

## General Disclaimer

### One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

SEVENTH QUARTERLY PROGRESS REPORT  
Covering the Period April 1, 1977, to June 30, 1977

on

**EVALUATION OF SELECTED CHEMICAL PROCESSES  
FOR PRODUCTION OF LOW-COST SILICON**  
(Phase II)

JPL Contract 954339

Silicon Material Task  
Low-Cost Silicon Solar Array Project

to

JET PROPULSION LABORATORY  
CALIFORNIA INSTITUTE OF TECHNOLOGY

by

J. M. Blocher, Jr., M. F. Browning, W. J. Wilson,  
and D. C. Carmichael

July 20, 1977

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, under NASA Contract NAS7-100 for the U.S. Energy Research and Development Administration, Division of Solar Energy.

The JPL Low-Cost Silicon Solar Array Project is funded by ERDA and forms part of the ERDA Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays.

BATTELLE  
Columbus Laboratories  
505 King Avenue  
Columbus, Ohio 43201



(NASA-CR-153907) EVALUATION OF SELECTED  
CHEMICAL PROCESSES FOR PRODUCTION OF  
LOW-COST SILICON, PHASE 2 Quarterly  
Progress Report, 1 Apr. - 30 Jun. 1977  
(Batelle Columbus Labs., Ohio.) 33 P HC  
P03/MF A01  
G3/44  
Unclas  
39176  
N77-28579

SEVENTH QUARTERLY PROGRESS REPORT  
Covering the Period April 1, 1977, to June 30, 1977

on

**EVALUATION OF SELECTED CHEMICAL PROCESSES  
FOR PRODUCTION OF LOW-COST SILICON**

(Phase II)

JPL Contract 954339

Silicon Material Task  
Low-Cost Silicon Solar Array Project

to

JET PROPULSION LABORATORY  
CALIFORNIA INSTITUTE OF TECHNOLOGY

by

J. M. Blocher, Jr., M. F. Browning, W. J. Wilson,  
and D. C. Carmichael

July 20, 1977

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, under NASA Contract NAS7-100 for the U.S. Energy Research and Development Administration, Division of Solar Energy.

The JPL Low-Cost Silicon Solar Array Project is funded by ERDA and forms part of the ERDA Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays.

BATTELLE  
Columbus Laboratories  
505 King Avenue  
Columbus, Ohio 43201

## TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGEMENT. . . . .	iii
ABSTRACT . . . . .	1
INTRODUCTION . . . . .	4
DESIGN OF THE EXPERIMENTAL FACILITY. . . . .	4
Process Flow Diagram - Materials/Energy Balance . . . . .	5
Instrumentation . . . . .	10
ZnCl <sub>2</sub> Recycle Alternatives. . . . .	10
ZnCl <sub>2</sub> Electrolysis. . . . .	12
Waste Processing. . . . .	13
DuPont Silicon. . . . .	14
Design Strategy . . . . .	14
Design of Specialized Units . . . . .	15
Operation Cost, Experimental Facility . . . . .	18
Plans for the Next Report Period. . . . .	20
EXPERIMENTAL SUPPORT PROGRAM . . . . .	20
Effect of Bed Particle Size . . . . .	21
Zinc Vaporizer. . . . .	24
Electrolysis of ZnCl <sub>2</sub> . . . . .	25
Removal of SiCl <sub>4</sub> From Cl <sub>2</sub> . . . . .	26
Solubility of ZnCl <sub>2</sub> in SiCl <sub>4</sub> . . . . .	26
Work Planned for Next Report Period . . . . .	27
REFERENCES . . . . .	28

LIST OF FIGURES

	<u>Page</u>
Figure 1. Process Flow Diagram for 25 MT/Year Silicon Facility (7/5/77) . . . . .	6
Figure 2. Description of Units and Associated Equipment - 25 MT/Year Facility (7/5/77). . . . .	11
Figure 3. Design Schedule, Experimental Facility (7/5/77). . . . .	17

LIST OF TABLES

Table 1. Material and Energy Flow Sheet - 25 MT/Year Silicon Facility (7/5/77) . . . . .	7
Table 2. Identification of Primary Design Responsibility by Item (7/5/77). . . . .	16
Table 3. Estimated Cost of Operation of Experimental Facility . . . . .	19
Table 4. Summary of Selected Miniplant Data. . . . .	23

### ACKNOWLEDGEMENT

The authors gratefully acknowledge the capable assistance of the following individuals in the performance of the work and preparation of this report: Mr. Erlan E. Rose, Mr. William B. Thompson, Mr. William A. Schmitt, Mr. James S. Fippin, Mrs. Pamela S. Kerbler.

SEVENTH QUARTERLY PROGRESS REPORT  
Covering the Period April 1, 1977, to June 30, 1977

on

EVALUATION OF SELECTED CHEMICAL PROCESSES  
FOR PRODUCTION OF LOW-COST SILICON

JPL Contract 954339

Silicon Material Task  
Low-Cost Silicon Solar Array Project

to

JET PROPULSION LABORATORY  
CALIFORNIA INSTITUTE OF TECHNOLOGY

from

BATTELLE  
Columbus Laboratories

July 20, 1977

ABSTRACT

During Phase I of this program (concluded in October of 1976), economic analyses and experimental work were carried out on the fluidized-bed zinc reduction of  $\text{SiCl}_4$  and on several modifications of the iodide process ( $\text{SiI}_4$  decomposition or reduction) which led to the selection of the fluidized-bed zinc reduction of  $\text{SiCl}_4$  as a promising candidate for supplying low-cost solar- or semiconductor-grade silicon. Phase II of the program, currently underway, has as its objective, designing an experimental facility (tentative 25 MT Si/year capacity) and carrying out an experimental program to support the design effort. Updates of plant and production cost estimates at the 1000 MT/year level are to be made based on the design experience.

During this quarter, the process flow diagram and materials/energy balances for the experimental facility were refined. Preliminary assessments were made of the instrumentation requirements. The alternative of marketing

the  $ZnCl_2$  by-product rather than recycling the zinc by electrolysis was considered and rejected.

A visit was made to the Bureau of Mines Station at Reno, Nevada, to obtain information on their fused-salt electrolysis of  $ZnCl_2$ . The requirements of a 25 MT Si/year experimental facility could be met with three 5000-ampere cells containing ~50 mole percent KCl in the  $ZnCl_2$ , operating at 500 C with current efficiencies of 95 percent and electrical energy utilization efficiencies of >85 percent at current densities of 2 amp/cm<sup>2</sup>. The cell design would be consistent with chlorination of the fine particulate suspended silicon that would be carried into the electrolytic cell in the experimental facility.

Design of the system for chlorine disposal has been greatly simplified by the finding that it will not be necessary to remove the  $SiCl_4$  from the chlorine if the hypochlorite product of disposal is used for local sewage plant effluent treatment as planned.

Information has been obtained from DuPont on the quality of the silicon they prepared by the batch-wise zinc reduction of  $SiCl_4$  and supplied to the semiconductor industry in the 1960's. Useful information was also obtained on the production process.

On the basis of contacts with four engineering firms and their proposals, Raphael Katzen Associates of Cincinnati, Ohio, has been chosen to supply chemical engineering design service for items of conventional design in the experimental facility, and Pace Engineering, Inc., of Beaumont, Texas, has been chosen to design the  $SiCl_4$  purification section of the experimental facility. Design of the unconventional items such as the fluidized-bed reactor and zinc handling system will be undertaken by Battelle's Columbus Laboratories personnel with ad hoc assistance where necessary. A chart of design responsibilities has been drawn up and a detailed time table established for conclusion of the overall design task by November 15, 1977.

Potential designs for an integrated fluidized-bed reactor/zinc vaporizer/ $SiCl_4$  preheater unit are being considered and heat-transfer calculations have been initiated on versions of the zinc vaporizer section.

Estimates of the cost of the silicon prepared in the experimental facility have been made for projected capacities of 25, 50, 75, and 100 MT/



of silicon. A 35 percent saving is obtained in going from the 25 MT/year to the 50 MT/year level. This analysis, coupled with the recognition that use of two reactors in the 50 MT/year version allows for continued operation (at reduced capacity) with one reactor shut down, has resulted in a recommendation for adoption of an experimental facility capacity of 50 MT/year or greater. At this stage, the change to a larger size facility would not increase the design costs appreciably.

In the experimental support program, the effects of seed bed particle size and depth were studied, and operation of the miniplant with a new zinc vaporizer was initiated, revealing the need for modification of the latter.

Experimental operation of a cell for the electrolysis of  $ZnCl_2$  by-product of the miniplant revealed no problems relative to the presence of zinc and finely divided silicon in the by-product. The cell will be redesigned in light of information obtained on the Bureau of Mines operation.

