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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
Fifth—Sixth Quarterly Progress Report, October 1, 1976—March 31, 1977

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April 29, 1977

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

Battelle Columbus Laboratories
Columbus, Ohio

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
Division of Solar Energy

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FIFTH-SIXTH QUARTERLY PROGRESS REPORT
Covering the Period October 1, 1976, to March 31, 1977

on

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FOR PRODUCTION OF LOW-COST SILICON**
(Phase II)

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

April 29, 1977

JPL Contract 954339

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April 29, 1977

ABSTRACT

The results of experimental work and economic analyses carried out during the first 12 months of this contract (Phase I) have led to Battelle's concentration on development of the zinc reduction of silicon tetrachloride on seed particles in a fluidized bed. A second year program (Phase II) has been initiated which consists of the design of a 25 MT/year experimental facility and supporting experiment effort.

During this quarter, the effort in the plant design portion of the program has been devoted to the (1) preparation of a detailed process schematic diagram; (2) determination of material flow and energy requirements; (3) conceptual design of major equipment items, including those unique to the facility; (4) contacts with industrial companies on equipment and processes for which experience is available; and (5) initiation of contacts with Battelle pilot plant design specialists, a

distillation consultant, and engineering firms. It is intended that a Columbus, Ohio-based engineering firm be employed to design standard items and prepare detailed engineering drawings of the entire plant.

The effort in the experimental support portion of the program has included a continuation of the following studies: (1) operating parameter optimization in the miniplant, (2) reactor design, and (3) condenser system design, including supplemental condensation experiments. In addition, a new zinc feed system has been devised and evaluated, and the construction of a system sufficiently large to obtain meaningful data on the electrolytic recovery of zinc from zinc chloride has been initiated.

As a result of these experimental support activities, deposition rates on the seed particles of 334 g/hr have been achieved in the miniplant at a bed efficiency of 62.1 percent. Further, total silicon recovery efficiencies as high as 97.7 percent of that predicted thermodynamically have been obtained and wall deposits as low as 3 percent of the product were observed.

The condensation studies have resulted in a condenser system for the miniplant that has been functioning satisfactorily and can be used as a guide for the design of a system for the 25 MT/year plant.

Zinc vaporization rates of ~40 g/minute were achieved in a newly designed unit operated at 1050 C (in current system, 1300 C is required to get this rate) which is more amenable to scaleup.

INTRODUCTION

This is the Fifth-Sixth Quarterly 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. A combined report is being issued to cover the period October 1, 1976, through March 31, 1977, as the project activity during the last quarter of 1976 was limited during a period of negotiations with reference to contract extension.

The overall objective of this program has been to evaluate (1) the fluidized-bed zinc reduction of silicon tetrachloride and (2) modifications of processes involving silicon tetraiodide, to determine whether any have the potential for supplying semiconductor-grade silicon at a cost below \$10/Kg (1975 dollars), and then to follow through with development of the process having the greatest potential. In the early days of the semiconductor silicon industry, certain versions of the zinc reduction of SiCl_4 process and the iodide process had been shown to be capable of supplying semiconductor-grade material.

During the first four quarters of this program, hereinafter referred to as Phase I, both economic and experimental evaluations were made of the candidate processes with the result that although all appeared to be technically feasible, only the zinc reduction of silicon tetrachloride in a fluidized bed of seed particles, with electrolytic recovery and recycle of the zinc at an estimated production cost of \$9.12/Kg⁽¹⁾, had the prospect of meeting the LSSA Project goals. The iodide processes were more expensive by at least a factor of two.

In the light of the Phase I work, the zinc reduction of silicon tetrachloride in fluidized particles was recommended for further development. Accordingly, JPL-ERDA has authorized Phase II of a projected five-phase program described in the following section.

Although not recorded in the Fourth Quarterly Report because of time limitations, the Phase I program was concluded with the submission to JPL of a 500+ g sample of silicon prepared on semiconductor-grade

silicon seed. With the exception of including that item for purpose of record, this report deals with the Phase II program.

PROGRAM OBJECTIVE AND APPROACH

The overall objective of the current program is the design, construction, and operation of a 25 MT/year experimental facility for the preparation of semiconductor-grade silicon by zinc reduction of silicon tetrachloride in a fluidized bed of seed particles. The program is divided into five phases:

Phase I (1976) - Process Selection

This phase has been concluded as discussed above.

Phase II (1977) - Design and Experimental Support

Phase II has as its major objective the design of the 25 MT/year facility. Provision is made for experimental work in support of the design program where the data required are not available, and for iterative product cost estimates at the 25 MT/year and 1000 MT/year levels as the design progresses. Also provided for in Phase II is the preparation (in the present or modified "miniplant") of demonstration quantities of the product for quality evaluation.

Phase III (1978) - Construction

Contingent upon the successful conclusion of Phase II, the 25 MT/year experimental facility would be constructed at Battelle's Columbus Laboratories.

Phase IV (1979) - Shakedown Operation

Phase IV would involve shakedown, debugging, and confirmation of operability of the facility.

Phase V (1980) - Experimental Operation

In Phase V, the experimental facility would be operated on a continuous basis (1) to provide semiconductor-grade silicon for the LSSA Project and (2) to obtain engineering and cost data for subsequent construction of larger production facilities elsewhere than at Battelle.

Work Plan for Phase II

Figure 1 presents the current work plan for Phase II. Although the details of the program and the accompanying indication of progress through March 31, 1977, will be better understood by the uninitiated after reading this report, the plan is presented here in this form, since the plans for the major lines of attack are readily apparent.

It will be noted that the program is divided into four tasks:

- (1) Experimental Support
- (2) Design
- (3) Economic Analysis
- (4) Representative Sample Preparation.

Although the economics of the process and the requirements for high purity in representative samples of the product (Tasks 3 and 4) are of constant concern, work during the report period was limited to design of the 25 MT/year facility and supporting experimental work (Tasks 2 and 1, respectively). Accordingly, this report is organized under those major headings. For clarity of presentation, the task order is reversed from that in Figure 1 which had been established in identifying the tasks for contractual purposes.

DESIGN OF THE 25 MT/YEAR FACILITY

In this section of the report, the background for the design of the 25 MT/year facility is presented briefly for the benefit of the

FIGURE 1. PROPOSED WORK PLAN FOR PHASE II (FY 77)

△ Milestones - Initiation and Completion Events

▲ Milestones - Date to be decided by JPL

▲ Completed milestones

— Major effort

--- Continuing effort as needed

3/31/77

uninitiated reader, followed by a description of the work accomplished in this area during the report period.

The basic chemical reaction for the process

was used by the Du Pont Company in the early days of the semiconductor industry as a batch process to produce semiconductor silicon in dendritic form in an open tube reactor^(2,3). They also investigated experimentally the use of a fluidized bed reactor⁽⁴⁾ with limited success. However, despite the potential advantages of the fluidized bed in continuity of operation and in yielding the product in dense granular form (Figure 2), it was never brought to commercial fruition. Indeed, Du Pont abandoned the production of silicon in view of a soft market at the time and for other reasons which, however, do not prejudice the eventual commercial success of the process.

It appears that only by deposition on seed particles in a fluidized bed can a zinc reduction process be used to meet the LSSA Project goals. However, certain limitations exist in the range of operation of the process which should be understood to appreciate the approach to process design. In the first place, the reaction [Equation (1)] is exothermic; that is, its thermodynamic efficiency decreases with increasing temperature. For example, with a stoichiometric feed, the calculated equilibrium efficiency⁽⁵⁾ is 81 percent at 1100 K (827 C), 72 percent at 1200 K (927 C), and 62 percent at 1300 K (1027 C). Thus, one would like to operate at the lowest possible temperature consistent with limitations of kinetics, about which less is known. However, limitations on the volatility of zinc and zinc chloride set definable lower limits. For example, at 1000 K (727 C), the ZnCl_2 dew point is reached for the equilibrium mixture (at 86 percent conversion), below which the condensation of liquid ZnCl_2 in the bed would cause loss of fluidization due to inter-particle agglomeration. Probably of greater concern is the dew point of zinc, which is 1181 K (908 C) for undiluted zinc vapor at 1 atm. Although some supercooling is necessary for condensation on

3484VD

13X

a. Macrograph of particles

3505VD

513X

b. Cross Section of Particles

FIGURE 2. SILICON PARTICLES FROM CURRENT PROGRAM
HAVING A COATING/SEED RATIO OF ~ 1 (RUN NO. 64)

surfaces, and greater supercooling for condensation of gas-borne droplets, problems with condensation can be experienced in the lower section of the fluidized bed (where the entering zinc stream is undiluted) at some ill-defined temperature below the zinc dew point. These problems take two forms:

- (1) Loss of fluidization due to bed agglomeration
- (2) Nucleation and growth of loose silicon crystallites on the zinc condensate in preference to deposition on the silicon seed particles. (Because two atoms of zinc are needed for each one of silicon, the zinc concentration enters kinetic expressions as a squared term, thus promoting the reaction in the region of highest zinc concentration.)

It is not clear as yet, to what extent the gas phase nucleation of silicon can occur by Equation (1) without the prior formation of gas-phase zinc condensate; however, the latter must definitely be avoided for highest efficiency of deposition on the seed particles. Accordingly, a reference fluidized-bed temperature of 1200 K (927 C) has been used in the current work.

Although continuous operation of the fluidized bed at high efficiency (to minimize the recycle of uncoated material) is of primary importance in meeting the program goals, all of the other aspects of the process must be considered in the design of the 25 MT/year facility. Figure 3 is a simplified block diagram of the process showing the major units and the flow of materials.

In a commercial plant, e.g., at a level of 1000 MT/year, the silicon tetrachloride would probably be prepared by the chlorination of SiO_2 + carbon mixtures. However, incorporation of that step in the 25 MT/year experimental facility is not justified. Accordingly, the feed for the 25 MT/year facility will be SiCl_4 purchased in bulk and purified by distillation. The SiCl_4 will meet the zinc reductant in the fluidized-bed reactor, the granular silicon product will be withdrawn semicontinuously, and the unreacted zinc and SiCl_4 recycled.

FIGURE 3. SIMPLIFIED PROCESS FLOW SHEET FOR ZINC REDUCTION OF SILICON TETRACHLORIDE

The by-product ZnCl_2 will be fed to an electrolysis cell* for the recovery and recycle of zinc. Although in a larger installation the by-product chlorine would be recycled to form SiCl_4 , current plans are to dispose of it in the 25 MT/year facility as sodium hypochlorite, a marketable commodity.

