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

Silicon Material Task, Low-Cost Solar Array Project
Eleventh-Twelfth Quarterly Progress Report, April 1–September 30, 1978

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

October 31, 1978

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

Battelle Columbus Laboratories
Columbus, Ohio

U.S. Department of Energy

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Solar Energy

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ELEVENTH-TWELFTH QUARTERLY PROGRESS REPORT
Covering the Period April 1 to September 30, 1978

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

October 31, 1978

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.

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ABSTRACT

This Eleventh-Twelfth Quarterly Report covers progress from April 1 to September 30, 1978, on development of a process for producing high-purity silicon by zinc reduction of silicon tetrachloride in a fluidized bed of seed particles to yield a free-flowing granular product. A final report, covering Phases I and II of the program and written in lieu of an Eleventh Quarterly Report, has been submitted to JPL for approval. Work in the eleventh quarter, detailed in the Final Report, is summarized herein for continuity.

Pending the outcome of negotiations on the actual construction of a 50 MT/year experimental process facility (EPF), progress has been made in finalizing the design of the facility so that bids can be obtained on construction of the various process units. The design is being done by Raphael Katzen Associates International, Inc., of Cincinnati, Ohio, in frequent consultation with Battelle-Columbus personnel. Major simplification of the design of the zinc/ZnCl₂ by-product recycle system has been effected by the recognition that the finely divided unreacted zinc can be maintained in suspension as a solid and not melted and coalesced until it reaches the electrolytic cells.

Further, two of the original four ZnCl_2 strippers (solids condensers) have been eliminated with the recognition that the small amount of ZnCl_2 that would escape a condenser operating just above the melting point of ZnCl_2 can be adequately handled downstream.

Two models have been made of the EPF, one of the Reactor/Recovery section for display purposes, and one of the entire plant to facilitate piping and wiring design and unit placement.

Cost estimates, based on the 50 MT/year design and extrapolated, with appropriate modifications, to the 1000 MT/year level, are reproduced from the Final Report for Phases I and II. Three design options are given with two sub-cases, leading to costs of \$7.35, \$7.61, \$8.33, \$8.71, and \$11.21 (1975 dollars) per kg of silicon, depending upon the size of the fluidized-bed reactors and ZnCl_2 electrolytic cells employed. The cost range of from \$8 to \$9 appears to be accessible in the 1985 time frame, with the \$7 to \$8 range as an eventual goal. An energy payback time of 5.9 months has been calculated.

Experimental work has continued in support of the design program. Fluidized-bed modelling studies have given limited evidence of particle size segregation in the fluidized bed, hopefully leading to avoidance of the eventual growth of a few "marbles" that might plug the product withdrawal system.

Although the electrolysis of ZnCl_2 in conjunction with chlorination of the particulate silicon reaching the electrolytic cell has been demonstrated, improved ventilation of the anode to remove chlorine and to promote mixing with the KCl additive will be needed for maximum power efficiency. Appropriate electrode design changes are being studied.

A number of alloys, and graphite and silicon carbide products have been subjected to compatibility tests with the process stream components, with encouraging results.

Melting of the product silicon granules has been found to decrease their zinc content from about 1500 ppm in the as-produced condition to an undetectable level (<6 ppm, atomic absorption) after fusion.

The fate of impurities on vaporization of the zinc has been studied with inconclusive results, suggesting a need for refinement of the experimental technique.

A gas-piston pump design for recirculating ZnCl_2/Zn mixtures has been tested successfully along with a valve for control of liquid zinc flow.

INTRODUCTION

This Eleventh-Twelfth Quarterly Report is the first 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. In the first phase of the program, the zinc reduction of silicon tetrachloride in a fluidized bed of seed particles was selected to be the most promising of several options studied, from the standpoint of technical and economic feasibility. Phase II of the program concentrated on development of the process and the design of a 50 MT/year silicon experimental process facility (EPF) for possible construction and operation at BCL.

This report covers some of the Phase II effort plus work through September, 1978, on Phase III of the program which is directed toward construction and operation of the experimental facility. The designation of this as the Eleventh-Twelfth Quarterly Report is made to reconcile its timing with the fact that a Final Report* was issued at the end of the Phase I/II work in lieu of a Quarterly Report.

Finalization of the EPF design has been initiated along with an experimental support program, pending conclusion of negotiations leading to actual construction of the EPF.

* Not yet published; draft submitted for approval.

DESIGN OF THE EXPERIMENTAL PROCESS FACILITY (EPF)

Completion of the final design of the 50 MT Si/year EPF is proceeding at Raphael Katzen Associates International, Inc. (RKAI), in cooperation with Battelle's Columbus Laboratories' (BCL) personnel. The design as it existed toward the end of Phase II is outlined in the Tenth Quarterly Report (April 30, 1978) and the Final Report. Hence, only changes in the design since that time will be discussed in any detail here. The major design alterations, made for purposes of economy or process simplification, are:

- (1) Redesign of the ZnCl_2/Zn condenser, transfer lines, and storage tank to operate at 350 C rather than at 500 C
- (2) Elimination of two of the original four zinc chloride strippers
- (3) Redesign of the electrodes in the cell for electrolyzing ZnCl_2
- (4) Refinement of the design of the waste disposal system.

These changes as reflected in the current process flow diagrams, Figures 1 through 5, will be discussed in turn. In addition to incorporating the changes in design, these process flow diagrams show the instrumentation, purge lines, and heat exchange systems. Further details on the above-mentioned design changes are given below.

