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EVALUATION OF SELECTED CHEMICAL PROCESSES FOR
PRODUCTION OF LOW-COST SILICON

MASTER

Nineteenth Quarterly Progress Report, April 1—June 30, 1980

By
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July 31, 1980

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

Battelle Columbus Laboratories
Columbus, Ohio

U.S. Department of Energy

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NINETEENTH QUARTERLY PROGRESS REPORT
Covering the Period April 1 to June 30, 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., M. F. Browning, and D. A. Seifert

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* Deceased May 15, 1980.

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ABSTRACT

Early in this report period, the PDU was operated for a short time (one-half hour) before downstream constrictions prompted termination*. The problem was traced to malfunction of the wetted-wall by-product condenser owing to the zinc chloride having a higher-than-anticipated viscosity near its melting point. Since then, a number of problems, minor in origin but major in effect, have hampered operation of the PDU. Steps are being taken to correct these deficiencies of design or mode of operation as they are revealed.

Mathematical models were developed for testing against the data on the removal of zinc from silicon granules by vacuum heat treatment. With a suitable model confirmed, it will be possible to extrapolate the results to the larger particle size and different zinc content expected in the eventual product.

* Run made on April 10, 1980 already mentioned in last Quarterly Report(1).

INTRODUCTION

This Nineteenth Quarterly Report is the seventh 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 areas of (1) evaluation of the direct-coupled induction-heated zinc vaporizer, and (2) elimination of residual zinc from the silicon product.

These topics are discussed in turn.

PDU ACTIVITIES

Activities during this report period continue to be concerned principally with shakedown of the PDU reactor, condenser and zinc feed systems. Insufficient by-product ZnCl_2 has been obtained to justify running the electrolytic cell.

Zinc Feed System

Operation of the alternative zinc feed system since the independent qualification of that system before April 1, 1980 has been carried out entirely in conjunction with attempts to operate the entire PDU. At times the zinc feed system has operated well in the experimental PDU effort during this quarter. Its malfunction was, however, responsible for cancellation of the most recent start-up attempt. Zinc leakage past the valve to the zinc supply caused premature filling of the displacement feeder and eventually, flooding of the tray vaporizer. The molten zinc overflowed the vaporizer into the vapor-transport tube which was at a high enough temperature to vaporize some of the metal, sending it into the reactor where part of it condensed at the silicon product drain port. The remainder was apparently carried through into the condenser where it formed dust with the ZnCl_2 and was carried through the system to the waste-product scrubbers.

Other more minor but yet time-consuming problems which were encountered in operating the zinc delivery system were breakage of quartz delivery tubes due to some accidental relative motion between the quartz vessels, leakage of liquid zinc from the graphite piping, due to imperfectly formed joints, or oxidation degradation of some of the graphite piping components as a result of long-term exposure to air at elevated temperature. This latter problem prompted the installation of an argon purge manifold adjacent to the graphite piping and the construction of an independently supported metal enclosure to contain the argon blanket.

Reactor-Condenser System

On April 10, 1980 the first successful 30-minute run was made in the PDU, as was discussed in our previous report. The circumstances surrounding the premature termination of that run due to excessive system pressure were examined, and it was concluded that two factors probably contributed to clogging of the waste vapor piping. First, it was found that the unreacted SiCl_4 vapors had cooled enough to condense before reaching the neutralizer drums. As a liquid, the SiCl_4 is too concentrated to be dispersed in the caustic suspension before reacting to form silicate products. Thus, the sparge tubes became clogged. This problem was dealt with by installing a trap in the waste vapor line immediately ahead of the neutralizer to remove the condensed SiCl_4 .

The second, more serious, reason for excessive pressure was found to be the accumulation of ZnCl_2 and zinc dust in the piping downstream of the stripper (vent condenser). It was determined that this build-up resulted from overloading the stripper. The excess ZnCl_2 load on the stripper was caused by a malfunction or improper operation of the wetted-wall condenser which severely limited the ZnCl_2 condensation at that point. As a result of recalculating the hold-up volume in the condenser tubes, recirculation experiments just prior to the subsequent PDU run attempt, and concurrent experimental determination of the viscosity of ZnCl_2 at 350 C (~ 1000 cp), it was concluded that the lack of a liquid seal in the condenser reservoir permitted the hot reactor effluent gases to by-pass the condenser and overload the stripper.

The work, including system modifications, required to prepare the PDU for operation after the successful 30-minute run included the following:

- (1) Replacement of quartz vessels in the zinc feed system--cracked due to back-up of liquid zinc and loss of heating.
- (2) Replacement of zinc feed system graphite piping and valve body which deteriorated after prolonged exposure to air at elevated temperatures*.

