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

Silicon Material Task, Low-Cost Solar Array Project

Tenth Quarterly Progress Report, January 1—March 31, 1978

By
J. M. Blocher, Jr.
M. F. Browning

April 30, 1978

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

Battelle Columbus Laboratories
Columbus, Ohio

U.S. Department of Energy

MASTER

Solar Energy

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TENTH QUARTERLY PROGRESS REPORT
Covering the Period January 1 to March 31, 1978

on

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

JPL Contract 954339

Silicon Material Task
Low-Cost Solar Array Project

to

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY

by

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ABSTRACT

Progress from January 1 to March 31, 1978, is reported in design of the 50 MT/year 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.

The design of the experimental facility has been concluded and sent to JPL for evaluation. It is also being critiqued by an independent pilot plant design group at BCL. Detailed analyses of equipment and construction costs have led to an estimate of \$1.5 million for construction of the facility in an available building at BCL.

Although the design was frozen for purposes of cost estimation, some improvements have been made since, and others are contemplated before it is necessary to freeze the design for construction. Representative flow sheets and related equipment drawings are shown in this report.

In the experimental support program, moving pictures have been taken of a full-scale mock-up of the 25 MT/year units (two) to be used in the 50 MT/year facility. Of the alternatives studied, a bed support (distributor plate), consisting of a round bottom with transition to the cylindrical wall through a conic section, appeared to give the best bed action.

It was found that a zinc vaporizer of 5.7-cm-diameter, 30-cm-long quartz tubing in which the zinc is heated by direct inductive coupling can easily support the 0.5 kg Zn/minute requirement of one of the 25 MT Si/year fluidized-bed reactors. The boiling rate can be controlled by power input, and it may even be possible to control the zinc inventory by the inductive characteristics of the load, although resistance-probed level control is presently planned.

Experimental runs in the electrolytic cell for recovering zinc from the $\text{ZnCl}_2/\text{Zn/Si}$ fluidized-bed by-product indicated that the small quantity of silicon "dust" in the by-product can indeed be chlorinated in the cell as planned (at least up to 3.4 percent of the granular silicon product) without build-up of silicon in the electrolytic cell.

Materials-compatibility tests are reported for stainless steels and other materials of interest in construction of the 50 MT/year facility.

Experiments are recorded in which certain design features of the facility were verified.

Additional quantities of quality-evaluation material were prepared in the miniplant and sent to JPL for evaluation.

INTRODUCTION

This Tenth Quarterly Progress Report covers the work at Battelle's Columbus Laboratories (BCL) for DOE/JPL on the Evaluation of Selected Processes for the Production of Low-Cost Silicon. In the first phase of this work, the zinc reduction of silicon tetrachloride in a fluidized bed of seed particles was selected to be the most promising of several options studied, from the standpoint of technical and economic feasibility. Accordingly, the second phase of this program has concentrated on the development of that process and the design of a 50 MT/year Si experimental facility for possible construction and operation at BCL.

As in the prior reports of this series, the results for the current quarter are presented and discussed in separate sections under Design and Experimental Support. The reader is assumed to have the background provided in the Fifth/Sixth through the Ninth Quarterly Reports.

DESIGN OF THE EXPERIMENTAL FACILITY

During the current quarter, the design of the 50 MT/year Si experimental facility was concluded and presented to JPL for evaluation. Three organizations have cooperated in formulating this design. The SiCl_4 purification system was the primary responsibility of Pace Engineers, Inc. (Pace), of Houston, Texas; the remainder of the more conventional aspects of the design were handled by Raphael Katzen Associates International, Inc. (RKAI), of Cincinnati, Ohio; and the less conventional aspects of the design and its overall integration were handled by BCL in cooperation with RKAI.

Representative flow sheets and drawings from the design package as it existed at the time were presented in the Ninth Quarterly Report. Since then, improvements and/or simplifications have been made in the design, and certain of those flow sheets and drawings have been superseded.

Accordingly, a few of the most significant drawings are reproduced here with explanatory notes so that the current status of the program may be appreciated by the reader. It is recognized that the drawings contain some detail that may not be legible at the scale used here; however, they are believed to be sufficiently informative for the present purpose. Detailed presentation and discussion of the design will be deferred for the final report.

50 MT/Year Si Facility Design

In general, the process provides for mixing purified silicon tetrachloride and zinc vapor in the lower part of a fluidized bed of silicon seed particles on which the reaction product accumulates as a relatively dense and adherent deposit. The by-product zinc chloride vapor and unreacted zinc vapor are condensed and routed to electrolytic cells for recovery and recycle of the zinc. The unreacted silicon tetrachloride is recycled to the purification unit. In a production plant, the chlorine from the zinc chloride electrolysis would be used to produce the make-up silicon tetrachloride by

reaction with metallurgical-grade silicon or with silicon carbide; however, in the experimental facility, it was deemed prudent to bypass this step, since silicon tetrachloride is readily available at a reasonable cost. Further, when the chlorination step is eventually undertaken for minimizing overall cost, the design can be based on well-established practice, which needs no verification in the experimental facility considered here. Accordingly, the chlorine from the electrolytic cells is converted to sodium hypochlorite for use locally in treating sewage plant effluent. The chlorine-to-hypochlorite conversion system is integrated in the waste treatment section of the facility with a system for neutralizing and disposing of the waste silicon tetrachloride from the purification system.

