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EVALUATION OF SELECTED CHEMICAL PROCESSES
FOR PRODUCTION OF LOW-COST SILICON. PHASE II

Silicon Material Task Low-Cost Silicon Solar Array Project

Eighth Quarterly Progress Report, July 1–September 30, 1977

By
J. M. Blocher, Jr.
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W. J. Wilson
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October 20, 1977

Work Performed Under Contract No. NAS-7-100-954339

Battelle Columbus Laboratories
Columbus, Ohio

MASTER

U.S. Department of Energy

Solar Energy

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EIGHTH QUARTERLY PROGRESS REPORT
Covering the Period July 1, 1977, to September 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

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from

BATTELLE
Columbus Laboratories

October 20, 1977

ABSTRACT

Progress from July 1 to September 30, 1977, is reported in the design of a large experimental facility for the preparation of high-purity silicon by the zinc vapor reduction of silicon tetrachloride in a fluidized bed of seed particles to form a free-flowing granular product. As of July 25, 1977, the capacity goal for the experimental facility was raised from 25 to 50 MT Si/year.

Process flow diagrams and materials/energy flow sheets have been revised to conform to the higher capacity and a plant layout has been developed for locating the facility within an available structure. A unit-by-unit review of instrumentation and other requirements has been made, with the inclusion of those items in the flow diagrams and flow sheets.

Alternative designs are presented for a silicon carbide-coated carbon-lined fluidized-bed reactor contained in hot-wall stainless steel, including alternative designs for zinc vaporizers based on detailed heat-transfer calculations. It should be recognized that the air ambient temperature limitations of stainless steel coupled with the high boiling point of zinc and high reaction temperature (to avoid by-product concentration) place limitations on the temperature gradients available for moving heat in a stainless steel-contained system; however, the limitations fall short of being prohibitive.

Although the concept of using a quick-response flash vaporizer with a metered feed of liquid zinc appears unobtainable except at prohibitively high vaporizer temperatures, it is believed that the situation can be accommodated. Hysteresis in the vaporizer has the compensating advantage of maintaining zinc vapor flow during the interruption in liquid flow as the metering device is being recharged.

A visit to Jones Chemicals, Inc., of Barberton, Ohio, was made to define conditions and equipment for the conversion of by-product chlorine to hypochlorite for use in the treatment of sewage effluent locally. The logistics of 19 percent NaOH delivery and pick-up of 14 percent NaOCl was worked out and equipment suppliers were identified. The economics of the exchange is yet to be addressed.

Heat dissipation requirements for the fluidized bed, Zn/ZnCl_2 condenser, and SiCl_4 waste disposal sections were established.

Recrystallinity and purity data were obtained for DuPont's silicon prepared by batchwise zinc reduction of SiCl_4 ; however, their data on minority carrier lifetime could not be located.

A preliminary safety review was made of the experimental facility.

During the report period, the miniplant was operated to (1) provide 2.2 kg of product for JPL evaluation, (2) evaluate methods of product withdrawal, and (3) test three zinc vaporizer concepts. Results of the zinc vaporizer tests were consistent with concurrent heat-transfer calculations. An average value of $\sim 450 \text{ Btu hr}^{-1} \text{ ft}^{-2} \text{ F}^{-1}$ for heat transfer from graphite to boiling zinc (1 atm) was determined.

Work was continued on the electrolysis of synthetic Zn/ZnCl₂ mixtures to develop base-line experience for comparison with the results of planned experiments with miniplant by-product containing suspended silicon and zinc.

It was found experimentally that the 1 percent residual NaOH used to stabilize the NaOCl in 14 percent hypochlorite is sufficient to avoid the precipitation of SiO₂ (hydrated) when Cl₂(g) containing 1 m/o SiCl₄(g) is reacted with 19 percent NaOH. This was a welcome result, as cloudiness in the hypochlorite delivered to local sewage treatment facilities would be undesirable, and its correction would represent an additional expense.

It is anticipated that approval of the subcontract arrangements with Pace Engineering, Inc., and Raphael Katzen Associates will be received early in October* and that the design work will then proceed rapidly to projected conclusion in February of 1978.

* Work was actually initiated by the middle of October after receipt of approval.

INTRODUCTION

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

This work is currently in the second phase, that of designing a large experimental facility for the preparation of silicon by the zinc vapor reduction of silicon tetrachloride on a fluidized bed of seed particles. The design of the experimental facility described in prior quarterly reports has been geared to a production level of 25 MT/year of silicon. However, as of July 25, 1977, a decision was made by JPL to double the size. Accordingly, this report deals with a 50 MT/year capacity.

The Fifth/Sixth Quarterly Report of this series (ERDA/JPL 954339-77/5,6, April 29, 1977) summarizes the prior work and plans for the current program through design (Phase II), construction (Phase III), shakedown (Phase IV), and experimental operation (Phase V) of the experimental facility. It was initially planned to conclude the final design of the experimental facility by November 15, 1977; however, a 3-month delay in approval of sub-contracting arrangements has moved the target date to February 15, 1978.

In writing this report, it is assumed that the reader will have the background of the Fifth/Sixth and Seventh Quarterly Reports. Accordingly, progress and status changes since the Seventh Quarterly Report are reported with a minimum of background, in two sections, Design of the Experimental Facility, and Experimental Support Programs.

DESIGN OF THE EXPERIMENTAL FACILITY

The current version of the process flow diagram for the 50 MT/year experimental facility is shown in Figure 1*. It differs from the July 5, 1977, version as follows.

- (1) The capacity has been increased from 25 to 50 MT/year.
- (2) The 50 MT/year capacity is obtained by operating two 25 MT/year deposition units in parallel, each having its own reactant vaporizer and by-product condensation systems for independent control. Reactant storage/purification and by-product disposal systems are common. Accordingly, a branching is shown at A1 (purified SiCl_4 storage) to A2 and A2' through A11' and A12'. Returns from the duplicate systems are shown as "From A11', A12'" and "From B3', B4'" at the appropriate locations. The projected use of duplicate 25 MT/year deposition reactors was justified by the fact that the 6.6-inch-diameter fluidized bed required is a logical next step from the 2-inch miniplant, and that having the duplicate systems will permit operation of one while the other is down for repair or modification.
- (3) The locations of indicators and controllers for level, pressure, flow, and temperature are shown.
- (4) Provisions are made as indicated for breathing of tanks where liquid level and/or temperature are subject to change, and the points of introduction of inert gas for purge and constriction tracing

* Figure 1 bears the date October 20, 1977, beyond the report period, to accommodate minor revisions made during writing of this report.

FIGURE 1. PROCESS FLCW DIAGRAM FOR 50 MT/YEAR SILICON FACILITY (10/20/77)

are indicated. It is anticipated that further refinements will be made in this area as the design progresses.

- (5) An emergency storage tank for SiCl_4 (C4) has been added to permit the storage of SiCl_4 from any other SiCl_4 tank that must be emptied for repair or other reasons.
- (6) The SiCl_4 (g) preheater, A14, is shown separate from the fluidized-bed reactor, although it may be integrated with the fluidized-bed reactor.
- (7) A heat exchanger (A10a) has been shown for the Zn/ZnCl_2 condenser (A10) to take care of and monitor the large negative heat flux at that point (18.5 kw for each 25 MT/year unit).

Tables 1 and 2 are the current versions of the mass flow and energy flow sheets in metric and English units, respectively. It should be noted that the quantities shown are totals for the pairs of duplicate 25 MT/year units where used.

Figure 2 shows a preliminary plant layout, drawn to give assurance that the 50 MT/year experimental facility could be fitted into an existing building that is potentially available for the purpose.

The following paragraphs are devoted to a discussion of the various aspects of the experimental facility design that received special attention during this report period.

Design/Operations Narrative

A step-by-step analysis of the design and operation of the 50 MT/year facility was made as an aid in crystallizing some of the concepts and uncovering items requiring more information. As this document is considered to be a "working paper", and as it has not been fully reviewed by Battelle personnel and subcontractors involved in the design, it will not be presented here. However, it should be noted that its availability is expected to enhance progress in design of the facility.