ZnCl_2/Zn Condenser Design

Initially this unit was to have operated as a wet-wall condenser for cooling the reactor by-products to ~500 C and thus condensing out the ZnCl_2 and zinc vapor as a liquid. The wet-wall medium was to have been recirculated ZnCl_2 at 500 C. Results of support experiments suggest that in ZnCl_2 /zinc mixtures held at 500 C (above both melting points), the

FIGURE 5. FLOW DIAGRAM OF THE WASTE TREATMENT SYSTEM

RAPHAEL KATZEN ASSOCIATES CONSULTING ENGINEERS CINCINNATI, OHIO U.S.A.			
REVISIONS NO. DATE BY			
1			
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DRAWN BY: MAN		DATE: 5-17-78	
CHECKED BY:		SCALE: None	
PROJECT: BATTELLE MEMORIAL INSTITUTE COLUMBUS, OHIO FLOW DIAGRAM WASTE TREATMENT SYS. DRAWING NO: WH-271-03			

zinc droplets tended to coalesce and settle. Consequently, since it is desirable to keep the zinc suspended so that it will circulate freely through the system, it was considered advisable to handle and store the ZnCl_2/Zn mixtures at 350 C (below the melting point of zinc) to maintain the zinc as fine particles in suspension. Furthermore, the lower temperature of 350 C made material selection for the ZnCl_2 recirculating pump in the condenser system less difficult, allowed the use of more conventional valves between the ZnCl_2/Zn storage tank and the electrolytic cells, and permitted elimination of graphite-lined transfer lines and storage tanks. In addition, Therminol cooling channels were relocated from internal axial orientation to the outer shell of the condenser to simplify operation and construction.

ZnCl_2 Stripper Revision

In the original flow sheet* duplicate condensers were provided for removing ZnCl_2 vapor from each of two process streams: (1) the recycled SiCl_4 from the reactor by-product and (2) the chlorine from the electrolytic cells. The duplicate condensers were to have been alternately cooled for condensation and heated to melt down and return the condensed ZnCl_2 . In this way the ZnCl_2 carry-over was to have been reduced to <0.05 percent. It was later decided that the amounts of ZnCl_2 ** that would escape condensation at just above the melting point should be easily handled, in one case as they reach the SiCl_4 condenser and form a very dilute slurry which would eventually exit with the bottoms of the SiCl_4 purification. In the other case, where the chlorine from the electrolytic cells is converted to NaOCl for use in local sewage effluent treatment***, the ZnCl_2 escaping

* E.g., Table 1 of the Eighth Quarterly Report.

** E.g., a few tenths of a percent of the ZnCl_2 reaching the condenser.

*** It will be recalled that this method of disposing of the by-product chlorine has been adopted only as an expedient in the 50 MT/year EPF. In the future, the chlorine will be used to generate SiCl_4 from metallurgical-grade silicon.

a condenser operating 10 degrees above the melting point (318 C) of ZnCl_2 would lead to a negligible 0.1 ppm in the hypochlorite solution. As the hypochlorite is used at 50 ppm in the sewage treatment, the zinc level is reduced to a totally negligible fraction (5×10^{-6} ppm) of the effluent entering the environment.

Electrolytic Cell Electrode Design

The design of the cell has been essentially finalized except for electrode design, which is currently the subject of support studies. The electrode design as originally conceived was determined in earlier support studies to have a higher-than-expected resistance, resulting in a reduced power efficiency. Trapped chlorine was thought to be the primary contributor to this condition even though the initial design included features to promote chlorine release. Recent support studies have tentatively confirmed this hypothesis.

Waste Disposal System Design

Changes in this system were all directed toward simplification of construction and operation. Most involved tray, solution inlet, and solution outlet relocation in the vent scrubber. In addition, control systems were simplified.

Design Status

In addition to implementing the design changes discussed above, RKAIH personnel, with BCL consultation, have completed several tasks as of the end of the current report period.

- (1) The engineering model is about 50 percent complete.
- (2) The plant layout has been finalized.
- (3) Design details of equipment in the Feed Preparation section are essentially complete (including SiCl_4 purification unit).

- (4) Design details of equipment in the Waste Disposal section are essentially complete.
- (5) Structural support designs have been essentially completed except for foundations.
- (6) Finalization of the design of the equipment in the Reactor/Recovery section is about 50 percent complete.
- (7) Significant progress has been made in finalizing piping, electrical, and instrumentation.

Tasks yet to be concluded are:

- (1) Completion of the engineering model
- (2) Finalization of Reactor/Recovery section design
- (3) Completion of piping, electrical, instrumentation, and foundation specifications.

MODELLING OF THE 50 MT Si/YEAR
EXPERIMENTAL PROCESS FACILITY

Modelling of the 50 MT/year facility has been undertaken with a dual purpose:

- (1) To facilitate (a) visualization of the relative size and positioning of the units and (b) layout of piping and related equipment within the available space
- (2) To provide a "showpiece".

A model of the Reactor/Recovery section made for display purposes was shown at the Tenth Project Integration Meeting at Pasadena, August 16 and 17, 1978. Figure 6 is a front view of that model. In Figure 7, a back view, the SiCl_4 vaporizer is on the far left and the fluidized-bed reactors are just to the right of the first flight of stairs. The zinc/ ZnCl_2 by-product condensers are on the upper level just to the right of the middle vertical column, and the ZnCl_2 strippers are shown in the center on the top deck together with a condenser for unreacted SiCl_4 on the right. Behind the condenser for unreacted SiCl_4 is a shorter condenser for the SiCl_4 produced in periodic chlorination of the wall deposit accumulated in the fluidized bed. The six 6000-amp electrolytic cells for recovering zinc and chlorine from the ZnCl_2 are visible in both figures on the intermediate access level, with the electrolysis feed tank above and the zinc storage tank below. The power supply for the electrolytic cells is visible to the far right. At floor level below the zinc storage tank are the zinc vaporizers feeding the fluidized bed. The product withdrawal systems are visible at the base of the fluidized beds.