Table 1 lists the major design parameters of the 50 MT/year Si experimental facility. It is to be noted that two 25 MT/year fluidized-bed units of 6.5-inch ID are used for flexibility and as a reasonable scale-up from the 2-inch ID reactor used in the miniplant. The capacity of each unit, 3.6 kg/hour, is a direct scale-up on an area basis from the 340 g/hour production level attained in the miniplant unit. The 63 percent SiCl_4 conversion per pass is a projection of miniplant experience; however, the seed requirements (5 percent of production) and the zinc recovery (95 percent) estimates are somewhat arbitrary at this point and subject to modification by experience.

In the discussion that follows, the process is divided into three sections -- Feed Preparation, Reaction and Recovery, and Waste Treatment.

Feed Preparation

Figure 1 shows the feed preparation section of the facility, with process flow rates tabulated at upper left. Silicon tetrachloride of the approximate analysis given in the Ninth Quarterly Report* is received in 40,000-pound tank trucks. This material is purified by distillation in two columns (light-end and heavy-end) with intermediate surge tank (T101 in the figure). A 92-percent center cut is taken, with 4 percent each of tops and

* Note that the typical analysis for As should have read 0.2 to 1.5 ppb.

TABLE 1. DESIGN PARAMETERS - 50 MT/YEAR
SILICON EXPERIMENTAL FACILITY

● On-stream factor	80 percent
● Zn/SiCl ₄ stoichiometry	2/1
● Reaction temperature	925 C
● Operating pressure	~1 atm above fluidized bed
● Conversion of SiCl ₄	63 percent per pass
● Production rate	7.20 kg/hour (16.8 g/hour/ cm ² cross section)
● Seed requirement (5 percent)	0.36 kg/hour
● Fluidized-bed reactors (two)	16.5-cm diameter
● SiCl ₄ purification by distillation	92 percent center cut
● Zinc recycle by electrolysis	Six 5000- to 6000-amp cells
● Zinc recovery	95 percent
● Cl ₂ disposal	Conversion to NaOCl

FIGURE 1. FEED PREPARATION

bottoms going to waste. The purified product from the top of the heavy-ends column goes to a feed tank that supplies each of the SiCl_4 boilers for the two 25 MT/year Si fluidized-bed units. As shown in Figure 1, the pure SiCl_4 storage tank is compartmentalized (tentatively in six sections) to permit independent qualification of lots of SiCl_4 before committing them to use. Nitrogen is provided to allow the various units to breathe to a vent system, the SiCl_4 condensate from which goes to waste. An emergency storage tank is provided so that the contents of units containing appreciable quantities of SiCl_4 can be conveniently drained if necessary. The individual compartments of the pure SiCl_4 feed tank can be drained to the SiCl_4 storage tank for repurification or to the SiCl_4 emergency storage tank as desired.

The feed preparation section is designed to operate at pressures of up to 60 psig.

Reaction and Recovery

Figure 2 shows the reaction and recovery section of the facility with process flow rates tabulated at upper left.

Purified SiCl_4 from the feed preparation section is held at constant level (pumped from storage) and constant pressure (power input-controlled) in the SiCl_4 boiler from where it is metered by gas-flow control into a pre-heater in the bottom section of the fluidized bed. Provision is made to introduce an inert gas at this point to avoid the problems inherent in systems consisting of all condensible vapors. A proportionate flow control provides for continuously bleeding part of the boiler contents to storage to prevent impurity build-up.

The SiCl_4 vapor entering the bed is met by an approximately stoichiometric* quantity of zinc vapor. The silicon product grows on silicon particles introduced as seed from the hopper shown atop the reactor adjacent to a sight

* Calculations have shown no economic advantage in deviating from stoichiometry, and the incidence of gas-phase-nucleated silicon tends to be increased on the zinc-rich side.

glass. The granular product is withdrawn from the bottom of the reactor at a rate equal to the production rate [controlled by maintenance of constant bed level (pressure-drop monitored)].

Provision is made to periodically chlorinate the fraction of the silicon that deposits on the fluidized bed wall so as not to have excessive build-up.

The zinc/zinc chloride component of the by-product is condensed in a large condenser/heat exchanger (to be discussed later) and flows through an electrolysis feed tank into a bank of electrolysis cells (to be discussed later). The SiCl_4 /inert gas component of the by-product is passed through alternately cooled (for condensation) and heated (for melt-down) ZnCl_2 strippers, and then through a glycol-cooled condenser to remove SiCl_4 for recycle. A possible simplification of the design is being considered, that of using single ZnCl_2 strippers operating just above the melting point and allowing the small amount of ZnCl_2 that escapes to condense (as a slurry) with the SiCl_4 .

An organic heat exchange fluid, Therminol*, is used to maintain proper temperature levels for condensation in the large Zn/ ZnCl_2 condenser and ZnCl_2 strippers, and for melt-down of the ZnCl_2 strippers.

