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DOE/JPL/954339-80/16,17

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

Sixteenth/Seventeenth Quarterly Progress Report for July 1–December 31, 1979

By
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March 7, 1980

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

Battelle
Columbus Laboratories
Columbus, Ohio

D15T-355
NT15-25

U.S. Department of Energy

Solar Energy

R98

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SIXTEENTH/SEVENTEENTH QUARTERLY PROGRESS REPORT
Covering the Period July 1 to December 31, 1979

on

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

JPL Contract 954339

Silicon Material Task
Low-Cost Solar Array Project

to

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY

by

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

March 7, 1980

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

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

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ACKNOWLEDGEMENT

The authors gratefully acknowledge the capable assistance of the following individuals in the performance of the work and preparation of this report: Mrs. Viki L. Breckenridge, Mr. Theodore B. Buyers, Mr. James S. Fippin, Mrs. Pamela S. Kerbler, Mr. David W. Pickett, Mr. Nicholas E. Popovich, Mr. Erlan E. Rose, Mr. David A. Seifert, Mr. Edgar A. Wasto, and Mr. Jack G. Wiley of Battelle's Columbus Laboratories; and Mr. W. R. Ackley and associates of Raphael Katzen Associates International, Inc., Cincinnati, Ohio.

TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGEMENT	ii
ABSTRACT	1
INTRODUCTION	2
PDU ACTIVITIES	3
EPSDU-to-PDU Design Changes Not Previously Recorded	4
Coating of the Fluidized-Bed Graphite Liner	8
Check of Therminol Heat-Transfer System	10
EXPERIMENTAL SUPPORT	10
Zinc Feed System Studies	10
Elimination of Residual Zinc from the Product	12
Prospects of Decreasing Residual Zinc Content of the Product	27
Post-Process Treatment of Product for Zinc Removal	28
Results from Other Laboratories	29
PLANS FOR NEXT PERIOD	30
REFERENCES	32

LIST OF FIGURES

	<u>Page</u>
Figure 1. PDU Flow Diagram, Reaction Section	5
Figure 2. PDU Flow Diagram, Reaction Product Treatment Section . .	6
Figure 3. PDU Flow Diagram, Heat-Transfer System	7
Figure 4. Idealized Run-98 Miniplant Product	15
Figure 5. Cross Section of Run No. 98 Particles	15
Figure 6. Cross Section of Agglomerate From Run 98	17
Figure 7. X-Ray Image of Zinc in Run-98 Particles	17
Figure 8. Electron Probe Traces of Run-95 Particle for Zinc . . .	19
Figure 9. Reactor Designs Used in Miniplant	25

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ABSTRACT

Construction of the PDU was completed during the report period, the fluidized-bed reactor was coated internally with silicon/SiC, and the operation of several systems was checked out. However, problems with the zinc feed system, unrelated to its basic operability, delayed introduction of zinc vapor to the PDU. At the end of the report period, the zinc feed system stood ready for tests of the control of zinc vapor feed rate by regulation of r.f. induction heating directly coupled to the liquid zinc.

A study of the zinc distribution in miniplant silicon products containing zinc at the 300 and 3000 ppm levels suggests that the occlusion of zinc is caused by zinc mist entrained from the vaporizer, and it should be possible to drive the level to below 300 ppm by proper equipment design and process control.

INTRODUCTION

This Sixteenth/Seventeenth Quarterly Report is the fifth of the Phase-III effort at Battelle's Columbus Laboratories (BCL) for DOE/JPL on the Evaluation of Selected Processes for the Production of Low-Cost Silicon. Phase III has as its ultimate objective the construction and operation of an Experimental Process System Development Unit (EPSDU) for the production of granular semiconductor-grade silicon by the zinc vapor reduction of silicon tetrachloride in a fluidized bed of seed particles.

Work during this report period was concentrated on completion of the construction of the Process Development Unit (PDU) consisting of four critical units of the EPSDU, the fluidized-bed reactor, the reactor by-product condenser, the zinc vaporizer, and the electrolytic cell. The critical units of the PDU are of the full-scale EPSDU design so that their operability in a batch mode (8-hour) can be evaluated and appropriate changes made, if necessary, prior to committing them to operation in the EPSDU. It is believed that in this way, considerable time can be saved in the initial operation of the EPSDU that might normally be taken in design modification activities.

A decision has been made that rather than to operate the PDU for a period of 4 months and then proceed to the construction of an EPSDU, the PDU operation will be continued through October of 1980 to obtain engineering data applicable to the EPSDU. Another change in plans was the decision to use high-purity seed and semiconductor-grade SiCl_4 and to obtain as much data on product purity as possible within the inherent limitations of the PDU design.

As the major project activity during the six months covered by this report related to the construction of the PDU, it was agreed with JPL that the issuance of a quarterly report at the end of September was not warranted. Accordingly, the two quarters are covered in this combined report.

In addition to the PDU construction, the experimental support activity was continued with the zinc feed system, and with elimination of residual zinc from the product.

These topics are discussed in turn.

PDU ACTIVITIES

The period covered by this report was marked by completion of construction of the PDU. When the PDU construction and installation schedule (See Figure 1 of the Fifteenth Quarterly Report⁽¹⁾) was set up, it was recognized that to achieve the start-up date of October 1, 1979 at the end of a brief 6-month design and construction period would require that no major delays be encountered in the shipment of materials and equipment, or for other reasons. Although some changes in design were made to permit substitutions for long-delivery materials, unforeseen delays of that nature, plus the need for correcting errors in fabrication which required returning some units to the vendors for reworking, resulted in an overall schedule slippage of about two months.