Methodology of Design

The approach to the design of the 25 MT/year experimental facility involves the following activities:

- (1) Drafting of a detailed flow sheet covering all aspects of the process
- (2) Calculating mass balances and energy balances throughout the system
- (3) Establishing conceptual design of individual units
- (4) Assigning materials of construction for the individual units and associated piping
- (5) Sizing of individual units based on volumetric capacity and/or mass and heat transfer requirements
- (6) Establishing operating parameters for individual units
- (7) Determining the requirements for instrumentation including safety interlocks
- (8) Analyzing overall safety requirements
- (9) Preparing engineering drawings of individual items of equipment.

It is planned that the fluidized-bed reactor, zinc/zinc chloride condenser, and the electrolysis cell be designed by Battelle personnel, but that the design of the more conventional items of equipment be farmed out to engineering firms. Outside assistance will be

* Electrolytic recovery of zinc from ZnCl_2 was carried out on a large scale in England with cells operating over 1 year. (6)

sought from those who have had appropriate experience in silicon tetrachloride distillation, in the handling of zinc liquid and zinc vapor, and in the disposal of chlorine and chloride wastes. Where the data are not available or cannot reasonably be estimated, experimental work or equipment modelling will be provided as needed.

To coordinate this activity will require that task assignments and schedules be drawn up to culminate in having the final design available by November 15, 1977, according to the overall program plan. In this connection, full advantage will be taken of the experience accumulated by Battelle's engineering group recently in coordinating the design and construction of three large pilot plants.

Progress Made During This Report Period

Work in the area of design during the current report period included:

- (1) Drafting of a process flow sheet
- (2) Determining mass/energy balances for all parts of the system except for Cl_2 and SiCl_4 waste disposal where additional experimental data are needed
- (3) Establishing conceptual design of major units
- (4) Preliminary equipment sizing for space allocation
- (5) Contacts with materials suppliers
- (6) Contacts with sources of technology in SiCl_4 distillation, waste disposal, and zinc handling,
- (7) Developing working arrangements with Battelle's engineering group.

Progress on these items will be discussed individually.

Process Flow Sheet

Although the block diagram of Figure 3 shows the major items of process equipment, it does not include some of the complexities

introduced by waste handling, storage, and the incomplete separation of process intermediates. Hence, the more detailed flow sheet shown in Figure 4 has been prepared. In this figure and in subsequent identifications, each piece of equipment has been assigned a letter-number designation according to its function and sequence. Units having an (A) designation are part of the silicon deposition system; (B), the zinc recycle system; (C), the SiCl_4 purification system; (D), the SiCl_4 waste disposal system; (E), the chlorine handling system; and (F) (together with E3), the system involved in periodic chlorination of the silicon deposited on the wall of the reactor. That system is denoted by dashed lines. The materials flowing through the process and their phase are noted adjacent to the line carrying them.

In the following paragraphs, a brief word description will be given of the function of the various units.

It is expected that the SiCl_4 fed to the 25 MT/year facility will be purchased and transported to the facility in skid-mounted tanks (C1) having about 2 weeks' capacity. From these the SiCl_4 goes to a reserve tank (C2) which receives recycled SiCl_4 and accommodates imbalances in the flow rates. The purification system (C3), to be designed outside of Battelle, is visualized to consist of two distillation columns with one intermediate holding tank. Impurities contained in the tops and bottoms from the columns will be discarded. Purified SiCl_4 will be held in a storage tank (A1) having 5 days' capacity and fed to an equilibrium boiler, provided with a liquid bleed designed to minimize the build-up of impurities. The fluidized-bed reactor (A3) is fed with the purified SiCl_4 , silicon seed particles, an inert bleed gas, and zinc vapor from a zinc flash vaporizer (A7). The product of deposition on the seed particles is allowed to cool (A8) and is periodically withdrawn (A9) from the reactor. Part of the reaction product builds up on the wall of the reactor and must be periodically removed by chlorination as noted above and described in greater detail later. The by-products of the deposition reaction go first to a

FIGURE 4. PROCESS FLOW DIAGRAM FOR 25 MT/YEAR SILICON FACILITY (4/1/77)

zinc/zinc chloride condenser (A10) where most of the zinc and zinc chloride are removed at 500 C and 327 C, respectively. However, zinc chloride condensation is not total, so a pair of condensers (A11 and A12) strip the remainder, at a condensing temperature below the melting point. Alternately, one of these units is being operated as a condenser while the other is being heated to melt down the contents for return to the recycle stream. It will be noted that provision is made for the carryover of a small amount of silicon "dust" (gas-phase-nucleated silicon, or silicon nucleated on condensed zinc) which escapes the zinc/zinc chloride condenser(A10) but which, it is anticipated, can be collected in (A11) or (12) and returned to be ultimately chlorinated by the by-product chlorine in the electrolytic recovery of zinc from zinc chloride. The off gas from the zinc chloride strippers (A11 and A12) flows through a condenser (A13) where most of the SiCl_4 is removed and routed to the reserve tank (C2). That which is carried with the inert gas goes to waste disposal.

Zinc and zinc chloride (together with some silicon dust) go from the condenser (A10) to an electrolysis feed tank (B1) having a 2-day capacity, where gravity separation of the zinc and zinc chloride can occur (the degree to which this occurs must be determined), with the zinc going to molten storage (A5) and the zinc chloride and silicon dust going to the electrolysis cell (B2) where the zinc is recovered and returned to zinc storage, and the silicon dust is chlorinated. It is contemplated that some of the zinc impurities will be removed at this point, but the details are not yet worked out. Owing to the fact that the electrolysis cell operates at 500 C, a small quantity of zinc chloride is carried in the chlorine stream. A pair of solids condensers (B3 and B4), similar to (A11) and (A12), are used to recover this zinc chloride by alternate condensation and meltdown. The chlorine gas from the electrolysis goes to waste disposal as discussed later.

Although it is anticipated that a large fraction of the zinc reductant will be recycled (as indeed it must for economy) provision is made for feeding make-up zinc through the hopper (A4) to the molten storage tank (A5). It is contemplated that the zinc flash vaporizer (A7) will be fed by a positive displacement pump (A6); however, this decision

is open pending further information on current technology for handling liquid zinc.

As noted above, the silicon deposited on the wall of the reactor (F1 in the chlorination mode) is chlorinated to SiCl_4 and discarded. This might occur once every 6 days. In Figure 3, the chlorination product, containing a trace perhaps of ZnCl_2 , is shown being fed through a ZnCl_2 stripper (F2) and the SiCl_4 recycle condenser (F3 in the chlorination mode). Whether or not this condenser is used for the double function or another condenser provided is still open.

All of the SiCl_4 wastes from the facility are routed to a holding tank (D1) having a 1-week capacity, where they are treated with hydrated lime to form a slurry mainly of SiO_2 , CaCl_2 , and water; however, some $\text{Ca}(\text{OCl})_2$ will be contained because of the residual unreacted chlorine from the wall deposit chlorination step.

The major by-product disposal consideration is the chlorine from the SiCl_4 fed to the process, and issuing from the electrolytic cell. This amounts to ~5 Kg of Cl_2 for every 1 Kg of silicon produced. At present, it is contemplated that it be disposed of by forming sodium hypochlorite solution, a marketable commodity. However, the options of using it to chlorinate metallurgical-grade silicon to supply SiCl_4 or collecting it as Cl_2 for resale are not ruled out. In a 1000 MT/year facility, the Cl_2 would undoubtedly be used to prepare the required SiCl_4 but in the 25 MT/year plant it does not appear to be the most economical approach and it is not required to demonstrate the practicality of the process.

For use in making hypochlorite, the residual SiCl_4 must be removed (to avoid turbidity in the product). Hence, a SiCl_4 removal unit (E4) is provided, whose details are not yet established; however, it is anticipated that the SiCl_4 will be removed by hydrolysis with water. Two factors of unknown impact operate at that point. In the first place, it is necessary to keep the hydrolysis product fluid, so some minimum quantity of water (well in excess of stoichiometric) is required. Further, the effect that this effluent, containing some dissolved chlorine, has on the operation of the SiCl_4 waste disposal (at D3) to which it is transferred (assuming that the water requirements of that system are supplied in full or in part by the hydrolysis slurry from E4) has yet to be determined.

The SiCl_4 -free chlorine will be reacted with 18 percent caustic solution to form a sodium hypochlorite solution containing 15 percent chlorine as $\text{NaOCl} + \text{NaCl}$.

Two-week storage capacities have been assigned to the input and output tanks of both the SiCl_4 and Cl_2 disposal systems.

Although the flow diagram of Figure 3 should represent the 25 MT/year facility with a reasonable degree of finality, it is obviously subject to revision as the design work proceeds.

Materials/Energy Balance

Table 1 gives the mass/energy flow sheet for the 25 MT/year facility. Data for equilibrium calculations and enthalpy balances were taken from the JANAF Thermochemical tables, and publications of L. P. Hunt, the data on ZnCl_2 being revised as indicated earlier⁽⁵⁾. The bases for some of the choices made in the mass flows are described later.

Included in Table 1 are the identify of the individual units, and the materials flowing into and out of each in terms of molar quantities, weight, temperature, and volume. In addition, the viscosities of liquids and gases are noted for purposes of calculating flow resistance. Viscosities of gas mixtures were calculated as

$$\mu_{\text{mix}} = \frac{\sum_i \mu_i M_i^{1/2} X_i}{\sum_i M_i^{1/2} X_i}$$

where μ_i = viscosity, M_i = molecular weight, and X_i = mole fraction of each of 1 ... i species.

Viscosity data were taken from sources noted in previous reports.

At the far right of the table are included values for the process energy change in each unit (+ = endothermic, - = exothermic).