Condensed zinc and ZnCl_2 , containing small quantities of suspended silicon "dust"**, flows from the electrolysis feed tank (provided with a load cell for content monitoring) to one or more of the electrolytic cells (to be discussed later). The liquid zinc entering the electrolytic cells plus that produced by electrolysis of the ZnCl_2 is withdrawn to the zinc storage tank by an overflow system whose height is chosen to prevent overflow when the zinc level has fallen to the point (still above the submerged outlet) that the head of ZnCl_2 (controlled via a level indicator) is insufficient to cause flow. Prevention of accumulation of impurities from the zinc is accomplished by periodic manual skimming of the zinc or ZnCl_2 content of the electrolytic cells. Zinc from the load-cell-monitored zinc storage tank is fed by gravity

* Monsanto Industrial Chemical Company.

** Gas-phase-nucleated silicon that does not accumulate on the seed particles.

to a constant level tank that feeds the zinc vaporizer. The zinc vaporizer (to be discussed later) is induction heated, directly coupled to the zinc so that the vaporization rate can be controlled by power input. It is possible that the zinc inventory in the vaporizer can be monitored by the current-voltage relationship in the induction heater instead of the constant level device.

Provisions are made for appropriate pressure equalization and venting of the reaction and recovery system.

Waste Treatment

The waste treatment section of the facility shown in Figure 3 has two primary functions: (1) to convert the chlorine from the electrolytic cells to hypochlorite that can be disposed of in treating sewage and (2) to neutralize and dilute the SiCl_4 waste (tops and bottoms from distillation and vented SiCl_4).

In removing the heat of reaction between chlorine and NaOH to form hypochlorite, air cooling of the hypochlorite has been combined with scrubbing of the air from the plant area in the large unit, E7, termed the Area/Vent Gas Scrubber. This scrubber is provided with two sets of perforated trays over which solution is recirculated in two respective loops. The bottom loop contains 1 percent NaOH* and the top loop, essentially 19 percent NaOH as it comes from the Caustic Storage Tank, E6. The solution in the bottom loop circulates across the trays and through one of two interchangeable** eductors (E8) where it meets and reacts with the chlorine from the electrolytic cells to form hypochlorite solution. The NaOH concentration in the lower loop is maintained at 1 percent by demanding overflow from the top (19 percent NaOH) loop.

* Equivalent to 14 percent NaOCl.

** Duplicates provided to allow for cleaning of accumulated hydrated SiO_2 from SiCl_4 hydrolysis.

STREAM NO.	(5)	(17)	(52)	(58)	(49)	(51)	(55)	(49)	(58)	(59)	(60)	(61)	(62)	(63)	(64)	(65)	(66)	(67)	(68)	(69)
DESCRIPTION	STORAGE TANK VENTS (3.4)*	PURIFICATION UNIT VENTS 14.0	CELLS VENTS 1.0	ELECTROLYSIS VENTS 1.8	CHLORINATION VENTS (18.3)*	LIQ WASTE VENT UP IN PLANT (50) MIN	LIQ WASTE	RECYCLE	SOLID WASTE TO SEWER	VENT TO SEWERS	WASH MAKE UP	HYPH. LOOP FEEDER	LOWER LOOP FEEDER	REDUCTOR VENT FEEDER	HYPHOSITE PRODUCT	INSIDE AIR	AREA VENTS	LIQ WASTE STORAGE	WASH MAKE UP	VENT TO ATMOSPHERE
SiCl ₄				87.4	(10.0)*			155,844 Δ	116/463 Δ				117	33	12					
H ₂ O ₂								180/152 Δ	3.0/134 Δ		101.9	11,450	603	1705	62					
Cl ₂								1852/1150 Δ	773/894 Δ				6804	1705	69.4					
H ₂ O ₂								7189 Δ	10.4 Δ				5372	2350	85.6					
H ₂ O ₂								7510/7645 Δ	105.0/5247 Δ		4345	48,820	44,921	12,518	453.2					
AIR										47						21,100	316	632		724.4
INERT GAS										2.3							21,100			42,707
TOTAL	(3.4)*	14.0	33	84.4	(58.3)*	357/610 Δ	1550/1100 Δ	12,601 Δ	1519/684 Δ	70	536.4	60,270	60,842	17,036	620.6	21,416	21,416	42,832	724.4	42,734
TEMP. °F	77	77	37	350	150	77	77	50	ATM	77					17.0					
PRESSURE PSIG	(0.4)		30	766	(2.5)			20		1.33						25,000	25,000	25,000		10,000
ACFM		.02				27/100 Δ	3/22		0.10/1.33 Δ		.89	100	100	20	1.01					
GPM																				

NOTES

- () INTERMITTANT OPERATION
 * 6 HRS. EVERY TWO WEEKS
 ** 10 HRS PER WEEK (CHLORINATION)
 Δ MAX. PEAK DURING CHLORINATION.

FIGURE 3. WASTE TREATMENT

The net hypochlorite solution production is pumped out of the lower loop and into the Hypochlorite Storage Tank as controlled by a constant level device. A flow of outside and/or inside air through the Area/Vent Scrubber cools the hypochlorite solution. Chlorine lost by volatilization from the lower trays is reabsorbed by the 19 percent NaOH in the upper loop. An exhaust blower, E9 ($\sim 10,000$ cfm), in the scrubber exit is used to move the air through the trays.

