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FINAL REPORT
Covering the Period October 9, 1975, to July 9, 1978

on

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

(Phases I and II)

JPL Contract 954339

Silicon Material Task
Low-Cost Solar Array Project

to

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY

from

BATTELLE
Columbus Laboratories

July 9, 1978

ABSTRACT

The zinc reduction of silicon tetrachloride in a fluidized bed of seed particles to yield a granular product was studied along with several modifications of the thermal decomposition or hydrogen reduction of silicon tetraiodide. Although all contenders were believed to be capable of meeting the quality requirements of the LSA Project, it was concluded that only the zinc reduction of the chloride could be made economically feasible at a cost below $10/kg silicon (1975 dollars). Accordingly, subsequent effort was limited to evaluating that process.

A "miniplant", consisting of a 5-cm-diameter fluidized-bed reactor and associated equipment was used to study the deposition parameters, temperature, reactant composition, seed particle size, bed depth, reactant throughput, and methods of reactant introduction. It was confirmed that the permissible range of fluidized-bed temperature was limited at the lower

end by zinc condensation (918 C) and at higher temperatures by rapidly decreasing conversion efficiency [by 0.1 percent per degree C from 72 percent (thermodynamic) at 927 for a stoichiometric mixture]. Use of a graded bed temperature (decreased temperature upwards permitted by decreased zinc dew point of the partially reacted mixture) was shown to increase the conversion efficiency over that obtained in an isothermal bed.

Other aspects of the process such as the condensation and fused-salt electrolysis of the $ZnCl_2$ by-product for recycle of zinc and chlorine were studied to provide information required for design of a 50 MT/year experimental facility, visualized as the next stage in the development. Direct induction coupling to the boiling zinc was demonstrated as a reliable means of supplying the large heat requirement at that point while maintaining control of the rate of vaporization. Both miniplant and full-scale (25 MT/year) mock-up studies were made of the fluidized-bed reactor design to permit a choice for the two reactors of the 50 MT/year facility.

A total of 6.1 kg of silicon was prepared on semiconductor-grade seed particles for submission to JPL. However, analyses by spark-source mass spectrograph, neutron activation, and atomic absorption are not yet definitive in terms of quality for solar cell use.

Design of the 50 MT/year experimental facility was completed with the cooperation of Raphael Katzen Associates International, Inc., of Cincinnati, Ohio, and Pace Engineers, Inc., of Houston, Texas. On the basis of that design, described in this report, cost estimates were made for silicon production at the 1000 MT/year level. Although the preparation of $SiCl_4$ will be by-passed by direct purchase at the 50 MT/year level, operation at the 1000 MT/year level contemplates the chlorination of metallurgical-grade silicon with the chlorine from electrolysis of the by-product $ZnCl_2$.

Projected silicon costs of $7.35 and $8.71 per kg (1975 dollars) for a 1000 MT/year facility were obtained, depending upon the number and size of the fluidized-bed reactors and $ZnCl_2$ electrolytic cells used. An energy payback time of 5.9 months was calculated for the product silicon.

In view of the favorable technical and economic indications obtained, it is recommended that construction and operation of the 50 MT/year experimental facility be implemented.

A. INTRODUCTION

When JPL, under NASA/ERDA (now DOE), initiated the Low-Cost Solar Array Project (LSA), Battelle's Columbus Laboratories (BCL) was given the task of evaluating certain silicon production processes as to their potential for meeting the quality and cost goals set by the LSA Project [semiconductor-grade silicon at $10/kg in 1985 (1975 dollars)]. The approach proposed by BCL was (1) to study two processes which were known to have yielded semiconductor-grade silicon in commercial operation during the early days of the semiconductor silicon industry, and (2) to evaluate the probable economic effects of potential process improvements. The two processes were

(1) Zinc reduction of silicon tetrachloride (DuPont)

(2) Thermal decomposition of silicon tetraiodide (Mallinckrodt).