TABLE 1. MATERIAL AND ENERGY FLOW SHEET (METRIC)
50 MT/YEAR SILICON FACILITY (REVISED 10/20/77)

(+ + = Materials In or Out) ℓ = liters, (l) = liquid phase

Input								Output						Process Heat	
Unit	Material	T, C	g mole hr ⁻¹	Kg hr ⁻¹	ℓ hr ⁻¹	Viscosity, cp	Material	T, C	g mole hr ⁻¹	Kg hr ⁻¹	ℓ hr ⁻¹	Viscosity, cp	Kcal hr ⁻¹	Kw	
A1 Pure SiCl ₄ Tank Capacity 5 days 8884.8 Kg 5921.2 ℓ	SiCl ₄ (ℓ)	25	435.72	74.04	49.36	0.45	SiCl ₄ (ℓ)	25	435.72	74.04	49.36	0.45	0.0	0.0	
A2 ⁺ SiCl ₄ Boiler (1.7 atm) Capacity 8 hrs 592.32 Kg 394.88 ℓ	SiCl ₄ (ℓ)	25	435.72	74.04	49.36	0.45	SiCl ₄ (ℓ) SiCl ₄ (g)	73.6 73.6	8.54 427.18	1.46 72.60	1.04 7154	0.3 0.012	3535.8	4.12	
A3 ⁺ Fluidized Bed Reactor	SiCl ₄ (g) → Inert Zn (g) → Si seed	73.6 25 927 25	427.18 25.64 354.34 12.82	72.60 25.64 55.86 0.36	7154 627.26 68390 0.150	0.012 0.019 0.085 ∞	Si prod. Si wall Si dust Inert SiCl ₄ (g) Zn (g) ZnCl ₂ (g)	927 927 927 927 927 927 927	269.14 7.68 5.12 25.64 158.06 316.10 538.24	7.56 0.22 0.14 25.64 26.86 20.66 73.36	3.16 3.08 3.06 102,208 26.86 20.66 73.36	0.046	461.2	0.54	
A4 ⁺ Zn Hopper	→ Zn (s)	25	26.92	1.76*	0.24*		Zn (s)	25	26.92*	1.76*	0.24*		0.0	0.0	
A5 ⁺ Zinc Molten Storage Capacity 2 days 2681.28 Kg 411.84 ℓ	Zn (ℓ) Zn (ℓ) Zn (s)	500 500 25	511.32 316.10 26.92*	33.44 20.66 1.76*	5.14 3.18 0.24*	3(.987) 3(.987) ∞	Zn (ℓ)	500	854.34*	55.86*	3.58*	3(0.987)	133.18*	0.154	
A7 ⁺ Zinc vaporizer (1.23 atm)	Zn (ℓ)	500	354.34	55.86	8.58	3(.987)	Zn (g)	927	854.34	55.86	68,390	0.085	26,240	30.50	
A8 ⁺ Silicon Cooler	Si prod.	927	269.14	7.56	3.16		Si prod.	25	269.14	7.56	3.16		-1445.2	-1.68	
A10 ⁺ Zn/ZnCl ₂ Condenser	Si dust Zn (g) Zn (ℓ) ZnCl ₂ (g) SiCl ₄ (g) Inert (g) ZnCl ₂ (ℓ)	927 927 500 500 327 327 327	5.12 316.10 316.10 538.24 158.06 25.64 5.38*	0.14 20.66 20.66 73.36 26.86 25.64 0.74*	0.06 3.18 3.18 33.18* 102,208 0.30*	0.046 3(.987) 3(.987) -1 0.021	Si dust Zn (ℓ) ZnCl ₂ (ℓ) ZnCl ₂ (g) SiCl ₄ (g) Inert (g)	500 500 500 327 327 327	5.12 316.10 316.10 538.24* 158.06 25.64 25.64	0.14 20.66 20.66 73.36* 26.86 0.74 25.64	3.06 3.18 3.18 33.18* 9318 0.06	0.013	-31,844*	-37.00*	
A11 ⁺ ZnCl ₂ stripper Cool cycle	SiCl ₄ (g) ZnCl ₂ (g) Inert (g) Si (s)	327 327 327 327	158.06 5.38 25.64 5.12	26.86 0.74 25.64 0.14	9318 0.021 0.06	0.021	ZnCl ₂ (s) SiCl ₄ (g) Inert (g) Si (s)	77 77 77 77	5.38 158.06 25.64 5.12	0.74 26.86 25.64 0.14	0.06 3278 0.06	0.013	-1027.0	-1.20	
A12 ⁺ ZnCl ₂ stripper Melt cycle	ZnCl ₂ (s) Si (s)	77 77	5.38* 5.12*	0.74* 0.14*	0.06*		ZnCl ₂ (ℓ) Si (s)	327 327	5.38* 5.12*	0.74* 0.14*	0.30* 0.06*	-1	43.58*	0.050*	
A13 SiCl ₄ recycle condenser	SiCl ₄ (g) Inert Inert	77 77 77	158.06 25.64 25.64	26.86 0.74 25.64	9318 0.013	0.013	SiCl ₄ (ℓ) SiCl ₄ (g) Inert(g)	0 0 0	155.22 2.84 25.64	26.38 0.48 25.64	17.24 640	0.018	-1613.0	-1.88	
A14 ⁺ SiCl ₄ Preheater	SiCl ₄ (g)	73.6	427.18	72.60	7154	0.012	SiCl ₄ (g)	927	427.18	72.6	24,754	0.0313	9010 (included in A3 heat)	10.47	
B1 ⁺ Electrolysis Feed Tank Capacity 2 days Si dust 6.8 Kg 2.8 ℓ Zn(ℓ) 931.68 Kg 152.64 ℓ ZnCl ₂ (ℓ) 3485.76 Kg 1434.24 ℓ	Si dust Zn(ℓ) ZnCl ₂ (ℓ)	500 500 500	5.12 316.10 532.86	0.14 20.66 72.62	0.06 3.18 29.88	0.06 3(0.987) -1	Si dust Zn(ℓ) ZnCl ₂ (ℓ)	500 500 500	5.12 316.10 532.86	0.14 20.66 72.54	0.06 3.18 25.88		0.0	0.0	
B2 ⁺⁺ Electrolysis Cell	Si dust ZnCl ₂ (ℓ) ZnCl ₂ (ℓ)	500 500 327	5.12 538.24 6.10	0.14 73.36 0.84	0.06 30.18 0.34	0.06 -1 -1	Zn(ℓ) (recycle) Zn(ℓ) (loss) SiCl ₄ (g) Cl ₂ (g) ZnCl ₂ (g)	500 500 500 500 500	511.32 26.92 5.12 528.00 6.10	33.44 1.76 0.38 37.44 0.34	5.14 1,270 34,218	3(0.987) 3(0.987) 0.032	51,320 (38,838)	59,640H (45.14) (ΔG°-nFE)	

* Average of intermittent operation.

† Total of duplicate units.

‡ Total of six units.

TABLE 1. MATERIAL AND ENERGY FLOW SHEET (METRIC) (CONTINUED)