Neutralization of the SiCl_4 wastes is taken care of in the system on the left of Figure 3. A solution of 2 percent NaOH circulates through the SiCl_4 Scrubber, D3, where the liquid SiCl_4 wastes are neutralized. SiCl_4 vapors in the vent gases are fed to one of a pair of interchangeable eductors, D6, through which the 2 percent NaOH solution circulates as the motive fluid. The net discharge from the SiCl_4 scrubbing system (~ 0.3 gpm) overflows to the sewer. No environmental problems should be caused by this amount of material, particularly since it will be heavily diluted with cooling water (e.g., 10/1) from the rest of the facility.

The heat of neutralization of the SiCl_4 is dissipated in a water-cooled exchanger, D5 (NaOH Recycle Cooler). The capacity of this exchanger is chosen to provide for the increased load during the periodic chlorination of silicon from the reactor walls.

Fluidized-Bed Reactor

Figure 4 shows the fluidized-bed reactor in greater detail than in Figure 2. SiCl_4 vapor enters at the bottom, is preheated in the graphite-granule-packed annulus, and enters the fluidized bed through outer ports in the rounded bottom distributor plate. Zinc vapor at just above its boiling point (918 C at 1.1 atm) enters the bed through a ring of inner ports in the distributor plate.

The fluidized-bed reactor is constructed of silicon-carbide-coated graphite or solid silicon carbide, encased in a No. 310 stainless steel shell provided with bellows to accommodate thermal expansion differentials.

FIGURE 4. 6.5" ID FLUIDIZED-BED REACTOR

Changes in the positions of the SiCl_4 inlet and reaction product outlet relative to the fixed zinc vapor inlet and the connecting equipment is accommodated in the assembly sequence and by means of appropriate slip joints in non-critical positions.

The graphite is rendered impervious by appropriate coating to avoid deleterious exposure of the stainless steel shell to zinc vapor. Tungsten coating of the stainless steel is being studied as additional protection.

Zinc Vaporizer

One of the more difficult aspects of the facility design has been the problem of supplying the high heat of vaporization of zinc while maintaining a limited zinc vaporizer inventory to minimize hysteresis in the vaporizer output response. To drive the heat of vaporization through graphite or silicon carbide requires bulky equipment, steep temperature gradients, and excessive zinc inventory. This problem has been solved, as discussed in the Experimental Support section of this report, by direct induction coupling to the zinc in a quartz vessel. The zinc vaporizer design shown in Figure 5 is patterned after the vaporizer tested experimentally.

The vaporizer is packed with graphite chips to facilitate heating before liquid zinc is added and to reduce the inventory of zinc in the vaporizer per unit effective volume. Carbon wool is contained in the compartment formed by a wier placed 4 inches from the exit end, to act as a demister for the zinc vapor. Entrained droplets of unvaporized zinc not only serve to carry over impurities, but they act as nucleation and growth sites for silicon needles and powders, which can escape deposition on the seed particles of the fluidized bed. The zinc vapor line is lagged with heaters until well inside the fluidized bed furnace, to prevent condensation of zinc.

It is planned that the zinc vaporization rate be controlled by power input, and although present plans call for constant level control, it is possible that the liquid zinc inventory in the vaporizer can be sensed by the current-voltage relationship in the converter, and the latter used for control.

FIGURE 5. ZINC VAPORIZER

Zinc-Zinc Chloride Condenser

As indicated in the general description above, the reaction product consists of ZnCl_2 vapor, unreacted zinc and SiCl_4 vapor, a small amount of entrained gas-phase-nucleated silicon powder, and inert purge gas. The condenser, shown in two sectional views at right angles in Figure 6, provides for recirculating the condensed zinc chloride to act as a fluid for wet-wall condensation. The reaction by-products enter the condenser at the lower left of the view on the left and are directed up the left-hand open channel and down the right by virtue of the seal made by the liquid ZnCl_2 in a pool at the bottom, at the level of the condensate outlet and above the bottom of the wedge-shaped barrier. Liquid ZnCl_2 , taken from below the surface of the pool is cooled by circulation through the graphite block (see open channels on right-hand drawing). At the top of the block it overflows the barriers and wets the condenser surfaces.

Therminol 88, an organic heat exchange medium, is used to remove heat from the condenser to a separate Therminol heat-exchange system. The graphite is to be impregnated and coated to render it impervious to the Therminol. However, an alternative to direct contact of the Therminol with the graphite block is being explored.

Zinc condensation occurs between about 800 and 690 C and ZnCl_2 condensation from 690 to 565 C. The gas leaving the condenser will be at about 510 C when it enters the ZnCl_2 strippers (shown in Figure 2) for removal of the remainder of the ZnCl_2 .

Electrolytic Cell

The cells for fused salt electrolysis recovery of zinc from the by-product ZnCl_2 are patterned after those being developed at the U.S. Bureau of Mines, Reno, Nevada,* for electromining zinc from sulfide ores. The present

* D. E. Shanks, F. P. Haver, C. H. Elges, and M. M. Wong, "Electrowinning Zinc from Zinc Chloride - Alkali Chloride Electrolytes", U.S. Bureau of Mines report, to be published.