The first was a batch process, carried out at atmospheric pressure in an open tube to yield a mass of dendrites of non-uniform quality. The second, carried out on a "hot wire" (hot rod) reactor similar to the Siemens reactor now used in the present trichlorosilane reduction process by most silicon producers, was energy intensive.

The major improvements considered were to substitute fluidized beds for the open-tube and hot-rod reactors and to apply hydrogen reduction in various forms to the iodide process in place of low-pressure thermal decomposition. Flow sheets were drawn for the various process options, major equipment items were identified and sized, and conventional cost-estimate procedures used to arrive at production costs, with the objective of choosing the most promising process for further development and eventual pilot plant operation contingent upon continued demonstration of potential.

This final report, covering the 2.5 years of project work, is divided into four main sections, relating to

(1) Evaluation of candidate processes

(2) Experimental development of the zinc reduction of silicon tetrachloride in a fluidized bed of seed particles

(3) Design of a 50 MT/year experimental facility

(4) Cost estimates for a 1000 MT/year facility.

These subjects are discussed in turn.

B. EVALUATION OF CANDIDATE PROCESSES

Six candidate processes, i.e., one variation of the zinc reduction process and five of the iodide process, were evaluated for economic feasibility. As detailed in the Second Quarterly Progress Report for this program(1)*, certain constraints and opportunities in the zinc reduction process prompted limiting the evaluation to one option, whereas in the case of the iodide process, a number of apparently competitive options were retained.

The probable technical feasibility of each of the six evaluated processes was established either by prior knowledge or by experimental verification as part of this program. The experimental work associated with the zinc reduction process will be covered in Section C of this report, whereas that associated with the variations of the iodide process will be reported in this section.

The six processes evaluated may be described briefly as follows:

Process A - Preparation of $SiCl_4$ by chlorination of SiO_2/carbon mixtures, zinc reduction of $SiCl_4$ in a fluidized bed of seed particles, and recycle of the zinc and chlorine by electrolysis of the by-product zinc chloride

Process B - Preparation of SiI_4 by iodination of the metallurgical-grade silicon produced from SiO_2 + carbon, thermal dissociation of SiI_4 in a "hot-wire" reactor at low pressure, and recycle of I_2 and unreacted SiI_4

Process C - Same as (B) except for direct iodination of SiO_2/carbon mixtures instead of metallurgical-grade silicon to form the SiI_4

Process D - Fluidized-bed hydrogen reduction of SiI_4 produced by reaction of by-product HI with

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* References are given at the end of this report.

metallurgical-grade silicon produced as in (B), recycle of unreacted SiI_4, separation of H_2/HI by low-temperature condensation, and recycle of H_2 and HI

Process E - Same as (D) except for scrubbing of the by-product HI from HI-hydrogen off-gas, followed by wet processing (chlorination of HI + drying of molten iodine under concentrated sulfuric acid), and recycling the iodine and dried hydrogen (iodination with I_2 instead of HI)

Process F - Same as (D) except H_2/HI by-product is recirculated to the iodination step after removal of unreacted SiI_4 but without H_2/HI separation.

Other alternatives were omitted from the detailed evaluation for a variety of reasons.(1)

A word is in order regarding the potential advantages and disadvantages of the various process options which justified their choice for economic evaluation.

(1) The fluidized-bed deposition reactor has the advantage of providing a large surface for heterogeneous reaction and hence a high rate of production per unit reactor volume. Facilitated handling of the granular silicon product is another advantage. A disadvantage is that in the iodide process, excess hydrogen is required for reasonable efficiency. Operation of a shallow fluidized bed under reduced pressure is possible, but considered to be economically impractical for that application.

(2) Direct halogenation of SiO_2 + carbon mixtures in place of metallurgical-grade silicon offers the possible economy of avoiding that arc-furnace processing. The advantage is clear for the

preparation of $SiCl_4$ (Process A), as the chlorination efficiency is high and the technique has been used commercially*, but the advantage is less pronounced for the iodide processes where the halogenation efficiency is lower and the loss (and cost of recycle) of costly iodine by entrainment in the CO by-product, or in the SiO_2/C ash residue may become a significant cost factor.

