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

Eighteenth Quarterly Progress Report for January 1—March 31, 1980

By
J. M. Blocher, Jr.
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May 15, 1980

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

Battelle
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Columbus, Ohio

U.S. Department of Energy

Solar Energy

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EIGHTEENTH QUARTERLY PROGRESS REPORT
Covering the Period January 1 to March 31, 1980

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

May 15, 1980

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ABSTRACT

Progress during this report period was marked by the initial operation of the PDU at about 50 percent of design capacity with indications that many aspects of the facility operated satisfactorily. However, a downstream constriction, the cause of which is being isolated, led to termination of the run after one-half hour of operation. In the light of observations made during earlier start-up efforts, several modifications of equipment and technique were made for improved operation.

Vacuum outgassing experiments (850 to 1100 C, 1 to 256 hours) were carried out on miniplant-produced granules containing 360 and 3900 ppmw of zinc in the deposited silicon. Treatment of the data so that it can be extrapolated to the expected product of the EPSDU awaits development of an appropriate model.

INTRODUCTION

This Eighteenth Quarterly Report is the sixth 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 shakedown operation 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.

It is planned that the PDU operation be continued through September of 1980 to obtain engineering data applicable to the EPSDU. High-purity silicon seed and semiconductor-grade SiCl_4 will be used so as to provide as much data on product purity as possible within the inherent limitations of the PDU design.

In addition to the PDU activities, the experimental support activity was continued in the area of elimination of residual zinc from the product.

These topics are discussed in turn.

PDU ACTIVITIES

Activities during this report period were concerned principally with shakedown operation of the PDU, concentrating on the reactor, condenser, and the zinc feed system.

Zinc Feed System

By January 1, 1980, most of the mechanical difficulties with the zinc feed system had been isolated and eliminated. Induction coupling experiments conducted early during the current quarter revealed that the design vaporization rate could not be achieved due to the combined effects of (1) decreased coupling with the larger coil designed for the PDU, (2) the formation of a parasitic plasma in the zinc vapor, and (3) electromechanical difficulties which limited the output power of the Thermionic converter used to supply the r.f. energy for induction heating. Zinc vaporization rates were limited to approximately 0.3 lb/minute, equivalent to 5 kw, or one-third of design capacity.

Although the engineers of the company that makes the induction heating equipment are confident that the problem of providing efficient inductive coupling can be solved, considerable time would likely be involved. Thus, to provide a zinc-feed system for immediate use in the PDU, an induction-heated graphite tray vaporizer with a displacement-driven feed was scaled up from that used in the miniplant, and was constructed to be compatible with the zinc melter and flow control valve already shown to be operational. This interim zinc feed system assembly is shown in Figure 1 with the details of the tray vaporizer and displacement feeder shown in Figures 2 and 3 respectively. This system was bench-operated successfully at vaporization rates in excess of 0.5 lb/minute within the present power capabilities of the induction unit before being connected to the fluidized-bed reactor for service during operation of the entire PDU.

FIGURE 1. ALTERNATIVE ZINC FEED SYSTEM

FIGURE 2. GRAPHITE TRAY ZINC VAPORIZER

FIGURE 3. LIQUID ZINC DISPLACEMENT FEEDER

Reactor-Condenser System

As of January 1, 1980, the reactor condenser stood ready for plant operation. The reactor graphite liner had been coated, as described in the Sixteenth/Seventeenth Quarterly Progress Report, with 1 to 4 μm of Si/SiC on its inside surfaces by thermal decomposition of SiHCl_3 at 700 to 750 C.

An initial charge of 250 pounds of zinc chloride needed for operation of the wetted wall condenser was prepared from commercial ZnCl_2 and miniplant by-product. A mixture of the salt from these two sources was melted and heated to 350 C in an auxiliary tank and sparged with argon to expel moisture, a procedure previously proven effective in preparing anhydrous ZnCl_2 for electrolytic cell studies. After being cooled, the tank of dehydrated ZnCl_2 was connected to the condenser sump tank and the ZnCl_2 remelted in preparation for PDU start-up.

Four efforts have been made to operate the PDU during this report period, the most recent resulting in 30 minutes of operation with both SiCl_4 and zinc being fed at a planned 50 percent of design capacity.

The initial start-up effort had to be cancelled when a pre-operation systems check showed graphite flange breakage at the by-product condenser vapor inlet and the reactor SiCl_4 inlet, and fracture of the quartz tube at the zinc vapor inlet to the reactor. Breakage of the graphite components is attributed to imperfect alignment of the graphite with stainless steel back-up flanges and stresses generated during heating of the bellows expansion joints. Breakage of the quartz is attributed to a weakness created during forming of a 90-degree bend at the reactor inlet adapter. After these breakages were repaired, the PDU start-up procedure was resumed but again had to be cancelled when a significant leak was discovered in the condenser heat transfer fluid (Therminol) system. A cracked silver solder joint between the heat transfer fluid distribution manifold and the condenser cooling coils was found to be the cause. As a consequence, all such joints were carefully examined and upgraded.