Although work had been started earlier to evaluate and optimize the performance of the zinc feed system remote from the PDU, delays and problems were encountered so that when the PDU construction had been completed, the zinc feed system was not considered sufficiently reliable to be used on the PDU. Accordingly, it was decided to continue to develop the zinc feed system until the reliability of its operation could be assured.

In this section of the report, several aspects of the PDU construction not covered in the last Quarterly Report are discussed. The zinc vaporizer qualification experiments are discussed under Experimental Support although they deal with a component of the PDU.

The process flow sheet was given as Figure 1, pages 6 and 7 of the Fourteenth Quarterly Report⁽²⁾. Changes in design of the individual units from those of the EPSDU design (given in the Phase I/II Final Report⁽³⁾ and the Eleventh/Twelfth Quarterly Report⁽⁴⁾), are also noted in the Fourteenth Quarterly Report⁽²⁾. Additional changes not previously recorded are noted below, followed by a section on the procedures used to coat the graphite liner of the fluidized-bed unit, and a discussion of tests on the Therminol heat-exchange system.

EPSDU-to-PDU Design Changes Not Previously Recorded

Figures 1, 2, and 3 are flow diagrams of the PDU incorporating the following changes made since Figure 1 of the Fourteenth Quarterly Report(2).

- (a) Therminol System: heat exchanger shown on discharge side of pump rather than suction side.
- (b) SiCl_4 supply system modified to show pressurized syphon feed of liquid to TET vaporizer rather than gravity flow.
- (c) Addition of argon purge to ZnCl_2 condenser shell.
- (d) Addition of temperature monitoring capability to electrolytic cell.
- (e) Addition of flow indicator and argon purge to chlorination gas supply.

As discussed in the text, but listed here for sake of completeness, the following additional changes were made:

- (a) Reactor liner material changed from "Graphitite-A" to Stackpole "2020", coated on the outside with carbonizable resin and on the inside with Si/SiC.
- (b) The stainless steel sheath protecting the graphite piping between zinc liquid tank and zinc flow control valve was eliminated.
- (c) Specifications on the quality of SiCl_4 and silicon seed materials were changed to high-purity SiCl_4 and semiconductor-grade silicon seed material.

FIGURE 2. PDU FLOW DIAGRAM, REACTION PRODUCT TREATMENT SECTION

FIGURE 3. PDU FLOW DIAGRAM, HEAT-TRANSFER SYSTEM

Coating of the Fluidized-Bed Graphite Liner

As pointed out in the Fourteenth Quarterly Report(2), the silicon carbide-coated graphite liner of the EPSDU design could not have been provided within the time allotted for PDU construction. Although Graphitite-A, a high-density impervious graphite from the Carborundum Company, was planned as a substitute, the promised delivery date on that material could not be met. Accordingly, a decision was made to go with available Stackpole 2020 graphite which is fine-grained ($<0.0043\text{cm}$), reasonably dense (1.72g/cm^3) but porous (19.2%), and to coat it to make it impervious. Its thermal expansion ($4.2 \times 10^{-6}/\text{C}$) is a reasonable match for silicon carbide ($4.9 \times 10^{-6}/\text{C}$), and is not far from that of silicon ($3.7 \times 10^{-6}/\text{C}$).

Sealing of the pores of the graphite liner is prompted by the desire to minimize contact between the zinc vapor on the inside of the reactor and the stainless steel shell surrounding it. Accordingly, the liner parts were coated externally with a carbonizable resin before assembly and then coated on the inside with silicon in situ after assembly.

The following 4 resins have been used to varying degrees at BCL for decreasing the permeability of graphite to gases:

(1) UCAR-15	Union Carbide Corporation
(2) UCAR-14	Union Carbide Corporation
(3) Resinex SC-1008	Monsanto Corporation
(4) Ironsides DP25-10	Ironsides Resins Company, Inc.

To study the suitability for the PDU application, coupons of Stackpole 2020 graphite were used to optimize the resin coatings for reduction of porosity. Various dilutions of the as-received resins with methylethyl ketone (MEK) were evaluated by coating the coupons, heating them in a controlled manner to $\sim 900\text{ C}$, and ultimately comparing their permeability with that of an uncoated coupon. The best results obtained thus far have been with UCAR-14 diluted in a ratio of 3 parts (volume) resin to 1 MEK and applied in two steps. The porosity of the 2020 graphite was reduced from 0.056 darcy to 0.003 darcy. UCAR-14 diluted with MEK as above was applied liberally to the graphite liner parts, air dried for 2 hours, and then dried

at 160 F for 2 hours. After cooling, a second coat was applied and dried in the same manner. The coating (2 layers) was then cured at 200 F in air for 12 hours.

After assembly of the externally coated graphite reactor liner, the reactor was heated with an argon purge to ~ 900 C at a rate of 100 degrees/hour to cure the resin coating and check operability and control of the reactor furnace. The reactor temperature was then lowered to 700-750 C for silicon coating of the graphite liner bore by thermal decomposition of trichlorosilane (SiHCl_3), 10 percent in argon, to further reduce porosity and to decrease the introduction of impurities from the liner. The coating run was conducted over a 72-hour period with SiHCl_3 being introduced alternately through (1) the product discharge port of the reactor (for coating of the main fluidized bed chamber), and (2) silicon tetrachloride (SiCl_4) inlet port (for coating of the graphite-packed SiCl_4 preheater section).