Choice of Process Scale

For purposes of economic evaluation, it was assumed that the overall requirement of 3000 MT/year of silicon would be produced at three sites with a capacity of 1000 MT/year each. This production is conveniently handled in the case of Process A with six fluidized-bed zinc reduction reactors, 15 inches in diameter, each producing 24 kg/hr of silicon (80 percent on stream) as estimated from related experience. Although the entire plant production might be handled by a single 37-inch-diameter reactor in the case of this mildly exothermic reaction, strongly endothermic reactions, such as the hydrogen reduction of SiI_4, impose restrictions on the diameter of the fluidized-bed reactor where the endothermic heat requirement is supplied through the wall (even after taking advantage of maximum permissible preheating). For this reason, it seemed expedient to limit the size of the fluidized-bed reactor to 15 inches in diameter and to proceed from that as a reference. Additional economies from reactor scale-up may be considered later.

Approach to Economic Evaluation

The economic evaluation of Processes A through F involved the following steps:

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* However, most technical-grade $SiCl_4$ is currently made in the U.S. by chlorination of Acheson-process silicon carbide for convenience.

(1) Determination of feasible pressure/temperature/composition ranges for operation of the candidate processes from thermodynamic data(2,3,4) by means of Battelle's EQUICA free-energy-minimization computer program and experimental verifications

(2) Drafting of mass flow and energy flow sheets for the candidate processes, showing the major process functions and the enthalpy changes involved at each step

(3) Sizing of the major items of equipment necessary for each process step in the light of cross sectional area requirements dictated by gas flow for the mass transfer equipment, and the heat transfer area requirements dictated by the enthalpy changes for each heat transfer unit

(4) Estimation of the cost of the large items of equipment and conversion of the total to a fixed capital investment in accordance with standard texts on chemical engineering estimation(5,6,7) and with prior experience at BCL

(5) Determination of the net process energy requirements based on the energy flow diagram with appropriate assumptions concerning process heat exchange, dissipating waste heat, and energy loss

(6) Determination of materials costs based on chemical market prices and mass flow requirements with appropriate assumptions relative to materials utilization efficiency

(7) Estimation of direct labor costs by visualizing the man-hour requirements for the various operations involved in each process

(8) Conversion of the fixed capital investment, manpower, materials, and utilities costs to estimated product costs in accordance with standard texts on chemical engineering cost estimation(5,6,7).

All costs are for January of 1975, as obtained directly from the records for that period, or as extrapolated from prior cost estimates by means of published cost indices.(8)

Table 1 gives the January, 1975, materials costs used in the calculations, together with the sources of information.

TABLE 1. MATERIALS COSTS, JANUARY, 1975

Material	Lot Size	Cost	Reference
Silicon (metallurgical grade	Tonnage	\$1.00/kg	(9)
SiO_2 - 99.5 percent 325 mesh	Carload	\$0.0125/lb	(10)
Carbon, pet. coke	Tonnage	\$0.01/lb	(11)
Hydrogen	Piped under fence	\$0.96/lb (\$0.50/100 SCF)	(12)
Iodine, crude	Drum	\$2.59/lb	(10)
$SiCl_4$, tech.	Drum	\$0.185/lb	(10)
Zinc	Prime Western, tonnage	\$0.392/lb	(13)

The values of \$0.03/kwh used for power cost in the estimates was obtained from a representative of the Columbus and Southern Ohio Electric Company, Columbus, Ohio, as typical for most areas of the United States except those served by hydroelectric power.

Although it was recognized that utilities other than electrical would be required, these requirements would be small relative to electrical and to simplify the analysis were not estimated. All process heat was assumed to be electrical. Fifty percent of the exothermic heat was assumed to be recoverable and a 10 percent loss was added to the net endothermic heat requirement to arrive at the total.