		Input							Output							Process Heat	
Unit	Material	T, C	g mole hr ⁻¹	Kg hr ⁻¹	l hr ⁻¹	Viscosity, cp			Material	T, C	g mole hr ⁻¹	Kg hr ⁻¹	l hr ⁻¹	Viscosity, cp		Kcal hr ⁻¹	Kw
B3 ZnCl ₂ Stripper Cool cycle	Cl ₂ (g)	500	528.00	37.44	34,218	0.032			Cl ₂ (g)	25	528.00	37.44	13,042	0.014			
	ZnCl ₂ (g)	500	6.10	0.84					SiCl ₄ (g)	25	5.12	0.88					
	SiCl ₄ (g)	500	5.12	0.88					ZnCl ₂ (s)	25	6.10	0.84				-2,480	-2.88
B4 ZnCl ₂ Stripper Melt cycle	ZnCl ₂ (s)	25	6.10*	0.84*					ZnCl ₂ (l)	327	6.10*	0.84*	0.34*	~1		46.6*	0.054*
C1 SiCl ₄ Storage Capacity = 2 weeks 17,646 Kg 11,746.8 l	+ SiCl ₄ (l)	25	309.12	52.52	35.02	0.45			SiCl ₄ (l)	25	309.12	52.52	35.02	0.45		0.0	0.0
C2 SiCl ₄ Reserve Capacity = 2 days 2572.8 l 3857.28 Kg	SiCl ₄ (l)	25	309.12	52.52	35.02	0.45											
	SiCl ₄ (l)	0	155.22	26.38	17.24	0.51											
	SiCl ₄ (l)	73.6	8.54	1.46	1.04	0.3			SiCl ₄ (l)	25	472.88	80.36	53.6	0.45		110.2	0.12
C3 SiCl ₄ Purification	SiCl ₄ (l)	25	472.88	80.36	53.6	0.45			SiCl ₄ (l)	25	435.72	74.04	49.36	0.45			
	SiCl ₄ (l) waste	25	37.16	6.32	4.22	0.45										to be determined -	
Energy balance: total of steps = 43,482 50.54 products - reactants = 43,490																	
Materials and Energy Balance for Cl ₂ -Handling System, SiCl ₄ /Cl ₂ Waste, Wall Deposit Chlorination																	
		Input							Output							Process Heat	
Unit	Material	T, C	g mole hr ⁻¹	Kg hr ⁻¹	l hr ⁻¹	Viscosity, cp			Material	T, C	g mole hr ⁻¹	Kg hr ⁻¹	l hr ⁻¹	Viscosity, cp		Kcal hr ⁻¹	Kw
D1** SiCl ₄ Waste Holding Tank Capacity = 1 week 1,266 Kg 846 l	SiCl ₄ (l)	25	37.16						SiCl ₄ (l)	25	44.42	7.54	5.04	0.45			
	SiCl ₄ (l)	0	7.26														
D2** Ca(OH) ₂ Slurry Tank	Ca(OH) ₂ (s)	25	99.20						Ca(OH) ₂ (s)	25	99.20						
	H ₂ O(l)	25	y (to be determined)						H ₂ O(l)	25	y (to be determined)						
D3** SiCl ₄ Waste Processing	SiCl ₄ (l)	25	44.42						Slurry	SiO ₂	25	47.68					
	SiCl ₄ (g)	0	2.84							CaCl ₂	25	97.28					
	SiCl ₄ (g)	0	0.42							Ca(OCl) ₂	25	1.92					
	Inert(g)	0	25.64							H ₂ O	25	99.20+y					
	Cl ₂ (g)	0	3.84							Inert(g)	25	25.64					
	Ca(OH) ₂	25	99.20														
	H ₂ O(l)	25	y														
D4** Waste Storage Tank Capacity = 2 weeks	SiO ₂	25	47.68						SiO ₂	25	47.68						
	CaCl ₂	25	97.28						CaCl ₂	25	97.28						
	Ca(OCl) ₂	25	1.92						Ca(OCl) ₂	25	1.92						
	H ₂ O	25	99.20+y						H ₂ O	25	99.20+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. MATERIAL AND ENERGY FLOW SHEET (METRIC) (CONTINUED)

Unit	Input						Output						Process Heat	
	Material	T, C	g mole hr ⁻¹	Kg hr ⁻¹	l hr ⁻¹	Viscosity, cp	Material	T, C	g mole hr ⁻¹	Kg hr ⁻¹	l hr ⁻¹	Viscosity, cp	Kcal hr ⁻¹	Kw
E5, E6 Caustic/Hypochlorite Reactor/Storage 3287.2 l/wk 19% NaOH 37563 l/wk 14% NaOCl	Cl ₂ (g) SiCl ₄ (g) NaOH H ₂ O	25 25 25 25	528.00 5.12 1,142.82 10,820.00	37.44 0.88 45.72 194.92	145.55	Soln.	Na ₂ SiO ₃ NaCl NaOCl NaOH H ₂ O	25 25 25 25 25	1.12 548.48 528.00 54.10 11,363.30	0.62 32.06 39.32 2.24 204.72	223.62		-13,022 (Cl ₂ + NaOH Soln. only)	-15.13
E7 Caustic Cooler (Refrig.)	E5, E6 Contents	25	to be determined				E5, E6 Contents	4	to be determined				-13,022 (Cl ₂ + NaOH Soln. only)	-15.13
F1** Reactor Wall Deposit Chlorination	Si(s) Cl ₂ (g) Zn	?*** 25 ?***	7.68 19.20 z		(neglected in Zn + Cl ₂ balance)		SiCl ₄ (g) Cl ₂ (g) ZnCl ₂ (g)	?*** ?*** ?***	1.68 1.84 z		(neglected in Zn + Cl ₂ balance)			
F3** SiCl ₄ /ZnCl ₂ Condenser	SiCl ₄ (g) Cl ₂ (g) ZnCl ₂ (g)	?*** ?*** ?***	7.68 3.84 z		(neglected in Zn + Cl ₂ balance)		SiCl ₄ (l) SiCl ₄ (g) Cl ₂ (g) ZnCl ₂ (s)	0 0 0 0	1.24 0.42 1.84 z		(neglected in Zn + Cl ₂ balance)			
F4** Cl ₂ Supply Capacity = 2 weeks 457.0 Kg 142.4 l	Cl ₂ (l)	25	19.2*	1.36*	0.24*		Cl ₂ (g)	25	19.2*	1.36*	469.20*			

* Average of intermittent operation.

** See footnote, page 2.

*** To be determined.

TABLE 2. MATERIAL AND ENERGY FLOW SHEET (ENGLISH)
50 MT/YEAR SILICON FACILITY (REVISED 10/20/77)

(→ = Materials In or Out) (l) = liquid phase

Input														Output													
Unit	Material	T, F	lb mole hr ⁻¹ x 10 ²	lb hr ⁻¹	ft ³ (gal) hr ⁻¹	Viscosity, cp	Material	T, F	lb mole hr ⁻¹ x 10 ²	lb hr ⁻¹	ft ³ (gal) hr ⁻¹	Viscosity, cp	Process Heat														
													Btu hr ⁻¹	Kw													
A1	Pure SiCl ₄ Tank Capacity 5 days 19588.8 lb 1,564.80 gal	SiCl ₄ (l)	77	96.060	163.24	(13.040)	0.45	SiCl ₄ (l)	77	96.060	163.24	(13.040)	0.45	0.0	0.0												
A2 [†]	SiCl ₄ Boiler (1.7 atm) Capacity 8 hrs 1306.0 lb 104.4 gal	SiCl ₄ (l)	77	96.060	163.24	(13.040)	0.45	SiCl ₄ (l) SiCl ₄ (g)	164.5 164.5	1.882 94.176	3.22 160.04	(0.274) 252.6	0.3 0.012	14031.2	4.12												
A3 [†]	Fluidized Bed Reactor	SiCl ₄ (g)	164.5	94.176	160.04	252.6	0.012	Si prod.	1701	59.336	16.66	0.1116															
		→ Inert	77	5.652		22.16	0.019	Si wall	1701	1.694	0.48	0.0028			→												
		Zn(g)	1701	188.350	123.14	2415.2	0.085	Si dust	1701	1.128	0.30	0.0022															
		→ Si seed	77	2.826	0.80	0.0052	∞	Inert	1701	5.652																	
								SiCl ₄ (g)	1701	34.846	59.22																
								Zn(g)	1701	69.688	45.54	3609.6	0.046	1830.2	0.54												
								ZnCl ₂ (g)	1701	118.662	161.74																
A4 [†]	Zn Hopper	→ Zn(s)	77	5.934*	3.88*	0.0084*		Zn(s)	77	5.934*	3.88*	0.0084*		0.0	0.0												
A5 [†]	Zinc Molten Storage Capacity 2 days 5910.8 lb 108.8 gal	Zn(l)	932	112.726	73.70	(1.358)	3(.987)	Zn(l)	932	188.350*	123.16*	(2.266)*	3(0.987)	528.6*	0.154*												
		Zn(l)	932	59.688	45.56	(0.840)	3(.987)																				
		Zn(s)	77	5.934*	3.88*	0.0084*	∞																				
A7 [†]	Zinc vaporizer (1.23 atm)	Zn(l)	932	138.350	123.14	(2.266)	3(.987)	Zn(g)	1701	188.350	123.16	2415.2	0.085	104,128.8	30.50												
A8 [†]	Silicon Cooler	Si prod.	1701	59.336	16.66	0.1116		Si prod.	77	59.336	16.66	0.1116		-5735.0	-1.68 →												
A10 [†]	Zn/ZnCl ₂ Condenser	Si dust	1701	1.128	0.30	0.0022		Si dust	932	1.128	0.30	0.0022															
		Zn(g)	1701	69.688	45.56			Zn(l)	932	69.688	45.54	(0.840)	3(.987)														
		ZnCl ₂ (g)	1701	118.662	161.74			ZnCl ₂ (l)	932	118.662	161.74	(7.972)*	-1														
		SiCl ₄ (g)	1701	34.846	59.22	3609.6	0.046	ZnCl ₂ (g)	621	1.186	1.64																
		Inert(g)	1701	5.652				SiCl ₄ (g)	621	34.846	59.22	329.0	0.021	-126,367.2*	-37.00*												
		ZnCl ₂ (l)	621	1.186*	1.62	(0.080)*	~1	Inert(g)	621	5.652																	
A11 [†]	ZnCl ₂ stripper Cool cycle	SiCl ₄ (g)	621	34.846	59.22			ZnCl ₂ (s)	171	1.186	1.64																
		ZnCl ₂ (g)	621	1.186	1.62	329.2	0.021	SiCl ₄ (g)	171	34.846	59.22	186.4	0.013	-4,075.4	-1.20												
		Inert(g)	621	5.652				Inert(g)	171	5.652																	
		Si(s)	621	1.128	0.32	0.0022		Si(s)	171	1.128	0.30	0.0022															
A12 [†]	ZnCl ₂ stripper Melt cycle	ZnCl ₂ (s)	171	1.186*	1.62*			ZnCl ₂ (l)	621	1.186*	1.64*	(0.080)*	~1	173.0*	0.050*												
		Si(s)	171	1.128*	0.32*	0.0022		Si(s)	621	1.128*	0.30*	0.0022*															
A13	SiCl ₄ recycle condenser	SiCl ₄ (g)	171	34.846	59.22	186.4	0.013	SiCl ₄ (l)	32	34.220	58.16	(4.554)	0.51														
		Inert	171	5.652				SiCl ₄ (g)	32	0.626	1.06	22.6	0.018	-6,401.0	-1.88 →												
								Inert(g)	32	5.652					→												
A14 [†]	SiCl ₄ Preheater	SiCl ₄ (g)	164.5	94.176	160.04	252.6	0.012	SiCl ₄ (g)	1701	94.176	160.0	874.2	0.036	35,752.0	10.47												
														(included in A3 heat)													
B1 [†]	Electrolysis Feed Tank Capacity 2 days Si dust 15.4 lb 0.1 ft ³ Zn(l) 2186.8 lb 40.4 gal ZnCl ₂ (l) 7685.8 lb 378.8 gal	Si dust	932	1.128	0.32	0.0022		Si dust	932	1.128	0.30	0.0022															
		Zn(l)	932	69.688	45.56	(0.840)	3(0.987)	Zn(l)	932	69.688	45.54	(0.840)	3(0.987)														
		ZnCl ₂ (l)	932	117.474	160.12	(7.894)	~1	ZnCl ₂ (l)	932	117.476	160.14	(7.894)	~1	0.0	0.0												
32 ^{††}	Electrolysis Cell	Si dust	932	1.128	0.32	0.0022		Zn(l)(recyc)	932	112.726	73.72	(1.358)	3(0.987)														
		ZnCl ₂ (l)	932	118.562	161.74	(7.972)	~1	Zn(l)(loss)	932	5.934	3.88	(0.072)	3(0.987)														
		ZnCl ₂ (l)	621	1.344	1.84	(0.090)	~1	SiCl ₄ (g)	932	1.128	1.94																
								Cl ₂ (g)	932	116.404	82.54	1208.4	0.032	203,654.2	59.64ΔH												
								ZnCl ₂ (g)	932	1.344	1.86			(154,121.6)	(45.14) ΔG--nFE)												