It will be noted that the energy balance (and indeed mass balance) has been carried only through parts of the facility that do not involve waste disposal. The omission in the latter section stems from the fact that, as noted above, the amount of water required for SiCl_4 hydrolysis is not known, nor is the amount of Cl_2 dissolved in

TABLE 1. MATERIAL AND ENERGY FLOW SHEET (Revised 4/1/77)

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 ⁻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 4442.4 Kg 2961.6 ℓ	SiCl ₄ (ℓ)	25	217.86	37.02	24.68	0.45	SiCl ₄ (ℓ)	25	217.86	37.02	24.68	0.45	0.0	0.0		
A2 SiCl ₄ Boiler (1.7 atm) Capacity 8 hrs 296.16 Kg 197.44 ℓ	SiCl ₄ (ℓ)	25	217.86	37.02	24.68	0.45	SiCl ₄ (ℓ) SiCl ₄ (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 ₄ (g) → Inert Zr (g) → Si seed	73.6 25 927 25	213.59 12.82 427.17 6.41	36.30 27.93 34,195 0.18	3577 313.63 34,195 0.075	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	134.57 3.84 2.56 12.82 79.03 158.05 269.12	5.78 0.11 0.07 15.43 10.33 36.68	1.58 0.04 0.03 51,104	0.043	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 1340.54 Kg 204.32 ℓ	Zn (ℓ) Zn (ℓ) Zn (s)	500 500 25	255.56 158.05 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 ₂ Condenser	Si dust Zr (g) ZrCl ₂ (g) SiCl ₄ (g) Inert (g) ZnCl ₂ (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 0.37*	0.03 15,104	0.046 -1	Si dust Zn (ℓ) ZnCl ₂ (ℓ) ZnCl ₂ (g) SiCl ₄ (g) Inert (g)	500 500 500 327 327 327	2.56 158.05 269.12* 2.69 79.03 12.86	0.07 10.33 36.68* 0.37 13.43	0.03 1.59 15.09* 4659	3(.98?) -1	-15,922*	-18.50*		
A11 ZnCl ₂ stripper Cool cycle	SiCl ₄ (g) ZnCl ₂ (g) Inert (g) Si (s)	327 327 327 327	79.03 2.69 12.82 2.56	13.43 0.37 0.37 0.07	4,655	0.021	ZnCl ₂ (s) SiCl ₄ (g) Inert (g) Si (s)	77 77 77 77	2.69 79.03 12.82 2.56	0.37 13.43 1639 0.07	2639	0.013	-513.5	-0.60		
A12 ZnCl ₂ stripper Melt cycle	ZnCl ₂ (s) Si (s)	77 77	2.69* 2.56*	0.37* 0.07*	0.03*		ZnCl ₂ (ℓ) Si (s)	327 327	2.69* 2.56*	0.37* 0.07*	0.15* 0.03*	-1	21.79*	0.025*		
A13 SiCl ₄ recycle condenser	SiCl ₄ (g) Inert	77 77	79.03 12.82	13.43 0.37	2,619	0.013	SiCl ₄ (ℓ) SiCl ₄ (g) Inert (g)	0 0 0	77.61 1.42 12.82	13.19 0.24 320	8.62 0.018	0.54	-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 ₂ (ℓ) 1724.88 Kg 717.12 ℓ	Si dust Zn(ℓ) ZnCl ₂ (ℓ)	500 500 500	2.56 158.05 266.43	0.07 10.33 36.31	0.08 1.59 14.94	0.08 3(0.98?) -1	Si dust Zn(ℓ) ZnCl ₂ (ℓ)	500 500 500	2.56 158.05 266.43	0.07 10.33 36.32	0.03 1.59 14.94	0.03 3(0.98?) -1	0.0	0.0		
B2 Electrolysis Cell	Si dust ZnCl ₂ (ℓ) ZnCl ₂ (ℓ)	500 500 327	2.56 269.12 3.05	0.07 36.68 0.42	0.03 15.09 0.7	0.03 -1 -1	Zn(ℓ) (recyc) Zn(ℓ) (loss) SiCl ₄ (g) Cl ₂ (g) ZnCl ₂ (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 0.44 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)

		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	264.00	13.72	17,109	0.032		Cl ₂ (g)	25	264.00	18.72	6,521	0.014	-1,240	-1.44
	ZnCl ₂ (g)	500	3.05	0.42				SiCl ₂ (g)	25	2.56	0.44				
	SiCl ₄ (g)	500	2.56	0.44				ZnCl ₂ (s)	25	3.05	0.42				
B4 ZnCl ₂ Stripper Heat cycle	ZnCl ₂ (s)	25	3.05*	0.42*				ZnCl ₂ (l)	327	3.05*	0.42*	0.17*	-1	23.3*	0.027*
C1 SiCl ₄ Storage Capacity = 2 weeks 8823.4 Kg 5383.4 l	SiCl ₄ (l)	25	154.56	26.26	17.51	0.45		SiCl ₄ (l)	25	154.56	26.26	17.51	0.45	0	0
C2 SiCl ₄ Reserve Capacity = 2 days 1279.2 l 1928.64 Kg	SiCl ₄ (l)	25	154.56	26.26	17.51	0.45									
	SiCl ₄ (l)	0	77.61	13.19	8.62	0.51									
	SiCl ₄ (l)	73.6	4.27	0.73	0.52	0.3		SiCl ₄ (l)	25	236.44	40.18	26.8	0.45	55.1	0.06
C3 SiCl ₄ Purification	SiCl ₄ (l)	25	236.44	40.18	26.8	0.45		SiCl ₄ (l)	25	217.36	37.02	24.68	0.45	to be determined	
								SiCl ₄ (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 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 683.2 Kg 455.5 l	SiCl ₄ (l)	25	18.58					SiCl ₄ (l)	25	17.22					
	SiCl ₄ (l)	0	3.63					SiCl ₄ (g)	25	6.62					
	SiCl ₄ (g)	0	1.63					Cl ₂ (g)	25	1.92					
	Cl ₂ (g)	0	1.92					Inert(g)	25	12.82					
	Inert(g)	0	12.82												
D2 Ca(OH) ₂ Reserve	Ca(OH) ₂	25	54.72+x					Ca(OH) ₂	25	54.72+x					
D3** SiCl ₄ Waste Processing Soln.	SiCl ₄ (l)	25	17.22					Slurry	SiO ₂	25	26.4				
	SiCl ₄ (g)	25	6.62						CaCl ₂	25	53.76 + 0.5x				
	Inert(g)	25	12.82						Ca(OC1) ₂	25	0.96 + 0.5x				
	Cl ₂ (g)	25	1.92						H ₂ O	25	54.72+x+y				
	HCl	25	10.24						Inert (g)	25	12.82				
	Cl ₂	25	x												
	H ₂ SiO ₃	25	2.56												
	H ₂ O	25	y-7.68												
	Ca(OH) ₂	25	54.72+x												
D4 Waste Storage Tank Capacity = 2 weeks	SiO ₂	25	26.4					SiO ₂	25	26.4					
	CaCl ₂	25	53.76 + 0.5x					CaCl ₂	25	53.76 + 0.5x					
	Ca(OC1) ₂	25	0.96 + 0.5x					Ca(OC1) ₂	25	0.96 + 0.5x					
	H ₂ O	25	54.72+x+y					H ₂ O	25	54.72+x+y					
E-Feed from Electrolysis Cell, B2:	SiCl ₄ (g)	25	2.56	0.44	6,521	0.014									
	Cl ₂ (g)	25	264.00	18.71											
E3 Cl ₂ Supply Capacity = 2 weeks 228.5 Kg 71.2 l	Cl ₂ (l)	25	9.6*	0.68*	0.212*			Cl ₂ (g)	25	9.6*	0.68*	234.60*			

* 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; D3 must also be adjusted to production versus chlorination real time values.

TABLE 1. (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
E4 SiCl ₄ Removal	SiCl ₄ (g)	25	2.56				H ₂ O	25	y-7.68					
	Cl ₂ (g)	25	264.00			Soln.	H ₂ SiO ₃	25	2.56					
	H ₂ O(l)	25	y				HCl	25	10.22					
	(y depends on fluidity of hydrolysis product, x on solubility of Cl ₂ therein; needs experimental determination)						Cl ₂	25	x					
							Cl ₂ (g)	25	264-x					
E5a Caustic Mix Tank	50% Na ₂ O	25	264-x			18%	Na ₂ O	25	264-x					
Capacity = 1 day	Soln. H ₂ O	25	909-3.44x			Soln.	H ₂ O	25	4145-15.7x					
1790 l H ₂ O	H ₂ O	25	3236-12.26x											
at x = 0														
E5b 50% Caustic Storage	50% Na ₂ O	25	264-x				Na ₂ O	25	264-x					
	Soln. H ₂ O	25	909-3.44x				H ₂ O	25	909-3.44x					
E5 Caustic Reactor	18% Cl ₂ (g)	25	264-x			15% Cl	NaCl	25	264-x					
	Soln. Na ₂ O	25	264-x			Soln.	NaOCl	25	264-x					
	H ₂ O	25	4145-15.7x				H ₂ O	25	4145-15.7x					
E6 Hypochlorite Storage	Capacity = 2 weeks, water content 25059 l at x = 0													
F1** Reactor Wall Deposit	Si(s)	927	3.84				SiCl ₄ (g)		3.84					
	Cl ₂ (g)	25	9.60				Cl ₂ (g)	***	1.92					
	Zn	927	z	(neglected in Cl ₂ and Zn balance)			ZnCl ₂		z	(neglected in Cl ₂ +Zn balance)				
F2** ZnCl ₂ Stripper, Offgas Cooler	SiCl ₄ (g)		3.84				SiCl ₄ (g)	77	3.84					
	Cl ₂ (g)	***	1.92				Cl ₂ (g)	77	1.92					
	ZnCl ₂ (g)		z	(neglected in Cl ₂ +Zn balance)			ZnCl ₂ (s)	77	z	(neglected in Cl ₂ +Zn balance)				
F3** SiCl ₄ Condenser	SiCl ₄ (g)	77	3.84				SiCl ₄ (l)	0	3.63					
	Cl ₂ (g)	77	1.92				SiCl ₄ (g)	0	0.21					
							Cl ₂ (g)	0	1.92					
Overall Balance	SiCl ₄	25	154.56				Si	25	134.57					
(verified for each element)	Inert	25	12.82				Zn	25	13.46					
	Si s&ed	25	6.41				Inert	25	12.82					
	Zn make	25	13.46				15% Cl ₂ Soln.	NaCl	25	264-x				
	H ₂ O	25	y					NaOCl	25	264-x				
	18% Na ₂ O	25	264-x					H ₂ O	25	4145-15.7x				
Caustic	H ₂ O	25	4145-15.7x											
	Ca(OH) ₂	25	54.72+x				Slurry	SiO ₂	25	26.4				
	Cl ₂	25	9.6					CaCl ₂	25	53.76 + 0.5X				
								Ca(OCl) ₂	25	0.96 + 0.5X				
								H ₂ O	25	54.72+x+y				

** See footnote, page 2.

*** To be determined.

that water. These unknown quantities have been carried through the materials balance algebraically in moles, however, so as soon as they are determined experimentally, the mass balance and energy balance can be concluded easily.

It should be noted that the closure (overall versus sum of steps) on the materials balance is ± 0.00 moles per hour over the entire system, and the energy balance is 21741 versus 21745 Kcal per hour over that part of the system not involved in waste disposal.

Although Table 1 was developed in scientific units for convenience in using the data sources, a separate version in engineering units was derived for design purposes, and is available to anyone who may be interested.

It should be noted that Table 1 includes two units not shown in Figure 3, i.e., Units E5a and E5b provided for storing 50 percent caustic and diluting it to 18 percent. Their functions in feeding E5 are obvious.