FIGURE 6. ZINC/ZnCl₂ CONDENSER

design is shown in Figure 7. Depending upon the current efficiency attainable, six 5000- to 6000-amp cells will be required for the 50 MT/year Si facility. They are of "cold"-wall construction, graphite lined, with graphite electrodes. The cathode contacts the liquid zinc pool at the bottom of the cell which is connected to the current supply via a plug of frozen zinc extending through the cell wall (shown at the bottom, but probably to be through the side). A cell voltage of 4.5 volts is anticipated at a current density of 10 to 12 amps/in.². Excess heat is removed through a heat exchanger (not shown) in the hollow anode. By means of electric contact level probes (of tungsten or graphite), not shown in the figure, upper and lower ZnCl_2 level limits are set to control the addition of ZnCl_2 to the cell. The zinc overflows automatically on balancing the hydrostatic head of the ZnCl_2 approximately at the ZnCl_2 lower level limit. Blockage of the zinc outlet and resulting excess accumulation of zinc in the cell would be indicated by a shorted cell as the zinc level reaches the anode.

The entire electrode assembly is removable through the cell roof to provide for ease of cell maintenance.

Plant Layout

Figure 8 shows the plan view of the facility, as designed to fit into an available building area at BCL. As the zinc and zinc chloride flow is by gravity*, the Zn/ZnCl_2 condenser, electrolysis feed tank, electrolytic cells, zinc storage tank, zinc level tank, and zinc vaporizer are on different levels. Accordingly, some of the associated units are not shown in the plan view of Figure 8 at the electrolytic cell level.

The layout is designed to permit ready access for SiCl_4 and NaOH delivery and for hypochlorite removal, and to minimize the length of connecting lines carrying zinc and zinc chloride.

* Except for pumped recycle of liquid ZnCl_2 in the wet-wall Zn/ZnCl_2 condenser.

FIGURE 7. ELECTROLYTIC CELL

FIGURE 8. PLAN VIEW

Cost of Experimental Facility

It should be re-emphasized that many of the details and most of the specifications in the design package have been omitted in the above discussion which has been presented primarily for orientation. However, on the basis of a detailed summation of the vendor-estimated costs for equipment of special design, price-list data for equipment of standard design, detailed costs of the instrument package, and construction costs based on standard construction cost-estimating techniques, RKAI arrived at an initial cost estimate of \$1,536,000, of which \$266,500 for the SiCl_4 purification system was estimated independently by Pace. The overall cost estimate arrived at by RKAI includes all procurement, installation, management, and tax costs for constructing this facility in an existing building by a company building the facility for its own use. A contingency item of \$191,139 is included.

Because of differences in overhead, fee structure, and labor rates, the cost of building the facility at BCL would be higher; however, removal of the contingency item, credit of certain economies agreed upon by BCL and RKAI, and adjustment for the differences mentioned above leads to a figure of \$1.5 million, which has been presented to JPL for budgetary purposes. This estimate is based on purchasing equipment from outside vendors, subcontracting a significant portion of the construction and installation to an outside contractor, BCL's involvement in construction and installation of nonconventional equipment, and overall management of the program by BCL personnel.

EXPERIMENTAL SUPPORT PROGRAM

During the period covered by this report, experimental support work has continued in the following areas:

- (1) Fluidized bed
- (2) Zinc Vaporizer
- (3) ZnCl_2 electrolysis
- (4) Materials compatability
- (5) Product Quality
- (6) Miscellaneous.

These are discussed individually below.

Fluidized Bed

A full-scale* mock-up of the fluidized-bed reactor has been studied with sand as the granular material ($d = \sim 2.5$ versus 2.4 g/cc for Si) and air as the fluidizing medium. Motion pictures were taken to record the bed action.

In most fluidized-bed chemical vapor deposition reactions, the gases enter the bed at considerably below the reaction (bed) temperature. Further, the reaction results in increased molar volume (products versus reactants). Thus, a large expansion occurs within the bed, and fluidization patterns obtained under operating conditions differ from those observed at ambient temperature and with no reaction. By contrast, the reactants in the present process enter the reactor at near bed temperature.** Further, for a 63 percent efficient reaction with stoichiometric feed:

* To make use of a convenient size of transparent plastic tubing as the wall of the mock-up, the diameter was 7 inches instead of 6.5 inches called for in the experimental facility design.

** This condition is necessitated by the high boiling point of zinc (918 C at 1.1 atm) and to prevent nucleation of micron-to-submicron silicon needles on droplets of zinc (or loss of fluidization with larger quantities).

a net isothermal decrease in molar volume of 21 percent* occurs. Thus, depending upon how rapidly the exothermic heat of reaction (that would cause compensating gas expansion) is extracted, relatively little change in volume occurs within the fluidized bed in the present process and the fluidization patterns seen at room temperature should approximate those at operating temperature**.

Distributor plates of alternative design were studied with varying particle size (180 μm and 715 μm), bed depth (0.6, 1.2, and 1.8 feet), and flow rates (20 cfm to 40 cfm). Without going into detail, it was concluded that the bed action, particularly with respect to particle circulation with the bed, was superior in the round-bottom support design, shown in Figure 9.

Figure 10 gives a typical sequence of frames from the motion pictures, showing first a collapsed bed, gradually expanding bed with the formation of a gas bubble, breaking of the bubble through the top of the bed with particles being carried well above the top of the expanded bed, and finally, a return of the bed to the collapsed condition. Obviously, the frequency of this cycle is dependent (in this model) primarily on bed height and gas flow. In the case of a gas flow of 28 scfm and a bed height of twice the reactor diameter, the sequence is repeated on the average of once in 0.7 second. Two aspects of particle circulation, not as observable in this sequence of frames as when viewing the motion picture, are (1) predominant motion of particles down the wall to the distributor and then rapidly up the middle and (2) absence of areas of stagnation (especially at the distributor/wall junction).