To spread the coating reaction over the entire reactor, the temperature was regulated to limit the rate of reaction so that the reactant was no more than 20 percent depleted at the exit. Monitoring of the coating reaction was done by condensing the SiHCl_3 and SiCl_4 in liquid argon, converting the hydrogen from the reaction $4\text{SiHCl}_3 \rightarrow \text{Si} + 3\text{SiCl}_4 + 2\text{H}_2$ to water, and measuring the dew point of the resulting gas.

Cylindrical graphite specimens suspended in the reaction chamber were examined after the coating run. A dense silicon coating of $1\mu\text{m}$ to $4\mu\text{m}$ thickness was observed, indicating successful coating of the reactor interior. Visual observation of the walls made with a borescope after the run showed the coating to be smooth and typical of silicon on graphite, with only few protruberances having formed, located at the entrance to the by-product discharge nozzle.

Check of Therminol Heat-Transfer System

Although it would be desirable to have the full heat load of normal PDU operation during the check-out of the Therminol heat-exchange system to the condenser, opportunity was taken of the delay in achieving rated vaporization rate from the zinc vaporizer to check the "idling" condition of the Therminol system. Gas burners were used to preheat the Therminol. Slow heating was used at first to cure and bake out the heat-transfer cement used to couple cooling coils to the condenser. Vigorous heating of the system was then carried out to raise the temperature of the entire condenser to 350 C. The five parallel heating circuits provided very uniform temperature over the entire condenser length. The Therminol flow appeared to be lower than expected but that problem was traced to the vendor's supplying an incorrect calibration of the target flow meter used to monitor the flow.

EXPERIMENTAL SUPPORT

Work in the area of experimental support during this report period was tailored to avoid interference with the PDU construction schedule. However, significant progress was made, as recorded below, in the following areas:

- (1) Zinc feed system studies
- (2) Elimination of residual zinc from the product.

Zinc Feed System Studies

Although a hastily assembled laboratory mock-up of the zinc vaporizer designed for the PDU had been satisfactorily operated to show that a vaporization rate of 1 lb/minute of zinc (PDU requirement) could be obtained by direct coupling of ~450kHz r.f. energy to the zinc, it was believed prudent to pretest the entire zinc feed system (melt down tank, intermittently operated liquid flow-control valve, and vaporizer with resistance-probe level sensing) before connecting it to the PDU fluidized bed.

Several shortcomings were detected and corrected in sequence and the revised system stood ready at the end of the report period for tests of the most critical point, i.e., whether the more loosely coupled coil of the energy-conserving PDU design would be equally effective, or whether unforeseen differences would be found. Unfortunately, the design shortcomings revealed in the initial check-out runs did not permit operation of the vaporizer for a sufficient length of time to reach that point in the evaluation.

The first problem related to a leaking joint at the point where the liquid zinc line joins the zinc-supply crucible. The joint design had been accepted as a less-than-optimum time-saving expedient to accommodate an existing crucible pending receipt of the more satisfactory crucible. When that problem had been corrected, it was found that the support of the zinc supply crucible and surrounding tank was more critical than anticipated, in that with a full load (500 pounds of zinc) it settled to the point of breaking a joint in the jacketed graphite delivery line for liquid zinc.

It was decided that since graphite does not oxidize readily at 500 C, it would be preferable to leave the line unjacketed and increase the size of the joint in question. With that problem corrected, and a less yielding tank support provided, a malfunction of the feed-control valve was noted (leakage through the seat). As the valve had experienced some unusual circumstances in the initial tests, it was not evident that the observed leakage represented a design deficiency. Hence, a replacement valve was made without modification and substituted. With the liquid zinc feed problems corrected, it was found that when the zinc vaporization rate approached ~30 percent of the design capacity, a constriction developed at the exit ($\Delta p = 5-6$ psig). This was traced to a subtle difference between the design of the PDU vaporizer and that of the laboratory mock-up that allowed a carbon-fiber disentrainment barrier to be dislodged and driven into the exit line, thus constricting it prohibitively.

Several additional operational problems relating to thermal expansion mismatches, and plugging of the zinc collection system were time-consuming in making the zinc feed system operational. On correction of these problems, the vaporizer was ready at the end of the report period for the induction-coupling experiments.

Elimination of Residual Zinc from the Product

Although only a few samples of the silicon product of the present process have been analyzed for zinc, the available data reflect residual zinc concentrations of from 360 to 3900 ppmw in the deposited product (after correcting for seed content). Depending upon how low the concentration can be driven, the residual zinc may or may not be subject to handling in the wafer or ribbon forming operation. However, it is prudent in the present program to decrease the zinc content to the maximum extent practical by appropriate choice of process design and operating parameters. It is also prudent to study techniques for reducing the residual zinc content still further by post-process treatment. Accordingly, a program is being undertaken with the objective of eliminating residual zinc from the product.

The approach is (1) to study the distribution of zinc in the product and to relate it to the process parameters which would then be appropriately modified, and (2) to study the rate of zinc evaluation on heat treating the product particles in a vacuum. Whether heat treatment in a vacuum or in an inert gas is chosen on the basis of economy, the rate of zinc removal will be limited ultimately by the rate of transport of zinc through the particles. This, and the convenience of being able both to evolve and to condense the zinc in small sealed ampoules, prompted the planned use of vacuum heat treatment in these studies.