Basis for Materials Balance. The hourly flow rates for the 25 MT/year facility are based on a production of 3.60 Kg/hour of silicon, ~7000 hours/year equivalent to ~80 percent on stream. Efficiencies of reaction or of condensation are based on what has been accomplished experimentally, or might reasonably be expected to be done.

A Zn/SiCl₄ ratio of 2/1 (i.e., stoichiometric) is used as that is very close to the point of maximum yield (2.01/1) per unit of gas flow through the fluidized bed unit. There is no economic advantage of operating off stoichiometry⁽⁷⁾, and a suspected technological advantage in operating on the low-zinc side has disappeared with improvements in reactor design. A bed deposition efficiency (fraction of silicon fed as SiCl₄ which is deposited as a dense coating on seed particles) of 60 percent was adopted. Efficiencies of 62 percent have been attained experimentally, and it should be possible to do better in a deeper bed. However, it was thought better at this stage in the design to use the conservative 60 percent figure rather than the higher experimental value, or the 72 percent 1200 K equilibrium figure used earlier. It was assumed that 1.8 percent of the silicon fed as

SiCl_4 would deposit on the wall (which has been validated experimentally), and 1.2 percent would be carried over as silicon dust; thus a total SiCl_4 conversion efficiency of 63.0 percent is assumed. A 2 percent inert gas introduction for "breathing" purposes was assumed; however, it has not yet been decided whether nitrogen can be used or whether argon (with recovery) must be used. Thus, the weight of inert is not tabulated. Viscosities are about equal.

The product was assumed to be 95 percent deposited material and 5 percent seed.

The pure SiCl_4 is assumed to come from a 92 percent heart cut in the distillation with ~4 percent tops and ~4 percent bottoms routed to waste.

The efficiency of chlorinating the silicon wall deposit was assumed to be 80 percent.

For convenience, condensers were assumed to operate at equilibrium efficiency at the stated temperatures and the electrolytic cell was assumed to operate at 100 percent current efficiency versus the 89.3 percent observed over 1 year's operation by Threlfall⁽⁶⁾.

Pressures are assumed for convenience to be 1 atm unless otherwise noted. Establishment of pressure differentials in the system will develop with the design.

Comments on Materials/Energy Balance. It should be noted that the mass and energy flows through the units involved in chlorination of the silicon wall deposit (F1 through F3, and E3) are recorded as though they were functioning continuously. Actually they will be operated for only a fraction of the silicon production time, for example, 8 hours out of each 6 days, or $8/(6 \times 24 - 8) = 6$ percent of the production time. The flow rates tabulated must be divided by that figure to obtain the real-time values during chlorination. Note that the waste processing systems undergo related perturbations.

It is noted that the SiCl_4 vaporizer and the zinc vaporizer, and the electrolytic cell are the major endothermic units. In the case of the electrolysis cell, the total (theoretical) enthalpy change is

29.82 kw. However, of this, 22.57 is required as low-voltage direct current to supply the Gibbs free energy change,

$$\Delta G/\text{mol} = -nFE$$

where n = number of charges per mole (two for Zn^{++})

E = cell voltage

F = 96,500 coulombs/equivalent.

Theoretically, the 7.25 kw difference could be supplied other than electrically; however, because of cell resistance, a large part if not all will be supplied electrically.

The major exothermic unit is the zinc/zinc chloride condenser which will probably require a separate heat exchange system, not shown.

The fluidized bed unit is practically adiabatic as pictured. In fact, the break even point is at about 62 percent conversion efficiency. Above this figure, the unit would be exothermic and below, endothermic. However, one can be misled if it is not realized that the exothermic enthalpy change for Equation (1), -32.58 Kcal/mol at 1200 K, is about compensated by the requirement for heating the $\text{SiCl}_4(\text{g})$ and inert gas to reaction temperature (the zinc is already at temperature). In reality, the exothermic heat of reaction cannot be used directly to heat the $\text{SiCl}_4(\text{g})$, as mixing the "cold" 346.8 K ($\sim 74^\circ \text{C}$) gas with the zinc vapor at 1200 K (927°C) would result in zinc condensation and the accompanying problems referred to above. Thus, in its simplest form, the fluidized-bed reactor would consist of separate endothermic (preheater) and exothermic (reaction) sections. The feasibility of heat exchange has not been assessed.

In all of the energy calculations referred to above, none has concerned the energy requirements relating to items such as loss through insulation, cooling of electrodes, and the heat involved in periodically heating and cooling solids condensers themselves (A10, A11, B3, and B4), i.e., independent of their contents.

Conceptual Design and Preliminary Sizing of Equipment

In order to permit long-range planning for space utilization at Battelle's Columbus Laboratories, conceptual designs were established and estimates made of the sizes of the equipment listed in Table 1 to determine whether the 25 MT/year facility would fit in a potentially available location which has the advantage of proximity to currently available facilities.

Equipment items whose size depends on volumetric capacity were sized on that basis, with consideration being given to the approximate thickness of insulation required. Units whose size is controlled by heat-exchange requirements were sized in proportion to the heat-exchange areas calculated to be required in the 1000 MT/year facility estimates⁽¹⁾. The size of the fluidized-bed reactor was estimated by extrapolation/interpolation from experience with units having related functions. The dimensions of the electrolytic cell were taken from the design of Threlfall⁽⁶⁾. Estimates of the size of electrical equipment associated with the electrolytic cell and fluidized-bed reactor are educated guesses based on related experience.

Table 2 gives the results of this exercise.

It was determined that the units in Table 2 would fit comfortably into the potentially available 50- x 60-foot area with 20 feet of head room below crane traverse. However, as the first-cut layout is subject to changes in the relative positions of several units, it will not be presented at this time.

Contacts With Materials Suppliers

Contacts were made with a number of suppliers of SiCl_4 . Although subject to change, it appears that purchasing "technical-grade" SiCl_4 from the Union Carbide Corporation and transporting it in skid-mounted 1400-gallon tanks from Sistersville, West Virginia, to Columbus, Ohio, is the most practical arrangement.

TABLE 2. PREDESIGN ESTIMATES OF EQUIPMENT SIZE

Unit	Name	Description	Size dia x ht (l), ft or l x w x ht, ft
A1	Pure SiCl_4 Storage	tank	5 x 6
A2	SiCl_4 Boiler	shell and tube	2 x 4
A3	Fluidized Bed Reactor	vertical tubular	2.5 x 14
A3a	Power Supply	box	6 x 6 x 7
A4	Zinc Hopper	hopper	(located above A5)
A5	Zinc Molten Storage	tank	3.5 x 5.5
A6	Zinc Pump	cylinder	2 x 4
A7	Zinc Flash Vaporizer	packed bed	2 x 7
A8, A9	Silicon Cooler, Storage	cylinders	(part of A3)
A10	Zinc/ ZnCl_2 Condenser	shell and tube	3 x 9
A11, A12	ZnCl_2 Stripper	cylinders	2 x 7
A13	SiCl_4 Recycle Condenser	shell and tube	1 x 4
B1	Electrolysis Feed Tank	tank	6 x 4.5
B2	Electrolysis Cell	per Threlfall ⁽⁶⁾	11 x 9 x 17 (including 6-ft electrode clearance)
B2a	Electrical Equipment	box	6 x 6 x 6
B3, B4	ZnCl_2 Stripper	cylinders	2 x 7
C1	SiCl_4 Bulk Storage	tank	5 x (10.6)
C2	SiCl_4 Reserve	tank	4 x 4
C3	SiCl_4 Purification	a. two columns b. tank	1.5 x 12 each 3.5 x 3.5
D1	SiCl_4 Waste Holding	tank	3 x 3
D2	Ca(OH)_2 Supply	hopper	1 x 2
D3	SiCl_4 Waste Processing	packed tower	1 x 8
E3	Cl_2 Supply	tank	2 x 5
E4	SiCl_4 Removal	packed tower	0.5 x 6
E5	Caustic Reactor	packed tower	0.5 x 5
E5a	Caustic Mix	tank	4 x 5
E5b	50% Caustic Storage	tank	5 x (15)
E6	Hypochlorite Storage	tank	6 x (18)
D4	Waste Storage	tank	8 x 8

Contact was made with several zinc suppliers, from which it was learned that Gulf-Western Industries (formerly New Jersey Zinc) licenses most of the technology in the handling of liquid zinc and zinc vapor, the latter in connection with distillation. Accordingly, tentative arrangements have been made to visit the facility at Palmerton, Pennsylvania, to discuss the technology and the availability and characterization of zinc for the 25 MT/year facility.

Contact has been made with the Diamond Shamrock Corporation on the subject of chlorine disposal and it is hoped that an arrangement can be made with a commercial outlet for the acceptance of sodium hypochlorite, 15 percent, prepared by reaction of the by-product chlorine with 18 percent caustic.

The requirement of about 10 pounds/hour of Ca(OH)_2 for disposal of waste SiCl_4 (plus some chlorine) is not great and can probably be handled through local channels. However, contact has been made with National Lime and Stone Company at Carey, Ohio, to investigate the arrangements for shipping larger quantities if necessary.

Contacts With Sources of Technology

Although the design of several items of equipment of the 25 MT/year facility such as the fluidized bed and zinc/zinc chloride condenser will require the background of those currently involved in the project, design experience for many other items can best be obtained elsewhere. Accordingly, arrangements are being made with Dr. Carl Yaws of Lamar University to act as a consultant on the design of the SiCl_4 purification system. Arrangements for the transfer of zinc-handling technology are mentioned above. It is believed that the Cl_2 disposal (hypochlorite generation) system may be available as a packaged unit.

In the areas requiring less specialized experience, it is planned that the services of Columbus-based engineering firms will be used. Theirs would be the task of producing the final engineering drawings, incorporating their own input, and those from the specialized areas noted above.

In implementing this arrangement, discussions are underway with Battelle's engineering group, who have recently concluded the design and construction of three large pilot plants under similar arrangements, so as to take advantage of their experience.

Plans for the Next Report Period

The plans for the next quarter on the design of the 25 MT/year experimental facility will include:

- (1) Complete negotiations and initiate design work with engineering firms
- (2) Complete preliminary design of specialized equipment
- (3) Complete the establishment of operating parameters for each equipment item
- (4) Develop preliminary instrumentation requirements
- (5) Develop a detailed schedule for completing the plant design by November 15, 1977.

EXPERIMENTAL SUPPORT PROGRAM

The experimental program in support of the 25 MT/year facility design has two major aspects:

- (1) Continued operation of the miniplant instituted toward the end of the Phase I program
- (2) Design and performance of ad hoc experimental work outside of the miniplant as required for design information.