* Average of intermittent operation.

- Total of duplicate units.

†† Total of six units.

TABLE 2. MATERIAL AND ENERGY FLOW SHEET (ENGLISH) (CONTINUED)

		Input						Output						Process Heat	
Unit	Material	T, F	lb mole hr ⁻¹ x 10 ²	lb hr ⁻¹	ft ³ (gal) hr ⁻¹	Viscosity, cp	Material	T, F	lb mole hr ⁻¹ x 10 ²	lb hr ⁻¹	ft ³ (gal) hr ⁻¹	Viscosity, cp	Btu hr ⁻¹	Kw	
B3 ZnCl ₂ Stripper Cool cycle	Cl ₂ (g)	932	116.404	82.56	1208.4	0.032	Cl ₂ (g)	77	116.404	82.54	460.6	0.014	-9,841.4	-2.88	
	ZnCl ₂ (g)	932	1.344	1.86			SiCl ₄ (g)	77	1.828	1.94					
	SiCl ₄ (g)	932	1.128	1.92			ZnCl ₂ (s)	77	1.344	1.86					
B4 ZnCl ₂ Stripper Melt cycle	ZnCl ₂ (s)	77	1.344*	1.86*			ZnCl ₂ (l)	621	1.344*	1.86	(0.090)*	~1	189.0*	0.054*	
C1 SiCl ₄ Storage Capacity = 18 days 50,000 lb 4,000 gal	SiCl ₄ (l)	77	68.150	115.80	(9.252)	0.45	SiCl ₄ (l)	77	68.150	115.96	(9.252)	0.45	0.0	0.0	
C2 SiCl ₄ Reserve Capacity = 2 days 8503.6 lb 679.6 gal	SiCl ₄ (l)	77	68.150	115.80	(9.252)	0.45	SiCl ₄ (l)	77	104.252	177.16	(14.160)	0.45	437.2	0.12	
	SiCl ₄ (l)	32	34.220	58.16	(4.554)	0.41									
	SiCl ₄ (l)	164.5	1.882	3.20	(0.274)	0.3									
C3 SiCl ₄ Purification	SiCl ₄ (l)	77	104.252	177.16	(14.160)	0.45	SiCl ₄ (l)	77	95.060	163.24	(13.040)	0.45	to be determined -		
	SiCl ₄ (l) waste	77						77	3.192	13.94	(1.114)	0.45			
C4 SiCl ₄ Emergency Storage Capacity = 1	SiCl ₄ (l)	77	--	--	--	--	Energy balance: total of steps = 172,550 50.54 products - reactants = 172,582								
Materials and Energy Balance for Cl ₂ -Handling System, SiCl ₄ /Cl ₂ Waste, Wall Deposit Chlorination															
		Input						Output						Process Heat	
Unit	Material	T, F	lb mole hr ⁻¹ x 10 ²	lb hr ⁻¹	ft ³ (gal) hr ⁻¹	Viscosity, cp	Material	T, F	lb mole hr ⁻¹ x 10 ²	lb hr ⁻¹	ft ³ (gal) hr ⁻¹	Viscosity, cp	Btu hr ⁻¹	Kw	
D1** SiCl ₄ Waste Holding Tank Capacity = 1 week 2795.5 lb 223.3 gal	SiCl ₄ (l)	77	8.192	13.92			SiCl ₄ (l)	77	8.192	16.64	(1.329)	0.45			
	SiCl ₄ (l)	32	1.600	2.72											
D2** Ca(OH) ₂ Slurry Tank	Ca(OH) ₂ (s)	77	21.870	16.21			Ca(OH) ₂ (s)	77	21.870	16.21					
	H ₂ O(l)	77	y (to be determined)				H ₂ O(l)	77	y (to be determined)						
D3** SiCl ₄ Waste Processing	SiCl ₄ (l)	77	9.792	16.64		Slurry	SiO ₂	77	10.512	6.32					
	SiCl ₄ (g)	32	0.626	1.06			CaCl ₂	77	21.446	23.81					
	SiCl ₄ (g)	32	0.092	0.16			Ca(OC1) ₂	77	0.424	0.61					
	Inert(g)	32	5.652				H ₂ O	77	21.870+y	3.94+0.18016y					
	Cl ₂ (g)	32	0.846	0.60			Inert(g)	77	5.652						
	Ca(OH) ₂	77	21.870	16.21											
D4** Waste Storage Tank Capacity = 2 weeks	H ₂ O(l)	77	y	0.18016y			SiO ₂	77	10.512	6.32					
							CaCl ₂	77	21.446	23.81					
							Ca(OC1) ₂	77	0.424	0.61					
							H ₂ O	77	21.870+y	3.94+0.18016y					

* 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 2. MATERIAL AND ENERGY FLOW SHEET (ENGLISH) (CONTINUED)