Silicon Products Available for Study. Two different types of product are available for study, both resulting from experimental runs in the "miniplant" during the period from October, 1976 to February, 1978. In the early runs, made with metallurgical grade seed material, the operating parameters of the miniplant were being varied in an effort to evolve an operative process. Semiconductor-grade seed was ultimately substituted and a set of nominal operating parameters adopted for the preparation of quality evaluation specimens for delivering to JPL. Table 1 lists the geneologies of these products with the particle sizes, seed contents, and analyses, where available. Some of the material in the quality evaluation series (Runs 91-98) was given a vacuum heat treatment, ostensibly to remove

TABLE 1. SILICON SAMPLES AVAILABLE FOR ZINC-CONTENT STUDIES

Run No.	Source of Seed ^(a)	Final ^(b) Diameter, μm	Seed ^(a) Content, Percent	Vacuum ^(c) Heat Treatment	Chlorine Content, ppmw, in Whole Particle	Zinc Content, ppmw		Method ^(d) of Analysis
						In Whole Particle	In Deposited Silicon	
50	Runs 43, 44 45, 46, 47	318	~50.0	No	-	180	360	AA
51	210 X 297 μm crushed semiconductor-grade silicon	350	63.0	No	5	20	54	SSMS
91	125 μm crushed semiconductor-grade silicon	147	61.6	No	-	-	-	-
92	Run 91	180	33.3	No	-	-	-	-
93	Run 92	206	22.6	No	30	3000	3900	SSMS
94	Runs 91, 92	188, 220	24.9	No	-	-	-	-
95	Run 94	226 258	14.7	No	30	1700	2000	SSMS
96	Run 94	242 274	12.0	No	20	2000	2270	SSMS
97	Run 96	315 347	5.6	Yes	100	1500 3000 1470	1590 3200 1560	AA SSMS NA
98	Run 96	286 317	7.4	Yes	-	2000 1520	2160 1640	SSMS NA

(a) The seed bed for Run No. 50 was made from the 250/295 μm sieve fraction of the products of Runs 34, 44, 45, 46, and 47. As the original seed for these products was metallurgical-grade silicon, and as the then-current interest was in process characteristics rather than product purity, no record was kept of the relative amounts of the precursors of Run 50 making up its seed bed. Thus, the seed content (fraction of metallurgical-grade silicon relative to total) cannot be calculated and is therefore estimated from metallographic observation of sectioned product particles.

(b) The particle diameter is calculated by assuming that the observed weight of 100 percent dense silicon is deposited uniformly on a spherical seed particle of diameter equal to the average of the screen sizes defining the initial seed bed. Where a seed bed for a given run contains products from two prior runs, two diameters are given for the product of that run (and subsequent runs of the series) calculated from the sizes and numbers (calculated from weight and size) of precursor particles on the assumption that the radial increment during deposition is uniform over all particles.

(c) 12 hour, 920 C, in vacuum

(d) AA = atomic absorption (Battelle-Columbus)

NA = neutron activation (Lawrence Radiation Laboratory⁽⁵⁾)

SSMS = spark source mass spectrometry (Battelle-Columbus)

surface zinc that may have condensed during termination of the miniplant runs. As it turns out, some of the residual zinc contained in the body of the particles may also have been removed in this heat treatment*.

In the case of the product for which comparative analyses are available (Run 97), the atomic absorption and neutron activation analyses are seen to be in good agreement.

Both the neutron activation and atomic absorption analyses give the average over many particles constituting the sample. By contrast, the spark source mass spectrometer analysis "sees" only parts of one or a few particles, and any inhomogeneity in the product would be reflected in the analysis. It is significant that the chlorine analysis is low, indicating that the zinc is present predominantly in the elemental form rather than as the chloride. This is borne out by the results of vacuum heat treatment in which a condensate of zinc forms with no evidence of the more volatile ZnCl_2 or SiCl_4 (a possible product of back reaction: $2\text{ZnCl}_2 + \text{Si} \longrightarrow \text{SiCl}_4 + \text{Zn}$).

Particle Structure. Figure 4 shows schematically the growth pattern for the sequence leading to the Run No. 98 product. Figure 5 is a photomicrograph showing two particles from the Run No. 98 product. The particles have been etched with an HF/HNO_3 mixture which does not reveal any structure in the semiconductor-grade silicon core, but dissolves out large ($1\text{--}10\mu\text{m}^2$) localized areas of deposited silicon. The ringed growth structure becomes clearly delineated.

Very little porosity is present in the as-deposited particles which measure 99.6 percent of theoretical density⁽⁴⁾ and some of that porosity is noted in the as-polished structure (see unetched (masked) area). However, the action of the HF/HNO_3 mixture in dissolving local areas of silicon is marked and rapid, implying that the silicon that dissolves out is highly defected and chemically active. Etching with HCl alone (which would dissolve exposed zinc) does not create similar voids. Thus, while zinc may be associated with the points at which the etching originates,

* If all of the weight loss during vacuum heat treatment is attributed to zinc, 1090 ppm was lost from the product of Run No. 97, and 1280 ppm from that of Run No. 98.

FIGURE 4. IDEALIZED RUN-98 MINIPLANT PRODUCT

FIGURE 5. CROSS SECTION OF RUN NO 98 PARTICLES

the large void fraction developed by the etch can not have been initially present and filled with zinc. Thus, the zinc must be contained in the pores that are visible on a macro scale in the as-polished condition or in a submicron defect structure not visible in the as-polished or HCl-etched condition.