* Small addition of inert gas neglected.

** This equivalence disappears as the size of the particles is decreased to where adhesive forces (temperature- and reaction-system dependent) become important.

FIGURE 9. DIAGRAM OF ROUND-BOTTOMED DISTRIBUTOR
USED IN MODEL STUDIES

FIGURE 10. TYPICAL SEQUENCE FROM MOTION PICUTRES OF THE
FLUIDIZED-BED MOCK-UP (see Figure 9)
(time interval = 0.375 second)

The capacity of the central outlet for silicon granule withdrawal was also studied. It was demonstrated that 20 x 30 mesh (590 x 840 μ m) sand equivalent to 13 kg/hour of silicon could be withdrawn through an 8-mm ID tube against a purge gas (argon) flow of 1 l/minute, and that the flow of material could be initiated and terminated at will without hang-up that might require vibration to alleviate. This rate of flow is 3.4 times the requirement for the experimental facility; however, since the probability of bridging increases with the spread of particle size, the experiment will be repeated with a particle size mix that more closely approximates that expected in the fluidized-bed product.

Zinc Vaporizer

As indicated earlier in this report and in more detail in the Ninth Quarterly Report, design of a low-inventory zinc vaporizer is subject to a number of serious constraints. With the thought that these might be removed by direct induction coupling to the zinc, a series of experiments was made to test the concept. Two configurations were studied, the first of which consisted of a pool of zinc in a 57-mm-diameter by 30-cm horizontal quartz cylinder and the second, a bed of graphite chips (1/4 to 3/8 inch)* in the same cylinder, into which liquid zinc was metered. In both cases, the zinc vapor was condensed and collected in a continuously weighed container. A 50-kw, 450 K hertz thermionic converter with an 18-turn, 3-inch diameter coil was used. In the first experiment, the boil-off rate as a function of power setting was reproducible within 15 percent at low rates of boil-off (20 and 40 g/minute). However, the reproducibility was lost when the zinc level dropped to less than half of its initial value, as might be expected at some point with the attendant decreased coupling. The major objective of the second experiment was to determine the vaporization capacity of the

* The graphite packing has the advantages of (1) permitting initial preheating of the vaporizer, (2) roughly doubling the apparent volume of zinc, and (3) acting as a demister for the zinc vapor.

packed-bed vaporizer configuration. It was found that the graphite-packed vaporizer could easily support zinc boil-off rates of 1/2 lb/minute and 1 lb/minute, the latter being the full rate for one 25-MT/year half of the 50 MT/year experimental facility. The difference in the coupling to the graphite-filled vaporizer made it impractical to measure the sensitivity of rate of vaporization to power input in this case. However, since the boil-off rate was power-sensitive at 1/10 the rate in the first experiment, it is believed that with appropriate coil configuration and power instrumentation, the rate of boil-off can be related to power input. In any event, it was demonstrated that a relatively small vaporizer can supply the needs of the experimental facility.

Further contact with representatives of the Lepel High Frequency Labs, Inc., confirmed the feasibility of controlling the rate of zinc vaporization by power input and indicated a high probability of success in monitoring the zinc inventory by the relationship between current and voltage settings of the converter.

Electrolytic Cell

A limited amount of work was done with the experimental electrolytic cell during this report period, pending its being refurbished to decrease corrosion by the evolved chlorine.

The cell used in the single run to be discussed below was approximately of the configuration depicted in Figure 20 of the Fifth/Sixth Quarterly Report. However, 5-inch-diameter horizontal electrodes in a Pyrex liner were used, approximating the Bureau of Mines' design.

In order to confirm the feasibility of chlorinating by-product silicon dust in situ, a 14-hour run was made at 100 amp, in which 1.4 kg of zinc was produced at 82 percent current efficiency in the electrolysis of miniplant $\text{ZnCl}_2/\text{Zn}/\text{Si}$ condensate. At the same time, 9.8 g of the suspended silicon was chlorinated, as determined by collecting and hydrolyzing the SiCl_4 , and calcining and weighing the oxidized product. On the basis of the

equivalency of the ZnCl_2 electrolysis with the product silicon, the observed chlorination would accommodate silicon dust in the amount of 3.4 percent of the granular silicon product without build-up of silicon dust in the electrolytic cell. This figure represents a 70 percent margin over the requirement assumed in the 50 MT/year facility flow sheet. However, the actual amount of silicon dust that will have to be handled cannot be determined short of actually operating a full-scale fluidized-bed reactor.

Materials Compatibility

A series of materials-compatibility runs was made to define the limitations of potential materials of construction for the experimental facility.

The order of stability of various stainless steels in air at 950 C was:

$$310 > 308 > 347 > 316 > 304$$

with the weight gain due to scale formation on the 310 SS being 2×10^{-6} g/cm²/hour. This rate of oxidation corresponds to ~ 0.002 inch per year penetration on the basis of the more conservative linear extrapolation. The anticipated lifetime would increase to the extent that corrosion follows a parabolic relation. Thus, 310 SS should be satisfactory in air-exposed structures at 950 C if proper support is provided to compensate for decreased strength and possible creep.