It was determined experimentally that the solubility of  $ZnCl_2$  in  $SiCl_4$  at room temperature is <0.2 percent, and that water hydrolysis of  $SiCl_4(g)$  is effective in removing it from  $Cl_2(g)$ .

## INTRODUCTION

This is the Seventh Quarterly Progress Report covering the work for JPL-ERDA at Battelle's Columbus Laboratories on the Evaluation of Selected Chemical Processes for the Production of Low-Cost Silicon.

The Fifth-Sixth Quarterly Report, dated April 29, 1977, summarized the work done in Phase I of this program (October, 1975, through September, 1976) in which the zinc reduction of silicon tetrachloride in a fluidized bed of seed particles was chosen for further study, together with progress through March 31, 1977, on Phase II of the program, which has as its objective the design of an experimental facility, nominally of 25 MT/year silicon capacity, to demonstrate the process and to provide a sound engineering basis for further scale-up. As the background for the Phase II program is fully summarized in the Fifth-Sixth Quarterly Report, it will not be repeated here, even briefly. Rather, this report will be limited to changes in process concept that have occurred, and progress that has been made in furthering the design task and in the experimental study of process parameters and equipment design. Accordingly, progress is reported in two sections, Design of the Experimental Facility, and Experimental Support Program.

### DESIGN OF THE EXPERIMENTAL FACILITY

Progress in the design of the experimental facility during the report period has involved (1) further definition of the process flow sheet and materials/energy balances, (2) preliminary assessment of the instrumentation required, (3) consideration of alternatives to  $ZnCl_2$  electrolysis for recycle, (4) procurement of additional information on  $ZnCl_2$  electrolysis, (5) definition of waste handling procedures, (6) collection of information on the silicon produced by zinc reduction of  $SiCl_4$  at DuPont, (7) identification of primary design responsibility for each major piece of equipment, (8) generation of a detailed time schedule with the objective of concluding the design by November 15, 1977, (9) negotiations with engineering companies and with Battelle

engineering groups to provide engineering support, (10) preliminary design of specialized equipment, and (11) estimates of the operations cost of the experimental facility versus size. These items will be discussed in turn.

Process Flow Diagram -  
Materials/Energy Balance

The April 1, 1977, revisions of the process flow diagram and materials/energy balance were presented as Figure 4 and Table 2, respectively, of the Fifth/Sixth Quarterly Report. Changes have been made since that time related mainly to the waste product handling (to be discussed in a separate section). Figure 1 presents the July 5, 1977,\* revision of the process flow diagram which differs from the April 1, 1977, version in that

- (1) A separate  $\text{SiCl}_4/\text{ZnCl}_2$  condenser (F3) has been provided to handle the product of the wall deposit chlorination, rather than to strip the  $\text{ZnCl}_2$  (if any) in a small unit (F2) and then use the main process  $\text{SiCl}_4$  recycle condenser (A13) to condense the  $\text{SiCl}_4$ , rerouted to waste disposal
- (2) Removal of the  $\text{SiCl}_4$  from the chlorine produced in the electrolytic cell has been eliminated, as  $\text{SiCl}_4$  will not be objectionable as an impurity in the contemplated use of the hypochlorite (to be discussed in a separate section)
- (3) Additional pumps and valves have been added (distinguished as manual and automatic), and flow controls have been added at certain points
- (4) A few corrections have been made in the diagram.

Table 1 presents the corresponding Materials and Energy Flow Sheet. It will be noted that the elimination of  $\text{SiCl}_4$  removal from the chlorine

---

\* Minor last-minute revisions were made in the figure, thus accounting for the revision date beyond the report period.

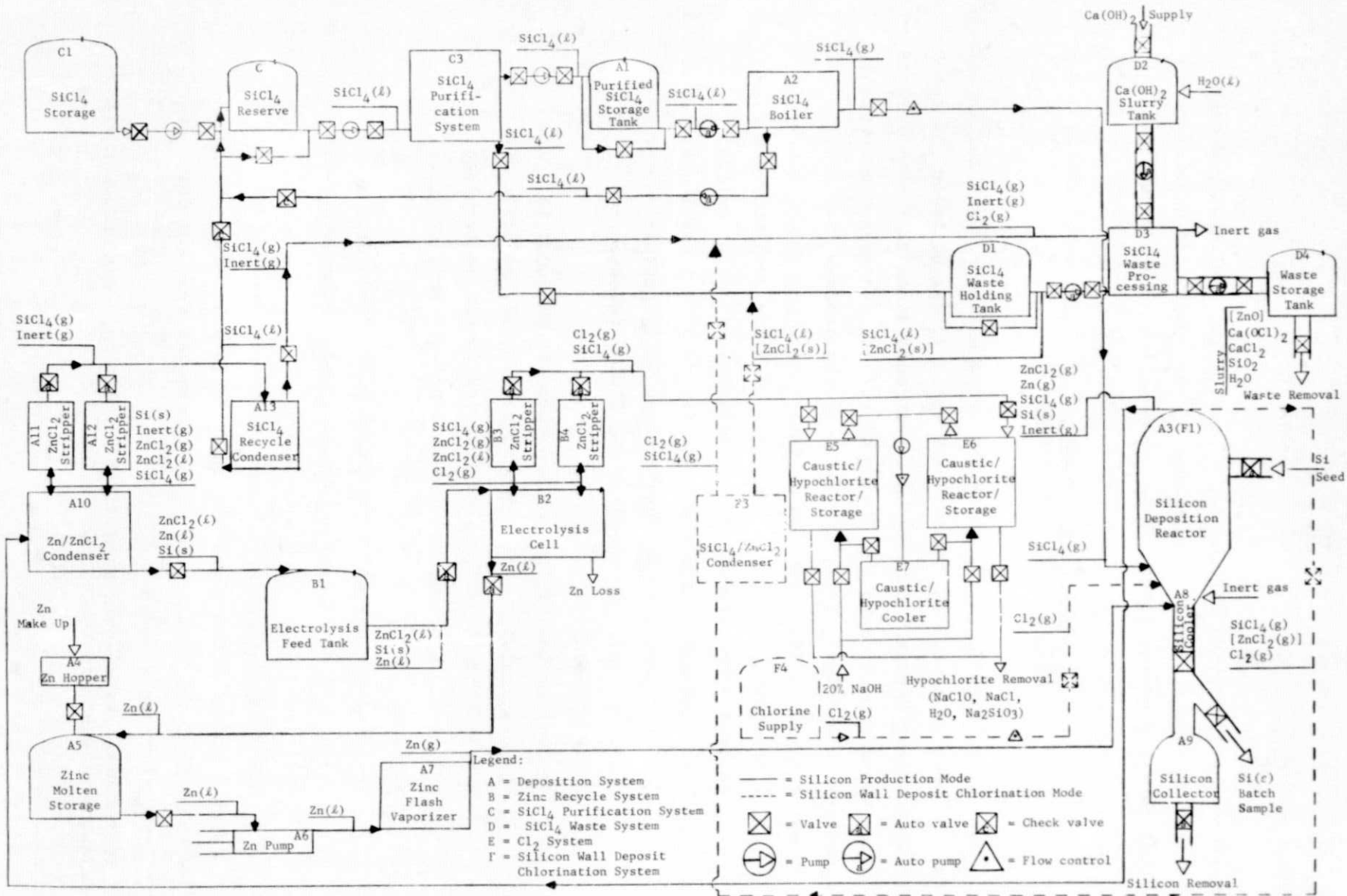


FIGURE 1. PROCESS FLOW DIAGRAM FOR 25 MT/YEAR SILICON FACILITY (7/5/77)

TABLE 1. MATERIAL AND ENERGY FLOW SHEET (Revised 7/5/77)  
 25 MT/Year Silicon Facility  
 (→ = Materials In or Out)  
 ℓ = liters (ℓ) = liquid phase