* It was reasoned that, although marginal, the graphite should have an experimentally useful life at 500 C. However, possible overheating in places not temperature monitored shortened that expectation.

- (3) Fabrication and installation of argon purge manifold and sheet metal shroud to provide inert atmosphere around zinc feed system graphite piping.
- (4) Replacement of graphite nozzles and flanges in condenser ZnCl_2 recirculation and overflow ports.
- (5) Installation of SiCl_4 liquid trap in waste treatment piping.
- (6) Increased cooling capacity of ZnCl_2 stripper.
- (7) Installation of pressure guage at discharge end of waste treatment piping.

Zinc chloride recirculation pumping experiments were performed immediately prior to the second PDU run attempt of the period. As a result of these experiments, it was established that, given sufficient suction head, the ZnCl_2 sump will deliver the molten salt to the top of the condenser. Continuous recirculation at the design rate was found not to be possible due to the higher than expected ZnCl_2 viscosity which resulted in an insufficient suction head to provide the flow required to supply the pump through the line connecting the condenser bottom with the pump sump. A purge atmosphere pressure equalization line between the sump tank and condenser bottom reservoir was also found to be necessary to prevent either loss of liquid or flooding of the condenser bottom reservoir.

In the subsequent PDU start-up, the operation proceeded normally through reactor heating while maintaining the condenser at operating temperature after the ZnCl_2 recirculation trials. This attempt had to be cancelled, however, when zinc could not be transferred to the displacement feeder due to plugging of the melter drain tube at a point inaccessible to auxiliary heaters. One heater element had burned out before, and heat from the remaining element was insufficient to hold the drain tube above the melting point of zinc.

After the reactor had cooled from this run attempt, it was discovered that, in addition to the usual cool-down breakage of the quartz vapor tube at the zinc inlet adapter, considerable damage had been done to the reactor shell

by high-temperature exposure to zinc chloride which may have been unknowingly introduced to the cold reactor shell during the condenser recirculation trials. In order to repair the leaks which developed in the reactor shell, the following procedures were required:

- (1) Replacement of the lower main reactor expansion bellows.
- (2) Welding in the bolts supporting the graphite reactor liner.
- (3) Complete seam welding of the center shell support collar to seal a leak that had been covered by the collar.
- (4) Rewelding a cracked longitudinal seam in the shell.
- (5) Rewelding portions of the shell top closure sealing band.

Advantage was taken of this down time to replace the stiff expansion bellows on the reactor TET inlet nozzle with a more flexible one. Additional work to forestall a recurrence of the backstreaming of ZnCl_2 included the installation of increased purge flow capacity to the reactor shell, the installation of sensitive pressure measuring devices to monitor shell pressure relative to reactor internal pressure, and modification of the PDU start-up procedure to provide for heating of the reactor to at least 400 C before beginning intensive heating of the condenser or condenser bottom reservoir.

A third attempt to operate the PDU this period was cancelled when high exhaust gas pressures were observed and stethoscopy indicated the reactor by-product gases were bubbling under the liquid seal at the condenser pass separator plate, rather than flowing through the condenser tubes. A thermocouple inserted inside the condenser shell against the graphite core (more strategically placed than the temperature sensors available before) indicated that the top of the condenser was not heated sufficiently and was probably clogging with solid ZnCl_2 . Additional insulation was added to the top portion of the condenser and the Therminol system heater controls were automated to permit continuous overnight heating of the system with a minimum

of attention. The reactor was maintained at an intermediate elevated temperature during these modifications to prevent fracture of the quartz vapor piping.

In a further attempt to operate the PDU, all proceeded well through reheating of the system, including the reactor, condenser and zinc feed vaporizer. With the top of the condenser at an adequate temperature (330 C), a confirmed full condenser reservoir and high purge gas flows through the reactor, stethoscopy indicated that the effluent gases were travelling through the condenser in the proper path. The operation was cancelled before introducing the bed when the pressure in the silicon product hopper rose to 15 psi and it was found that the zinc vaporizer and zinc vapor tube were flooded with molten zinc due to continued leakage of the zinc supply valve. As discussed above, the increased pressure in the product hopper was found to be due to condensation of zinc vapor at the product withdrawal valve which blocked the purge gas flow path. The purge gas in the product withdrawal tube had not yet been raised to operating level which would normally prevent the zinc vapor from entering the product withdrawal system. The premature presence of zinc vapor in the reactor may have also contributed to the dusting problem in the waste vapor neutralizer.

A significant amount of work, including removal of zinc from the silicon product withdrawal apparatus, replacement of broken graphite reactor nozzle liners, replacement of the quartz envelope of the zinc vaporizer and zinc vapor tubing, as well as repair of the zinc liquid control valve, was required to restore the PDU to operational status. This work was well under way at the close of the report period.