About 0.2 percent of the product of Run 98 was present in the seed material as agglomerates. Figure 6 shows the cross section of a typical agglomerate which is found to consist of a cluster of silicon granules bound together by a weblike network of silicon. Although not visible in Figure 3, the silicon forming the walls of the voids contains many faceted particles of the type observed in the past to have been associated with the formation of silicon by reaction of $\text{SiCl}_4(\text{g})$ with liquid zinc. Although the agglomerates are totally coated with silicon and are inert to dilute HCl, the fragments of crushed agglomerates react with HCl to release gas bubbles presumably hydrogen, by the reaction $2\text{HCl} + \text{Zn} = \text{H}_2 \uparrow + \text{ZnCl}_2$, indicating the presence of residual occluded zinc.

The structure of the agglomerates and the presence of residual zinc suggests that the agglomerates may have formed when "large" droplets of liquid zinc reached the fluidized bed from the zinc vaporizer, with silicon being formed in sufficient quantity to bond the particles together and completely coat the agglomerates before the zinc had entirely evaporated.

Electron Microprobe Examination of Particles. Particles from Runs 93, 95, 97, 98, and 50 were examined with the electron microprobe (EM) to study the distribution of zinc. Figure 7 shows an image of the particle from Run 98 created by X-ray emission from the zinc contained in the particle. The larger white spots are evidence of high concentrations of zinc. The fine white dots are background.

Figure 8 shows three parallel EM traces across a Run 95 particle about $15\mu\text{m}$ apart. The silicon trace is the relatively steady line extending from one edge of the particle to the other. The background of the widely fluctuating zinc trace (at higher sensitivity) would mask zinc concentration of <400 ppm. However, many segregated zinc peaks were seen corresponding to concentrations as high as 2.6 percent in the 0.7 to $1.0\mu\text{m}^3$ spot volume. Some particles showed zinc peaks at the particle surface (edge of the cross section) and some did not. Others showed zinc on one side of a particle

4999 VD

50X

FIGURE 6. CROSS SECTION OF AGGLOMERATE FROM RUN 98

5034 VD

500X

FIGURE 7. X-RAY IMAGE OF ZINC IN RUN 98 PARTICLE

cross section and not on the other. Since zinc peaks as narrow as $2.6\mu\text{m}$ are observed, the resolution is good, and, as indicated by the differences in the parallel traces of Figure 8, the residual zinc in the particles examined is highly segregated.

It is unfortunate that the optical imaging device was not operative when these scans were made, so the high concentration of zinc cannot be correlated with the growth ring structure. However, such a correlation is suggested and may eventually be found as it is in the area of growth interruption where the greatest porosity appears to be.

In the case of particles from Runs 93, 95, 97 and 98, the zinc is definitely not present as a uniformly distributed 1500 ppm or whatever the concentration may be. Without making a large number of scans of the particles from Runs 93, 95, 97, and 98, it would not be possible to confirm any differences that might be attributable to differences in average zinc content. By contrast, it was difficult to find any zinc in particles from Run 50 whose average zinc content was 360 ppm in the deposited silicon. The few peaks that were found were perhaps twice the 400 ppm background, but because of some unexplained iron inclusions in the Run 50 product* at which the zinc background is raised, it cannot be concluded that the observed peaks are actually attributable to zinc. A concurrent scan of zinc and iron, which was not made at the time, would be needed to settle that point.

It can be concluded, however, that the Run-50 product did not contain the localized high concentrations of zinc associated with the particles from Runs 93, 95, 97, and 98.

Correlation with Run Conditions. In light of the above observations, it becomes of interest to identify the difference between Runs 50 and 51 and the others, which might account for the dramatic difference in the residual zinc content, and which might shed light on the reason for the occluded zinc being widely segregated rather than uniformly distributed, as would be the case for zinc trapped in a uniform defect structure.

Table 2 lists the factors in the miniplant operation that relate to the zinc feed system and that might be expected to influence the mode and degree of zinc occlusion. They are: (1) reactor/zinc vaporizer design,

* Possibly originating the metallurgical grade seed.

FIGURE 8.

TABLE 2. SUMMARY OF RUN CONDITIONS BELIEVED
TO INFLUENCE RESIDUAL ZINC CONTENT

Run No.	Reactor ^(a) Design	Seed Bed	Bed (b) Temperature, °C		Zinc Flow Rate, g/minute	Zn/SiCl ₄ Mole Ratio	Zinc Content of ^(c) Deposited Silicon, ppmw
			Bottom	Top			
50	A	From Runs 43, 44, 45, 46, 47 (250 X 297µm) Metallurgical- Grade Silicon	927	927	33.7	1.79	360
51	A	~270µm Semiconductor- Grade Silicon	927	927	19.5	1.63	(54)
91	B	~125µm Semiconductor- Grade Silicon	925	890	36	1.95	-
92	B	Run 91	930	890	34.9	1.91	-
93	B	Run 92	920	900	36.3	2.05	(3900)
94	B	Runs 91, 92	920	900	36	1.94	-
95	B	Run 94	925	900	36	2.09	(2000)
96	B	Run 94	920	900	36	2.03	(2270)
97	B	Run 96	930	900	26.8 ^(d)	1.51 ^(d)	1560
98	B	Run 96	925	900	35.8	1.96	1640

Footnotes appear on the following page.