Unit	Material	T, F	Input				Material	T, F	Output				Process Heat	
			lb mole hr ⁻¹ x 10 ²	lb hr ⁻¹	ft ³ (gal) hr ⁻¹	Viscosity, cp			lb mole hr ⁻¹ x 10 ²	lb hr ⁻¹	ft ³ (gal) hr ⁻¹	Viscosity, cp	BTU hr ⁻¹	Kw
E5, E6 Caustic/Hypochlorite Reactor/Storage 8684 gal/wk 19% NaOH 5925 gal/wk 14% NaOCl	Cl ₂ (g) SiCl ₄ (g) NaOH H ₂ O	77 77 77 77	116.40 1.13 251.34 2385.36	82.55 1.92 100.80 429.75			Na ₂ SiO ₃ NaCl NaOCl NaOH H ₂ O	77 77 77 77 77	1.13 120.92 116.40 12.37 2505.15	1.38 70.69 86.67 4.95 451.33			-51,676 (Cl ₂ +NaOH soln. only)	-15.13
E7 Caustic Cooler (Refrig.)	E5, E6 Contents	77	to be determined				E5, E6 Contents	40	to be determined					
F1** Reactor Wall Deposit Chlorination	Si(s) Cl ₂ (g) Zn	*** 77 ***	1.694 4.232 z				SiCl ₄ (g) Cl ₂ (g) ZnCl ₂ (g)	*** *** ***	1.694 0.846 z					
					(neglected in Zn + Cl ₂ balance)						(neglected in Zn + Cl ₂ balance)			
F3** SiCl ₄ /ZnCl ₂ Condenser	SiCl ₄ (g) Cl ₂ (g) ZnCl ₂ (g)	*** *** ***	1.694 0.846 z				SiCl ₄ (l) SiCl ₄ (g) Cl ₂ (g) ZnCl ₂ (s)	32 32 32 32	1.600 0.094 0.846 z					
					(neglected in Zn + Cl ₂ balance)						(neglected in Zn + Cl ₂ balance)			
F4** Cl ₂ Supply Capacity = 2 weeks 1007.50 lb 37.62 gal	Cl ₂ (l)	77	4.232*	3.00*	(0.112)*		Cl ₂ (g)	77	4.232*	3.00*	16.570*			

* Average of intermittent operation.

** See footnote, page 2.

*** To be determined.

Fluidized-Bed Reactor

A tentative design of the fluidized-bed reactor (25 MT/year capacity in each of two for 50 MT/year facility) is shown in Figure 3. It is constructed of graphite-lined stainless steel, and provided with either a coaxial zinc vaporizer, or an external zinc vaporizer. The fluidized-bed support plate has 12 appropriately sized holes for $\text{SiCl}_4(\text{g})$ injection on a ring about 0.25 the distance from the outer wall to the center. An inner ring of eight holes, 0.6 of the distance to the center provides for zinc vapor introduction. In the initial version, an inert-gas-purged tube was provided at the center of the support plate for periodic withdrawal of the granular silicon product during operation, so as to maintain an effectively constant bed depth as the seed grows during production. This design also permits the use of an off-center withdrawal tube, if difficulty is encountered in withdrawing product from the central area where the concentration of low volatile zinc is highest.

To minimize carbon contamination of the product in a carbon-lined system, the use of a silicon carbide coating is an obvious possibility. However, providing a match between the thermal expansions of silicon carbide and graphite is difficult, as high-expansion graphite becomes less available as the size is increased. Accordingly, the concept of providing a silicon carbide-coated graphite felt sleeve liner is being considered to accommodate TCE mismatch. Obviously, this liner must also protect the stainless steel wall from the reaction mixture.

Zinc Vaporizer

Although the concept of graphite-lined stainless steel is attractive for the parts of the experimental facility involving $\text{ZnCl}_2(\text{g})$ and $\text{Zn}(\text{g})$ at high temperatures, certain limitations must be considered. Important among these is the temperature limitation of stainless steel in contact with air, about 980 to 1000 C depending upon the alloy. As the boiling point of zinc at atmospheric pressure is 908 C, and it rises to 917 C and 925 C for 1.1

FIGURE 3. FLUIDIZED-BED REACTOR - 25 MT/YEAR CAPACITY (9/19/77)

and 1.2 atm, respectively, this does not leave much of a ΔT available for driving in the high heat of vaporization of zinc (27.5 kcal/g mole). Accordingly, to have a zinc vaporizer coaxial and integral with the fluidized-bed unit requires that the vaporizer section be of larger diameter than the fluidized-bed section in order to provide the required area in a reasonable length. Figure 4 is an example of such a vaporizer. It consists of a stack of circular graphite trays from which the zinc boils. The trays have access ports to a central plenum chamber connected with the zinc vapor inlets of the fluidized-bed support plate. The trays of the vaporizer are connected by raised downcomers so that upper trays are filled before zinc flows to lower trays. With the proper balance of vaporizer temperature and liquid zinc feed rate, one or more of the bottom trays are kept "dry". The rate of flow of zinc to the vaporizer is 4.29 l/hour or $\approx 1.2 \text{ cm}^3/\text{second}$, a moderate rate.

It will be noted that the design shown in Figure 4 provides for axial location of the product withdrawal tube. As indicated above, while this is desirable from the standpoint of ease of construction, it may be necessary to locate the product withdrawal tube in the SiCl_4 -rich area to avoid plugging of the withdrawal tube by condensed zinc. This question will receive further attention.

With the recognition that the ΔT 's available in the stainless steel-contained integral coaxial zinc vaporizer are too low to enable the unit to function as a flash vaporizer (low inventory of zinc), attention was directed to assessing the feasibility of a quartz-enclosed, tray-type vaporizer in which higher ΔT 's could be developed. Figure 5 is a sketch of such a unit.

Table 3 gives the characteristics of a tray-type vaporizer having three graphite trays, 6 inches wide, the length being determined by the choice of ΔT to be used. The 50 MT/year experimental facility would have two such vaporizers, one for each fluidized bed and each having a capacity of 61.57 lb Zn/hr.

It can be seen from the information in Table 3 that the range of size and ΔT is practical. However, the inventory will lead to significant hysteresis in vapor flow once the metered flow of liquid zinc is changed.

SCALE: 1/4 inch = 1 inch

FIGURE 4. CANDIDATE DESIGN OF REACTOR BOTTOM SECTION (ZINC VAPORIZER) (9/19/77)

FIGURE 5. CANDIDATE DESIGN FOR TRAY-TYPE ZINC VAPORIZER (10/20/77)

TABLE 3. CHARACTERISTICS OF 61.57 lb hr⁻¹
TRAY-TYPE ZINC VAPORIZER*

Temperature Differential, F	40	100	150	200	250	300
Tray Length Required, inches	44.4	22.2	14.8	11.1	8.9	7.4
Time to Boil Off First 0.3 cm at Initial Rate on Termination of feed, minutes	13.5	6.7	4.5	3.4	2.7	2.2
Additional Time, minutes, to reach x percent of initial rate, x = 5	53.8	26.9	18.0	13.5	10.8	9.0
x = 1	82.8	41.4	27.6	20.7	16.6	13.8

* Three trays, 6 inches wide by 2(inches) long, steady-state boiling reached with bottom tray dry; top two trays each covered with 0.7 cm liquid zinc. When feed is cut off, 0.3 cm thickness of zinc boils off at full rate with trays fully covered. Then surface tension maintains level at 0.4 cm as tray coverage decreases and rate of vaporization decreases in direct proportion. Conservative heat transfer coefficient of 300 BTU hr⁻¹ ft⁻² F⁻¹ used.

The times necessary to boil out two components of the inventory after feed termination are given. The first covers boiling of the thickness increment due to the provision of a 0.3-cm-high lip on the downcomer. During the time this material is boiled off, the tray area is fully covered, and boiling occurs at full capacity. At a thickness estimated to be about 0.4 cm, the film starts to retreat, its thickness being maintained by surface tension. During this period, the rate of vaporizer output decreases in proportion to the plate coverage. The times necessary to boil away this layer to 5 percent and 1 percent of coverage (i.e., to 5 percent and 1 percent of the initial vaporization rate) are given in the table. It should be noted that the values in Table 3 are based on the assumption of uniform tray surface temperature. In actual practice where the conductively transferred heat is driven in from the tray edge, a gradient will be present from the edge to the middle where the rate of vaporization per unit area will be less than that near the tray edges. As the tray width is increased, one reaches a point (depending on the tray cross section) where the relative contribution of the middle zone is impractically low. Differential heat-transfer calculations are being made to assess this factor. It is quite possible that trays less than 6 inches in width and proportionately longer than those given in Table 3 would be preferred. Such a change would not alter the numbers given for the boil off of inventory, as long as (1) the length is varied inversely as the width and the area remains constant and (2) the effective ΔT 's for boiling are those given.