The second start-up of the PDU proceeded successfully to the point of starting to feed both SiCl_4 and zinc vapors to the reactor. Leakage of zinc vapors into the reactor furnace area prompted immediate termination of the run. This problem was traced to a design deficiency which allowed the

compression on the packing of the zinc vapor inlet gland to relax sufficiently during reactor heat-up to permit a zinc vapor leak. The zinc inlet port was redesigned to incorporate three independently acting seal points; a primary seal between the quartz zinc-vapor-inlet tube and the graphite reactor liner, and two secondary seals, one between components of the stainless steel reactor shell and one between the zinc-vapor-inlet tube and the stainless steel reactor shell. A cross-section of this gland detail is shown in Figure 4.

The third PDU start-up effort was cancelled as a result of a broken quartz tubulation in the zinc liquid feed train which caused loss of argon purge and bed support to the zinc side of the reactor distributor plate. Resultant clogging of the zinc distribution ports and the apparent residual strain resulting from in situ repair of the fractured quartz tubulation caused the zinc vaporizer shell (quartz) to fracture when purge gas pressure was increased in an attempt to free the clogged ports.

In light of the experience gained and operational problems (bed removal) encountered during these attempted start-ups, the PDU operating procedure and start-up sequence was revised (1) to make charging of the bed material the last operation before starting to feed the SiCl_4 and zinc reactants and (2) to greatly increase the purge flow through the silicon product drain port during bed charging.

As discussed above, breakage of graphite flanges and nozzle liners at the SiCl_4 inlet and exhaust-gas exit ports of the reactor has continued to be a problem during reactor heating and cooling. Steps being taken to render these joints less susceptible to breakage include replacement of the relatively stiff expansion bellows in the nozzle shells with more flexible ones and the addition of support structures to limit and permit control of movement of the stainless steel nozzle flanges during reactor heating and cooling. Since the replacement bellows will require several weeks to procure, the flange support and control structures were fabricated at BCL and installed in advance to permit continued operation of the PDU. It is planned to operate the PDU with just the flange control/support structures as long as breakage of the graphite nozzle liners can be avoided since the liners must be removed (in two cases destructively) to permit installation of the replacement bellows.

FIGURE 4. REACTOR ZINC VAPOR INLET ADAPTER

Start-up of the reactor-condenser system was achieved on April 10, 1980 by careful manipulation of the flange supports in conjunction with the revised procedure mentioned above. Both SiCl_4 and zinc were fed to the reactor for a period of 30 minutes at rates of 40 and 33 lb/hour, respectively (Zn/SiCl_4 ratio = 2.14 vs. 2.00 stoichiometric). Purge gas flow and pressure data indicated that bed fluidization was being maintained almost entirely by the reactants. Considerable difficulty was encountered during the operating period with excessive system pressure caused by clogging of (1) the vapor outlet pipe from the stripper, and (2) the waste vapor tube at the $\text{Ca}(\text{OH})_2$ mixture interface in the neutralizing tank. This tendency for the system pressure to increase was kept in check by proper manipulation of flow control valves and waste discharge nozzles. However, one or both of these clogging conditions eventually caused enough pressure build-up to slow the vaporizer purge gas to the point that back-diffusing zinc vapor condensed in the inlet, thus blocking the purge gas flow and forcing termination of the run.

It was subsequently found that blockage at the stripper outlet was caused by a build-up of ZnCl_2 which was carried through the stripper due either to insufficient stripper capacity or overloading of the stripper caused by possible malfunction of the wet-wall condenser. Although the stripper temperature reached 200 C, i.e., higher than desired, the vapor pressure of ZnCl_2 at 200 C is insignificant (10^{-5} torr). Therefore, the gas was not being effectively cooled in the stripper.

Draining of the fluidized bed after the reactor had been cleared of both zinc and SiCl_4 vapors was much more easily accomplished than in previous start-up efforts, presumably as a result of an improvement in the alignment of sections of the product withdrawal tube and the modified start-up procedure which kept the bed material out of the discharge tube until it was heated to the reactor temperature. It was, however, necessary with the fine-particle (150 to 400 μm) somewhat acicular starting bed material to decrease the purge gas flow through the discharge tube drastically (to 0.02 ft/second through the open tube) to allow the bed to drop. As the growing bed particles become larger and more spherical, greater latitude in the purge gas flow should be available in preventing back diffusion of condensible zinc and zinc chloride during bed withdrawal under operating conditions.