Work Performed During This Report Period

During this report period, experimental work in the miniplant related to improvement of fluidized-bed reactor design, improvement of by-product condensation and recovery, and increasing the reactant throughput and product yield. Auxilliary experiments were performed in developing a new zinc vaporizer and in determining the nature of and the conditions for forming silicon from the reaction of zinc with SiCl_4 independent of the presence of the fluidized bed. The importance of such competing reactions has been pointed out above; i.e., to be economically feasible, the process must maximize the fraction of silicon deposited as a dense coating on the seed particles and minimize the fraction deposited elsewhere or entrained as gas-phase-nucleated particles.

Although experiments with the electrolysis of synthetic by-product mixtures of $\text{ZnCl}_2 + \text{Zn} + \text{Si}(\text{dust})$ were carried out under the Phase I program⁽¹⁾. The electrolytic recovery of zinc from the actual miniplant by-product remains to be done. That task, envisioned to be part of Phase I, was deferred in the effort to maintain operability of the miniplant and increase the rate of deposition to permit preparation of the 500-g quality-evaluation sample delivered to JPL at the conclusion of Phase I. Accordingly, preparations for electrolysis experiments involving the miniplant by-product have been made as described in this report.

Operation of the Miniplant

In the following sections of this report, data are given from the Phase I work as well as from Phase II for purposes of comparison. Further, Run No. 51 of Phase I was concluded too late to be included in the Fourth Quarterly Report.⁽⁸⁾ As the primary purpose of Run No. 51 was to prepare material for quality evaluation, the results of that run are discussed separately, followed by discussion of the Phase II work.

Preparation of Quality Evaluation Sample. Run No. 51 was made at 927 C with a ~200-g, 149-x-297- μ seed bed of crushed and screened semiconductor-grade silicon. The run was made at a feed rate of 308.5 g/hour of silicon as SiCl_4 , with a Zn/SiCl_4 ratio of 1.64/1 (2/1 = stoichiometric), until exhaustion of the zinc supply terminated the run after 3.85 hours. Silicon was obtained on the seed particles as a dense coating at a rate of 128.4 g/hour, representing a net efficiency for this product of 41.6 percent, or 67.2 percent of that theoretically available (thermodynamically calculated conversion efficiency = 61.9 percent). In addition to the product collected on the bed, an additional ~10 percent of the silicon fed was collected downstream of the bed as a powder in various stages of aggregation.

As it was inconvenient to progressively withdraw the bed product during this run, the increased bed volume (~3.5X) exceeded the capacity of the reactor and 141 g of product was blown out of the bed at some time(s) during the run. This resulted in a higher ratio of deposited material to seed in the product than the 71 percent that would have been obtained had no blowover occurred. If all of the blowover occurred three quarters of the way through the run (assuming constant deposition rate), 72.5 percent of the product would be deposited material.

A 500+ g sample of the seed bed with its deposited silicon was forwarded to JPL for evaluation.

Spark-source mass spectrometric and emission spectrographic analyses were made of the product of Run No. 51, its seed material, and

a sample of the zinc reductant used. Although there was some indication that aluminum, iron, and some magnesium had been transferred from the zinc, it was clear that the sample(s) had been contaminated during preparation (grinding) for analysis. Further, the mass spectrometer suffered from memory problems, having been committed to the plutonium laboratory where cleaning of the source was inadequate.

As a new mass spectrometer has been installed to replace the one that had been moved to the plutonium laboratory, additional analyses of the product silicon will be made to identify sources of contamination. These will be reported later.

Progress With the Miniplant in Phase II. At the inception of Phase II, several changes were made in the miniplant to improve its operability and efficiency. These included

- (1) Substitution of a multiple inlet hemispherical bed support for the two-inlet conical reactor bottom used in Phase I (problems with the fabrication of quartz that prevented effective use of the hemispherical bed support in Phase I have been overcome)
- (2) Lengthening of the reactor by ~30 percent and the expanded section by ~70 percent to reduce bed "blowover" at high reactant throughput
- (3) Modification of the reactor outlet system to favor return of blown over material to the bed
- (4) Provision of baffles in the zinc/zinc chloride condenser to reduce by-passing of the condenser surfaces, and provision of a secondary trap for gas-borne ZnCl_2 dust.

The miniplant as presently constituted is pictured in Figure 5. Its major components are essentially those described in the Third Quarterly Progress Report⁽⁷⁾. Liquid SiCl_4 in a tank on a scale is fed through a flexible Teflon tube to a flowmeter, to a flash vaporizer, and through a preheater section below the fluidized-bed support. Liquid zinc

3481VD

FIGURE 5. MINIPLANT

- (1) Dust Trap
- (2) Secondary ZnCl_2 Condenser
- (3) Zn/ZnCl_2 Primary Condenser
- (4) Condensate Pot
- (5) Fluidized Bed/Furnace
- (6) Zinc Feeder
- (7) Induction-Heated Zinc Vaporizer
- (8) SiCl_4 Supply
- (9) SiCl_4 Flash Vaporizer
- (10) SiCl_4 Preheater

is fed to an induction-heated graphite boat where it vaporizes to enter the reactor and mix with the SiCl_4 above the fluidized-bed support. The reaction by-products pass through the zinc/zinc chloride condenser, the secondary ZnCl_2 condenser, and a glass wool-packed dust trap to a cooled condenser for collecting the unreacted SiCl_4 . A small stream of argon (3 to 5 mole percent of the reactant mixture) is provided as a breather gas to stabilize operation of the system.

Figure 6 shows the fluidized-bed reactor with the hemispherical bed support having one axial inlet and four planetary inlets ("Design A" of Figure 2 of the Third Quarterly Progress Report⁽⁷⁾). Provision has been made for feeding either the zinc or the SiCl_4 through the axial inlet, and several runs have been made in each mode. In switching the reactants from axial to planetary inlets, compensation is made for the flow differential by adjusting the size of the orifices.

The SiCl_4 and zinc feed systems and the Zn/ZnCl_2 condenser systems are essentially as depicted in the Third Quarterly Progress Report⁽⁷⁾ except for the addition of the secondary condenser and baffles noted above. Five slanted baffles, with their gas passages and liquid drain holes staggered, surround the central finger of the condenser at 6-inch intervals so as to promote a tortuous gas flow path and increase condensation efficiency.

In the Phase II work with the miniplant, the following parameters and reactor design factors were studied:

- (1) Hemispherical versus conical bed support
- (2) Axial zinc versus axial SiCl_4 introduction
- (3) Graded temperature bed
- (4) Reactant throughput
- (5) Bed particle size
- (6) Gas-phase nucleation of silicon
- (7) Zinc/ ZnCl_2 condensation efficiency.

The conditions and data for the nine runs made during Phase II (together with certain Phase I data) are given in Table 3. The results relative to the factors listed above are discussed individually below.

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3281VD

FIGURE 6. FLUIDIZED-BED REACTOR WITH HEMISPHERICAL
BED SUPPORT HAVING ONE AXIAL INLET AND
FOUR PLANETARY INLETS

TABLE 3. SUMMARY OF SELECTED MINIPLANT DATA

(Runs through No. 51 were made during Phase I with the double inlet cone-bottom reactor, Runs Nos. 52 through 68 were made during Phase II with the five-inlet hemispherical-bottom reactor. [Runs Nos. 54, 55, 58, 59, 61, 63, 65, and 67 were experiments outside of the miniplant.] Runs Nos. 43 and 44 were made with ~25 percent argon, and Nos. 45 and subsequent runs with 3 to 6 percent argon bleed gas.)

Run No.	Bed Data			Temperature, C	Time, hrs	Mole Ratio Zn/SiCl ₄	Si as S:Cl ₄ , g/hr	Axial Inlet Reactant	Bed Deposition, g/hr	Percent Bed Efficiency	Total Product ^(a) , g/hr	Percent Total ^(a) Efficiency	Percent of Product			Equilibrium Efficiency, percent	Bed + Equilibrium, percent	Total ^(a) + Equilibrium, percent	Remarks
	Initial Size, μm	Initial Weight, g	Final Weight, g										Bed	Wall	Dist				
Phase I																			
43	164 x 225	240	445	927	2.20	1.702	222.8	---	93.0	41.6	(b)	(b)	(b)	(b)	(b)	61.7	67.3	(b)	Reported in Phase I Final Report
44	149 x 250	240	425	927	1.95	1.642	234.0	---	95.0	40.6	(b)	(b)	(b)	(b)	(E)	60.1	67.5	(b)	Reported in Phase I Final Report
45	149 x 250	240	340	927	0.83	1.856	266.0	---	120.5	42.1	(b)	(b)	(b)	(b)	(E)	68.1	61.9	(b)	Reported in Phase I Final Report
47	177 x 250	240	517	927	1.47	1.967	462.5	---	188.2	40.7	(b)	(b)	(b)	(b)	(b)	71.2	57.2	(b)	Reported in Phase I Final Report
51	250 x 297	203	697	927	3.85	1.640	308.5	---	128.4	41.6	(b)	(b)	(b)	(b)	(E)	61.9	67.2	(b)	Data not in Phase I reports
Phase II																			
52	149 x 297	244	544	927	2.05	1.66E	299.0	SiCl ₄	148.7	49.73	178.0	59.5	83.5	9.6	6.5	62.3	79.1	94.7	Experimental problems with first hemispherical reactor run
53	149 x 297	240	803	927	3.00	1.747	363.2	SiCl ₄	187.7	51.0	219.0	59.5	85.7	5.3	9.0	65.2	78.1	91.2	Successful run - hemispherical bed support
56	149 x 297	500	711	Graded ^(d)	1.07	1.922	341.7	Zn	196.8	57.6	243.8	71.4 ^(c)	(80.7) ^(c)	(13.5) ^(c)	(5.8) ^(c)	74.2	77.6	96.2	Experimental problems with first graded temperature run
57	149 x 297	500	787	927	1.50	1.783	367.7	Zn	191.3	52.0	219.5	59.7	87.2	3.0	9.8	66.1	78.6	90.3	Base run for comparison with graded temperature
59	149 x 297	500	812	Graded ^(d)	1.50	1.773	364.2	Zn	268.2	57.2	221.0	60.7	94.2	3.3	2.4	67.1	85.0	90.2	Graded temperature
62	149 x 297	500	876	Graded ^(d)	1.50	1.577	471.3	Zn	251.0	53.2	283.2	60.1	88.6	4.2	7.2	61.5 ^(e)	86.6 ^(e)	97.7 ^(e)	Graded temperature, increased feed
64	149 x 297	500	932	Graded ^(d)	1.40	2.149	554.0	Zn	344.0	62.1	392.9	70.9	87.6	4.0	8.4	77.0 ^(e)	80.6 ^(e)	92.1 ^(e)	Graded temperature, increased feed
66	149 x 297	519	927	Graded ^(d)	1.30	2.216	544.4	Zn	313.4	57.6	356.9	65.5	87.8	3.0	9.2	78.4 ^(e)	73.4 ^(e)	83.5 ^(e)	Graded temperature, confirmatory, lengthened reactor
68	297 x 590	350	688.1	Graded ^(d)	1.18	2.117	565.7	Zn	285.7	50.5	366.1	64.7	78.0	7.8	14.2	76.3 ^(e)	66.2 ^(e)	84.8 ^(e)	Graded temperature, increased particle size

(a) "Total" silicon does not include uncollected amount in Zn/ZnCl₂ condenser.