FOOTNOTES FOR TABLE 2

- (a) Runs 50 and 51 were made with a cone-bottom reactor of Design A, Figure 9. Runs 91-98 were made with a hemispherical bed support of Design B, Figure 9.
- (b) The "graded bed temperature" was used in Runs 91-98 as it had been found in the interim to increase the overall efficiency and rate of deposition of silicon due to the equilibrium shift to the right of the exothermic reaction

with decreasing temperature.

- (c) The zinc content is given for the "most reliable" analysis available. The parenthetical values are from spark-source mass spectrometry, the limitations of which are discussed in the text.
- (d) Zinc feed rate intended to be that of preceeding run; wrong gear ratio on displacement feeder inadvertently used.

(2) fluidized bed temperature, (3) origin of seed bed, (4) rate of zinc input, and (5) stoichiometry.

Table 2 also repeats analyses given in Table 1.

The obvious correlations of residual zinc content in Table 2 are with (1) reactor design (See Figure 9 for design), (2) use of the graded bed temperature, and, possibly, (3) with stoichiometry. As will be discussed below, all of these correlations are in the direction expected and it is impossible at this point to assess the contribution of the individual factors to the incidence of residual zinc in the product.

Additional Observations. The assumption that at least a portion of the zinc is distributed in a network of very fine surface-connected porosity is strongly supported by the observation that when the vacuum heat-treated products of Runs 97 and 98 were exposed to air, they experienced a pronounced temperature rise, from 39 C to 109 C in the case of the Run 98 product for which the temperature rise was measured. Assuming that all of the heat went into raising the temperature of the silicon, this amounts to 350 calories per mole of silicon. If the thermal effect is due to the oxidation of silicon in air ($\Delta H_f \text{SiO}_2 = 204.53 \text{ Kcal/mole}$), this corresponds to $350/204,530 = 0.17$ percent of the silicon oxidized or 0.02cc of silicon per mole.

If the oxidized silicon formed the walls of 0.01 μm -diameter capillaries originally occupied by the 1380 ppm zinc that was evolved from the deposited silicon in the heat treatment, 29 monolayers of silicon would have been oxidized to account for the heat effect, a reasonable possibility. By contrast, if only the outer surface of fully dense silicon particles of this size were oxidized to produce the heat, 300 monolayers would have to be oxidized which is improbable. Further, the outer surface had already been exposed to air. The pores vacated by the zinc represent the only "nascent" surface. Capillaries smaller than 0.01 μm would require the oxidation of proportionately fewer monolayers of silicon.

It is also possible that the oxidation of freshly exposed zinc contributed to the effect. With a heat formation of 83.2 Kcal/mole, the oxidation of 0.275g of zinc per mole of silicon would be required. However, only 1640 ppm of zinc or 0.046g zinc per mole of silicon remained, not enough to account for the entire heat effect.

Discussion. All of the observations recorded above are consistent with the following postulated mechanism for the occlusion of zinc.

It is suggested that the zinc leaves the flash vaporizer in the form of monatomic zinc vapor and an unknown quantity of zinc mist of various droplet size. When the droplets enter the fluidized bed and contact the bed particles at 920 to 930 C, i.e., 12 to 22 C above the normal boiling point of liquid zinc, the droplets tend to evaporate.

"Small" droplets are believed to evaporate rapidly without leaving appreciable zinc in the product. (It should be noted, however, that any non-volatile impurities in the zinc could be transferred to the product by the evaporation of even "small" droplets.)

"Medium" droplets can cool and wet the silicon and can remain on the surface or be partially absorbed in the very fine interconnected pore structure of the deposited silicon of the particles, or can be concentrated as a meniscus between two temporarily agglomerated particles. These particles then circulate through the bed in the usual manner while the silicon deposits on the exposed zinc and the contained liquid zinc evaporates. During this time, silicon is being deposited on the particles by reaction of SiCl_4 . If the evaporation is sufficiently protracted, the occluded zinc will be trapped in the particles before it has completely evaporated. It should be noted that the acicular silicon that characteristically deposits on liquid zinc exposed to SiCl_4 results in porous structure and in that way can act as a sponge for the next droplet of zinc that hits the particle. In that sense, the mechanism is self enhancing.

"Large" droplets will wet and agglomerate several particles, which together can circulate as a unit pending evaporation of the zinc. The deposition of silicon on the agglomerate by reaction of SiCl_4 with Zn(g) to give the normal product, or with Zn(l) to form larger faceted silicon grains, can first bond the agglomerate together permanently and ultimately coat it over to entrap the remaining zinc.

It now becomes of interest to consider how the factors listed in Table 2 might contribute to the occlusion of zinc by the postulated mechanism. Higher rates of zinc vaporization or higher partial pressures of zinc in the feed gas (higher Zn/SiCl_4 mole ratio) would be expected to raise the occluded

zinc level. The variations in zinc feed rate are not such as to reveal a corresponding correlation. The suggested correlation with stoichiometry is not strong; however, it is in the right direction and consistent (to the extent that one can accept the 20 ppm SSMS value for the product of Run 51). In this connection, it is interesting to note that a definite difference exists from layer to layer in the porosity developed by the HF/HNO₃ etch as shown in Figure 2. The most porous layer corresponds to that (Run 96) deposited at the highest Zn/SiCl₄ ratio. It remains to be seen whether or not this apparent correlation is significant.