Unit	Input							Output						Process Heat	
	Material	T, C	g mole hr <sup>-1</sup>	Kg hr <sup>-1</sup>	ℓ hr <sup>-1</sup>	Viscosity, cp	Material	T, C	g mole hr <sup>-1</sup>	Kg hr <sup>-1</sup>	ℓ hr <sup>-1</sup>	Viscosity, cp	Kcal hr <sup>-1</sup>	Kw	
A1 Pure SiCl <sub>4</sub> Tank Capacity 5 days 4442.4 Kg 2961.6 ℓ	SiCl <sub>4</sub> (ℓ)	25	217.86	37.02	24.68	0.45	SiCl <sub>4</sub> (ℓ)	25	217.86	37.02	24.68	0.45	0.0	0.0	
A2 SiCl <sub>4</sub> Boiler (1.7 atm) Capacity 8 hrs 296.16 Kg 197.44 ℓ	SiCl <sub>4</sub> (ℓ)	25	217.86	37.02	24.68	0.45	SiCl <sub>4</sub> (ℓ) SiCl <sub>4</sub> (g)	73.6 73.6	4.27 213.59	0.73 36.30	0.52 3577	0.3 0.012	1767.9	2.05	
A3 Fluidized Bed Reactor	SiCl <sub>4</sub> (g) → Inert Zn (g) → Si seed	73.6 25 927 25	213.59 12.82 427.17 6.41	36.30 27.93 27.93 0.18	3577 313.63 34,195 0.075	0.012 0.019 0.085 ∞	Si prod. Si wall Si dust Inert SiCl <sub>4</sub> (g) Zn (g) ZnCl <sub>2</sub> (g)	927 927 927 927 927 927 927	134.57 3.84 2.56 12.82 79.03 158.05 269.12	3.78 0.11 0.07 12.82 13.43 10.33 36.68	1.58 0.04 0.03 51,104	0.046	230.6	0.27	
A4 Zn Hopper	→ Zn (s)	25	13.46*	0.88*	0.12*		Zn (s)	25	13.46*	0.88*	0.12*		0.0	0.0	
A5 Zinc Molten Storage Capacity 2 days 1340.64 Kg 204.92 ℓ	Zn (ℓ) Zn (ℓ) Zn (s)	500 500 25	255.66 158.05 13.46*	16.72 10.33 0.88*	2.57 1.59 0.12*	3(.98?) 3(.98?) ∞	Zn (ℓ)	500	427.17*	27.93*	4.29*	3(0.98?)	66.59*	0.077*	
A7 Zinc vaporizer (1.23 atm)	Zn (ℓ)	500	427.17	27.93	4.29	3(.98?)	Zn (g)	927	427.17	27.93	34,195	0.085	13,120	15.25	
A8 Silicon Cooler	Si prod.	927	134.57	3.78	1.58		Si prod.	25	134.57	3.78	1.58		-722.6	-0.84 →	
A10 Zn/ZnCl <sub>2</sub> Condenser	Si dust Zn (g) ZnCl <sub>2</sub> (g) SiCl <sub>4</sub> (g) Inert <sup>2</sup> (g) ZnCl <sub>2</sub> (ℓ)	927 927 927 927 927 327	2.56 158.05 269.12 79.03 12.82 2.69*	0.07 10.33 36.68 13.43 0.37* 0.15*	0.03 51,104 0.046	-1	Si dust Zn (ℓ) ZnCl <sub>2</sub> (ℓ) ZnCl <sub>2</sub> (g) SiCl <sub>4</sub> (g) Inert (g)	500 500 500 327 327 327	2.56 158.05 269.12* 2.69 79.03 13.43	0.07 10.33 36.68* 0.37 13.43	0.03 15.09* 4659	0.021	-15,922*	-18.50*	
A11 ZnCl <sub>2</sub> stripper Cool cycle	SiCl <sub>4</sub> (g) ZnCl <sub>2</sub> (g) Inert (g) Si(s)	327 327 327 327	79.03 2.69 12.82 2.56	13.43 0.37 4,659 0.03	0.021		ZnCl <sub>2</sub> (s) SiCl <sub>4</sub> (g) Inert (g) Si(s)	77 77 77 77	2.69 79.03 12.82 2.56	0.37 13.43 2639 0.07	2639	0.013	-513.5	-0.60	
A12 ZnCl <sub>2</sub> stripper Melt cycle	ZnCl <sub>2</sub> (s) Si(s)	77 77	2.69* 2.56*	0.37* 0.07*	0.03*		ZnCl <sub>2</sub> (ℓ) Si(s)	327 327	2.69* 2.56*	0.37* 0.07*	0.15* 0.03*	-1	21.79*	0.025*	
A13 SiCl <sub>4</sub> recycle condenser	SiCl <sub>4</sub> (g) Inert	77 77	79.03 12.82	13.43 2,639	0.013		SiCl <sub>4</sub> (ℓ) SiCl <sub>4</sub> (g) Inert <sup>2</sup> (g)	0 0 0	77.61 1.42 12.82	13.19 0.24 320	8.62	0.51 0.018	-806.5	-0.94 →	
B1 Electrolysis Feed Tank Capacity 2 days Si dust 3.36 Kg 1.4 ℓ Zn(ℓ) 495.89 Kg 72.32 ℓ ZnCl <sub>2</sub> (ℓ) 1724.88 Kg 717.12 ℓ	Si dust Zn(ℓ) ZnCl <sub>2</sub> (ℓ)	500 500 500	2.56 158.05 266.43	0.07 10.33 36.31	0.03 1.59 14.94	0.03 3(0.98?) -1	Si dust Zn(ℓ) ZnCl <sub>2</sub> (ℓ)	500 500 500	2.56 158.05 266.43	0.07 10.33 36.32	0.03 1.59 14.94	-1	0.0	0.0	
B2 Electrolysis Cell	Si dust ZnCl <sub>2</sub> (ℓ) ZnCl <sub>2</sub> (ℓ)	500 500 327	2.56 269.12 3.05	0.07 36.68 0.42	0.03 15.09 0.17	0.03 -1 -1	Zn(ℓ)(recyc) Zn(ℓ)(loss) SiCl <sub>4</sub> (g) Cl <sub>2</sub> (g) ZnCl <sub>2</sub> (g)	500 500 500 500 500	255.66 13.46 2.56 264 3.05	16.72 0.88 0.44 18.72 0.42	2.57 0.135 17,109	3(0.98?) 3(0.98?) 0.032	25,660 (19,419)	29.82ΔH (22.57) (ΔG=-nFE)	

\* Average of intermittent operation.

TABLE 1. (CONTINUED)

Unit	Input							Output					Process Heat	
	Material	T, C	g mole hr <sup>-1</sup>	Kg hr <sup>-1</sup>	ℓ hr <sup>-1</sup>	Viscosity, cp	Material	T, C	g mole hr <sup>-1</sup>	Kg hr <sup>-1</sup>	ℓ hr <sup>-1</sup>	Viscosity, cp	Kcal hr <sup>-1</sup>	Kw
B3 ZnCl <sub>2</sub> Stripper Coil cycle	Cl <sub>2</sub> (g)	500	264.00	18.72	17,109	0.032	Cl <sub>2</sub> (g)	25	264.00	18.72	6,521	0.014	-1,240	-1.44
	ZnCl <sub>2</sub> (g)	500	3.05	0.42			SiCl <sub>4</sub> (g)	25	2.56	0.44				
	SiCl <sub>4</sub> (g)	500	2.56	0.44			ZnCl <sub>2</sub> (s)	25	3.05	0.42				
B4 ZnCl <sub>2</sub> Stripper Meit cycle	ZnCl <sub>2</sub> (s)	25	3.05*	0.42*	ZnCl <sub>2</sub> (ℓ)	327	3.05*	0.42*	0.17*	-1	23.3*	0.027*		
C1 SiCl <sub>4</sub> Storage Capacity = 2 weeks 8823.4 Kg 5883.4 ℓ	SiCl <sub>4</sub> (ℓ)	25	154.56	26.26	17.51	0.45	SiCl <sub>4</sub> (ℓ)	25	154.56	26.26	17.51	0.45	0	0
C2 SiCl <sub>4</sub> Reserve Capacity = 2 days 1279.2 ℓ 1928.64 Kg	- SiCl <sub>4</sub> (ℓ)	25	154.56	26.26	17.51	0.45								
	SiCl <sub>4</sub> (ℓ)	0	77.61	13.19	8.62	0.51								
	SiCl <sub>4</sub> (ℓ)	73.6	4.27	0.73	0.52	0.3	SiCl <sub>4</sub> (ℓ)	25	236.44	40.18	26.8	0.45	55.1	0.06
C3 Cl <sub>2</sub> Purification	SiCl <sub>4</sub> (ℓ)	25	236.44	40.18	26.8	0.45	SiCl <sub>4</sub> (ℓ)	25	217.86	37.02	24.68	0.45	to be determined -	
							SiCl <sub>4</sub> (ℓ)waste	25	18.58	3.16	2.11	0.45		
Energy balance:													total of steps = 21739	25.26
													products - reactants = 21745	

Materials and Energy Balance for Cl<sub>2</sub>-Handling System, SiCl<sub>4</sub>/Cl<sub>2</sub> Waste, Wall Deposit Chlorination