Another model, made for engineering purposes, includes the entire facility and structural elements of the existing building in which it is to be housed. As indicated earlier, this model is about 50 percent complete in that (1) site details have been modelled, (2) essentially all the structural support and equipment have been located, and (3) piping has been initiated.

FIGURE 6. MODEL OF REACTOR/RECOVERY SECTION
 OF 50 MT/YEAR EPF (4333VD)

FIGURE 7. MODEL OF REACTOR/RECOVERY SECTION OF
50 MT/YEAR EPF (CLOSE-JP) (4334VD)

COST OF INSTALLING THE 50 MT/YEAR
EXPERIMENTAL PROCESS FACILITY AT BATTELLE

In the Tenth Quarterly Report, an estimate of \$1.5 million was given for the cost of installing the 50 MT/year experimental facility at Battelle. This estimate was prepared by the project staff on the basis of (1) the detailed costs of equipment, instrumentation, piping, wiring, and related items provided by RKAI and (2) appropriate modifications for BCL overhead and manpower rates where the use of BCL manpower is anticipated. This estimate was transmitted to JPL for budgetary purposes. Subsequently, an independent analysis was made by the Pilot Plant and Research Facilities group at BCL which resulted in a cost estimate within about 3 percent, i.e., \$27,000 higher than that obtained earlier.

ECONOMIC ANALYSIS OF SILICON PRODUCTION
AT THE 1000 MT/YEAR LEVEL

One of the objectives of the design of the 50 MT/year EPF was to provide a firmer basis on which to estimate production costs at the 1000 MT/year level, which should be more reliable than those given in the Second Quarterly Report. For that purpose, the costs of individual items of capital equipment in the 50 MT/year design were scaled to an appropriate larger size by the relation

$$\text{relative cost} = (\text{relative capacity})^{0.6}$$

and then multiplied by the number of units required to meet the 1000 MT/year capacity.

At the same time, the manpower, materials, and utilities costs were revised on the basis of the 50 MT/year design and experience gained since the earlier cost estimates were made.

Table 1 lists the items of equipment for the 50 MT/year EPF on which the estimates for the 1000 MT/year plant are based.

Three cases are defined as follows:

Case I

- (1) Six parallel feed preparation and deposition systems (17-inch-diameter fluidized-bed reactors)
- (2) Twelve 60,000-amp electrolytic cells for zinc recycle
- (3) One common waste disposal system
- (4) One common chlorine supply system (for chlorination of wall deposit)

Case II

- (1) Two parallel feed preparation and deposition systems (29-inch-diameter fluidized-bed reactors)
- (2) Twelve 60,000-amp electrolytic cells for zinc recycle, with an option of two 360,000-amp cells

TABLE 1. LIST OF EQUIPMENT FOR THE 50 MT/YEAR EXPERIMENTAL FACILITY UPON WHICH THE COST ESTIMATES FOR A 1000 MT/YEAR PLANT ARE BASED

Item No.	Description (a)	Estimated Item Cost	Item No.	Description	Estimated Item Cost
C1	SiCl ₄ Storage Tank 4,600 gal 7' D x 16' T/T	\$ 7,000	A6	Zinc Level Tanks includes heaters and controls	\$ 3,500
C2	Not Used		A7	Zinc Vaporizer includes power supply and temperature controls	15,000
C3	SiCl ₄ Purification Section	57,227	A8	Silicon Product Coolers	800
C4	SiCl ₄ Emergency Storage Tank 4,600 gal 7' D x 16' T/T	7,000	A9	Silicon Collectors	300
C5	Purification Feed Pump 30 gpm 30' TDH 1.5 SG 1-1/2 hp	760	A10	Zinc/ZnCl ₂ Condensers	15,800
C6	SiCl ₄ Feed (Metering) Pump 1/2 hp 13 pgh	1,100	A11	ZnCl ₂ Strippers	13,320
C7	Not used		A12	Not used	
C8	Vent Condenser 37 sq ft 2 pass on tube side 15° < in horizontal	1,300	A13	SiCl ₄ Condenser	1,700
	Refrigeration System 5T 10 hp	6,500	A15	ZnCl ₂ Circulating Pumps 2.4 gpm	1,500
A1	Pure SiCl ₄ Storage Tank 6' D x 10' T/T	6,000	A17	Therminol Cooler (Hot Circuit) 120,000 Btu/hr	1,900
A2	SiCl ₄ Boiler 2.75' D x 3' T/T 4 kW, includes heater and controls	1,400	A19	Therminol Cooler (Cold Circuit)	800
A3	Fluidized Bed Reactors	22,500	A20	SiCl ₄ Boiler Blowdown Pump Automatic Control	1,700
	Seed Addition Hopper	1,000	A21	Therminol Cooler Blower 500 acfm, 8" WG, 1-1/2 hp	1,000
	Furnace 80 kW, includes all necessary controls	21,500	A22	Hot Circuit Head Tank 1.5' C x 3.75' T/T, includes heater and controls	800
A4	Zinc Hopper	500	A23	Therminol Blowdown Tank 2.75' C x 3' T/T, includes heater and controls	1,100
A5	Zinc Molten Storage Tank 20 kW, includes heaters and controls	17,600			

(a) Items indicated as "not used" were either dropped from the original 50 MT/year facility design or will not be used in a 1000 MT/year plant.