(b) Silicon product other than bed not recorded.

(c) Temperature too low at inlet; zinc condensation = excessive wall deposit and sintered bed.

(d)

Location	Run No. 56	59	62	54	66	68
Below bed	927	927	966	966	938	949
Bottom of bed	850	900	915	912	916	914
Top of bed	800	850	860	870	880	880
Expanded section	800	850	800	820	900	880
"Equilibrium" temperature	877	910	910 ^(e)	910 ^(e)	910 ^(e)	910 ^(e)

(e) Shading "equilibrium" temperature by (e.g.) 15 C upward would lower calculated equilibrium efficiency by ~1.5 percentage points.

In several cases, limited data availability precludes an accurate assessment of the relative contribution of these factors, but in most cases significant conclusions can be defined and others reasonably inferred.

Before the factors are treated individually, a brief summary of the effect of these factors and the equipment modifications described above on the overall performance of the miniplant is given to inform the casual reader. The overall operability of the plant has been considerably improved over that experienced in Phase 1, in that all experiments were terminated essentially as planned except for two minor problems. The by-product condensate collection system was shown not to be the problem once thought, but with minor revisions in design and operating parameters, the collection system performs satisfactorily and provides the basis for the design needed in the 25 MT/year facility. Fluidized-bed reactor wall deposit, an obvious undesirable feature, has been shown experimentally to be as low as 3 percent of the silicon product. Further, there is every reason to assume that this percentage of wall deposit will decrease with the increase of reactor size. Silicon dust, another undesirable product, was indicated to have been reduced to as low as 2.4 percent of the silicon product, which prompts optimism that this factor can be controlled to the extent required for economical operation.

In addition to these improvements in operability, silicon deposition rates in the 2-inch diameter miniplant reactor have been as high as 344 g/hr, which provides an experimental verification for the 6- to 7-inch reactor size selected for the 25 MT/year facility. The potential economics of the zinc reduction system have been strengthened further by achieving an experimental silicon bed efficiency of 62 percent and a total silicon efficiency of 97.7 percent of that predicted thermodynamically.

Hemispherical Versus Conical Bed Support. Although the potential advantages of the hemispherical bed support had been well

known from previous experience, it was not possible to obtain trouble-free operation with such reactors in Phase I and their use was reluctantly abandoned. Part of the problem lay in the difficulty of fabricating a suitable inlet configuration within the confines of the 2-inch-diameter quartz. With this difficulty overcome, use of the hemispherical bed support was reinstituted.

Comparison of the results of Runs No. 52 and 53 with those of the Phase I series demonstrates the gain in SiCl_4 -to-silicon conversion efficiency in going to the new reactor. That is, deposition on the bed was 79.1 and 78.1 of that thermodynamically predicted for these runs as against a maximum of 67.5 in the pilot runs with the conical bed support. This gain was accompanied by a smoother bed action, reflecting the capacity of the multiple-inlet hemispherical bed support for higher reactant throughput.

A significant drawback of the new reactor with the SiCl_4 fed through the axial inlet was the deposition of silicon on surfaces contiguous with one more of the four planetary zinc inlets, resulting in growth of tubular accretions extending into the bed. Apparently, when the zinc vapor dispersion in the bed is reduced below some critical value, either because of flow imbalance among the four inlets or the inherently poorer particle movement at or near the reactor wall, silicon deposition occurs preferentially nearer the zinc inlet. Preferential deposition in areas of high zinc concentration occurs because two zinc atoms are required for each SiCl_4 molecule to form one atom of silicon. Accordingly, the inlet configuration was reversed to feed the zinc through the axial inlet.

Axial Zinc Versus Axial SiCl_4 Inlet. In Run No. 56 and subsequent runs, the zinc was fed through the axial inlet. Two significant improvements resulted from this change: (1) elimination of the growth of reaction-sintered silicon at the zinc inlet and (2) reduction in the amount of silicon deposited on the reactor wall, particularly in

the inlet area. To have the reactor wall clear of deposited silicon over 30 percent of the active bed length was not unusual.

Comparison of the results of Runs No. 57 and 53 indicates that the silicon conversion efficiency was not significantly altered by the change, although the use of a deeper starting bed in Run No. 57 which may have increased efficiency early in the run masks the results with reference to such a conclusion. However, the shorter run with the deeper starting bed may well be the equivalent of the longer run with the shallower starting bed. It is believed that the effect on efficiency of changing to the axial zinc feed is minimal if not positive. The improvement with reference to elimination of undesirable deposition at the reactant inlet is compelling.

Graded Temperature Bed. As pointed out above, the exothermic nature of the zinc-reduction of SiCl_4 reaction leads to decreased equilibrium efficiency with increased temperature; thus it is desirable to operate at the lowest possible bed temperature consistent with reaction kinetics. However, the danger of condensing zinc in the bed requires a bed temperature (allowing for some supercooling) of not much below 908 C at 1 atm and with increasing operating pressure, even higher (e.g., 927 C at 1.23 atm). However, as the zinc is diluted by the SiCl_4 and as its partial pressure is further reduced by reaction, a lower bed temperature can be tolerated. Thus, if provision is made for cooling the bed preferentially toward the top, a higher net deposition efficiency should result. There is a limit to how far this can be carried as shown below.

For example⁽⁸⁾, with an undiluted stoichiometric feed, $2\text{Zn(g)} + \text{SiCl}_4\text{(g)}$, at 1 atm, the zinc dew point of the (unreacted) mixture is 1142 K (869 C), i.e., 39 degrees below the boiling point of zinc (the dew point of undiluted zinc vapor). As the reaction proceeds, the dew point falls off progressively as shown in Table 4.

In implementing experiments to test the graded-temperature concept, it was necessary to provide a deeper bed so that the gradient could be established immediately. Thus, it was necessary to shorten

TABLE 4. ZINC DEW POINT AS A
FUNCTION OF CONVERSION
EFFICIENCY

(Zn/SiCl₄ = 2, p = 1 atm)

Conversion, percent	Zinc Dew Point	
	K	C
0	1142	869
25	1124	851
50	1097	824
70	1062	789
75	1050	777

the run time so as not to exceed the reactor capacity as the result of growth of the bed.* A compromise was reached in establishing a run time of ~1.5 hours as a reasonable period for obtaining meaningful data. This would be accompanied by a ~60 percent increase in bed depth.

In the first run with the graded bed, No. 56, the bed was over-cooled, resulting in zinc condensation, and before the next graded-temperature run was made, a reference run (No. 57) was made at the usual bed temperature of 927 C. The following run (No. 59**) resulted in an increase in bed efficiency from 52 percent (No. 57) to 57.2 percent (No. 59). It should be noted that the directly measured bed efficiency is a valid basis for comparison in runs for which the feed stoichiometry is comparable. The ratio of bed efficiency to equilibrium efficiency reflects the expected increased bed efficiency by use of a lower temperature for calculation of the equilibrium efficiency. The selection of the effective bed temperature in the calculations for graded temperature

* It is not convenient at this time to introduce a mechanism for withdrawing product continuously to maintain constant bed depth.

** "Run" No. 58 was an experiment outside of the miniplant.

run is somewhat subjective, of course. In the region of interest here, the calculated equilibrium efficiency increases about 1 percentage point for each 10 C drop in temperatures.

Reactant Throughput. With the next run in the miniplant (No. 62), the throughput of SiCl_4 was increased by 29 percent with a resulting increase in deposition rate on the bed of 20.6 percent. Part of the loss of efficiency can be accounted for in the lower Zn/SiCl_4 ratio. The data actually indicate that the bed efficiency relative to that thermodynamically predicted increased, but this is subject to question because of the problem of choosing the effective equilibrium temperature. The fact that the percentage of product collected as dust increased (7.2 versus 2.4) can be interpreted as an indication of reduced bed efficiency as the result of the increased throughput.

Since problems associated with higher Zn/SiCl_4 ratios experienced earlier should be ameliorated by the use of axial zinc vapor injection, a return was made to near-stoichiometric feed ($\text{Zn/SiCl}_4 = 2.0$) near where (2.01) it has been shown⁽⁷⁾ that the greatest yield of silicon per unit volume of reactant gas can be obtained.

Although in Run No. 64 the silicon throughput was increased over that of Run No. 62 by 17.5 percent, the total throughput in moles of gas per hour was increased by 41.5 percent as a result of a change in the Zn/SiCl_4 ratio from 1.577 to 2.149. The resultant bed deposition rate of 344 g/hr was the highest achieved thus far. However, it was evident that the capacity of the reactor was being reached, as about 20 percent of the bed had been blown into the crossover line. The fact that the material blown out of the bed contained particles of varying thickness of deposit indicated that the transfer occurred progressively during the run.

The next run (No. 66) was made under approximately the same conditions as Run No. 64 with a reactor 2 inches longer to decrease the carry-over of bed material. A substantial decrease was recorded in the efficiency as percent of theoretical, which can be attributed

to carry-over of bed material into the condenser where it is not accounted for in the total. This conclusion is supported by the presence of a considerable amount of bed material at the condenser inlet. This loss of bed to the condenser is thought to be the result of a spontaneous release of back pressure that occurred during the run.

It was concluded from these experiments that, with the $149 \times 297 \mu\text{m}$ seed particles, the capacity of the reactor was being reached or exceeded at the reactant throughput rates used in Runs No. 64 and 66, i.e., 2.8 linear feet per second (at 910 C) or about 56 pounds of silicon fed per hour per square foot of reactor cross section.

Bed Particle Size. With the limitation of the system established for the $149 \times 297 \mu\text{m}$ seed particle size, the following run (No. 68) was made with $297 \times 590 \mu\text{m}$ particles, i.e., an increase in average diameter of about a factor of 2 which should ultimately allow the throughput to be increased by a factor of 4 to reach the same limitation. However, the throughput of the present system is limited by the capacity of the zinc vaporizer, a limitation to be relieved with the installation of a new vaporizer as discussed below.