The difference in reactor design shown in Figure 9 would certainly appear to be significant. The eventual adoption of Design B in preference to Design A was a two-step transition. An alternative to the cone design was being sought which would be more amenable to scale-up. Accordingly, a multiple-inlet hemispherical bed support was first adopted similar to Design B but with the zinc vapor supplied to the four planetary inlets and silicon tetrachloride fed from the preheater below through the single central inlet. After problems were encountered with deposition of silicon on the bed support in the areas of zinc entry, the configuration of Design B was adopted which delayed mixing of the reactants until they were well into the bed and prevented silicon deposition at the support plate. A basic difference between Designs A and B relative to the zinc occlusion problem is the fact that Design A, which was used in preparing the low-zinc products, provided a larger (lower velocity) section for disentrainment for droplets of liquid zinc generated by the flash vaporizer, and thus favors a lower amount of residual zinc in runs made with that design.

At a zinc feed rate of 30g/minute, near that used in the preparations, it is calculated that ≤ 467 zinc droplets would remain entrained in Design B, while ≤ 78 zinc droplets would remain entrained in Design A.

Designs A and B differ further in the fluidization pattern developed and the partial pressure of zinc in the region immediately surrounding the zinc inlet. It could be reasonably agreed that in Design B the particles spend a longer time in contact with zinc on the average than in Design A.

Another factor that is believed to be significant is the adoption of the graded temperature bed for the runs in which the high residual zinc contents were recorded. When a silicon particle with occluded liquid zinc

FIGURE 9. REACTOR DESIGNS USED IN MINIPLANT

(Material = Quartz unless specified, Scale = $\sim 1/2$)

leaves the high temperature section of the bed and enters the section below the boiling point of zinc at the prevailing pressure ambient*, spontaneous boiling of the zinc would cease and the transfer of zinc away from the particle would be limited to diffusion into the gas stream or reaction with SiCl_4 to form volatile ZnCl_2 . In short, the time for zinc evaporation would be protracted and the residual zinc content increased.

This simple picture is complicated by the possibility that the effective vapor pressure of the zinc absorbed in fine connected porosity of the silicon particles may be significantly lower than the equilibrium vapor pressure for zinc, thus lowering the tendency for spontaneous evaporation at the prevailing temperature.

Dushman⁽⁵⁾ gives the following equation for the lowering of the vapor pressure of a liquid absorbed in capillaries:

$$\ln P/P_0 = \frac{-2\sigma V \cos \theta}{rRT}$$

where P = vapor pressure of absorbed liquid

P_0 = equilibrium vapor pressure of the liquid

σ = surface tension (700 dyne cm^{-1} for Zn at b.p.)

V = molar volume of zinc = 10.7 cm^3 at b.p.

θ = wetting angle, assumed = 0 for wetting

r = radius of capillary, cm

T = °K

Substituting for P_0 , the equation for the equilibrium vapor pressure of zinc near its boiling point,

$$\ln P_0 = \frac{-13870}{T} + 11.744,$$

one gets the values given in Table 3 for the predicted boiling point rise as a function of pore size.

* B.p. = 908 C at 1.0 atm, 918 C at 1.1 atm.

TABLE 3. INCREASE IN ATMOSPHERIC BOILING POINT
OF ZINC DUE TO ABSORPTION IN PORES

Pore Diameter, μm	ΔT_{bp} , C
∞	0
1.0	0.3
0.1	3.1
0.08	3.8
0.06	5.1
0.04	7.7
0.03	10.2
0.02	15.3
0.01	30.6

Thus, for a sufficiently fine pore structure, the tendency for spontaneous evaporation of the zinc can be negated in a 1 atm ambient at several degrees above the normal boiling point.

Conversely, under these conditions zinc can be condensed into pores at temperatures several degrees above the nominal boiling point from an ambient containing zinc at a partial pressure of one atmosphere. Whether this "non equilibrium" condensation is operative in the areas of the zinc inlet is not known. If it were not for the clear evidence of the participation of zinc droplets in the formation of the agglomerates, one might be tempted to assign the zinc occlusion mechanism entirely to this non-equilibrium condensation in pores.

Prospects for Decreasing the Residual Zinc Content of the Product

If the above-suggested droplet entrainment mechanism for the occlusion of zinc in the product is valid, two levels of improvement can be anticipated. In the first place, providing for the disentrainment of the larger zinc mist droplets can be expected to decrease the residual zinc content dramatically by assuring instant evaporation of the surviving

zinc droplets on contact with the silicon particles. Secondly, decreasing the quantity of zinc that is carried to the fluidized bed as a mist will not only decrease the quantity of occluded residual zinc, but will decrease proportionately the residue of other non-volatile contaminants carried in the zinc mist.

By providing for mist disentrainment (or evaporation) and by eliminating the graded-temperature bed (at least tentatively), it should be easily possible to reduce the residual zinc to the ≤ 360 ppmw level observed in the product of Run 50. Decreasing the generation of zinc mist in the vaporizer would not only permit greatly reduced residual zinc levels, but may permit return to the graded bed temperature concept for increased SiCl_4 utilization efficiency per pass. In this connection, related information will be sought from staff members at Aerojet General who have done considerable research on the elimination of sodium mist.

It should be noted that the zinc vaporization and transfer system in the PDU provides a greater opportunity (much longer line) for the evaporation of mist droplets than was provided in the miniplant. Further, some packing is provided for disentrainment by impingement. However, the line velocities are somewhat higher than in Design B of Figure 8, so it is too early to predict the net effect on mist generation and transport.