TABLE 1. (Continued)

Item No.	Description	Estimated Item Cost	Item No.	Description	Estimated Item Cost
A24	Start-Up Heater 29 kW	\$ 2,000	D8	Makeup NaOH Metering Pump 1/2 hp	\$ 1,700
A25	Hot Circuit Pump	2,900	E1	Not Used	
A26	Cold Circuit Pump	1,400	E2	Not used	
A27	SiCl ₄ Feed Pump 1 gph @ 48' TDH	300	E3	Not used	
B1	Electrolysis Feed Tank 20 kW, includes heaters and controls	17,600	E4	Not used	
B2	Electrolysis Cells	9,700	E5	Not used	
A-F	Power Supply 160 kW	15,300	E6	Caustic Storage Tank 12,000 gal capacity 12' D x 14'6" T/T	8,500
	Bus	7,600	E7	Final Vent Gas Scrubber 7'6" D x 17'4" T/T four polypropylene trays Teflon mist eliminator	14,000
B3	ZnCl ₂ Strippers	4,480	F8-162	Eductor Penberthy Series 60 Size LL-2"	300
B4	Not used		E9	ID Fan 10,000 acfm @ 15" WG 50 hp	6,800
F3	Not used		E10	Primary Loop Recirculation Pump 100 gpm @ 100' TDH 8 hp	1,890
F4	Chlorine Supply Tank	500	E11	Secondary Loop Recirculation Pump; 100 gpm @ 30' TDH 2 hp	1,830
D1	Not used		E12	Makeup NaOH Metering Pump 54 gph 1/2 hp	1,700
D2	Not used		E13	Fill/Drain Pump 100 gpm @ 30' TDH 2 hp	1,830
D3	Primary SiCl ₄ Vent Scrubber 3' D x 4'4" T/T, flat bottom	1,000	E14	Not used	
D4	Not used				
D5	NaOH Recycle Cooler Plate and Frame Exchanger	5,100			
D6-162	Eductor Penberthy Series 60 Size LL-1-1/2"	140			
D7	Primary Scrubber Recirculation Pump; 20 gpm @ 125' TDH 2.5 hp	1,160			

- (3) One common waste disposal system
- (4) One common chlorine supply system

Case III

- (1) One feed preparation and deposition system (41-inch-diameter fluidized-bed reactor)
- (2) One 720,000-amp electrolytic cell for zinc recycle, with an option of six 120,000-amp cells
- (3) One common waste disposal system
- (4) One common chlorine supply system.

Except for the use of fewer (12 versus 30) larger electrolytic cells, Case I is essentially that adopted for the original cost estimate. Case II reflects the savings that accrue from going to fewer (two versus six) and larger (29-inch versus 17-inch) fluidized-bed reactors and associated equipment.

Case III represents the minimum-cost option, which would use a single 41-inch-diameter fluidized bed and one 720,000-amp electrolytic cell. Fluidized beds of that size are operated in the petrochemical industry and preliminary calculations have shown that extraction of the exothermic heat of reaction does not constitute a size limitation, even at 60-inch diameter. Bipolar electrolytic cells of up to 10^6 equivalent amp are under construction for the electrolytic recovery of aluminum. Thus, although Case III is a large extrapolation from the technology anticipated for use at the 50 MT/year level, it appears to be ultimately accessible.

Since some optimum multiplicity of units will be required to maintain a steady operation, more than a single unit should be operated at a given site, even at the 1000 MT/year/unit level. Case III would envision operating three 1000 MT/year units at one site to fulfill the 3000 MT/year goal of the LSA Project.

It should be noted that although the purchase of SiCl_4 is planned at the 50 MT/year level, the SiCl_4 will be generated at the 1000 MT/year level by reaction of metallurgical-grade silicon with chlorine from the

electrolytic cells. However, the capital, labor, materials, and manpower requirements of that operation have not been calculated in detail. Instead, all of these costs are included in a materials cost for SiCl_4 , calculated at lowest market price plus 20 percent credit for on-site manufacture instead of purchase. The resulting SiCl_4 material cost of \$1.69 per kg of silicon product is assumed to be constant for the three cases. This is equivalent to the assumption that the size of the SiCl_4 preparation unit(s) does not change from Case I to Case III, a conservative position.

Since the raw material is factored in as SiCl_4 , rather than as metallurgical-grade silicon and chlorine, a \$0.37/kg Si credit is given for the by-product chlorine.

Table 2 gives the equipment costs, scaled as indicated above, for Cases I, II, and III for each of the six sections of the plant.

Table 3 gives the manpower breakdown and costs for the three cases.

The materials requirements given in Table 4 are essentially the same for the three 1000 MT/year cases as those for the 50 MT/year facility except for the nitrogen blanket gas whose requirement was scaled up from the 50 MT/year level by $(\text{relative use}) = (\text{relative size})^{0.5}$. For simplification, the utility costs given in Table 5 are assumed to be common to the three cases, a conservative position. Process energy requirements for Items 1 through 7 and part of 8 are assumed to be constant with scale; however, as heat losses per unit volume decrease with increasing size, the overall kw per kg of silicon also decreases. The heat losses from process units and from line tracing (Items 9 and 10) were scaled on the basis of $\text{area} \propto \text{volume}^{2/3}$, i.e.,

$$(\text{relative loss}) = (\text{relative size})^{2/3}$$

Although it will not be necessary in the 1000 MT/year facility to convert the chlorine from the electrolytic cells to NaOCl , a vent and area gas scrubber of the same size as used in the 50 MT/year facility for the scrubbing and waste disposal functions will be required for the 1000 MT/year facility. Hence, the energy requirement for the 50 hp blower was distributed over the 144 kg/hour silicon output of the 1000 MT/year facility.

TABLE 2. EQUIPMENT COSTS (1975 DOLLARS) BY GROUPS FOR
50 MT/YEAR EXPERIMENTAL FACILITY AND 1000 MT/
YEAR PLANT -- CASES I, II, AND III*

Equipment Group	50 MT/Year ^(a) Equipment Cost in 1975 Dollars	1000 MT/Year Equipment Cost in 1975 Dollars		
		Case I	Case II	Case III
A - Reaction/Recovery	\$173,360	\$1,724,106	\$1,111,023	\$ 841,998
B - Zinc Recovery	84,554	835,200	673,224	374,967
C - Feed Preparation	66,288	831,030	539,795	399,994
D - Waste Processing	7,573	45,697	45,697	45,697
E - Vent Scrubbing	30,446	30,446	30,446	30,446
F - Chlorination	410	2,474	2,474	2,474
	<u>\$362,631</u>	<u>\$3,468,953</u>	<u>\$2,402,659</u>	<u>\$1,695,576</u>
			\$2,208,372 ^(b)	\$1,830,824 ^(c)

(a) Includes items used only in 1000 MT/year facility.