Unit	Input							Output					Process Heat	
	Material	T, C	g mole hr <sup>-1</sup>	Kg hr <sup>-1</sup>	ℓ hr <sup>-1</sup>	Viscosity, cp	Material	T, C	g mole hr <sup>-1</sup>	Kg hr <sup>-1</sup>	ℓ hr <sup>-1</sup>	Viscosity, cp	Kcal hr <sup>-1</sup>	Kw
D1** SiCl <sub>4</sub> Waste Holding Tank Capacity = 1 week 633 Kg 423 ℓ	- SiCl <sub>4</sub> (ℓ)	25	18.58				SiCl <sub>4</sub> (ℓ)	25	22.21	3.77	2.52	0.45		
	SiCl <sub>4</sub> (s)	0	3.63											
D2** Ca(OH) <sub>2</sub> Slurry Tank	- Ca(OH) <sub>2</sub> (s)	25	49.60				Ca(OH) <sub>2</sub> (s)	25	49.60					
	- H <sub>2</sub> O(ℓ)	25	y (to be determined)				H <sub>2</sub> O(ℓ)	25	y (to be determined)					
D3** SiCl <sub>4</sub> Waste Processing	SiCl <sub>4</sub> (ℓ)	25	22.21			Slurry	SiO <sub>2</sub>	25	23.84					
	- SiCl <sub>4</sub> (g)	0	1.42				CaCl <sub>2</sub>	25	48.64					
	SiCl <sub>4</sub> (g)	0	0.21				Ca(OCl) <sub>2</sub>	25	0.96					
	- Inert(g)	0	12.82				H <sub>2</sub> O	25	49.60+y					
	Cl <sub>2</sub> (g)	0	1.92				Inert(g)	25	12.82					
	Ca(OH) <sub>2</sub>	25	49.60											
D4** Waste Storage Tank Capacity = 2 weeks	H <sub>2</sub> O(ℓ) <sup>2</sup>	25	y											
	SiO <sub>2</sub>	25	23.84			SiO <sub>2</sub>	25	23.84						
	CaCl <sub>2</sub>	25	48.64			CaCl <sub>2</sub>	25	48.64						
	Ca(OCl) <sub>2</sub>	25	0.96			Ca(OCl) <sub>2</sub>	25	0.96						
	H <sub>2</sub> O	25	48.60+y			H <sub>2</sub> O	25	49.60+y						

\* Average of intermittent operation.

\*\* Hourly rate of F units to be divided by (chlorination time/silicon production time) to get real-time rates during chlorination; D1-D4 must also be adjusted to production versus chlorination real-time values.

TABLE 1. (CONTINUED)

Unit	Input					Viscosity, cp	Output					Process Heat	
	Material	T, C	K mole hr <sup>-1</sup>	Kg hr <sup>-1</sup>	l hr <sup>-1</sup>		Material	T, C	g mole hr <sup>-1</sup>	Kg hr <sup>-1</sup>	l hr <sup>-1</sup>	Viscosity, cp	Kcal hr <sup>-1</sup>
E5, E6 Caustic/Hypochlorite Reactor/Storage 15,750 l wk <sup>-1</sup> 20% NaOH	-Cl <sub>2</sub> (g)	25	264.00			Soln.	Na <sub>2</sub> SiO <sub>3</sub>	25	2.56				
	-SiCl <sub>4</sub> (g)	25	2.56				NaCl	25	274.24				
	NaOH	25	571.41				NaOCl	25	264.00				
	H <sub>2</sub> O	25	5074.69				H <sub>2</sub> O	25	5346.37				
							NaOH	25	28.05				
E7 Caustic Cooler (Refrig.)	E5, E6 Contents	25	to be determined			E5, E6 Contents	4	to be determined					
F1** Reactor Wall Deposit Chlorination	-Si(s)	?***	3.84			SiCl <sub>4</sub> (g)	?***	3.84					
	Cl <sub>2</sub> (g)	25	9.60			Cl <sub>2</sub> (g)	?***	1.92					
	-Zn	?***	z	(neglected in Zn + Cl <sub>2</sub> balance)		ZnCl <sub>2</sub> (g)	?***	z	(neglected in Zn + Cl <sub>2</sub> balance)				
F3** SiCl <sub>4</sub> /ZnCl <sub>2</sub> Condenser	SiCl <sub>4</sub> (g)	?***	3.84			SiCl <sub>4</sub> (l)	0	3.63					
	Cl <sub>2</sub> (g)	?***	1.92			SiCl <sub>4</sub> (g)	0	0.21					
	ZnCl <sub>2</sub> (g)	?***	z	(neglected in Zn + Cl <sub>2</sub> balance)		Cl <sub>2</sub> (g)	0	1.92					
F4** Cl <sub>2</sub> Supply Capacity = 2 weeks 228.5 Kg 71.2 l	-Cl <sub>2</sub> (l)	25	9.6*	0.68*	0.212*	Cl <sub>2</sub> (g)	25	9.6*	0.68*	234.60*			

\* Average of intermittent operation.

\*\* See footnote, page 2.

\*\*\* To be determined.

greatly simplifies the process. Although it is believed that the materials flow aspects of the waste processing section of the plant will be modified little, if at all, in the future, the energy balance has not yet been made, owing to uncertainties in the heats of reaction of some of the aqueous reactions. These calculations will be deferred.

The estimates of equipment size (presented as Table 2 of the Fifth/Sixth Quarterly Report) have been revised and are included with information on instrumentation in Figure 2.

### Instrumentation

As pointed out above, the needs for automatic fluid flow control in the experimental facility have been identified and the locations denoted on the process flow diagram, Figure 1. Instrumentation for pressure and temperature indication and control will be assessed with the design of individual units. A preliminary draft of a chart (Figure 2) delineating the control functions required for each unit has been made.

Discussions have been initiated with Beckman Instruments of Los Angeles, California, with regard to some of the less conventional instrumentation, such as the level indicator for the high-temperature fluidized bed. These discussions will be pursued further as the design progresses.

### ZnCl<sub>2</sub> Recycle Alternatives

Because of the complexity of recycling the zinc component\* of the ZnCl<sub>2</sub> by-product of the fluidized-bed unit, consideration was given to the alternative of treating the ZnCl<sub>2</sub> as a co-product, disposing of it commercially, and crediting the return toward the cost of purchasing new zinc.

The possibility of burning ZnCl<sub>2</sub>(g) to pigment-grade ZnO was ruled out early, as that reaction is very inefficient; indeed, the reverse reaction,

---

\* Recycling the Cl<sub>2</sub> in the experimental facility has already been ruled out, because the technology of SiCl<sub>4</sub> manufacture is already well in hand and adding that complexity to the experimental facility was not justifiable.



Unit	Name	Description	Size, dia x ht (L), ft or L x W x ht, ft	Materials Construction	Control Functions			Indicating Functions			Operation		Features			
					Temp.	Pressure	Quantity	Level	Time	Flow	Temp.	Pressure		Quantity	Level	Flow
A1	Pure SiCl <sub>4</sub> Storage	Tank	5 x 6	CS												---
A2	SiCl <sub>4</sub> Boiler	Shell and tube	2 x 4	CS	X	X		X	X	X			X	X	X	Timed blowdown, equilibrium boiler
A3(F1)	Fluidized Bed Reactor	Vertical tubular	2.5 x 14	SS - SiC-coated graphite liner	X			X		X			X	X	X	Several pressure and temperature taps
A4	Zinc Hopper	Hopper	(located above A5)	CS												Lock system
A5	Zinc Molten Storage	Tank	3.5 x 5.5	SS - graphite liner	X					X					X	---
A6	Zinc Pump	Cylinder	2 x 4	SS - graphite liner	X			X	X	X					X	Positive displacement, 2 units
A7	Zinc Flash Vaporizer	Packed bed	2 x 7	SS - graphite liner and packing	X						X		X		X	Inductive or resistive heat
A8, 9	Silicon Cooler, Storage	Cylinder	(part of A3)	SS						X		X				Solids system
A10	Zinc/ZnCl <sub>2</sub> Condenser	Shell and tube	3 x 9	SS - graphite liner	X					X				X	X	Several temperature taps, temperature gradient
A11, 12	ZnCl <sub>2</sub> Stripper	Cylinder	2 x 7	CS - graphite liner	X				X					X	X	Timed cycle, solids condenser
A13	SiCl <sub>4</sub> Recycle Condenser	Shell and tube	1 x 4	CS	X					X					X	---
B1	Electrolysis Feed Tank	Tank	6 x 4.5	SS - graphite liner	X					X	X				X	---
B2	Electrolysis Cell	per Threifall and Bureau of Standards	11 x 9 x 17 (including 6-ft electrode clearance)	SS - graphite liner	X	X		X		X				X	X	ZnCl <sub>2</sub> and Zn levels, DC power equipment
B3, 4	ZnCl <sub>2</sub> Stripper	Cylinder	2 x 7	CS - graphite liner	X				X					X	X	Timed cycle, solids condenser
C1	SiCl <sub>4</sub> Bulk Storage	Tank	5 x (10.6)	CS							X					Supplied by SiCl <sub>4</sub> manufacturer
C2	SiCl <sub>4</sub> Reserve	Tank	4 x 4	CS							X					---
C3	SiCl <sub>4</sub> Purification	a. two columns b. tank	1.5 x 12 each 3.5 x 3.5	CS											X	Design: Pace Engineering, Inc.
D1	SiCl <sub>4</sub> Waste Holding	Tank	3 x 3	CS - elastomer liner						X						Discharge flow control
D2	Ca(OH) <sub>2</sub> Slurry Supply	Tank	2 x 3	CS - elastomer liner						X						Discharge flow control, mixer
D3	SiCl <sub>4</sub> Waste Processing	Packed tower	1 x 8	CS - elastomer liner				X					X			Flooded bottom
D4	Waste Storage	Tank	8 x 8	CS - elastomer liner							X					---
E5	Caustic/Hypochlorite Reactor	Tank	6 x (18)	Plastic/fiber reinforced							X				X	---
E6	Caustic/Hypochlorite Reactor	Tank	6 x (18)	Plastic/fiber reinforced							X				X	---
E7	Caustic/Hypochlorite Cooler	Flat plate exchanger	---	Elastomer/titanium	X				X	X					X	---
F3	SiCl <sub>4</sub> /ZnCl <sub>2</sub> Condenser	Shell and tube	---	CS	X					X					X	---
F4	Cl <sub>2</sub> Supply	Cylinders	2 x 5	CS - elastomer liner						X						Commercial supplier

