MASTER

LOW COST SILICON PROCESS DEVELOPMENT
Phase III: Process Optimization and Evaluation
THIRD QUARTERLY
TECHNICAL PROGRESS REPORT

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PROJECT DESCRIPTION

The goal of the Low Cost Silicon Process Development project is to determine technical and economic feasibility of a tribromosilane-based process for the production of Solar Cell Grade Silicon. To accomplish this project goal, three principal tasks have been defined: 1) an experimental chemistry task; 2) a mini-plant design and construction task; and 3) a mini-plant operation and evaluation task. The scope of the experimental chemistry task includes optimization of the process with design verification studies at bench scale level. The mini-plant design task is focused on construction of a flexible, cost effective mini-plant. The final task is concerned with the generation of sufficient high quality process data through mini-plant operation to support an accurate assessment of the potential of the process for meeting DOE silicon material quality and cost goals.

SECTION I

INTRODUCTION

Low cost silicon process development work began in 1977 at the J. C. Schumacher Company. Current process optimization and evaluation work described in this report is sponsored by the Solar Energy Research Institute under DOE/SERI Contract XS-9-8279-1. The contract period is June 1979 through September 1980.

1.1 Process Description

The J. C. Schumacher Company's low cost silicon process is based on the silicon-bromine-hydrogen chemical system. The favorable characteristics of this system make possible the generation of a high purity, granular polycrystalline silicon product from metallurgical grade silicon in a closed-loop process. The process chemistry was described in detail in the progress report ⁽¹⁾ issued in October 1979.

1.2 Project Objective

The goal of this project is to determine the technical and economic feasibility of the J. C. Schumacher process for continuous, closed-loop production of low cost polycrystalline silicon suitable for use in photovoltaic applications. Earlier phases of the program focused on unit operations but did not address process integration. In this phase an experimental mini-plant having all necessary chemical processing units and instrumentation to demonstrate the complete process will be designed and constructed. The design effort has been supported by experimental chemistry studies to obtain necessary data not available in the literature.

1.3 Technical Approach

As described above, the three main areas of technical effort include the experimental chemistry studies, the design and construction of the mini-plant, and the mini-plant operation and process analysis.

Several alternative approaches to the final design of the mini-plant have been investigated. The versatile nature of the bromine system chemistry presents a broad spectrum of processing alternatives. Although it is beyond the scope of this effort to fully characterize each specific effect of the many competing chemical reactions in the bromine-hydrogen-silicon system, the operating yield and cost parameters of the alternative processing schemes can be defined and analyzed.

From the results of the experimental chemistry studies and supporting cost estimates, a cost effective set of processing conditions has been selected as a basis for the mini-plant design. The completed mini-plant will now be operated as an experimental tool to investigate the overall silicon production process. Based on the data obtained, a process feasibility analysis will be conducted.

SECTION 2

EXPERIMENTAL CHEMISTRY TASK

The experimental chemistry task was completed during the third quarter of the project. The silicon production reactor study was concluded with a material balance and yield test. The analytical methodology sub-task was completed with the final calibration of the gas chromatograph.

2.1 Product Reactor Optimization

Silicon production by both the thermal disproportionation and hydrogen reduction of tribromosilane have been reported previously ⁽¹⁾. During the second quarter of the project a silicon production reactor design was developed to operate at very low residence times. Subsequently, tests showed good stability and fluidization in the range of residence times of interest. Plans were then made to conduct a comprehensive material balance test in this reactor. The final reactor design is illustrated in Figure 1. The experimental arrangement is shown in Figure 2.

The experiment was conducted to determine silicon yield of the hydrogen reduction of tribromosilane in a fluidized bed at a residence time of 0.008 second. The experimental conditions are reported in Figure 3. The results of the material balance test showed an overall mass balance of 97.8 percent. The silicon yield was 31.3 percent when computed on the basis of conversion of tribromosilane to silicon by the reaction given below.

59.5 g of silicon as tribromosilane was fed to the reactor system during the test and 18.7 g of the available silicon was actually deposited as product. These results are shown in further detail in Figure 4.

VARIABLE CROSS SECTION SILICON PRODUCT REACTOR

FIGURE 1

EXPERIMENTAL APPARATUS FOR THE VARIABLE CROSS SECTION REACTOR
SILICON PRODUCTION TESTS.

FIGURE 2

REACTOR DATA *

Inlet diameter	10 mm
Exit diameter	68 mm
Length of Variable Section	60 mm
Length of hot zone	100 mm
Operating Temperature	$1100 \pm 30^{\circ}\text{C}$
Silicon Charge (40-60 mesh)	232.2g
Operating Pressure	about 775 mm Hg

FEED PREHEATER *

Exit Temperature	$850 \pm 25^{\circ}\text{C}$
Inlet Temperature	$105 \pm 5^{\circ}\text{C}$

FEED *

Hydrogen	1.78g/min.
Tribromosilane	13.92g/min.
Silicon tetrabromide	1.28g/min.
$\text{H}_2/\text{HSiBr}_3$ Ratio (Molar Basis)	23

TOTAL TEST TIME

45 min.

* Experimental conditions used for material balance test in a variable cross section reactor for the production of silicon by hydrogen reduction of tribromosilane.

FIGURE 3 - Material Balance Test Conditions

Total Input 996.2g

Total Output 975.1g

Overall mass balance: 97.5% recovery

Silicon yield: 31.3% recovery

FIGURE 4 - Overall Material Balance Test Results

2.2 Gas Chromatograph Calibration

The gas chromatograph is the primary on-site instrument used to evaluate the chemical composition of the process streams in the experimental mini-plant.