(b) Based on two 360,000-amp cells instead of twelve 60,000-amp cells.

(c) Based on six 120,000-amp cells instead of one 720,000-amp cell.

*CE Equipment Index: 1975 - 191.6; 1978 (February) - 233.8; factor - 0.8195.

TABLE 3. MANPOWER BREAKDOWN AND COSTS^(a,b)

Operation	Manhours per Day					
	Case I		Case II		Case III	
	Skilled	Semi-Skilled	Skilled	Semi-Skilled	Skilled	Semi-Skilled
Feed Preparation	12	11	4	12	4	12
Vaporization	12	11	4	12	4	12
Deposition	12	19	4	12	4	12
Condensation	12	11	4	12	4	12
Electrolysis	18	18	4	12	4	12
Waste Treatment	8	8	4	12	4	12
Product Handling		36		16		16
Raw Material Handling		36		16		16
	74	150	24	104	24	104
Dollars per day	\$ 1,178.4		\$ 636.8		\$ 636.8	
Dollars per year	\$420,689		\$227,338		\$227,338	

(a) Labor hours/process based on Peters and Timmerhaus⁽¹⁾ number of operator hours/major process step.

(b) Labor rate based on Peters and Timmerhaus⁽¹⁾ adjusted to 1975 dollars:

Skilled - \$6.60/hour
Semi-Skilled - \$4.60/hour

TABLE 4. MATERIALS COST (1975 DOLLARS)

Material	Requirement per kg Si	Unit Cost, dollars	Cost/kg Si, dollars
SiCl_4	15.68 lb	$0.135 \times 0.8^{(a)}$	1.69
Zinc	0.54 lb	0.39	0.21
Caustic (50% aq. NaOH)	2.4 lb	0.063	0.15
Argon	3.1 scf	0.016	0.05
Nitrogen	7.6 scf	0.003	0.02
Chlorine	2.04 lb	0.067	0.14
			<u>2.26</u>

(a) Credit for on-site manufacture.

TABLE 5. UTILITIES COST (1975 DOLLARS)

Item(a)	Requirement/kg Si		
1. Zinc Electrolysis	21.56 kwh	(b)	
2. Zinc Vaporization	4.24 kwh		
3. Zinc Melting	0.02 kwh		
4. SiCl ₄ Vaporization	0.00 kwh	(c)	
5. SiCl ₄ Preheating	1.45 kwh		
6. Fluidized-Bed Reduction Reaction	0.00 kwh	(d)	
7. SiCl ₄ Purification	1.80 kwh	(e)	
8. Pumps, Blowers	4.0 kwh		
9. Heat Losses from Process Units	1.94 kwh		
10. Line Tracing	1.24 kwh		
11. Instrumentation	0.21 kwh		
Subtotal Electrical	36.46 kwh @ \$0.03		= \$1.094
12. Cooling Water	180.0 gal @ \$0.04/1000		= \$0.007
13. Process Water	2.6 gal @ \$1.00/1000		= \$0.003
TOTAL UTILITIES			\$1.104

(a) Primarily endothermic process heat in Items 1 through 8, except for Item 1 which includes resistive heat loss; heat losses from process units, insulated to OSHA standards, are included in Item 9.

(b) At 2 kwh/lb Zn.

(c) 0.63 kwh supplied by heat exchange with Zn/ZnCl₂ condenser.

(d) Exothermic reaction.

(e) Additional 3.8 kwh supplied by heat exchange with Zn/ZnCl₂ condenser.

It was assumed that the instrumentation power costs for one of the six sections of the 1000 MT/year facility in Case I would equal that for the 50 MT/year facility and that this cost would remain the same for Cases II and III, again a conservative position.

Table 6 gives the fixed capital investment costs for Cases I, II, and III based on Table 2.

Table 7, in the Lamar University format⁽²⁾, gives the total product cost on the basis of Tables 3, 4, 5, and 6. It can be seen from the data of Table 7 that for all of the cases analyzed, the cost of silicon produced by the fluidized-bed zinc reduction of SiCl_4 falls near the \$10/kg silicon LSA goal, with Cases II and III beating the goal by \$1.29 and \$2.65, respectively. Case II is a reasonable expectation for 1985 and Case III is a logical long-range goal.

The options on electrolytic cell size described previously for Cases II and III as indicated in Table 7 reflect a decrease of \$0.38/kg of silicon and an increase of \$0.26/kg of silicon in product cost, respectively. The options are presented because the trade-offs with cell size are not yet clearly understood and, consequently, data of this type are required to give insight into the effect of cell size on product cost.

Energy Payback

The process energy requirements (exclusive of pumping of utility water and other minor items) from Table 5 total 36.46 kwh/kg silicon. To this must be added the energy requirement of the metallurgical-grade silicon used, that of the make-up chlorine, make-up zinc, and that of the NaOH used to neutralize the chloride and chlorine wastes. Table 8 gives the energy requirements per kg of silicon. At 12,000 MT silicon per peak megawatt (60,000 MT/average mw, 0.0167 kw/kg), the power generation credit is 12.10 kw/month, whence the payback time is 5.9 months. The power generation rate is the equivalent of about 50 percent silicon material loss in the fabrication of 0.0254-cm-thick cells generating 0.1 kw/m² over 1825 hours/year.