Post-Process Treatment of Product for Zinc Removal

Although it is hoped that post-process treatment of the product can be avoided, experiments are planned to evaluate this route to decreasing the residual zinc content.

It was shown that exposure to vacuum at 920 C for 12 hours was effective in decreasing the residual zinc content from 2740 to 1590 ppmw in the deposited silicon of Run 97 and from 3020 to 1640 ppmw in the deposited silicon of Run 98.

Additional vacuum heat treatment runs are being planned with smaller quantities of material, not only to assess the efficiency of the vacuum heat treatment as such, but to study the diffusion of zinc through the silicon particles, which is expected to limit the rate of zinc removal

whether vacuum or inert gas is used to sweep the evolved zinc away from the product particles.

The procedures and results of this effort will be described in the next Quarterly Report.

Results from Other Laboratories

During this report period, results have been obtained from other laboratories relating to the quality of the silicon product of the Battelle process. The implications of these results are discussed below.

Fabrication and Testing of Solar Cell from Product. One of the intriguing implications of the above-suggested mechanism for zinc occlusion is the prospect that on suppression of the zinc mist, a proportionate decrease in the level of non-volatile impurities contained in that mist will occur.

It was therefore comforting to learn that from the product of miniplant Run No. 97, containing 1470 ppmw zinc, a web dendrite was pulled successfully at Westinghouse and five solar cells were fabricated which averaged 12.8 percent AM-1 efficiency after correction for the expected effect of providing an antireflective coating.⁽⁶⁾

Although the Run-97 product was given a 6-hour heat treatment by Westinghouse in argon at 1290 C to remove the zinc, in other respects the material was handled in the same way as was their practice for semiconductor-grade feed, and gave comparable results. The resistivity of the intentionally doped material (0.24 Ω -cm, vs 9 Ω -cm calculated) indicated a degree of autodoping which can be expected to decrease on refinement of the process, as by suppression of zinc mist, etc.

Preparation of Seed Material. As an integral part of the process, it is planned to comminute and recycle a portion of the product, e.g., 5 percent or less as seed. It is therefore necessary that the comminution process introduce a minimum of contaminants or that the contaminants be removed by treatment subsequent to comminution.

In preparation for use as seed in the quality evaluation runs, high-purity semiconductor-grade silicon was crushed in a jaw crusher to provide 105 x 149 μ m powder. As contamination was expected, the comminuted

product was subjected to a leaching process, previously used at Hemlock Semiconductors.⁽⁷⁾ The comminuted product in 400 to 500g batches one-inch deep in a polyethylene dish was covered with one inch of 48 percent HF for 16-24 hours with stirring every 4 to 6 hours. After draining and washing with deionized water, the material was similarly exposed to 50-50 HF/conc H_2SO_4 , drained, rinsed six times with deionized water, and air dried.

Spark source mass spectrometric analyses at BCL revealed no residual contamination in the crushed and leached material. Samples of the product before crushing, after crushing but before leaching and after crushing and after leaching were submitted by JPL to Lawrence Livermore Laboratories for neutron activation analysis. The results, reproduced in Table 4, indicate that contamination with material of the jaw crusher did indeed occur, up to the hundreds and thousands of parts per million for iron, chromium, and nickel. However, after the leach treatment, the original purity was essentially restored.

On the basis of these data, it is believed that an automated crushing, screening and cleaning line can be devised for low-cost recycle of part of the product as seed.

PLANS FOR NEXT PERIOD

The following activities are planned for the period January through March of 1980:

- (1) With conclusion of the zinc vaporizer qualification tests, the vaporizer and its associated feed system will be attached to the PDU and the shake-down series of silicon-preparative runs initiated.
- (2) Studies of the removal of residual zinc from the silicon product will be continued.
- (3) Information will be obtained on the elimination of mist in sodium technology which should be applicable to minimizing the quantity of zinc mist entering the fluidized bed reactor.

TABLE 4. EFFECT OF CRUSHING AND SUBSEQUENT LEACHING OF
SEMICONDUCTOR-GRADE SILICON, MICROGRAMS/GRAM(8)

(Preliminary First-Count Results)

Element	Before Crushing	After Crushing Before Leaching	After Crushing After Leaching
Na	0.0463±0.0016	1.43±0.16	0.07±0.15
K	N.D.	1.31±0.43	0.095±0.097
Sc	0.000180±0.000056	N.D.	N.D.
Cr	0.0434±0.0050	1071±9	<0.044
Fe	<0.56	6502±72	<1.2
Ni	<0.46	80±25	<1.3
Co	N.D.	2.57±0.05	N.D.
Cu	<0.040	17.6±1.6	1.03±0.19
Zn	<0.025	2.8±0.7	<0.13
Ga	N.D.	0.204±0.021	N.D.
As	N.D.	1.630±0.019	0.00119±0.00030
Br	0.000970±0.000079	0.0050±0.0078	0.0162±0.0067
Zr	<0.12	<4.0	<0.41
Mo	<0.009	4.16±0.17	<0.029
Cd	0.0091±0.0018	0.15±0.13	N.D.
Sb	0.000262±0.000050	0.411±0.006	0.00012±0.00020
La	N.D.	0.0059±0.0010	0.00050±0.00010
Ta	0.0234±0.0006	0.198±0.018	N.D.
W	0.00575±0.00016	6.378±0.045	0.0744±0.0007
Au	0.000483±0.000007	0.0240±0.0004	0.000810±0.000017

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