Electrolytic Cell System

Although the electrolytic cell was ready for operation at the beginning of this report period, its operation must await the availability of the ZnCl_2 by-product of the operating PDU. An initial charge of zinc metal, made during cell assembly to provide electrical contact to the cathode and a seal to prevent the ZnCl_2 salt from entering the zinc discharge port, was melted in situ during the first reactor/condenser start-up effort. The cell has since been maintained at 460 C by using the base heaters to maintain the zinc in the liquid state. A minimal argon purge has been maintained to prevent oxidation of the molten zinc. The liquid-solid transition and seal in the zinc cathode connection appears to be performing satisfactorily, showing no evidence of leakage or deterioration. An initial salt charge for the electrolytic cell consisting of 68.2 w/o ZnCl_2 and 31.8 w/o KCl (1.2/1 mole ratio) has been prepared in the ZnCl_2 storage tank and is being held in the molten state in readiness for operation of the cell. The KCl addition to the initial salt charge is necessary to (1) decrease cell resistance, and (2) reduce the vapor pressure of the ZnCl_2 (1)

Plans for PDU Operation

With the progressive solution of the various operational problems associated with this unique chemical process, it is anticipated that the planned 8-hour batch-wise runs can be made to obtain engineering data which will be valuable in the design and eventual operation of the EPSDU.

It is believed that the control now provided over the position and alignment of the flanged connections during start-up and cool-down of the reactor will provide the margin necessary to avoid the breakage that has characterized the initial start-up experience.

Data from the 30-minute run are being examined to determine whether the inability of the ZnCl_2 stripper to handle the ZnCl_2 load was due to an inherent limitation of stripper capacity or to an overload attributable to possible malfunction of the wet-wall condenser.

EXPERIMENTAL SUPPORT

Although plans were made for the experimental operation of a direct-coupled zinc vaporizer for eventual replacement of the tray-type unit installed in the PDU as a temporary expedient, no actual experimental work was done in this area during the report period. Effort in the Experimental Support Program was limited to the area of elimination of residual zinc from the Product.

Elimination of Residual Zinc From The Product

As discussed in the last Quarterly Progress Report⁽²⁾, the product of the earlier miniplant contained from 360 to 3900 ppmw of second-phase residual zinc in the deposited silicon*. The level of contamination varied with reactor configuration and process conditions in such a way as to suggest that the zinc occlusion had its origin in zinc mist droplets entrained in the vapor from the flash vaporizer used in the miniplant zinc-vapor feed system.

That the residual zinc is not grossly detrimental to the quality of the product has been shown by the work at Westinghouse⁽³⁾ in which the efficiency of web-dendrite solar cells made from the zinc-reduction-process material was distinguishable from that of those made from semiconductor-grade silicon.

The evolution of zinc in the silicon melting process (i.e., the very mechanism by which its content in the silicon wafer or web is reduced to negligible levels), is obnoxious from the standpoint of the crystal pullers.** Thus, an effort is being made (1) to reduce the zinc level by appropriate process design and control, and (2) to study methods of post-process treatment for zinc removal.

Progress in the area of post-process treatment will be discussed below.

* After having corrected the average analysis for seed content.

** Except for the heat-exchange ingot casting method, where much larger amounts of zinc are said to be tolerable.

Post-Process Treatment

Work reported earlier has shown that the residual zinc in the mini-plant product is a highly segregated second-phase material, entrapped in the silicon. On the assumption that any process for removing it will ultimately be limited by the rate of transport of zinc through the silicon particles, studies are being made of the vacuum heat treatment of representative materials as a function of time and temperature in the hope that correlations can be developed which will permit extrapolation to particles of different size and initial zinc content as a function of temperature.

It would be desirable for such a study, to synthesize perfectly spherical silicon particles with uniformly dispersed initial zinc content at the levels of interest. These particles could be synthesized only in the mini-plant (or similar reactor), and such is not now available. Accordingly, the current heat-treatment studies are being made with the products of prior mini-plant runs.

The products of the miniplant runs were not made with the objective of providing particles for the heat-treatment studies, and they suffer several limitations:

- (1) The seed particles are irregular and the final particles only approach being spherical.
- (2) The size of seed and of final particles of a given lot cover a broader range than desired.
- (3) The silicon was deposited in layers in a sequence of runs under varying conditions. Portions of a given lot came to the final step by different sequences. Only the average zinc content can be measured.
- (4) The products of Runs 97 and 98 had already been given a vacuum heat treatment in which part of the residual zinc was removed. These lots underwent a temperature rise on exposure to air (e.g., from ~30 C to ~100 C) suggesting surface and internal pore oxidation which may impart a non-representative diffusivity.

Despite the limitations of these materials, it was thought desirable to obtain information on their vacuum heat treatment for zinc removal and to make an effort to extrapolate the data with whatever qualifications may be imposed by the above-listed limitations.