In exposure of molybdenum* and stainless steels (304 and 310) to graphite at 950 C for 76 hours in argon, the molybdenum picked up negligible weight, whereas the carbon pick-up by the 304 and 310 SS corresponded to 0.86 and 0.14 inch per year, respectively, of Fe_3Cr formation (linear extrapolation). Thus, it is concluded that 310 SS will be marginally acceptable for use in contact with graphite at 950 C with air on the outside; however, care will be necessary to avoid long-term thermal excursions above that level to avoid excessive carburization.

Samples of 304 SS were exposed to the miniplant by-product condensate at 350 C [below the melting point of zinc (429 C)] and 500 C in argon for

* Potential coating for stainless steel.

100 hours with the thought that bare stainless steel might be substituted for graphite-lined stainless steel in certain cases. The condensate contains zinc chloride, zinc, and some finely divided silicon in the approximate weight ratio of 77/22/0.1. A coating of the θ phase (~ 6 a/o Fe) in the Zn-Fe system formed; however, spectrographic analysis revealed no iron, nickel, or chromium in the condensate. On the basis of the more conservative linear extrapolation, the θ -phase formation corresponded to 0.05 and 0.2 inch per year at 350 C and 500 C, respectively. On the basis of parabolic extrapolation, the rate would be 0.007 and 0.026 inch per year. In light of this and prior information, it was thought to be feasible to use stainless steel in contact with zinc chloride, but probably not in contact with zinc, at up to 500 C.

In further exploration of this prospect, the compatibility of 304 SS with the by-product condensate at 350 C for 270 hours was studied. No appreciable change was noted in the appearance of the 304 SS coupon except for its acquisition of a zinc-rich (θ -phase) coating which probably accounts for the very slight weight increase corresponding to $<3 \times 10^{-5}$ inches per year, linear, or $<5 \times 10^{-4}$ inches per year, parabolic, growth. The latter data, indicating arrested corrosion, are not entirely consistent with the former; however, the difference may be a question of limit of error. On the basis of structural considerations alone, it would appear that a stainless steel rather than the more expensive graphite-lined tank would be suitable for storing the condensate at 350 C. It remains to be determined whether impurities would be transferred from the stainless steel which cannot be tolerated. Further, if unlined stainless steel is contemplated, where apparently feasible, it would be prudent to recheck the corrosion rates using welded specimens.

Two design features of the 50 MT/year facility require the cooling of graphite by Therminol (high-temperature organic heat transfer medium mentioned earlier). It is probably necessary* to render the graphite impervious to Therminol to prevent contamination of the process stream even though this

* It is conceivable that small quantities of leakage might be tolerated if self-healing reactions occur on the process stream side or if the evolution of volatile material is slow and free of deleterious impurities.

material contains only carbon, hydrogen, oxygen, and silicon in excess of 1 ppm.* To accomplish this, coating/impregnation of the Therminol side of the graphite surface with a carbonizable resin or pyrolytic graphite (PyC) was explored. The following resins were evaluated.

Cement No. 15	- Union Carbide Corporation, Cleveland, Ohio
Cement No. 14	- Union Carbide Corporation, Cleveland, Ohio
BKS-2600 Phenolic Plastic	- Union Carbide Corporation, Cleveland, Ohio
Resinox Resin SC 1008	- Monsanto, New York, New York
Ironsides Resin FF-17	- Ironsides, Columbus, Ohio
Ironsides Resin DP 25-10	- Ironsides, Columbus, Ohio

Coated crucibles were filled with Therminol, heated to 370 C, and observed for penetration and/or leakage.

In this brief study, only PyC imparted the required imperviousness to the graphite. Cement No. 15 and Resinox provided the best protection under the conditions tested although it was tentatively concluded that if their curing cycle, dilution, and method of application were optimized, any of these resins could provide the protection required.

As pointed out in an earlier section of this report, an alternative to direct contact of the Therminol with the graphite is being considered which will be reported later.

Product Quality

To provide JPL with material for quality evaluation, Runs 96, 97, and 98 were made in the miniplant during the report period. Figure 11 (a continuation of Figure 8 of the Ninth Quarterly Report) shows the "geneology" of this material. In Runs 97 and 98, the content of semiconductor-grade seed in these products was reduced to 5.6 percent and 7.4 percent, as the

* Mg, Fe, and Cu were below the detection limit of 100 ppmw. Silicon was present at 80 ppmw.

458 g of 105 x 149 μ m semiconductor-grade seed
(Run 91)

FIGURE 11. PREPARATION OF QUALITY EVALUATION MATERIAL

(The upper number in each group is the weight of the starting material, the middle number in parentheses is the run number, and the lower number is the weight of the product of that run. The bracketed number is the seed content of that product in percent. The notes to the right indicate disposition.)

weighted average particle size increased from 120 μm to 307 μm and 278 μm , respectively.