In the differential heat-transfer calculations, the contribution of radiant heat will also be assessed. This contribution would be appreciable to the bottom tray (graphite, $\epsilon^* = 0.9$ to graphite), but would be only about one third as large to the top tray (graphite, $\epsilon = 0.9$ to zinc, $\epsilon = 0.3$) for given heat source and heat sink temperatures.

The zinc vaporizer will be fed with liquid zinc at 500 C by means of a mechanically controlled displacement metering device as discussed in the next section.

* Emissivity.

Zinc Liquid Feed System

A candidate design for the liquid zinc feed system is shown in Figure 6. It consists of a motor-driven piston which displaces a ~0.5-hour charge of zinc from the cylinder into the vaporizer. To ensure controlled flow of liquid zinc to the vaporizer in droplets, the tube between the cylinder and the vaporizer must be slanted upward and the exit end constricted, otherwise initiation of flow would empty an uncontrolled length of the tube at the exit end. In general, the size of the orifice required is a function of the surface tension of the liquid. Experience with zinc in the miniplant has shown that an orifice of 2-mm diameter is effective in ensuring dropwise flow of zinc at the rates used in the miniplant. This factor will be less critical, of course, with the higher flows used in the experimental facility. During the time the piston is withdrawn and the cylinder recharged, the inventory in the zinc vaporizer provides for essentially constant* vapor feed rate. The piston also serves as a seal against the zinc supply in the reservoir to the left. It is obvious that the filling of the cylinder must be limited either on the basis of an allotted time for a known rate of filling, or by means of a level detector, otherwise after complete filling, the head in the cylinder could build up to the point of initiating flow independent of the position of the piston.

The reservoir to the left provides a constant head of zinc to control the rate of flow to the displacement cylinder during its charging so that a timed recharging cycle can be used. It remains to be determined whether the constant-level reservoir can be eliminated by filling the cylinders directly from the molten zinc storage tank, A5 (of variable liquid head), using a level indicator on the cylinder with feedback to the piston activating mechanism.

A mock-up of the zinc vaporizer design will be evaluated on the experimental support program.

* The filling time must be minimized to accommodate the effect of decreasing vaporization from partially filled trays in the vaporizer.

FIGURE 6. LIQUID ZINC FEED SYSTEM (10/24/77)

Control of the zinc vapor feed rate by means of a limited-inventory vaporizer coupled with a liquid metering device was adopted after calculation of the requirements for orifice control and measurement of zinc vapor feed. Rejection of the latter concept was based on the fact that the high boiling point of zinc (908 C at 1 atm, 917 C at 1.1 atm, and 925 C at 1.2 atm) does not allow for (1) development of the pressures required for orifice metering and control within the temperature constraints of stainless steel containmnet, and (2) 1200 K (927 C) operation of the fluidized bed free of zinc mist. If the boiling point of zinc were 100 C lower, orifice control and metering of the vapor might be practical, which would have eliminated the necessity for mechanical feed devices of the type contemplated in Figure 6. Although perhaps less desirable, it is believed that a workable device for mechanical displacement feed can be devised for the 50 MT/year facility, as considerable success has been achieved with that approach in the miniplant.

Chlorine Disposal

The by-product chlorine from the electrolysis of $\text{ZnCl}_2(\ell)$ for zinc recycle is to be converted to sodium hypochlorite for use in local sewage treatment plant chlorination.

A trip was made to Jones Chemicals, Inc., Barberton, Ohio, Division, to discuss the logistics of their delivering NaOH solution and picking up NaOCl solution, together with the equipment requirements for making the conversion. Units E5, E6, and E7 are the ones involved in this operation. E5 and E6 are 12,000-gallon, fiberglass-reinforced bisphenyl resin tanks provided with sparging tubes for chlorine input, and other appropriate fixtures. A 5-10 hp (refrigeration) water chiller is used to cool a titanium heat exchanger through which the hypochlorite solution is pumped to dissipate the heat of reaction (626 BTU/lb Cl_2). A solution containing 19 percent NaOH would be converted to one containing about 14 percent NaOCl and about 1 percent residual NaOH for stabilization. Provision is made in the piping/pumping

system for filling or emptying* either tank and transferring the contents of either tank to the other. Chlorination would be initiated with 7500 gallons of 19 percent NaOH in E5 and 3500 gallons of 19 percent NaOH reserve in E6. After about 6 days of chlorination, the NaOCl concentration will have risen to 14 percent and the volume to 8000 gallons, at which point the chlorine will be routed to E6. Two tank trucks of 4000-gallon capacity each will deliver 7000 gallons of 19 percent NaOH to E6 and withdraw 8000 gallons of the 14 percent NaOCl from E5 for local distribution. Then 3500 gallons in E6 will be routed to E5 as reserve for the next cycle. Details on the heat exchanger and other auxilliary items for the operation were obtained.

The economics of the NaOH/NaOCl exchange will be worked out.

Heat Dissipation, Fluidized-Bed Reactor

Heat transfer calculations were made for dissipating, from the walls of the fluidized-bed reactor, the exothermic heat of the reaction

It was concluded that this amount of heat can readily be transferred by radiation to the wall of the containment vessel, and that the graded bed temperature, found to be conducive to increased reaction efficiency, can be established by a corresponding temperature gradient in the adjacent heat sink.

Zn/ZnCl₂ Condensation

Recalculation of the condensation pattern in the Zn/ZnCl₂ condenser has shown that at an effective surface temperature of 477 C, it should be capable of removing 99.9 percent of the zinc and 99.8 percent of the ZnCl₂

* Two low-level outlets will be provided, one about 12 inches above the bottom to prevent delivery of sludge, and one at the bottom for drainage.

from the SiCl_4 passing through, leaving only 0.1 and 0.2 percent, respectively, to be handled by the solids condensers, A11 and A12. The allowance of 1 percent residual ZnCl_2 condensation in A11 and A12 in the Mass/Energy Flow Sheets, Tables 1 and 2, is based on a conservative approach.

SiCl_4 Waste Disposal

An estimate was made of the enthalpy change for the reaction

at 298 K which effectively takes place in the SiCl_4 waste disposal system. The result for the 50 MT Si/year facility requiring the disposal of 8.1 kg h^{-1} of SiCl_4 is $-4300 \text{ Kcal h}^{-1}$ or $-17,000 \text{ BTU h}^{-1}$ which can be handled by $\sim 100 \text{ gal h}^{-1}$ water cooling at $\Delta T = 20 \text{ F}$.

DuPont Silicon

The following information was obtained from DuPont on specifications for the silicon produced there in the 1950's by batchwise zinc reduction of silicon tetrachloride.

TABLE 4. SPECIFICATIONS FOR DUPONT SILICON

	Grade I	Grade II	Grade III	Solar Cell Grade
Boron Content (ppb)*	1	1 to 3	6 to 11	---
Minimum Resistivity for Top 60 Percent of Crystal (ohm cm)				
"P" Type	100	50	25	---
"N" Type	25	15	5	0.5

* Calculated from resistivity of float-zoned bar cut from Czochralski crystal.

It was not possible to locate data on the minority carrier lifetime of this material, nor on the history of a given lot subsequently used in characterized solar cells. It is understood that cells with AML efficiencies of 10 to 12 percent were being obtained.

It can be seen from the data of Table 4 that the product covered a wide range of characteristics, presumably stemming from the batchwise mode of operation, and perhaps from uncontrolled variables. It is anticipated that a material of more uniform quality will be obtained in the essentially continuous operation of the 50 MT/year experimental facility.

Safety Review

A preliminary review of the safety aspects of the 50 MT/year experimental facility was conducted by the safety personnel of Battelle's Columbus Laboratories, with the primary objective of evaluating the feasibility of locating the facility in an existing building on the Columbus site as opposed to the pilot plant area at Battelle's West Jefferson (Ohio) facility. In addition to citing the standard requirements for handling of chlorine gas and molten zinc, information was requested on industry practice for dealing with SiCl_4 spills, and incorporation of such information in the plant design was requested. As a first step, an emergency SiCl_4 storage tank, C4, equal in capacity to C1 has been provided so that the contents of any tank containing SiCl_4 can be pumped to C4 in an emergency.

Contacts with SiCl_4 suppliers have revealed that diking of individual units, and application of coarse water spray and, occasionally, soda lime are effective measures in dealing with SiCl_4 leaks and spills.