TABLE 6. FIXED CAPITAL INVESTMENT

Cost Item		Case I	Case II	Case III
Direct Cost (D)				
1. Purchased equipment (E)		\$ 3,468,953	\$ 2,402,659	\$1,695,576
2. Installation of E	40 percent of E	1,387,581	961,064	678,230
3. Instrumentation (Installed)	25 percent of E	867,238	600,665	423,894
4. Piping (Installed)	60 percent of E	2,081,372	1,441,595	1,017,346
5. Electrical (Installed)	15 percent of E	520,343	360,399	254,336
6. Buildings and Services	47 percent of E	1,630,408	1,129,250	796,921
7. Yard Improvements	10 percent of E	346,895	240,266	169,558
8. Service Facilities	50 percent of E	1,387,581	961,064	678,230
9. Land	6 percent of E	208,137	144,160	101,735
TOTAL DIRECT COST		\$11,898,508	\$ 8,241,122	\$5,815,826
Indirect Cost (I)				
1. Engineering and Supervision	15 percent of E	\$ 520,343	\$ 360,399	\$ 254,336
2. Construction Expenses	14 percent of E	485,653	336,372	237,381
TOTAL D AND I		\$12,904,504	\$ 8,937,893	\$6,307,543
Contractor's Fee	10 percent of D and I	\$ 1,290,450	\$ 893,789	\$ 630,754
Contingency	10 percent of D and I	\$ 1,290,450	893,789	\$ 630,754
Fixed Capital Investment - 1000 MT/year		\$15,485,404	\$10,725,471	\$7,569,051

TABLE 7. PRODUCT COST (\$/kg SILICON)

Cost Item	Case I	Case II	Case III
1. Direct Manufacturing Cost (Direct Charges)			
1. Raw Materials - from design	\$2.26 ^(a)	\$2.26 ^(a)	\$2.26 ^(a)
2. Direct Operating Labor - from design	0.42	0.23	0.23
3. Utilities - from design	1.10	1.10	1.10
4. Supervision and Clerical, 15 percent of 1.2	0.06	0.03	0.03
5. Maintenance and Repairs, 10 percent of fixed capital (50 percent labor, 50 per- cent materials)	1.55	1.07	0.76
6. Operation Supplies, 20 per- cent of 1.5	0.31	0.22	0.15
7. Laboratory Charge, 15 per- cent of 1.2	0.06	0.03	0.03
8. Patents and Royalties, 3 percent of product cost	0.34	0.26	0.22
2. Indirect Manufacturing Cost (Fixed Charges)			
1. Depreciation, 10 percent of fixed capital	\$1.55	\$1.07	\$0.76
2. Local Taxes, 2 percent of fixed capital	0.31	0.22	0.15
3. Insurance, 1 percent of fixed capital	0.16	0.11	0.08
4. Interest, 8 percent of fixed capital	1.24	0.87	0.62
3. Plant Overhead, 60 Percent of Labor in 1.2 + 1.4 + 1.5	\$0.75	\$0.48	\$0.38
4. By-Product Credit - From Design	-\$0.37 ^(b)	-\$0.37 ^(b)	-\$0.37 ^(b)
4A. Total Manufacturing Cost, 1 + 2 + 3 + 4	\$9.74	\$7.58	\$6.40

TABLE 7. (Continued)

Cost Item	Case I	Case II	Case III
5. General Expenses			
1. Administration, 6 percent of manufacturing cost	\$0.59	\$0.45	\$0.38
2. Distribution and Sales, 6 percent of manufacturing cost	0.59	0.45	0.38
3. Research and Development, 3 percent of manufacturing cost	<u>0.29</u>	<u>0.23</u>	<u>0.19</u>
6. Total Cost of Product, 4A + 5	<u>\$11.21</u>	<u>\$8.71</u>	<u>\$7.35</u>
		(\$8.33) (c)	(\$7.61) (d)

(a) Includes all cost (operating and capital investment) for the manufacture of SiCl_4 used.

(b) Credit for by-product chlorine; see text.

(c) Based on the use of two 360,000-amp cells instead of twelve 60,000-amp cells.

(d) Based on the use of six 120,000-amp cells instead of one 720,000-amp cell.

TABLE 8. ENERGY REQUIREMENTS, kwh/kg Si

Item	Basis	Energy Requirement, kwh/kg Si
Process	Table 5	36.46
Make-up Cl ₂	2.04 lb/kg Si @ 1.54 kwh/lb ^(a)	--- ^(b)
NaOH	2.4 lb/kg Si @ 1.37 kwh/lb ^(a) ; 97 percent utilization	3.29
Make-up zinc	0.54 lb/kg Si @ 2 kwh/lb ^(c)	1.08
Metallurgical-grade Si	1.27 kg/kg Si @ 23.97 kwh/kg ^(d) ; 95 percent utilization	30.44
		<u>71.27</u>

(a) Reference (3).

(b) Co-product of NaOH production.

(c) Conservative estimate of 2 kwh/lb Zn adopted on basis of 1.6 kwh/lb projected by U. S. Bureau of Mines, Reno, Nevada⁽⁴⁾.

(d) Reference (5).

The difference between the 5.9 months calculated above and the 2 months calculated earlier is the result of a more realistic estimate of the power efficiency of the ZnCl₂ electrolysis step, of including the energy requirements of the make-up zinc and the caustic used to neutralize the waste SiCl₄ and Cl₂ which had not been included earlier, making a more detailed examination of power losses from the 1000 MT/year plant, and adopting a more realistic value for the loss of material in manufacture of the cell from the polycrystalline product. Although not as optimistic as the 2 months estimated earlier, the 5.9-month energy payback time is presumed to be an acceptable value.