One-gram or 0.5-gram samples of silicon from miniplant Runs No. 50, 96, and 98 were placed in one end of 5-mm diameter x 30-cm long fused quartz tubes and sealed under vacuum after warming to below red heat with the glass blower's torch. The ends of the tubes containing the samples were placed in controlled temperature furnaces with the other end protruding from the furnace. Condensation of the zinc occurred in a sharp ring adjacent to the hot zone. After heat treatment at various times and temperatures, the tubes were cut open and the condensed zinc leached out with several portions of 0.1 N HCl. Atomic absorption analysis was used to determine the quantity of zinc evolved, which should be reliable to 1-2 ppmw in the original silicon.

The data are presented in Table 1 in terms of the fraction of zinc retained after the heat treatment. The data are presented here in raw form, pending the development of a satisfactory model for use in generalizing the data so that the time of outgassing of any given product can be predicted as a function of particle size, zinc content, and temperature.

Treatments of similar problems in the literature for outgassing of spherical particles⁽⁴⁾ contain the implicit assumption that all of the contained diffusing species is dissolved in the major phase, and that the concentration gradient varies continuously with time. It was first reasoned that if the second phase were highly enough dispersed, the trend of average concentration with time would be similar. Indeed, the above data seemed to correlate reasonably well on that basis. However, such a model was deemed deficient and it was decided that since outgassing may need to be carried to a much lower value (e.g., 5 percent or 10 percent of that contained in the experimental samples), and that larger particles will be involved in practice, a more rigorous model should be developed.

TABLE 1. VACUUM HEAT TREATMENT OF SILICON GRANULES

Source of Silicon, Description	Temperature, C	Time, Hour	Zinc Evolved, ΔC		Residual Zinc, $C/C_o(a)$
			ppmw	ppmw/hr	
<u>Run 50</u>					
$C_o = 150$ ppmw	900	1	4.7	4.7	0.97
Seed dia = $207\mu m^{(b)}$		4	12	3.0	0.92
Particle dia = $319\mu m^{(b)}$		16	30	1.9	0.80
		64	70	1.1	0.53
		256	120	0.5	0.20
<u>Run 96</u>					
$C_o = 2250$ ppmw	900	1	50	50	0.98
Seed dia = $125\mu m^{(b)}$		4	146	36	0.94
Particle dia = $260\mu m^{(b)}$		16	366	23	0.84
		64	720	11	0.68
		256	1340	5	0.40
<u>Run 50</u>					
$C_o = 150$ ppmw	850	16	17	1.1	0.89
Seed dia = $207\mu m^{(b)}$	900	16	11	2.6	0.73
Particle dia = $319\mu m^{(b)}$	950	16	35	2.2	0.77
	1000	16	59	3.7	0.61
	1050	16	111	6.9	0.26
	1100	16	124	7.8	0.17
<u>Run 98</u>					
$C_o = 1400$ ppmw	850	24	28	1.2	0.98
Seed dia = $125\mu m^{(b)}$	900	24	55	2.3	0.96
Particle dia = $300\mu m^{(b)}$	950	24	140	5.8	0.90
	1000	24	290	12.1	0.79
	1050	24	690	28.8	0.51
	1100	24	1080	45.0	0.23

(a) Initial concentration = C_o ; Residual zinc = $(C_c - \Delta C)/C_o$.

(b) Tentative values, pending verification.

Three cases are being considered:

- (1) Zinc highly dispersed as a second phase in spherical particles; rate of outgassing limited by diffusion through the silicon between the retreating two-phase front and the outer surface.
- (2) Zinc trapped in silicon surrounding pores of connected porosity; rate of outgassing limited by diffusion through the silicon surrounding the pores (negligible resistance to flow in the connected porosity)
- (3) Zinc contained solely in connected porosity; rate of outgassing limited by the permeability of the connected porosity.

Data on the diffusivity and solubility of zinc in silicon are available in the literature which, with the degree of conformance of the data to the models, will aid in the choice of model and provide a better basis for extrapolation.

It is also planned to perform a few more ΔC -vs.-time experiments at higher temperatures, in which the residual zinc concentration will be carried to lower values (e.g., 48-100 hours at 1050 C). The observed presence or absence of a sharp drop in the rate of zinc evolution should be useful in clarifying the model.

PLANS FOR NEXT PERIOD

The following activities are planned for the period April 1 through June 30, 1980:

- (1) Continued work will be directed toward improving the operability of the PDU with the objective of making 8-hour runs.
- (2) Studies of the removal of residual zinc from the silicon product will be continued to the extent necessary to permit extrapolation of the present data.
- (3) Information will be collected on the elimination of mist from boiling metals.

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