FIGURE 2. DESCRIPTION OF UNITS AND ASSOCIATED EQUIPMENT  
25 MT/YEAR FACILITY (7/5/77)

chlorination of ZnO to ZnCl<sub>2</sub> proceeds readily without requiring a reducing agent to accept the oxygen.

Although at the 3000 MT/year Si level, the U.S. ZnCl<sub>2</sub> market, 44,000 MT/year, would be severely perturbed by the addition of the molar equivalent quantity of ZnCl<sub>2</sub>, marketing the 242 MT/year of ZnCl<sub>2</sub> from a 25 MT/year silicon facility would be practical. For the purpose of analyzing the economic feasibility of such a move, an estimate of the value of the ZnCl<sub>2</sub> co-product equal to about 35 percent that of the contained zinc in an "across the fence" operation was obtained from a principal supplier of ZnCl<sub>2</sub> to the industry.

The major incentive in marketing versus recycling the by-product is the elimination of the high capital cost of the ZnCl<sub>2</sub> electrolysis and a large fraction of the associated manpower. It is speculated that elimination of the zinc recycle would require purification by distillation of all of the zinc equivalent stoichiometrically to the product silicon. If it is assumed (1) that the capital cost of the distillation is 25 percent that of the electrolysis, (2) that the manpower needed for distillation is only 40 percent of that required for electrolysis, and (3) that the power costs are roughly the same, the 35 percent salvage value of zinc in ZnCl<sub>2</sub> leads to a silicon product cost of \$9.82 versus the \$9.12 originally estimated in the Second Quarterly Report. On that basis, there would be no economic incentive for discarding the ZnCl<sub>2</sub> electrolysis even if the market could absorb the by-product.

In the case of the experimental facility where the materials costs are a smaller fraction of the total, the simplification of the process by elimination of the electrolytic recycle results in an almost equal product cost. Although this option should be kept in mind, the necessity of using electrolysis at the 1000 MT/year level makes it advisable to adopt its use at this time.

#### ZnCl<sub>2</sub> Electrolysis

With the decision to retain the concept of fused-salt electrolysis for recycle of the zinc in the experimental facility, it became of interest

to obtain detailed information on the work at the Reno, Nevada, Station of the U.S. Bureau of Mines. In that work, the electrolysis is part of a process for recovering zinc from zinc sulfide ore concentrates as an alternative to the air-polluting roasting process. The initial laboratory work with a 10-amp cell is described in a paper by F. Haver, et al.<sup>(1)</sup>, and subsequent work on a 1500-amp cell is described by D. Shanks, et al.<sup>(2)</sup>, in a paper which should be published within a few months. Pending the availability of that report, a trip was made to the Reno Station to discuss their work. Briefly summarized, it should be possible to handle the requirements of a 25 MT/year silicon facility with three 5000-ampere cells operating at 500 C from a 50 mole percent  $ZnCl_2/KCl$  mixture at a current density of 2 amp/cm<sup>2</sup> and a current efficiency of 95 percent, with an energy consumption of below 5.5 Kwhr/kg Zn, i.e., >85 percent electrical energy efficiency. The cathodes of each of the three cells would consist of 50-cm x 50-cm (or equivalent) plates of graphite submerged horizontally in the electrolyte about 1.25 cm above graphite anodes extending just above the pool of zinc in the bottom of the cells. The cathodes would be provided with grooves on the underside, slanted upward from one side to the other, and possibly provided with vent holes to aid in sweeping chlorine from the cathode surface. Circulation of the electrolyte within the cell would be provided by the "pumping" action of the chlorine gas evolution as it sweeps from one side of the cathode face to the other.

One of the major problems with the Bureau of Mines operation arose from the fact that their cell is "open", i.e., loosely baffled, and is therefore subject to back diffusion of air, leading to the formation of a zinc oxide "scum" on the electrolyte surface. The fact that we will be dealing with a closed system avoids that problem.

#### Waste Processing

During the current report period, attention has been given to the provisions necessary for proper disposal of the chlorine evolved from the  $ZnCl_2$  electrolysis, and it is believed that a reasonable arrangement has been

devised. As the details have not as yet been worked out, no names will be mentioned; however, the arrangement in principle involves accepting 20 percent caustic solution from a vendor, chlorinating it to form sodium hypochlorite solution until the caustic level is reduced to 1 percent NaOH and then returning it to the vendor for use in chlorinating sewage plant effluent locally.

The 18.7 kg/hour of chlorine from the electrolytic cell will contain about 0.4 kg/hour of  $\text{SiCl}_4$ . This would lead to 0.23 percent  $\text{Na}_2\text{SiO}_3$  in the hypochlorite (from  $\text{SiCl}_4 + 6\text{NaOH} = \text{Na}_2\text{SiO}_3 + 4\text{NaCl} + 3\text{H}_2\text{O}$ ), which should not be a problem. However, consideration must be given to the amount of zinc as a "heavy metal" that is carried into the sewage plant effluent by this route. The contamination of the hypochlorite with zinc would come by inefficient removal of zinc in the  $\text{ZnCl}_2$  strippers (B3 and B4) above the electrolytic cell. Since in the treatment of sewage plant effluent, 50 ppm of hypochlorite solution is used, a maximum heavy metal specification of 0.01 ppm in the effluent would allow for 0.15 mole percent  $\text{ZnCl}_2$  in the chlorine, and it should be possible to hold it below that level, if necessary, by providing a bag filter in the chlorine stream. Specifications for permissible heavy metals in the sewage plant effluent are being obtained to determine whether a problem exists in this area that would require additional attention.

#### DuPont Silicon

Information has been obtained directly from the DuPont Company on the characterization of the material they prepared by zinc reduction of  $\text{SiCl}_4$  and supplied to the early semiconductor industry. Information on the resistivity, boron content, and on several questions regarding the process itself were obtained. Receipt of information on minority carrier lifetime is pending. This information will be compiled and presented later when it is complete.

#### Design Strategy

The design tasks involved in Phase II of this program fall under three categories:

- (1) Conventional Chemical Engineering, non-specialized
- (2) Conventional Chemical Engineering, specialized
- (3) Unconventional Chemical Engineering (specialized).

For most efficient progress to the final design, it is planned that the design of process equipment involving conventional, non-specialized chemical engineering (Category 1) be "farmed out" to a locally based engineering firm, that the  $\text{SiCl}_4$  purification which falls under Category 2 be assigned to a company with expertise available in the area, and that Battelle retain responsibility for the design of the unconventional items, Category 3.

Discussions have been held with three engineering firms in the Columbus-Cincinnati area and each have submitted a proposal for work in Category 1. On the basis of this information, Raphael Katzen Associates of Cincinnati, Ohio, has been selected to provide the conventional non-specialized chemical engineering services.

Pace Engineering, Inc., of Beaumont, Texas, has been selected for design of the  $\text{SiCl}_4$  purification section of the experimental facility because of the availability in their area of the expertise required for this specialized design.