EXPERIMENTAL SUPPORT PROGRAM

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

- (1) Fluidized-bed modelling
- (2) Zinc chloride electrolysis
- (3) Materials compatibility
- (4) Product quality
- (5) Purification of zinc during vaporization
- (6) Valving and pumping of zinc and zinc chloride.

In cases where details are given in the Final Report for Phases I and II, only a brief summary is given here.

Fluidized-Bed Modelling

A series of experiments was performed in the 7-inch-diameter fluidized-bed model*. The purpose of these experiments was to study fluidization and product withdrawal. The action of the bed at fluidizing gas flows approximating those expected in the 50 MT/year facility was violent with slugging and spouting taking place regularly. The motion of the bed particles was generally down the walls of the bed and up through the central portion of the bed. Silica sand from various sources was used as the dummy bed. The particle size distribution, estimated to be similar to that expected in the 50 MT/year reactors after starting with 100 μm seed particle and coming to nearly steady state was as shown in Table 9. Product withdrawal was studied using a 0.409-inch-ID withdrawal tube with purge gas flows ranging from 1 to 4 l/minute. Intermittent withdrawal at low average withdrawal rates (5 to 7 g/minute) of samples equal to ~1 percent of the bed gave evidence of loss of smaller particles in the lower part of the bed at the higher purge flow.

* Full-scale model of the twin 25 MT/year reactors to be used in the 50 MT/year facility.

TABLE 9. PARTICLE SIZE DISTRIBUTION
FOR MODELLING EXPERIMENTS

Particle Size Range, μm	Weight, percent
105- 149	3.5
149- 210	6.5
210- 279	16.9
279- 420	19.5
420- 590	32.0
590- 840	16.5
840-1000	3.5
1000-1190	1.3
1190-1410	0.3

Average product withdrawal rates comparable to those expected in the 50 MT/year facility (50-60 g/minute) were achieved by fully opening the withdrawal tube for about 1 out of every 15 seconds for time periods sufficient to withdraw about 10 percent of the bed per sample (actual rate during 1-second period was 750 to 900 g/minute). Very little segregation in the bed was evidenced even at the higher withdrawal tube purge flow rates, although there did appear to be some correlation with purge flow rate. It must be noted, however, that each sampling reduced the total bed size, and that the dummy bed differed from that of the planned facility in that no particle growth occurred in the dummy bed. In addition, it was observed that the overall particle size distribution of the bed shifted with time toward the smaller size fractions due to attrition, and that some of the smallest particles were elutriated from the bed.

Despite the observed reduction in segregation with an increase in withdrawal rate, it is believed that the segregation effect is sufficient to preclude the growth of a few "marbles" to the point that the product discharge port is blocked. If the withdrawal rate were continuous instead of intermittent, this conclusion is further strengthened in that the rate

required by one of the 25 MT/year reactors of the 50 MT/year facility would be considerably less than the actual rate associated with the higher average rate evaluated. In addition, as the size of a particle increases beyond the largest employed in the simulated dummy bed, the tendency of that particle to segregate and be removed preferentially should significantly increase.

Further experiments are to be carried out with a few (e.g., 0.1 percent of the "marbles" (e.g., 3000 to 4000 μm) in the dummy bed.

Zinc Chloride Electrolysis

Work with the electrolysis of the zinc chloride by-product of prior miniplant operation is detailed in the Final Report, with the following major conclusions:

- (1) The miniplant by-product condensate can be electrolyzed to recover zinc and chlorine from the contained ZnCl_2 without apparent interference (such as cell shorting) by the contained suspended zinc and silicon dust.
- (2) Silicon dust suspended in the by-product condensate can be chlorinated in the electrolytic cell at least up to 3.4 percent of the silicon production of the fluidized bed.
- (3) Cell voltages were higher than those experienced by the Bureau of Mines work; this is believed to relate partly to electrode resistance loss and perhaps to less efficient mixing of the ZnCl_2 with the KCl electrolytic inventory. Solution of this problem is being pursued.
- (4) The projected electrical energy requirement of about 2 kwh per pound of zinc electrolyzed appears to be reasonable.

Currently work is being conducted in a small size (1000 ml) electrolytic cell to evaluate electrode configuration as a means of

optimizing power efficiency. It is hypothesized that chlorine entrapped at the face of the horizontally positioned anode is the primary cause for the higher-than-expected cell resistance observed in the experimental work. Vertically positioned electrodes could obviously minimize this problem, but would replace it with an equally or more serious problem -- rechlorination of the zinc formed at the top of the electrodes. Accordingly, a compromise between the vertical and horizontal positioning, or other means of ventilating the space between the electrodes is being explored.

Materials Compatibility

Although tentative selection of construction materials for the Reactor/Recovery section of the demonstration facility were made in Phase II work based on compatibility tests, it was considered advisable to confirm these earlier selections as well as evaluate additional candidates before finalizing the choice of materials. Accordingly, stainless steel, chromium, and nickel-base superalloy specimens are being exposed to, e.g., Zn vapor at 900 C, Zn/ZnCl₂ product from the miniplant at 350 C, and Zn granules at 350 C. The purpose of these experiments is to determine (1) what measures must be taken to prevent degradation of the reactor containment structure by accidental exposure to Zn vapor, and (2) whether lowering the temperature of the ZnCl₂ by-product to 350 C in the condenser may permit simplification of the condenser design and elimination of the use of liner materials in the condenser recirculation pump, ZnCl₂ transfer pipes, and the ZnCl₂ storage tank. It is expected that the results of these exposure tests will be available at the end of October and will be included in the next Quarterly Report.