Design Schedule

Table 5 gives the current assignments for design responsibility by item, and Figure 7 gives the current schedule for conclusion of the design task. With minor exceptions, Figure 7 differs from the July 5, 1977, version (Figure 3, Seventh Quarterly Report) by setting back the dates for design

conclusion by 3 months to compensate for the delay in approval of the sub-contract arrangements.

With the design subcontractors applying the concentrated effort anticipated from early October, it should be possible to have the individual items designed by the end of January, and the overall design concluded by the middle or the end of February, 1978.

Plans for the Next Report Period

The following items are planned for next quarter relative to design of the 50 MW/year experimental facility.

- (1) On approval of the subcontracting agreements, these firms will be brought into the design task rapidly in accordance with the schedule in Figure 7.
- (2) Continuation of the Battelle effort on the design of items of specialized equipment in accordance with Figure 7.

TABLE 5. IDENTIFICATION OF PRIMARY DESIGN
RESPONSIBILITY BY ITEM (10/20/77)

I. "Off Shelf" Purchases

A1, A4, C1, C2, C4, D1, D2, D4, E5, E6, 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, A10a, A11, A12, A13, A14, B1, B3, B4, D3, F3

Level controls in A3, A5, A6, B1, B2

III. Battelle's Columbus Laboratories

A2, A3, A6, A7, B2

IV. Pace Engineering, Inc.

C3

V. Supplied by Materials Manufacturers

F4

Underlined items require extensive BCL involvement.

* Letter codes refer to major equipment items cited in Figure 1 and Tables 1 and 2. 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 is changed and items in earlier designs are dropped, new items are assigned new code numbers rather than vacated numbers, to avoid confusion of the records.

* Δ = completed item; Δ = target item.

FIGURE 7. DESIGN SCHEDULE, EXPERIMENTAL FACILITY
(10/20/77)

EXPERIMENTAL SUPPORT PROGRAM

During this report period, the miniplant was operated with semiconductor-grade seed material to prepare silicon for quality evaluation. Several experiments were carried out in support of the zinc vaporizer and electrolytic cell design efforts and in clarifying the requirements for by-product chlorine disposal. This work is described below.

Miniplant Operation

In three of the runs (Nos. 86, 87a, and 88) made in the miniplant this quarter, semiconductor-grade seed was used to provide material for JPL's use in quality evaluation. The total quantity shipped was 2.2 kg, containing about 50 percent of deposited material. Although it is anticipated that the fraction of deposited material will be increased in the future (to >95 percent in the 50 MT/year experimental facility), accretion was limited in these three runs due to three factors:

- (1) The limited availability of semiconductor-grade seed of the desired particle size
- (2) The lack of a suitable product withdrawal system
- (3) The limited amount of zinc available in the zinc vaporizer.

The seed material used in the runs mentioned above was prepared from semiconductor-grade silicon by hand grinding in an agate mortar. The crushed material was screened to isolate a usable fraction (149 x 420 μm). Stainless steel screens were used, with the solder seams and brass rims coated with epoxy to prevent contamination from these materials. Following screening, the seed was treated 24 hours in HF and 24 hours in 50 percent HF-H₂SO₄ with intermittent agitation, and then washed with deionized water and dried. Seed preparation by means of an impact mill is being evaluated as an alternative to the tedious and potentially more contaminating hand grinding. Mass

spectrometric analyses of the seed material from both the agate mortar and impact mill operations are pending with those of the fluidized-bed product. Receipt of the mass spectrometric results has been delayed pending the development of a technique for forming contamination-free electrodes of the silicon granules. The procedure used with the Siemens product* is, of course, inapplicable with the granular fluidized-bed product. Several options are being considered. Forming a pressed ingot from mixture of granules with graphite or silver has been used before in the semiconductor industry in analyzing high-purity granules. Sintering the granules together thermally just below the melting point, or by chemical transport in, e.g., trichlorosilane at lower temperatures are alternatives being considered.

The first product withdrawal scheme used (Runs 82 and 83) in the three preparation runs was a simple overflow arrangement, a 5-mm-ID tube extending from a point just above the desired expanded bed height, down the side of the reactor, and to a collecting vessel beside the reactor. Despite a purge of inert gas through the tube** that would be enough to prevent back diffusion in a quiescent situation, ZnCl_2 entered the tube, condensed at the colder end, and plugged it off early in the run, so that the overflow of silicon product was prevented. It is believed that the pressure differentials during fluctuations of the bed were sufficient to cause "breathing" of the withdrawal tube to the location at which ZnCl_2 condensation was noted. Breathing to the point of ZnCl_2 condensation might be avoided by maintaining the product in the withdrawal tube at a level well within the hot zone thus increasing the gas-flow resistance of the withdrawal tube; however, to do this would require periodic controlled withdrawal of the product, thus negating the automatic action desired in the simple overflow arrangement.

* Slicing an electrode from the Czochralski or float-zoned crystal, or from the as-deposited material.

** Short of preventing flow of particles down the tube.

In Run No. 89, the withdrawal tube was moved to the point at which the hemispherical bed support meets the cylindrical fluidized-bed reactor tube wall. This portion of the bed is exposed primarily to SiCl_4 vapor so that the concentration of $\text{ZnCl}_2(\text{g})$ [or $\text{Zn}(\text{g})$] is very low and the condensation plugging hazard is greatly reduced. With the withdrawal tube maintained full of product except during periods of withdrawal, no condensation was noted and product was withdrawn successfully during and after the run. It remains to be seen whether this arrangement would be effective if the product outlet were moved to near the zinc inlet where the zinc condensation is high and where the possibility of zinc condensation in the withdrawal tube would be enhanced.

With the potential availability of larger quantities of seed of smaller particle size, and with some of the pressure for prompt supplying of product relieved, it will be possible to use the product of one run as seed in the next two, etc., and to build up the final increment ratio in that way. In this mode of operation, the increment per run would be limited only by the capacity of the zinc vaporizer, and the final increment ratio by the final particle size that can be fluidized effectively. A disadvantage in operating this way is that undetected contamination in an early run of the series carries into all of the subsequent product. Some compromise will be reached in planning future materials preparation runs based on consideration of all of the factors involved.

It is significant that the shallower beds used for the quality-evaluation runs (because of limited seed availability) led to decreased SiCl_4 conversion efficiency, increased amounts of silicon dust, and increased deposition of silicon on the reactor wall, thus confirming the predictions from earlier runs with decreased bed height that increased efficiency and decreased silicon dust production can be expected on going from the miniplant to the deeper beds of the experimental facility. The degree of improvement to be expected depends upon how rapidly the curve is levelling off at the higher bed levels employed in the miniplant. The impact of this factor cannot be established with certainty from the data now available.

Heat Transfer Coefficient,
Graphite to Boiling Zinc

In work with the SNAP-8* power system, heat fluxes of over 1000 BTU $\text{hr}^{-1} \text{ft}^{-2} \text{F}^{-1}$ were obtained for mercury boiling in stainless steel tubes. However, the flow velocities and accompanying pressure differentials are too high to be considered for the zinc vaporizer of the 50 MT/year experimental facility. Further, the quality of the vapor emerging from the narrow tube was less than 100 percent. As the presence of zinc mist in the vapor entering the fluidized bed can be expected to nucleate dendritic, and ribbon-like silicon which remains entrained and is lost to the fluidized bed product, the use of a vaporizer similar to that for SNAP-8 was rejected. However, the data indicated that it should be possible to obtain heat transfer coefficients of the order of 500 BTU $\text{hr}^{-1} \text{ft}^{-2} \text{F}^{-1}$ with boiling zinc under conditions compatible with other aspects of the experimental facility design.

By contrast, the heat transfer coefficient calculated for the 1-inch-diameter packed bed vaporizer discussed on page 24 of the Seventh Quarterly Report was only $\sim 120 \text{ BTU hr}^{-1} \text{ft}^{-2} \text{F}^{-1}$ based on wall area alone, and would have been even lower if the area of the packing were included. It is evident that, in this case, the zinc was in poor contact with the internal surfaces. Zinc does not wet graphite and its high surface tension near the melting point, 700 dyne cm^{-1} **, supports a large radius of curvature on exposed unsupported surfaces. Thus the observed behavior of the packed bed vaporizer is understandable.

The heat transfer coefficient from graphite to boiling zinc with an identifiable confined surface area was measured in a subsequent experiment. Zinc was boiled at atmospheric pressure from a 1-inch-diameter graphite pot with a zinc depth of about 8 inches. Differential thermocouples were provided for measuring the temperature drop between the graphite wall and the body of the zinc. Based on the rate of evaporation and measured temperature

* A. J. Sellers, M. R. Wong, and G. M. Thur, USAEC Report No. ANL-7100, pp 573-632 (1965).