Staff members of Battelle's Columbus Laboratories have had experience in the design of CVD fluidized-bed reactors and associated equipment, and would therefore take the major responsibility for the items of unconventional design, seeking assistance on an ad-hoc basis as needed, for example as in the design of the electrolytic cell for  $\text{ZnCl}_2$  recycle discussed above.

The assignment of responsibility for the design of individual items and systems is given in Table 2.

Figure 3 is the design schedule that has been adopted so as to have a final design of the experimental facility available by November 15, 1977.

#### Design of Specialized Units

Design activities on the unconventional items during the report period have been concentrated on the zinc vaporizer and the fluidized-bed reactor. Several options are being considered in each case, and their

TABLE 2. IDENTIFICATION OF PRIMARY DESIGN  
RESPONSIBILITY BY ITEM (7/5/77)

I. "Off Shelf" Purchases

A1, A4, C2, D1, D2, D4, E5, E7\*

Except as indicated under Group II -

1. All heating and cooling systems
2. DC power supply
3. All pumps, valves, flow controls, and level controls
4. Pressure, temperature, quantity, time, and alarm instrumentation.

II. Raphael Katzen Associates

A5, A8, A9, A10, A11, A12, A13, B1, B3, B4, D3, E5, E6, F3

Level controls in A3, A6, B2

III. Battelle's Columbus Laboratories

A2, A3, A6, A7, B2

IV. Pace Engineering, Inc.

C3

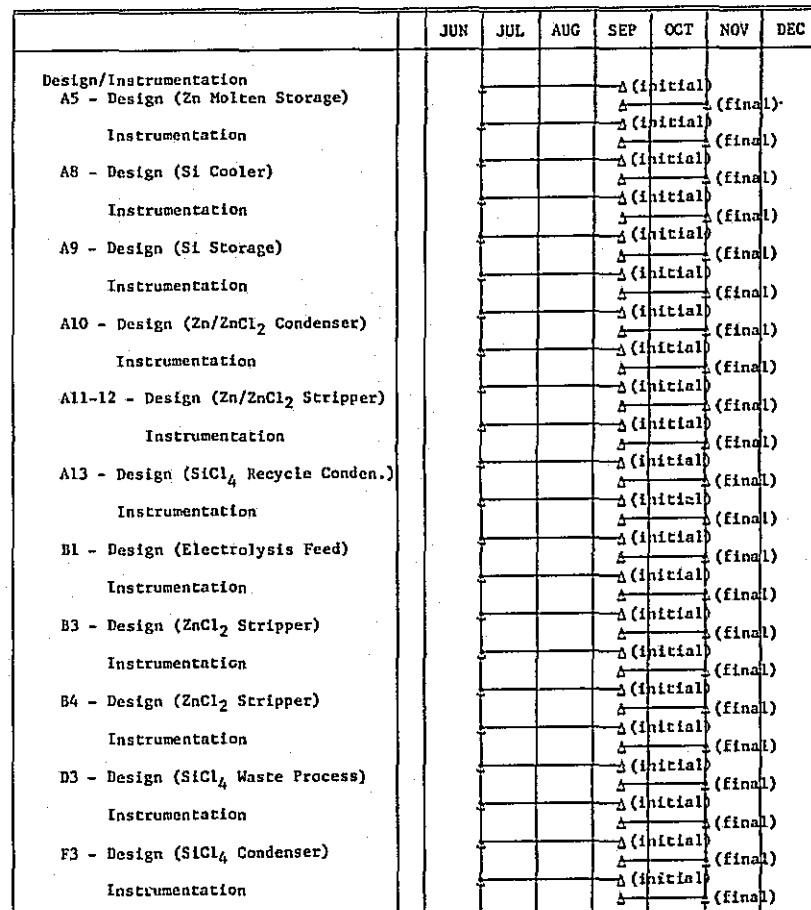
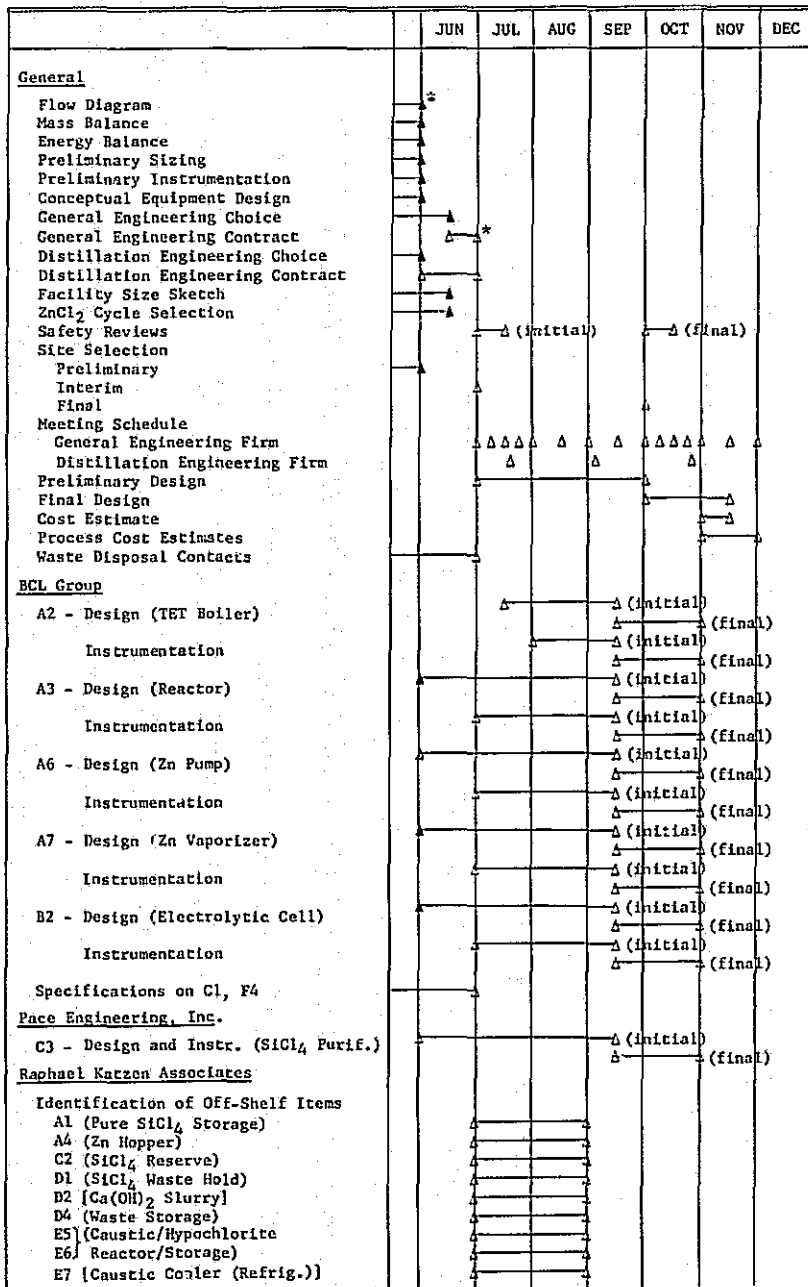
V. Supplied by Materials Manufacturers

C1, F4

Underlined items require extensive BCL involvement.

---

\* Letter codes refer to major equipment items cited in Figure 1 and Table 1. It will be noted that certain items in the letter sequences are "missing", such as E1 to E4. This is explained by the fact that as the design changes, items in earlier designs are dropped and new items are assigned new code numbers, rather than vacated numbers. This is done to avoid confusion of the records.



\* ▲ = completed item; ▲ = target item.

FIGURE 3. DESIGN SCHEDULE, EXPERIMENTAL FACILITY  
(7/5/77)

advantages and disadvantages noted, with the objective of evolving a design with the greatest probability for success. To avoid the problem of piping zinc vapor over significant distances, the concept of including the zinc vaporizer,  $\text{SiCl}_4$  preheater, and the fluidized-bed reactor in an integrated unit is being studied. The feasibility of such an arrangement is challenged by the high boiling point (908 C at 1 atm, 918 C at 1.1 atm) of zinc and its high heat of vaporization (27.5 Kcal/g mole). It is essential that heat transfer be maximized to avoid the necessity of excessively high temperatures at the heat source and further aggravation of an already limited situation with regard to choice of materials of construction. Heat transfer calculations have been made on two versions of a zinc vaporizer and it is believed that a suitable design will emerge. The design of this composite system will be reported when further crystallized.

#### Operation Cost, Experimental Facility

In response to a JPL request, estimations were made as a function of capacity, of the cost of the silicon prepared in the course of operating the experimental facility at Battelle's Columbus Laboratories. The initial projection of a 25 MT/year level for the experimental facility had been somewhat arbitrary. The additional information was desired so that JPL can make logical decisions relative to cost versus projected silicon needs.