At approximately the same reactant flow conditions used in Run No. 66, essentially no material was blown out of the bed. However, the bed efficiency dropped substantially to 50.5 percent from 57.6 percent (which itself is an artificially depressed figure because of bed loss in the prior run). The decrease in efficiency of deposition on the bed was reflected in the collection of an increased amount of dust downstream. Further, an increase in the rate of formation of silicon deposited on the wall was observed.

The decreased bed efficiency is attributed tentatively to the decreased surface area of the bed in Run No. 68. Owing to the use of a decreased initial bed volume, 285 cc versus 410 cc (as a further precaution against blowover) together with the increased particle size (area per unit volume of particles decreased by $\sim 1/2$), the bed area at the initiation of Run No. 68 was about $1/3$ that of Run No. 66. However, as the run progressed, the area ratio probably approached $1/2$ since

with part of the bed blown out of the reactor in the prior run, the effective bed heights may well have been equivalent toward the end of the run.

The results of the single run must be interpreted with caution. However, the effect of bed area on bed deposition efficiency is of obvious importance in economical operation of the process. Fortunately, decreases in bed area due to increased particle size in the size range from 200 to 1000 μm contemplated for the 25 MT/year reactor are easily compensated for by increased bed height, as the reactor diameter is increased (with the same L/D) from that of the miniplant (2 inches). To the extent that the heterogeneous reaction predominates, a deep bed of large particles can yield the equivalent of a shallow bed of fine particles. However, it should be noted that the surface area per unit volume of reactant gas in the bed is important in limiting gas-phase nucleation of silicon (i.e., the so-called "homogeneous" reaction). Unfortunately, this factor is not a function of bed height and subject to improvement with scale-up. Thus, attention will be given to these factors in future work with the miniplant and related experiments.

Preliminary information on the gas-phase nucleation of silicon is reported in the next section.

Sampling of Gas-Phase Nucleated Silicon. In Run No. 53, provision was made for sampling the by-product stream just above the bed with the objective of estimating the quantity and assessing the form of whatever fine particulate silicon is generated within the fluidized bed but is not deposited on the particles as a dense coating. A gas-purged tube extending into the region above the expanded bed and connected through a valve to an evacuated reservoir was suddenly evacuated to collect a sample.

Except for some particles from the fluidized bed, the silicon collected by the sampling probe consisted of spheriodal particles in the micron range as shown in the scanning electron micrograph, Figure 7. The fact that no larger crystalline particles of silicon were observed

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1000X

FIGURE 7. SCANNING ELECTRON MICROGRAPH OF GAS-BORNE SILICON PARTICLES IN RUN NO. 53 BY-PRODUCT STREAM (1 mm - 1 μ m)

is taken to indicate that the by-product stream was effectively quenched and that essentially no reaction occurred beyond that in the fluidized bed. In this connection, it is of interest to compare the analysis of the sample with that calculated for the overall by-product of Run No. 53.

Owing to the fact that zinc and zinc chloride are not collected from the Zn/ZnCl_2 condenser at the end of each run, experimental values for these components of the by-product cannot be obtained. However, they can be calculated based on assumed stoichiometry. To obtain the calculated composition of the by-product stream it is assumed that all of the SiCl_4 , except that trapped, reacted to produce silicon on the bed, on the wall, or as dust. The amount of dust was found by subtracting the experimental weights of the bed and wall deposits from the total. The zinc chloride produced and the zinc consumed were determined from stoichiometry, and the residual zinc from the total of the zinc fed during the run. Table 5 gives the results.

TABLE 5. BY-PRODUCT COMPOSITION AS DETERMINED FROM ASPIRATED SAMPLE AND OVERALL RUN DATA

Material	Composition, percent	
	Aspirated Sample	Overall Run
ZnCl_2	61.4	65.8
Zn	13.6	10.9
Si dust	1.1	1.1
SiCl_4	23.9	22.2

The results for the aspirated sample are subject to some uncertainty in the amount of zinc that should be attributed to an unanalyzed 3-g plug at the aspirator inlet. The data of Table 4 are based on the assumption that the plug was 1/2 zinc and 1/2 fluidized

bed particles. Assumption of a lower zinc content would improve the agreement. The apparent agreement must be further qualified by uncertainty in the by-product collection which would affect material balance.

Although the above calculations must be viewed with caution, they lead to the distribution of silicon product given in Table 6.

TABLE 6. DISTRIBUTION OF SILICON PRODUCT
IN RUN NO. 53

Source	Weight, g	Percent of Total Si	Percent of Collected Si(c)
Bed	563.0	78.4	85.7
Wall	35.0	4.9	5.3
Collected particulate	59.1	8.2	9.0
Uncollected particulate(a)	60.7	8.5	
Total(b)	717.8	100.0	

(a) Presumably left unrecovered in condenser, calculated by difference.

(b) Calculated by assumed 100 percent conversion of SiCl_4 fed minus that trapped.

(c) These data recorded in Table 2.

An overall silicon deposition efficiency, including the "uncollected" particulate silicon, equal to 99.5 percent of the thermodynamic equilibrium yield is calculated.

It is difficult to accept the presence of as much as 8.5 percent of the total silicon as remaining in the condenser. This would require a weight ratio Si/ZnCl_2 in the condenser (where most of the ZnCl_2 resides) of 0.0096, whereas samples cored from the condensate from Runs No. 49-51 showed a ratio of only 0.0019 in the top of the condenser and 0.0026 in the bottom, or an average of 23 percent of the required value. Since the condensate from Runs No. 53 through 59 was drained out of contact with air, for use in electrolysis experiments, no analyses were taken.

Most of the particulate silicon is believed to be carried through the zinc/zinc chloride condenser into the traps, as will be discussed in the next section of this report; however, because of the importance of the yield of silicon in forms other than as deposited on the fluidized-bed particles, attention will be directed in the future to obtaining more quantitative results on the overall balance.

Before leaving the subject, it should be pointed out that if the nucleation of the silicon dust is dependent upon prior condensation of zinc from the vapor phase, reduction in silicon dust formation can be obtained simply by giving greater attention to gas temperatures and bed temperature. For example, the SiCl_4 preheating may actually be inadequate in the miniplant as presently constituted.

It should be recognized that the amount of zinc condensation from the gas phase needed to give the observed behavior would be miniscule. A 1000-atom zinc nucleus for each 1- μm silicon particle would have required condensation of only 2×10^{-7} percent of the zinc fed in Run No. 53.

Condensation Efficiency. In the Phase I program, problems had been experienced with the free flow of liquid zinc/zinc chloride mixtures particularly in the crossover line and condenser inlet of the miniplant, and concern was expressed that the condensate might not drain freely, as required for operation of the electrolytic zinc recovery system. However, it was learned that if the slope of the transfer lines

exceeds some minimum (perhaps the angle of repose of the associated particulate silicon) free flow is obtained. Further indication that no serious problem existed in this area was obtained when the condenser contents from Runs No. 52 through 59 were found to drain cleanly at <500 C into the transfer vessel which will be used to feed the electrolysis cell. Inspection of the condenser surfaces showed then to be clean and not obviously restricted relative to heat transfer.

As noted previously, the condensation of liquid zinc and zinc chloride is not complete, some of the material (mostly zinc chloride) being collected downstream of the condenser. Two steps were taken at the inception of Phase II to (1) improve condensation of Zn/ZnCl₂ as liquid and (2) avoid carryover of ZnCl₂ into the SiCl₄ condenser. The addition of a trap (secondary condenser) accomplished the second objective, and the improvement relative to the first, attributed to the addition of baffles, is shown by the data of Table 7.

TABLE 7. FRACTION OF Zn/ZnCl₂/Si BY-PRODUCT COLLECTED IN CONDENSER AND TRAPS

Sources of Condensate	Percent at Stated Location	
	Condenser	Trap(s)
Runs No. 49-51 (Phase I)	91.9	8.1 (single trap)
Runs No. 52-59 (Phase II)	94.7	5.3 (two traps)

The gain in condenser efficiency is even more significant, as the average rate of flow through the condenser was 3 percent higher in Runs No. 52 through 59 than in Runs No. 49 through 51.

In the case of the condensate from Runs No. 49 through 51, the core samples taken for zinc, ZnCl₂, and silicon analyses permit calculation of the efficiency of condensation of zinc and zinc

chloride based on the stoichiometric relation to the amount of silicon formed. The amount calculated on the basis of stoichiometry, 11.344 Kg, agreed almost exactly with that observed, 11.345 Kg, although the agreement must be considered in light of the problems in collection and sampling.

Form of Condensate Collected in Traps. The material collected in the traps consists mainly of ZnCl_2 with small amounts of zinc and silicon. For example, in Run No. 57 the first and second traps contained 88.7 weight percent ZnCl_2 , 7.9 percent zinc, and 3.4 percent silicon. A scanning electron micrograph (SEM), Figure 8, of this material after water and acid leach (to remove ZnCl_2 and zinc, respectively, and leave silicon) shows the same finely divided silicon pictured in Figure 7. It is obvious that much of the particulate silicon, once generated, is carried through the system virtually unchanged, although evidence for some particle growth is suggested by comparison of Figures 7 and 8. The zinc and zinc chloride particles must also be of very small size as they escape the condenser, although no SEM's were made of this material.

By contrast, small crystallites of silicon can be found in the material collected at the condenser inlet where the residue is at a higher temperature and can grow by heterogeneous reaction with the unreacted SiCl_4 and zinc. Figure 9 is a SEM of this material. As long as excessive growth does not occur, it should be possible to move this material from the condenser into the electrolytic recovery unit with the large amount of associated liquid zinc chloride.

SEM's corresponding to Figures 8 and 9 were obtained for Run No. 64 which showed the same features except that, in the particular area examined, the average particle size of the dust trap product appeared to be slightly smaller.

Auxilliary Experiments

In this section of the report, experimental work carried on outside of the miniplant is discussed.

3453VD

2000X

FIGURE 8. SILICON RESIDUE FROM DUST TRAP, RUN NO. 57

3456VD

FIGURE 9. PARTICULATE SILICON COLLECTED AT CONDENSER INLET, RUN NO. 57

Reaction of $\text{SiCl}_4(\text{g})$ With Liquid Zinc. In the first run (No. 54) of a series of experiments made to determine the character of silicon deposited by the zinc reduction of SiCl_4 other than in the area of the fluidized bed, SiCl_4 gas (~33 percent in argon) was bubbled through liquid zinc at 740 C through a tube with a 1-mm orifice initially 12.5 cm below the surface of the zinc. The average argon flow was 124 cc/minute over a period of 213 minutes of uneventful operation. A total of 5.4 g of silicon was collected representing a SiCl_4 conversion efficiency of 53 percent. Most of the product (74 percent) was recovered from the liquid zinc (after solidification) as free-flowing 60 to 400 μm crystallites such as those shown in Figure 10.