Two commercially available carbon-impregnated graphite materials were investigated as possible candidates for lining selected tanks and reactors. The two Carborundum "Graph-i-tite" materials, Grade "A" for amorphous carbon-impregnated and Grade "B" for graphite-impregnated, both proved to be completely impervious to helium (0.0000 Darcy) at room temperature over test times of 24 hours. Both were exposed to molten Zn at 500 C

for 7 hours and then analyzed by spark source mass spectrometry. Specimens of "Graph-i-tite A" material, 1/2-inch by 1/4-inch by 1/4-inch, appeared to absorb about 110 ppmw of Zn compared to 2 ppmw for comparable samples of the "Graph-i-tite B" material. Other major impurity concentrations, e.g., 5-10 ppm B, 20-100 ppm Na, 10-20 ppm Si, 30-60 ppm Cl, 20-40 ppm Mg, and 3-7 ppm S, were not measurably affected by the exposure to molten Zn.

A second candidate for lining critical parts of the EPF was evaluated. Nitride-bonded silicon carbide re-fired in oxygen was determined to have a permeability to helium at room temperature of 0.0000 Darcy after 24 hours of testing. A 0.0045 Darcy permeability was measured on material that had not been oxygen re-fired, thus demonstrating the effectiveness of the oxide glaze in re-firing.

Product Quality

Details of several analyses of quality evaluation specimens of miniplant silicon containing as little as 5.6 percent seed material are given in the Final Report. It is concluded that zinc is the major impurity, being present to the extent of 1500 ppmw even after vacuum heat treatment for 1 hour at 920 C. Fusion of the silicon under argon reduced the zinc content to an undetectable <6 ppmw by atomic absorption analysis. Atomic absorption analyses agreed with neutron activation analysis at the 1500 ppm level for which a comparison was made.

Purification of Zinc During Vaporization

The expected purification of the recycled zinc feed material on vaporization was investigated by means of a simple distillation experiment. Zinc, containing 194 ppm Fe, 14 ppm Pb, and 5 ppm Cd, was recovered from operation of the miniplant electrolytic cell, and 55 percent was boiled off at 1 atm pressure (908 C) under an argon blanket in quartz apparatus. The condensate was found to contain 28 ppm Fe, 8 ppm Pb, and 6 ppm Cd while the

residue contained 423 ppm Fe, 24 ppm Pb, and 0.5 ppm Cd as determined by atomic absorption. This indicates that low volatility impurities are indeed concentrated in the heel during vaporization and that highly volatile impurities such as Cd are concentrated in the vapor.

Table 10 compares the results with those to be expected for single-plate distillation on the basis of vapor pressure and activity data. In this tabulation, α is the ratio of the vapor pressure of the more volatile to the less volatile component.

As can be seen from the results of Table 10, more iron and lead were carried into the condensate than would have been expected from volatilization alone. The results could be accounted for by mechanical carry-over of 9 percent of the initial material in the case of iron, which is remotely possible. However, the required 37 percent carry-over in the case of lead is inconsistent with the value for iron carry-over, and difficult to visualize physically. The agreement of the α values for cadmium is definitely within experimental effort, as 1 ppm error in the cadmium analysis would lead to $\alpha = \infty$ based on initial and condensate analyses.

In view of the discrepancies in the above results, the experiment will be repeated with additional precautions taken to avoid the mechanical carry-over of material from the heel.

Valving and Pumping of Zinc and Zinc Chloride

One of the major items covered in the support effort during this period was the evaluation of a newly designed pump and valve for handling the molten ZnCl_2/Zn (plus small percentage of Si) by-product from the reactor. The pump is required to recirculate the ZnCl_2/Zn from the bottom to the top of the condenser since this liquid is used to wet the condenser surfaces. Plans are to use the valve in selected areas in the zinc recovery section of the facility. Both were constructed of graphite with the valve being full size and the pump $\sim 1/8$ (volume basis) that required in the

TABLE 10. RELATIVE VOLATILITY (α) OF ZINC COMPONENTS

Element	α , Based on Analyses of Heel and Initial Material	α , Based on Analyses of Condensate and Initial Material	Vapor Pressure Ratio ^(a)	Activity Ratio ^(b)	α , Theoretical
Fe	--(c)	8.0	$\frac{\text{Zn}}{\text{Fe}} = 1 \times 10^{10}$	$\frac{\text{Fe}}{\text{Zn}} = 10^{(d)}$	1×10^9
Pb	3.0	2.5	$\frac{\text{Zn}}{\text{Pb}} = 2200$	$\frac{\text{Pb}}{\text{Zn}} = 35$	63
Cd	>3	3.5	$\frac{\text{Cd}}{\text{Zn}} = 4.06$	$\frac{\text{Cd}}{\text{Zn}} = 4.0$	16

(a) Data from Stull and Sinke⁽⁶⁾.

(b) Data at infinite dilution from R. Hultgren, et al.⁽⁷⁾, except as indicated.

(c) Intractable; analysis indicated more total iron in heel than was present in initial material.

(d) Data not available at zinc-rich end of the system; $\gamma = 10$ estimated.

50 MT/year facility. The valve and pump were assembled into a loop having a ~9-foot head (equivalent to that required by the ZnCl_2/Zn condenser) with a by-product supply and collector tank. The valve performed satisfactorily and the pump, after a few modifications in the control and activation auxiliary equipment were made, delivered at approximately the design rate. Considerably more confidence in the operability of this pump was achieved by this effort since valuable operational experience was gained and design deficiencies identified that will be corrected in the final design.

PLANS FOR FUTURE WORK

Work planned during the next report period includes:

- (1) Completion of the 50 MT/year EPF design including the model
- (2) Acquisition of bids from commercial suppliers for all equipment, and multiple bids where appropriate
- (3) Acquisition of multiple bids from mechanical contractors on the construction of the EPF
- (4) Placement of equipment on order as soon as JPL provides BCL with appropriate authorization
- (5) Continuation of the support studies to resolve design problems or optimize operation as the need becomes apparent.

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