Although it is expected to be less of a problem in the larger experimental facility, condensation of zinc on the product (as semicontinuously withdrawn from the tube at the bottom of the bed) was observed in the miniplant. In the extreme, condensation of zinc or ZnCl_2 has been observed to plug the withdrawal tube. Proper operation of the product withdrawal system depends upon balancing the purge gas flow in the exit line so that pressure surges in the reactor do not drive the zinc or ZnCl_2 vapor down the withdrawal tube to where the temperature of the tube and its contents is below the dew point of the vapor. This requires a balance of purge rate. It is obvious that the product should be withdrawn slowly and as nearly continuously as possible. Surges of product result in displacement of the vapor in the interstices. High rates of purge are beneficial in limiting penetration of vapor into the withdrawal tube as the pressure at the bottom of the bed fluctuates. However, cooling of the exit tube increases with increasing purge, driving the zone at the dew point of the vapor closer to the reactor and making it more accessible to condensation during pressure surges. Clearly, a balance must be struck. Independent heating of the product withdrawal tube would be beneficial; however, this is not easily done in the design configuration shown in Figure 4 where the SiCl_4 preheater surrounds the tube.

The actual zinc content of the granular silicon is uncertain, spark source mass spectrometric analyses ranging from 140 to 3000 ppmw. A series of experiments is being run to determine (1) what part of the zinc is on the surface (e.g., as condensate), (2) what part has been entrapped in the growing granules, and (3) what part can be removed by a simple heat treatment.

As it was not possible in the work done by Dow Corning/Westinghouse and by Motorola (DOE/JPL LSA Task I) to dope silicon with zinc due to the high volatility of the latter, it is not known to what extent zinc is detrimental to solar cell performance, nor to what extent its content must be limited to avoid problems in wafer or ribbon growth. It is expected that information on these points will be forthcoming from JPL and its contractors.

in evaluation of the 6.1 kg of silicon granules supplied. In the meantime, spark-source mass spectrometric analyses have been run at BCL to obtain information on the purity of the product.

To avoid possible contamination in melting, most of the analyses made at BCL have been run on as-produced granules, pressed into high-purity graphite powder in a polyethylene disc to form an electrode for use in the mass spectrometer. The basic problem with this procedure is that only one or a few granules are "seen" in the analysis and, of these, only the outer layers are analyzed. Thus, a given analysis cannot be assumed to be representative of a lot, nor can the contribution of impurities from the seed be traced from one run to the next in a sequence of the type shown in Figure 11.

It is too early to base conclusions on the results of the analyses of the materials that have been sent to JPL. Blanks and other samples of high-purity, single-crystal silicon are being run to assess the reliability of the analyses and to explain the observed inconsistencies.

In the best analyses (indicative of what may be ultimately attainable), only zinc (140 ppmw), sulfur (2 ppmw), chlorine (20 ppmw), and iron (<3 to 5 ppmw) are consistently above 1 ppmw.

Miscellaneous

During this report period, experiments were conducted to test or verify certain design features of the 50 MT/year facility.

In two areas of the waste treatment section of the 50 MT/year unit, reaction of the waste with a sodium hydroxide solution in eductors is planned. On the basis of prior experience with mixing SiCl_4 and NaOH solutions, it was feared that plugging of this type of device might preclude its use. Accordingly, it was considered prudent to evaluate its use before a final design was adopted. A model LL 3/4 eductor* was determined to effectively handle SiCl_4 gas (at 65 g/minute) in a ~50 mole percent SiCl_4/N_2 stream when contacting water, without any evidence of plugging. Treatment with NaOH

* Mart Engineering Company, Cincinnati, Ohio.

should be even less of a problem, because of greater solubility (as sodium silicate) of the hydrolysis product.

In the 50 MT/year facility, a few graphite slip joints have been used for simplicity of design. These are located in areas where liquid zinc chloride provides a seal. It was determined that liquid ZnCl_2 at 700 C under approximately a 2-inch head would not penetrate a graphite slip joint having a 0.007-inch clearance.

The potential for penetration of graphite by the Therminol heat-transfer solution and the need for extracting heat from the anode of the electrolytic cell has prompted the evaluation of an alternative design. This involves the use of a metal-enclosed Therminol exchanger positioned in a well in the graphite, packed with copper shot to improve heat transfer. This system has been used satisfactorily at BCL but whether or not it is practical to use under the particular heat transfer conditions of the 50 MT/year facility for which it is being considered will depend on the overall heat transfer coefficient that can be achieved. This cannot be calculated with any degree of confidence, and consequently, must be determined experimentally. Plans are to accomplish this during the next quarter.

PLANS FOR THE NEXT REPORT PERIOD'

50 MT/Year Si Facility Design

Work planned for the next report period in the area of design includes

- (1) Critique of the RKAI and Pace designs by BCL personnel
- (2) Refinement of cost estimates for the 50 MT/year experimental facility
- (3) Revision of cost estimates for a 1000 MT/year facility
- (4) Review of equipment design with the objective of simplifying and improving.

Experimental Support

Work planned for the experimental support area includes

- (1) Continued operation of the experimental ZnCl_2 electrolysis cell to obtain general operating experience and specifically to evaluate the extent of sludge formation
- (2) Continued study of the full-scale mock-up of the fluidized bed
- (3) Determination of the reliability and meaning of the analytical results on the miniplant product
- (4) Determination of the conditions for essentially freeing the product of zinc
- (5) Verification of inventory and rate of vaporization control of the zinc vaporizer via electrical parameters of the induction heating system

- (6) Continued evaluation of Therminol/graphite heat transfer methods not involving direct contact
- (7) Continued improvement in the resin coating of graphite to render it impervious to Therminol.