Another 19 percent of the silicon product was collected over a 10-cm length of the tube above the orifice of the liquid zinc as a mixture of dendritic material and fragments of spherical shells as shown in Figures 11 and 12.

The remainder of the silicon (7 percent) collected as a spongy material (presumably interlocked needles) in a gas eddy zone (enhanced mixing, lower temperature) at the outlet of the reactor.

These operations suggest that, at 740 C, silicon formed in bubbling SiCl_4 through liquid zinc yields reasonably equiaxed crystals on the inside wall of the gas bubbles, and that these are easily broken up to distribute the crystallites throughout the liquid zinc.* Once the gaseous reactants emerge from the liquid without having come to equilibrium dendritic forms can occur on further reaction.

Supplemental By-Product Condensate Experiments. Four experiments were made independent of the miniplant to partially mock up the miniplant configuration and trace the form of the zinc/zinc chloride/silicon condensate toward the exit of the crossover line where problems had been encountered with free flow of the condensate in the past.

* Although beyond the scope of this program, it is interesting to speculate on the possibility of basing a silicon production process on this phenomenon. A greater depth of liquid and greater agitation would be required to increase conversion efficiency [which might approach 100 percent, allowing $\text{ZnCl}_2(\ell)$ to form].

3/31VD

(SEM)

50X

FIGURE 10. SILICON CRYSTALLITES RECOVERED FROM ZINC THROUGH WHICH SiCl_4 WAS BUBBLED AT 740 C, RUN NO. 54

3359VD

8X

FIGURE 11. SILICON DENDRITES AND SHELL FRAGMENTS
COLLECTED ABOVE ZINC SURFACE, RUN NO. 54

3357VD

87X

FIGURE 12. SILICON COLLECTED ABOVE ZINC
SURFACE, RUN NO. 54

In the simplest form of the experiment, preheated zinc and silicon tetrachloride vapor were fed into one end of a 36-cm length of 25-mm Vycor tubing inclined at 20 degrees to horizontal (as is characteristic of the crossover line) and heated to different temperatures. A condenser and dust trap in series were provided downstream. It was intended that the complication of simultaneously feeding known quantities of zinc chloride be added later to more closely simulate the by-products of the fluidized bed; however, the condensation problem in the miniplant diminished in severity with better recognition of some of the requirements, and the supplemental experiments were not carried beyond the simplified stage.

Data were taken with Zn/SiCl_4 ratios of 1.58 through 2.2 and with tube temperatures of 730 to 930 C; however, insufficient data are available to resolve the relative effects (kinetic/thermodynamic) of flow rate, Zn/SiCl_4 ratio and reaction temperatures on the results. For that reason, only data on the form of the silicon and the location of the zinc and zinc chloride condensates are presented.

Table 8 gives the results of the experiments most significant in terms of by-product condensation.

Figures 13 through 16 show that the same types of crystallites, i.e., acicular and more equiaxed forms, can be found in all of the products regardless of tube temperature, although a greater fraction of whiskers may have been present in the lower temperature run (No. 61). Bundles of knit whiskers are also observed similar to that shown in Figure 17. An interesting aspect of the delayed reaction in Run No. 60 (presumably due to the low Zn/SiCl_4 ratio) was the presence in the condenser of some ribbon shaped crystals (Figure 18). Evidence of gas-phase nucleation is obtained in the spheriodal micron-size particles recovered from the condenser in Run No. 61 (Figure 19) at the lower tube temperature.

In summary, the lowest tube (crossover line) temperature appears to favor the growth of whiskers and gas-phase-nucleated particles (and incidentally the highest conversion of SiCl_4 to silicon). At

TABLE 8. BY-PRODUCT EXPERIMENTS

Run No.	Temperature, C	Location and Quantity of Product/By-Product			
		Silicon		ZnCl ₂	Zn
55	826-856	Tube,	90%	Condenser and dust trap, 99%	Condenser end of tube, 19% Condenser, 81%
58	892-930	Tube,	97%	Condenser, 70% Dust trap, 30%	Condenser end of tube, 28% Condenser, 66%
60	906-924	Tube,	61%	Condenser, 70%	Condenser, 86%
		Condenser,	38% (a)	Dust trap, 30%	Dust trap, 13%
61	732-800	Tube,	95%	Condenser, 70%	Tube, 14%
		Dust trap,	1%	Dust trap, 30%	Condenser, 69%
					Dust trap, 12%

(a) Zn/SiCl₄ ratio = 1.53 versus 1.8 to 2.2 in other runs; may have suppressed kinetics resulting in some reaction in condenser.

3436VD

21X

FIGURE 13. SILICON DEPOSITED IN TUBE,
SUPPLEMENTAL RUN NO. 55

3448VD

21X

FIGURE 14. SILICON DEPOSITED IN TUBE,
SUPPLEMENTAL RUN NO. 58

3461VD

100X

FIGURE 15. SILICON DEPOSITED IN TUBE,
SUPPLEMENTAL RUN NO. 60

3464VD

53X

FIGURE 16. SILICON DEPOSITED IN TUBE,
SUPPLEMENTAL RUN NO. 61

3441VD

23X

FIGURE 17. KNIT SILICON WHISKERS DEPOSITED
IN TUBE, SUPPLEMENTAL RUN NO. 58

3423VD

500X

FIGURE 18. RIBBON SHAPED SILICON WHISKERS DEPOSITED
IN TUBE, SUPPLEMENTAL RUN NO. 60

3470VD

2000X

FIGURE 19. SPHEROIDAL SILICON PARTICLES RECOVERED
FROM CONDENSER, SUPPLEMENTAL RUN NO. 61

higher temperatures a greater portion of the silicon tends toward the larger nodular forms.

In the lowest temperature run, a portion of the unreacted zinc condensed in the tube, its saturation pressure having been exceeded.

It is evident from the above and from work with the miniplant, that heterogeneous growth of whiskers and other macrocrystalline forms of silicon must be prevented to permit free flow of the by-product. This means bringing the reaction as close to equilibrium as possible within the fluidized bed and maintaining the by-product at temperature (to avoid further [exothermic] reaction with decreasing temperature), until the by-product can be quenched at the condenser surface. Near horizontal orientation of condenser and transfer surfaces should be avoided to promote flow of the condensate (liquid zinc and zinc chloride plus some particulate silicon). The amount of particulate silicon in the condensate should obviously be minimized.

Evaluation of New Zinc Flash Vaporizer. As indicated above, the induction-heated graphite tray used to vaporize zinc in the miniplant is limited in capacity and not subject to scaleup. Accordingly, a flash vaporizer of different design was tested independently. It consists of an induction-heated 12-inch length of 1 inch ID x 1.5-inch OD graphite tubing packed with 1/8 x 1/4-inch crushed graphite contained in a quartz envelope. A positive displacement zinc feeder similar to that on the miniplant is used to feed liquid zinc to a point 1.5 inches below the upper level of the packing. The vaporized zinc flows to a condenser which can be removed and weighed to confirm the zinc flow. The temperature of the vaporizer is read optically and two axially located thermocouples are provided 2 inches and 5 inches, respectively, above the bottom of the vaporizer for use in detecting flooding of the vaporizer as indicated by a tendency of the thermocouple in question to drop toward the boiling point of zinc (908 C).

Three runs were made with the test unit, with the results noted in Table 9.

TABLE 9. EVALUATION OF ZINC FLASH VAPORIZER

Run No.	Vaporizer Temperature, C	Vaporization Rate, g/min	Remarks
63	965 maximum	16	Check-out Maximum not reached
65	965 maximum	~20	Upper limit
61	1056 maximum	32	Upper limit not reached owing to unrelated operational problems

Thus, zinc vaporization rates of ~40 g per minute can probably be reached in the test unit at temperatures in the neighborhood of 1050 C, whereas 1300 C is required in the miniplant. Accordingly, a flash vaporizer based on the test unit is being designed, for use in the miniplant, that will have a capacity in the range of 60 g/minute.

Electrolytic Recovery of Zinc from ZnCl_2 . As mentioned above, electrolysis experiments had been performed during the Phase I work on the electrolytic recovery of zinc from synthetic by-product mixtures, which were consistent with the results of Threlfall⁽⁶⁾. That is, no complications appeared to exist in the basic electrolytic zinc recovery reaction due to the presence of small quantities of silicon. Electrolytic zinc recovery experiments using actual miniplant by-product mixtures are part of the planned experimental support program of Phase II.

The electrolytic cell, with electrode area and spacings patterned after the work of Threlfall⁽⁶⁾ is shown in Figure 20.

Provisions are made for draining the miniplant by-product from a transfer vessel into the cell for the electrolysis experiments. The chlorine liberated from the ZnCl_2 , plus SiCl_4 resulting from

FIGURE 20. SCHEMATIC DIAGRAM OF ZINC CHLORIDE
TO ZINC RECOVERY SYSTEM

chlorination of the particulate silicon will be vented and the zinc will be drained from the lower section of the cell by means of a plug valve to a storage vessel.

The electrolytic cell is graphite lined, and the zinc storage vessel is presently provided with a Pyrex liner, for which quartz liners will be substituted when experiments requiring maintenance of higher purity levels are carried out. Provisions have been made for lining the upper by-product transfer vessel with graphite, if necessary, although for the first experiments, the by-product from Runs 52 through 59 is contained in the unlined stainless steel vessel. Since the transfer vessel will be operated at temperatures only slightly above the melting point of ZnCl_2 , it has yet to be determined whether impurities are introduced into the system from the stainless steel that are not readily removed by the electrolytic operation.

Initially provisions are being made to monitor the following:

- (1) Equipment temperature
- (2) Electrolysis current and voltage
- (3) Quantity of by-products -- zinc, chlorine, ZnCl_2 , and SiCl_4
- (4) Quantity of Zn/ZnCl_2 condensate electrolyzed
- (5) Examination of residuals, if present.

It is planned that this work will be underway in the month of April.

Work Planned for Next Report Period in Experimental Support

Program. Plans for experimental support activity next quarter include:

- (1) Continue reactor design studies as required
- (2) Continue condenser studies as required
- (3) Complete zinc flash vaporizer design evaluation
- (4) Initiate studies on the recovery of zinc from the $\text{Zn/ZnCl}_2/\text{Si}$ by-product condensate

- (5) Study removal of SiCl_4 from $\text{Cl}_2/\text{SiCl}_4$ mixture simulating material processed in E4
- (6) Prepare material for purity evaluation to identify problem areas
- (7) Continue fluidized-bed operating parameter optimization.

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