In making the calculations, the process flow sheet of Figure 1 was assumed. High-purity zinc and technical-grade  $\text{SiCl}_4$  were assumed to be purchased from appropriate sources at January, 1975, prices and no credit was taken for by-products. That is, the hypochlorite formed from the by-product chlorine was assumed to be traded for the caustic solution used in its disposal.

In general, the estimates were made on the basis of those in the Second Quarterly Progress Report (April 8, 1976) for a 1000 MT/year facility. The production costs for a 25 MT/year facility were established first and then extrapolated to the 50, 75, and 100 MT/year levels. A 10-year amortization of capital cost was assumed, and it should be recognized that amortization over a shorter time would not only raise the cost, but diminish the relative cost advantage of increased facility size.



The personnel assigned to the 25 MT/year facility comprise (1) four shifts of two technicians and a shift leader each, (2) a plant engineer, and (3) appropriate support staff. An extra technician (40 hours per week) and an appropriate support staff factor were added for each increment of facility size. Capital investment costs were increased by the 0.6 power of the size using the 25 MT/year cost as the base, e.g., ratio of capital costs =  $(C_{50}/C_{25})^{0.6}$ . A maintenance and repair cost of 9 percent of the capital investment was used. This is a lower percentage than was used in estimating the production costs for the 1000 MT/year facility, but certain items involved in this item for the 1000 MT/year facility are covered in the labor-related costs for the experimental facility.

The results of this exercise are given in Table 3.

TABLE 3. ESTIMATED COST OF OPERATION OF EXPERIMENTAL FACILITY

Items	\$ /kg of Si			
	25 MT/Year	50 MT/Year	75 MT/Year	100 MT/Year
Materials	4.54	4.54	4.54	4.54
Utilities	0.38	0.38	0.38	0.38
Capital-related	9.88	7.49	6.37	5.67
Labor-related	28.86	15.52	11.08	8.86
Others	0.82	0.82	0.82	0.82
TOTAL	44.48	28.75	23.19	20.77

It will be noted that the greatest saving (i.e., 35 percent) results in the first increment from 25 to 50 MT/year, primarily as a result of a 46 percent reduction in labor-related costs coupled with a 24 percent reduction in capital-related cost. It is significant that the 50 MT/year facility would use two fluidized-bed reactors and provide the flexibility of continued operation with one reactor down, albeit on a limited basis. In the light of

these economic and operational factors, it is recommended that a size larger than the 25 MT/year level be adopted for the experimental facility, if such a decision is found to be consistent with other aspects of the program objectives.

### Plans for the Next Report Period

Plans for next quarter relative to the design of the experimental facility include:

- (1) Conclusion of agreements with engineering firm subcontractors and initiation of design work in accordance with the schedule of Figure 3
- (2) Continuation of design effort by BCL groups on specialized equipment as indicated in the schedule of Figure 3
- (3) Initiation of safety review of plant design
- (4) Implementation of anticipated early decision on the size of the experimental facility.

### EXPERIMENTAL SUPPORT PROGRAM

The experimental support program associated with the design of the experimental facility comprises two major aspects:

- (1) Operation of the miniplant with the 2-inch-diameter fluidized-bed system
- (2) Performance of ad hoc experimental work outside of the miniplant as required for design information.

During this report period, several runs were made in the miniplant to determine the effect of bed particle size on the deposition efficiency of silicon. Additional runs were made to study the operation of a new flash vaporizer.

Auxilliary experiments were concentrated on the electrolysis of molten zinc chloride. Brief experiments were carried out to confirm the insolubility of  $ZnCl_2$  in  $SiCl_4$  (up to then, and in deriving the process flow sheet of Figure 1, negligible solubility has been assumed). Additional experiments were carried out to devise a means of recovering  $SiCl_4$  from the chlorine by-product, initially thought to be necessary to yield a hypochlorite solution for which a use could be found.

#### Effect of Bed Particle Size

At the conclusion of last quarter, experimental work in the mini-plant had demonstrated the advantages of providing the fluidized-bed reactor bed support with a central zinc vapor inlet and introducing the  $SiCl_4$  through four surrounding inlets. Not only was efficiency increased, but the troublesome deposition of silicon on the surface of the reactor contiguous with the inlets was eliminated. Deposition on the wall was restricted to the area above the bed. The use of a graded bed temperature was also shown to be beneficial in taking advantage of the increased thermodynamic conversion with decreasing temperature. Deposition rates of useful product on the fluidized-bed particles of up to 344 g/hour were obtained which extrapolates directly to 3.78 kg/hour in a 6.6-inch-diameter reactor, i.e., the production level required for the projected 25 MT/year facility. It was evident that at this throughput the capacity of the 2-inch fluidized-bed reactor was being reached because excessive "blow-over"\* of the bed was noted. Hence, experiments were initiated with particles of a larger size than those used before (149 x 279  $\mu m$ ), to decrease the loss of particles from the fluidized bed. In addition, larger particles are of interest because a typical bed of a continuously operated unit would be expected to contain a particle size distribution of roughly 200 to 1200  $\mu m$  in order to obtain the volume increase in seed and the silicon deposition rates per unit size desired. Not only was

---

\* It should be noted that the term "blow-over" refers to an inertial transfer of bed material to the exit line due to surges in the bed rather than to elutriation in the sense that the terminal velocity has been exceeded.

the particle size increased to reduce "blow-over", but a shallower bed was used in Run No. 68 reported last quarter. Data from Run No. 68 and earlier runs together with those of subsequent runs made during the current report period are given in Table 4. As the result of the change to larger particles and shallower bed, a decrease in bed efficiency\* was recorded and increases in silicon dust production and wall deposit were noted. Total  $\text{SiCl}_4$ -to-Si conversion efficiency was not changed. Subsequent runs were made in an effort to distinguish the relative significance of particle size (specific surface area/bed volume) and bed depth. Run No. 69 made with the larger particle size and with a 96 percent increase in initial bed weight (and depth) gave increased bed efficiency and decreased wall deposit, but with little effect on the fraction of product collected as dust. Part of the increased efficiency resulted from an inadvertent increase in Zn/ $\text{SiCl}_4$  ratio from 2.1 to 2.6 (raising the predicted equilibrium conversion efficiency by about 10 percentage points). Thus, Run No. 72 was made to avoid this complication. Unfortunately, one of the  $\text{SiCl}_4$  inlets plugged\*\* with an unidentified (carbonaceous?) residue not encountered before. Although the results are supportive of the final conclusion, it was thought best to make another run (No. 78) to obtain data free of qualification. Comparison of Run No. 78 with Run No. 68 indicates that the bed efficiency was increased, and the wall deposit (most above the initial bed level) decreased. However, the fraction of silicon collected as dust was not affected. Despite the increase in efficiency relative to Run No. 68, the efficiency levels did not reach those characteristic of the runs made with smaller particle size, e.g., Run No. 64. It is probable that increased bed efficiency and overall conversion efficiency would be obtained by going to even deeper starting beds than those being used (as would be done in scale-up, or as could be done if a continuous product withdrawal system were to be installed in the miniplant). However, the formation of silicon

---

\* Silicon collected on the bed particles relative to that fed as  $\text{SiCl}_4$ .

\*\* Distortion of the inlet flow pattern resulted in wall deposit in that area, normally absent.

TABLE 4. SUMMARY OF SELECTED MINIPLANT DATA

(Runs made in hemispherical-bottom reactor with 3 to 6 percent argon bleed gas. Data for Runs Nos. 69, 72, 78, and 79 added this report period. Runs Nos. 60, 61, 63, 67, 70, 71, and 73-77 were experiments outside of the miniplant.)