Electrolytic Cell System

A lack of sufficient by-product zinc chloride has prevented operation of the electrolytic cell during this Quarter. The initial charge of ZnCl_2 -KCl salt mixture was introduced into the cell when the ZnCl_2 storage tank began leaking. Stress-corrosion cracking of the stainless steel vessel was apparently promoted by welding of tabs to its surface to secure heating elements and by intermittent contact between the elements and the vessel skin possibly leading to local overheating. A new ZnCl_2 storage tank was

fabricated with a layer of asbestos paper between the tank skin and the heating elements and a modified heater design which eliminated the requirement for welded tabs to secure the heater.

Shortly after the salt mixture was introduced into the electrolytic cell, both base heaters burned out at the point where their leads emerged from the graphite liner. These heaters had been operating continuously for several months before salt was introduced into the cell. It is not known whether a direct relationship exists between the presence of the salt mix in the cell and heater burn-out because there was no evidence of salt leakage. There is, however, evidence of trapped moisture in the system which may have come from the insulation. The burned out cartridge heaters were removed from the cell and replaced with similar units whose leads are encased in quartz tubes to inhibit recurrence of the problem. Both the zinc and salt mixture solidified when the heaters were lost. Remelting, which will not be attempted until the cell is to be operated, will be a test of the cell's design and durability.

EXPERIMENTAL SUPPORT

Owing to the emphasis on the PDU activity, activity in the Experimental Support area was limited during the Quarter.

Direct-Coupled Induction-Heated Zinc Vaporizer

As a result of concentrating the experimental effort on the operation of the PDU, only a minimal effort was directed to the study of the direct-coupled zinc feed system.

A zinc feed system similar to that initially constructed for use in the PDU and later replaced with the current feed system was set up in an area remote from the PDU for the purpose of working out the bugs originally encountered. As an expedient, the system was set up so that vaporization could be studied but no provisions were established for measuring vaporization rate.

As discussed in earlier reports, one of the major problems encountered with the direct-coupled zinc feed system was the formation of a plasma in the zinc vaporizer section which robbed the system of power (decreased vaporization rate) and interfered with the level control mechanism. During consultation with the manufacturer of the radio frequency generator being used, it was suggested that the plasma should be less of a problem if a saturable core reactor control system were used instead of the electronic system associated with the generator being used.

Accordingly, the current studies of the direct-coupled system are being carried on using a 50 kw generator with a saturable core reactor control. The results of the exploratory effort to use this system were very encouraging in that a plasma did not form at the unknown but substantial vaporization rate achieved, and a simulated zinc level indicator system also appears to function as expected.

Plans are to continue this work as time permits by expanding the system capability to include a vaporization rate monitoring scheme.

Vacuum Heat Treatment of Product Silicon to Remove Residual Zinc

In the last Quarterly Report⁽¹⁾, raw data were given for the removal of residual zinc from miniplant product silicon as a function of time and temperature. In order to extrapolate these data to the larger particles expected as a product of the PDU/EPsDU and on a commercial scale, it will be necessary to have a model for the transport of zinc in the silicon granules, assumed to be the rate-limiting process.

During this report period, mathematical models were developed for the following cases:

- (a) 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.
- (b) 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.

- (c) Zinc contained solely in connected porosity; rate of outgassing limited by the permeability of the connected porosity.

To test the consistency of the results, the extrapolation of each model to the simpler thin sheet model (infinite radius of curvature) was tested and found to be valid. The sign and magnitude for the deviation from the thin sheet model for finite and increasing radius of curvature were also consistent with the geometry (spherical for Cases (a) and (c), cylindrical for Case (b)).

The models will be presented in detail when the data have been tested against them. Results are pending for an additional run at 1050 C, for 4, 20, 75, 100 and 125 hours, in which at some point the zinc content of the particles should have been exhausted suddenly after a gradual decline. In the prior runs, the zinc content was not carried below about 20 percent of its initial value.

ERRATUM

In the discussion on Page 12 of the last Quarterly Report⁽¹⁾ on the quality of the miniplant product, an error was made. The statement should have read (paragraph 3) "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 indistinguishable from that of those made from semiconductor-grade silicon."

* Reference (3) of the last Quarterly Report⁽¹⁾.

PLANS FOR NEXT PERIOD

The following activities are planned for the period July 1 through September 30, 1980:

- (1) Continued work 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, to the extent necessary to permit extrapolation of the present data.
- (3) Collection of information on the elimination of mist from boiling metals.

REFERENCE

- (1) Eighteenth Quarterly Progress Report, DOE/JPL 954339-80/18, May 15, 1980.