** Extrapolated from data of D.W.G. White, Trans. AIME 236, 796 (May, 1966).

differentials, an average value of $467 \text{ BTU hr}^{-1} \text{ ft}^{-2} \text{ F}^{-1}$ was calculated. Thus, it appears reasonable to use a value of $450 \text{ BTU hr}^{-1} \text{ ft}^{-2} \text{ F}^{-1}$ for vaporizer design where contact with the graphite can be assured over the given area.

Zinc Vaporizer

As indicated earlier, a major objective of the zinc vaporizer design work has been to evolve a "flash vaporizer", i.e., a vaporizer with low inventory which would not experience a large hysteresis in vapor output with changes in the metered rate of liquid input. As it is also desirable to minimize the length of line through which the zinc vapor must flow, designs that might be integrated into the lower part of the fluidized-bed reactor are favored.

With the above objectives in mind, three types of zinc vaporizers were evaluated in the miniplant. The first, a radiation-heated packed bed, was discussed in the Seventh Quarterly Report. At a feed rate of 40 g hr^{-1} and short of the capacity desired, it appeared to be on the verge of flooding. Additional preheating was provided in the SiCl_4 stream to decrease the cooling effect of the SiCl_4 in the annulus surrounding the zinc vaporizer, but the subsequent results were inconclusive. As heat transfer calculations showed the difficulty of driving heat into the packing in such a design*, that approach was deferred. However, an annular packed bed may still be practical.

In the second design evaluated, zinc was fed to the top end of a ~ 146 -inch-long tube formed between a spiral groove (5 mm x 5 mm) in a graphite rod (~ 12 -inch-long x ~ 1.4 -inch-diameter) and the radiatively heated quartz wall. The vapor exit was from the bottom through a central ~ 0.31 -inch-diameter hole connected also with 0.060-inch-diameter ports spaced every ~ 8 inches along the length of the spiral. The surface tension of the zinc is such that a minimum opening of ~ 5 -mm diameter is required for zinc

* The packing might be used effectively to disperse the zinc, but the major heat transfer must occur from the wall.

"droplets" to flow under their own head. This fact limits the pitch of the spiral to 4 per inch, and with a wall temperature of 975 C, the dwell time of the zinc droplets in the tube was too short to achieve complete vaporization before reaching the bottom of the spiral. At a temperature of 1098 C, this vaporizer had a capacity of 42 g zinc per minute which would be adequate for operation of the miniplant, but the operating temperature was deemed excessive for some of the designs visualized for the experimental facility. Hence, it would be necessary to increase the dwell time of zinc in the spiral. Use of a larger diameter spiral with the same pitch to reduce the slope and hence the velocity of the droplets, and/or a longer spiral would be appropriate for a scaled up system, but could not be used in the confines of the miniplant heaters. Thus, attention was directed to a third alternative, a stacked tray arrangement.

In the stacked tray vaporizer, the trays, consisting of parallel grooves (5 mm x 5 mm) in a 1.4-inch-diameter graphite rod, again surrounded by a quartz chamber, were connected by staggered downcomer holes of 5-mm diameter. At a temperature of 980 C and a feed rate of 15 g per minute, the top tray flooded. Although the head on the flooded tray could have been allowed to build up until flow was achieved, such a procedure is inconsistent with minimizing the zinc inventory in the vaporizer so that it can be treated as a "flash" vaporizer.

To avoid upper tray flooding under the above conditions, two staggered 6-mm openings were added to each tray as downcomers. At a wall temperature of 980 C, the vaporizer performed satisfactorily at 22 g per minute but appeared to be on the verge of flooding (liquid zinc reaching the bottom without having vaporized), i.e., the provision of the additional downcomers resulted in an overcorrection. On the basis of a $450 \text{ BTU hr}^{-1} \text{ ft}^{-2} \text{ F}^{-1}$ heat transfer coefficient, the observed performance implies that 23 percent of the available tray area was covered with zinc. It was evident that to promote complete tray coverage and maximum area utilization, downcomers with raised lips would be required in future designs despite their leading to increased inventory.

At this point, the miniplant had to be readied for the preparation of quality-evaluation material, and as a completely satisfactory alternative vaporizer design was not yet available, the induction-heated (1350 C) single-tray vaporizer used in previous work with the miniplant was installed. It performed satisfactorily as before; however, the desire to lower the vaporizer temperature as much as possible has dictated the planned testing of a tray-type vaporizer of larger area, based on the information covered in the design section of this report. Accordingly, a new vaporizer for the miniplant is being constructed along the lines of Figure 4 which will provide two trays nominally 5 inches long by 1.5 inches wide. The upper tray will have a 0.1-inch riser to restrict overflow to the lower tray. A carbon wool-packed section of the vapor outlet will provide for de-misting of the vapor. It is desirable that droplets of zinc be removed from the vapor to avoid the potential for formation of silicon on the droplets rather than on the bed particles with subsequent loss of product by entrainment as "dust". It is anticipated that the new vaporizer will be evaluated early in October.

Electrolysis of Zinc Chloride

In accordance with information obtained from the U.S. Bureau of Mines in Reno, Nevada, during the visit noted in the Seventh Quarterly Report, the experimental zinc electrolysis cell was revised to conform to the Bureau of Mines' electrode configuration. Horizontal electrodes with slanted chlorine vent channels on the underside of the anode were provided. With a 1/1 mole ratio synthetic ZnCl_2/KCl mixture, 16 hours of uneventful operation at 100 amp (0.8 amp/cm^2) and 5 V were achieved when a malfunction of the electronic section of the electrolyte level indicator led to the cell's being overfilled and forced termination of the run. Corrosion of the stainless steel in direct contact with the fused salt mixture required extensive repair of the cell.

The refurbished cell was supplied with a high- and low-level resistance-activated indicator, and a gas bubbler (pressure responsive) liquid head indicator.

Further experiments in the refurbished cell with synthetic ZnCl_2/KCl mixtures were likewise terminated when the stainless steel containment vessel corroded through on contact with the salt mixture. In this case, the salt mixture had been blown over the wall of the graphite liner on the chlorine-outlet side of the electrode assembly because of the foam formed in the salt mixture at that point. The formation of such a foam in the chlorine emergence area has been observed in the Bureau of Mines work; however, it was hoped that it would not be as troublesome in the closed cell design as it was in the open cell work at the Bureau where the formation of zinc oxide/hydroxide is a factor.

Before starting another campaign on the electrolysis of synthetic ZnCl_2/KCl mixtures scheduled for October, a greater freeboard will be provided above the salt mixture to accommodate the effects of foaming.

Chlorine Disposal

In the disposal of chlorine by the formation of hypochlorite for projected use in treatment of sewage plant effluent, it is desirable that the properties of the hypochlorite not differ visibly from those of the product currently in use. For example, the presence of cloudiness due to SiO_2 precipitate would be undesirable. Accordingly, chlorine containing about 1 mole percent SiCl_4 was bubbled into initially 20 percent NaOH for conversion to hypochlorite. In one experiment, at 0.8 mole percent SiCl_4 in the Cl_2 , the reaction proceeded to 1.0 percent residual NaOH^* and the product was the normal clear straw-colored solution. Although the limit of SiCl_4 tolerance was not determined, the precipitation of SiO_2 (hydrated) at 1 percent SiCl_4 in Cl_2 is not a problem.

* About 1 percent of residual NaOH is necessary to prevent spontaneous decomposition of the NaOCl .

Work Planned for Next Report Period

The following work is planned for the next report period.

- (1) Operation of the miniplant to provide material for quality evaluation will be continued.
- (2) The characteristics of the new zinc vaporizer (low-temperature/tray-type) will be determined.
- (3) Operation of the electrolysis cell on synthetic ZnCl_2/KCl mixtures will be continued to provide a data base for comparison with the miniplant by-product, containing some silicon.
- (4) Compatibility and reactant-exposure tests will be run with potential materials of construction to support design activities.
- (5) The fluidized-bed design (25 MT/year) for the experimental facility will be modelled to check reactant flow/mixing and particle motion.
- (6) The essential design elements of the positive displacement zinc feeder described in this report will be modelled to evaluate their feasibility.
- (7) Other experiments will be performed as may be needed in support of the design work.