The chromatograph planned for use during the Development Test and Demonstration Run Task was calibrated during the third quarter of the project. Samples having known compositions of tribromosilane and silicon tetrabromide were analyzed on a Varian 3700 chromatograph employing a thermal conductivity type detector. Output signals were recorded and integrated with a Varian 9176 Recorder. The system's differential sensitivity was calculated for a range of known compositions using standardized analytical techniques. The differential sensitivity is a correction factor which compensates the system output for the physical differences between tribromosilane and silicon tetrabromide. The results of this work showed that the chromatograph is less sensitive to tribromosilane than to silicon tetrabromide. The correction factor was determined to be 1.49 and is used as a multiplier to compensate for the lower system sensitivity to tribromosilane.

SECTION 3

EXPERIMENTAL MINI-PLANT DESIGN & CONSTRUCTION

The third quarter was highlighted by the commissioning of the mini-plant utility systems. The detailed design task was finished following a complete redesign of the equipment support structure. This redesign effort was forced by a vendor default. The installation of process equipment and piping was started and reached the 75% complete mark during the quarter.

3.1 Process Design Task

There were no changes or modifications to the process design basis or to the mini-plant process design during the third quarter. The design basis was established and reported in the first quarterly report,⁽¹⁾ and the final process design was presented in the second quarterly report⁽²⁾. The final process design and mechanical specifications are shown in the SCC Silicon Mini-Plant Mechanical Flow Diagram in Figure 5.

3.2 Detailed Design Task

The detailed design for the mini-plant was completed during the first part of the quarter. A delay occurred when the support structure material vendor defaulted. A redesign was completed to enable the use of different structural members.

3.2.1 Structural Design

The equipment support structure was redesigned to utilize a 1 5/8 x 1 5/8 inch slotted channel material as the load carrying beam column members. Structural tubing had been planned for this application, but the supplier of the connector fittings failed to meet the shipping date.

3.2.2 Piping Design

No changes were made to the piping design during the quarter.

3.3 Equipment Procurement

Purchase orders were issued for all outstanding items during the quarter. Delivery of all significant process equipment occurred on schedule with the exception of the chemical reactors and the metering pumps. These items are rescheduled for early March and the vendors commitment is firm. At the end of the quarter 85% of the material purchased for the mini-plant had been delivered.

3.4 Mini-Plant Construction

The construction of the mini-plant reached the 80% completion level during the quarter. Delays in shipment of reactors and metering pumps caused a 3 week slip in the scheduled completion date. Completion of the mini-plant is now expected by March 20. Photographs illustrating construction progress are shown in Figures 6 through 11. No delays are forecast in the supply of silicon samples or other scheduled tasks and milestones.

3.4.1 Utility System Construction and Commissioning

All utility systems were installed and commissioned during the quarter. These systems include circulating coolant, inert gas and vacuum, electric power supply, plant ventilation, and fire control. Portions of the utility systems are shown in Figures 7, 9, and 11.

3.4.2 Process Module Construction and Commissioning

The hydrogen scrubbing and recompression module and the purification module mechanical systems were completed during the quarter. Commissioning activities were not undertaken because of delays in completion of the other process modules. As explained in section 3.3, the delivery of reactors and metering pumps fell three weeks behind schedule.

FIGURE 6 - View showing distillation columns, product cooler and circulating coolant distribution equipment.

FIGURE 7 - Upper sections of the distillation columns shown with column vent piping in place.

FIGURE 8 - The hydrogen scrubbing columns, by pass valving and gas preheater are shown.

FIGURE 9 - The lower by-pass piping on the hydrogen scrubbing columns are shown. The mini-plant vacuum pump is shown on the left. The hydrogen recycle compressor is on the right.

FIGURE 10- View showing the distillation column valving and the thermosyphon reboiler.

FIGURE 11- The reactor exit gas condenser is shown here. The synthesis reactor is shown on the left.

SECTION 4

DEVELOPMENT TESTS AND DEMONSTRATION RUN TASK

The start of the Development Test and Demonstration Run Task is dependent on the completion of the mini-plant construction. The initial steps of plant operation were originally scheduled for mid-March, however, a three week schedule slip has occurred as explained in Section 3. The scheduled availability of silicon samples, mini-plant operating data and results should not be delayed by these events because there is still room for a compensating schedule compression during the fourth quarter.

SECTION 5
CONCLUSIONS

Significant highlights and conclusions from third quarter work appear below:

- 5.1 The mass balance experiment using the variable cross section product reactor was completed.

- 5.2 The experimental chemistry task of this project was completed.

- 5.3 All outstanding purchase orders for mini-plant equipment and start-up chemicals were placed.

- 5.4 The equipment shelter structure and equipment support structure was erected.

- 5.5 The utility systems were installed and commissioned.

- 5.6 The purification module and the hydrogen scrubbing and compression module were mechanically completed.

- 5.7 The mini-plant start-up plan was finalized.

SECTION 6
PLANNED ACTIVITY

6.1 Experimental Chemistry Task

- The experimental chemistry task has been completed and no additional activity is forecast.

6.2 Mini-Plant Design and Construction Task

- Construction of the mini-plant will be completed.
- Hydrostatic and vacuum testing of the mini-plant will be completed.
- The mini-plant will be commissioned.

6.3 Development Test and Demonstration Run Task

- Mini-plant development tests and demonstration runs will be executed.
- Feed rates and composition will be determined.
- Effluent rates and composition will be determined.
- Chemical make-up requirements will be determined.
- A technical feasibility study will be performed.
- An economic feasibility analysis for the process will be completed.

REFERENCES

1. E. Moore, et al, First Quarterly Technical Progress Report,
Contract DOE/SERI XS-9-8279-1, October 1979.
2. E. Moore, et al, Second Quarterly Technical Progress Report,
Contract DOE/SERI XS-9-8279-1, December 1979.