, heat solids to 750°C	1	Net heat input = BTU/min Solids = 1.5 to 3.0 T/hr	Inner wall is SS 347 L or 321L outer wall is brick- lined CS

WET PLANTEQUIPMENT LIST

DESIGNATION	NAME	NO. REQD.	CAPACITY	MATERIALS
<u>Equipment</u>				
<u>Miscellaneous</u>				
M14	Gas Scrubber, Tower, Liquid Sprayed	1	6000 cfm input, 100GPM liquid flow	FRP tower with plastic or S.S. distributors
M15	Screw Feeder to NaF Hopper with Variable Speed Drives	1	10 T/hr	SS
M16	Precipitator screw feeder with Variable Speed Drive	1	10 T/hr by 75 ft	SS
M17	Blower for Scrubber Vent (Induction Fan)	1	5000 cfm	SS
M18	Vent Stack	1	2 ft dia x 50 ft	SS
M19	Semi-autogenous Ball Mill with Trammel Discharge at 10 Mesh	1	2 T/hr solids avg max = 5 T/hr solids	SS shell and trammel rubberlined shell and lifters

REDUCTION PLANTEQUIPMENT LIST

DESIGNATION	NAME	NO. REQD.	CAPACITY	MATERIALS
P1	Scrubber Pump	1	25 GPM	Carbon Steel
M1	SiF ₄ Gas Filter (Dry)	2		Remove all submicron particulate at 64 cfm Gas Flow rate, replaceable filter media
M2	Vacuum Pump and Motor	1	Evacuate 65 cu ft at STP to 0.2 Torr in 6 min.	Pump equipped with particulate filter or inlet, must handle corrosive gas SiF ₄ but dry
M3	Fluidized Bed Pit	1	11 ft x 11 ft x 16½ ft deep with -48 mesh sand filled to 13 ft level when expanded to 50% porosity	
M4	Fluidized Bed Turbo-Blower	1	7500 cfm at 200 °C	ΔP = 7 psig avg. with motor for peaking to 8 psig Temp = 200 °C, SS Motor = 400 HP

REDUCTION PLANTEQUIPMENT LIST

DESIGNATION	NAME	NO. REQD.	CAPACITY	MATERIALS
M5	Fluidized Bed Vent Induced Draft Fan	1	3000 Cfm Max Δ P = 0.5 psig	SS 25 HP motor
M6	Wet Scrubber	1	3000 Cfm inlet 4000 Cfm exhaust	FRP 25 HP motor
M7	Soaking Pit	1	6 ft x 6 ft x 17 ft deep	Brick lined for 1450 ^o F duty, equipped with adjustable gas burner to 1.25 million Btu/hr max
M8	Soaking Pit Vent Fan	1	2500 acfm @ 225 ^o C	S.S.
M9-B	Reduction Pot Bottom (per sketch, fig. A-4)	20	3 ft dia x 13 ft	Nickel 1/8" inner cladding with 3/8" shell of SS 321L or SS 347L
M9-T	Reduction Pot Top (per sketch, fig. A-4)	20	3 ft dia x 5 ft	SS 321L or 347L

REDUCTION PLANTEQUIPMENT LIST

DESIGNATION	NAME	NO. REQD.	CAPACITY	MATERIALS
M10	Electric Melting Furnace for Sodium	1	20 kw	With vacuum sealed 100 lb capacity lock hopper, SS
M11	Electronic Platform Scale to Weigh Na filling Pots with Readout and Printer	1	3000 lb	SS deck
M12	Bridge Crane with Mounted Operator Cab 35 ft span, 30 HP motor	1	10 Ton	Standard
M13	Pot Unload/Reload Station Consisting of a 20 unit Pot Storage rack and a Platform 20 ft x 30 ft x 14 ft with 6 dismount stations	1		CS
M15	Nitrogen Actuated Liquid Sodium Pump-Variable Flow Rate	1	40 lb /min (5 GPM)	Special
M16	Liquid N ₂ Reservoir	1	10 tons	Standard pkg unit