Run No.	Bed Data			Temperature, C	Time, hrs	Mole Ratio Zn/SiCl <sub>4</sub>	Si as SiCl <sub>4</sub> , g/hr	Axial Inlet Reactant	Bed Deposition, g/hr	Percent Bed Efficiency	Total Product <sup>(a)</sup> , g/hr	Percent Total <sup>(a)</sup> Efficiency	Percent of Product			Equilibrium Efficiency, percent	Bed + Equilibrium, percent	Total <sup>(a)</sup> + Equilibrium, percent	Remarks
	Initial Size, μm	Initial Weight, g	Final Weight, g										Bed	Wall	Dust				
Phase II																			
59	149 x 297	500	812	Graded <sup>(b)</sup>	1.50	1.773	364.2	Zn	268.2	57.2	221.0	60.7	94.2	3.3	2.4	67.3	85.0	90.2	Graded temperature
62	149 x 297	500	876	Graded <sup>(b)</sup>	1.50	1.577	471.3	Zn	251.0	53.2	283.2	60.1	88.6	4.2	7.2	61.5 <sup>(c)</sup>	86.6 <sup>(c)</sup>	97.7 <sup>(c)</sup>	Graded temperature, increased feed
64	149 x 297	500	982	Graded <sup>(b)</sup>	1.40	2.149	554.0	Zn	344.0	62.1	392.9	70.9	87.6	4.0	8.4	77.0 <sup>(c)</sup>	80.6 <sup>(c)</sup>	92.1 <sup>(c)</sup>	Graded temperature, increased feed
66	149 x 297	519	927	Graded <sup>(b)</sup>	1.30	2.216	544.4	Zn	313.4	57.6	356.9	65.5	87.8	3.0	9.2	78.4 <sup>(c)</sup>	73.4 <sup>(c)</sup>	83.5 <sup>(c)</sup>	Graded temperature, confirmatory, lengthened reactor
68	297 x 590	350	688.1	Graded <sup>(b)</sup>	1.18	2.117	565.7	Zn	285.7	50.5	366.1	64.7	78.0	7.8	14.2	76.3 <sup>(c)</sup>	66.2 <sup>(c)</sup>	84.8 <sup>(c)</sup>	Graded temperature, increased particle size
69	297 x 590	685	814.5	Graded <sup>(b)</sup>	0.42	2.634	517.7	Zn	311.0	60.1	387.1	74.7	80.3	5.6	14.1	85.6 <sup>(c)</sup>	70.2 <sup>(c)</sup>	87.3 <sup>(c)</sup>	As 68, with deeper bed, higher Zn/SiCl <sub>4</sub> ratio
72	297 x 590	621.5	1032.9	Graded <sup>(b)</sup>	1.28	2.224	557.4	Zn	320.6	57.5	387.8	69.6	92.7	5.0	12.3	78.6	73.1	88.5	Check 69, Zn/SiCl <sub>4</sub> as in 68, operational problems
78	297 x 590	641.6	982.5	Graded <sup>(b)</sup>	1.08	2.178	579.5	Zn	314.6	54.3	383.7	66.2	82.0	3.6	14.4	77.7	69.9	85.2	Check 69, 72
79, 80, 81	ABORTED RUNS WITH NEW ZINC VAPORIZER (SEE TEXT)																		

(a) "Total" silicon does not include uncollected amount in Zn/ZnCl<sub>2</sub> condenser.

(b)

Location	Run No.	59	62	64	66	68	69	72	78
Below bed		927	966	966	938	949	927	927	948
Bottom of bed		900	915	912	916	914	915	911	912
Top of bed		850	860	870	880	880	880	880	893
Expanded section		850	800	820	900	880	890	890	899
"Equilibrium" temperature		910	910 <sup>(c)</sup>	910 <sup>(c)</sup>	910 <sup>(c)</sup>	910 <sup>(c)</sup>	910 <sup>(c)</sup>	910 <sup>(c)</sup>	910 <sup>(c)</sup>

(c) Shading "equilibrium" temperature by (e.g.) 15 C upward would lower calculated equilibrium efficiency by ~1.3 percentage points.

dust may well be a function of the specific surface area of the bed particles, and not subject to improvement with a deeper bed of larger particles. This factor will be investigated further as there is some (as yet unknown) limit to the amount of silicon dust that can be handled as a by-product by chlorination in the electrolytic cell as now planned; beyond this limit additional facilities for dust handling would be required.

### Zinc Vaporizer

As pointed out in the Fifth/Sixth Quarterly Report, the zinc vaporizer used in the miniplant was not well suited to scale-up; it consisted of an induction-heated graphite tray fed with liquid zinc by a positive displacement metering device. Accordingly, experiments outside of the miniplant with a packed bed vaporizer were conducted and the results reported. With a 25-mm-ID graphite tube packed with 3-mm to 6-mm crushed graphite, a vaporization rate of about 2 kg/hour was obtained in <20 cm active depth at a temperature of 1056 C, i.e., 148 degrees above the normal boiling point of zinc. Since the same vaporization rate in the tray-type miniplant vaporizer required a surface temperature of 1350 and since the packed-bed configuration appeared to be more subject to scale-up, a packed-bed vaporizer, 25-mm ID x 30.5 cm in length, was installed in the miniplant below the fluidized-bed support plate. Three differences exist between the new vaporizer and that tested in the laboratory:

- (1) The 3-mm to 6-mm graphite packing is contained in a quartz rather than graphite tube
- (2) Heating is by radiation through the quartz envelope rather than by direct induction heating of the graphite tube
- (3) The liquid zinc is introduced above the packing rather than from an orifice immersed in the packing.

In the first run (No. 79), an adverse procedural judgment was made which resulted in loss of control. In the second run (No. 80), the inlet orifice was plugged on heat-up from residual zinc in the vaporizer which

zinc and silicon dust on freezing and remelting would lead to inhomogenities in the material charged to the electrolytic cell, and the core sample analyses may not have been totally representative. The overall recovery values of 94 and 93 percent of the zinc contained as Zn and as  $ZnCl_2$  in the original are similarly uncertain.

Owing to the high resistivity of the  $ZnCl_2$  without salt additives, the overall energy utilization efficiency was low, about 9 to 11 percent, much more resistive heat being generated than was necessary to maintain the cell at 500 C. Addition of KCl or other salts as practiced by the Bureau of Mines would increase the energy efficiency by decreasing resistivity. An ideal balance would be obtained at the point that the resistive heat is just sufficient to offset the heat lost in maintaining the cell at 500 C.

The electrolytic cell is being redesigned in accordance with Bureau of Mines practice, and it is expected to be operable by the third week in July.

#### Removal of $SiCl_4$ From $Cl_2$

Before it was found that the hypochlorite from  $Cl_2$  disposal could be used for local sewage plant effluent chlorination without removing the  $SiCl_4$ , experiments were run to determine whether the  $SiCl_4$  could be removed by water scrubbing (hydrolysis of the  $SiCl_4$ ). It was determined that no more than a gram of water per liter of  $Cl_2$  would be needed to effectively remove the  $SiCl_4$  without forming a gel of hydrolyzed  $SiO_2$  of prohibitively low fluidity.

#### Solubility of $ZnCl_2$ in $SiCl_4$

In work with the design thus far, it has been assumed that  $ZnCl_2$  is insoluble in  $SiCl_4$  up to the boiling point of the latter. However, it was recognized that in separating the unreacted  $Cl_2$  from the  $SiCl_4$  obtained in the silicon wall deposit chlorination, any  $ZnCl_2$  that was formed from chlorination of residual zinc would be more easily handled if it had some solubility in liquid  $SiCl_4$  whereupon it could be transferred in solution to

the waste disposal system (D1-D3). Thus a simple solubility experiment was performed in which 0.29 g of anhydrous  $ZnCl_2$  powder was introduced into 144.9 g of  $SiCl_4$  at ambient temperature and mixed over a period of several hours. No significant change in the quantity of  $ZnCl_2$  was noted during this time. It was concluded that the solubility, if any, of  $ZnCl_2$  in  $SiCl_4$  at room temperature is significantly less than 0.2 percent by weight. Despite the lack of solubility of  $ZnCl_2$  in  $SiCl_4$  and forfeiture of the option of condensing it in solution, it is believed that the small amount of  $ZnCl_2$  that might be involved in the silicon wall deposit chlorination operation can be washed down by the condensing  $SiCl_4$  and easily transferred as a dilute slurry to the waste disposal system.

#### Work Planned for Next Report Period

Plans for experimental support activity next quarter include:

- (1) Check out operability of new zinc vaporizer after providing supplemental  $SiCl_4$  preheating
- (2) Procure semiconductor-grade seed material and make a series of purity evaluation runs to provide material for Task II as requested by JPL, and to provide information on impurity levels
- (3) Complete remodelling of the  $ZnCl_2$  electrolysis cell and operate to optimize design parameters and to provide information on the chlorination of by-product silicon dust
- (4) Model proposed design of the fluidized bed reactor for the experimental facility
- (5) Determine compatibility of selected materials as needed to support design activities
- (6) Perform such other experiments as may be indicated for support of the design work.



#### REFERENCES

- (1) Haver, F. P., Shanks, D. E., Bisby, D. L., and Wong, M. M., "Recovery of Zinc from Zinc Chloride by Fused-Salt Electrolysis", U.S. Bureau of Mines Rept. Invest. 8133, 16 pages (1976).
- (2) Shanks, D. E., et al., (Report on 1500-amp  $ZnCl_2$  electrolysis cell) U.S. Bureau of Mines, to be published, 1977.