The labor rates employed for manpower cost estimates were $6.60/hour for skilled operators and $4.60/hour for unskilled operators.

The cost of recovering iodine from iodine and iodide wastes of $0.20/pound was estimated from prior experience at BCL with a large iodide process titanium pilot plant(14) and confirmed as being consistent with industrial experience(15).

Any interest cost on the "capital investment" in the initial inventory of iodine in Processes B through F would eventually be offset by the increased value of the upgraded iodine.

Except for the cost of refrigeration units which were obtained by quotation, the costs of equipment, once sized, were taken from References 5 and 6 or, in the case of fluidized-bed reactors, halogenation furnaces, a scraper-condensers, and a centrifugal compressor for iodine/SiI_4, were based on BCL experience with similar units.

The following simplifying assumptions were made:

(1) Rather than to cost out the equipment and processing for $SiCl_4$ production from Cl_2, SiO_2, and carbon, that cost and others associated with $SiCl_4$ production were entered as a materials cost for all of the $SiCl_4$ used, but with a 20 percent credit for on-site production. Metallurgical-grade silicon from SiO_2 + carbon was similarly introduced, but at cost.

(2) The permissible volumetric throughput of fluidized-bed reactors and iodination reactors was assumed to vary approximately inversely as the square root of the average molecular

weight, i.e., approximately inversely as the average viscosity.

(3) Common heat transfer coefficients were assumed:

(a) 70 BTU $hr^{-1}ft^{-2}F^{-1}$* for gasses high in H_2

(b) 3 BTU $hr^{-1}ft^{-2}F^{-1}$ for higher molecular weight gases

(c) 3 BTU $hr^{-1}ft^{-2}F^{-1}$ for high molecular vapors condensing to solids in a scraper condenser

(d) 30 BTU $hr^{-1}ft^{-2}F^{-1}$ for high molecular weight material being vaporized from its liquid.

Having these values and an estimated available ΔT for each heat-transfer step, the heat-transfer areas required were estimated.

(4) A 20-plate distillation column having an HETP of 1 foot per plate at unit reflux was assumed to be adequate for the purification of $SiCl_4$ and SiI_4/I_2, taking a center cut of 90 percent (5 percent tops, 5 percent bottoms). The permissible boil-up rate, well short of flooding, was based on BCL experience(14).

(5) The flow charts to be presented in the following pages for the six candidate processes were simplified by the deletion of minor species such as $SiCl_2(g)$, $SiI_2(g)$, $SiH_2I_2(g,\ell)$, $SiHI_3(g,\ell)$, and monatomic iodine. $SiCl_2$ and SiI_2 would be expected to back react with $ZnCl_2$ or HI, I_2, respectively, on cooling. SiH_2I_2 and $SiHI_3$ were assumed to behave as SiI_4 for the purpose of the

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* In retrospect and on further study of heat transfer to hydrogen, this value is concluded to be too high, attainable only at Reynolds numbers for flow above 10,000, i.e., above the flow rates that would be used. The net effect of using a lower value, e.g., h = 20, would be to increase the required size of the heat transfer equipment in Processes C through F and hence the capital costs and product costs above those calculated.

economic analysis; however, a detailed plant design would have to take the properties of these species into consideration. Although the above minor species were ignored in the sizing of equipment, etc., they were used in the thermodynamic calculations of equilibrium conversion efficiency.

(6) The reaction efficiencies and the enthalpies of reactions and phase changes at any given point were taken as those calculated for equilibrium conversion.

Results of Economic Analysis

The six processes for which process cost estimates were made are discussed below in turn. A brief description of the process is given, followed by a flow sheet. In the case of Process A, tables listing (1) major equipment costs, (2) materials and energy costs, and (3) manpower costs are included. The reader is referred to Reference (1) for the corresponding tables for Processes B through F.

Tables listing (4) fixed capital investment and (5) product costs for all of the processes are then presented with a discussion of the relative merits of the processes with regard to dollar costs and energy burdens.

As noted above, a 24-kg/hour silicon fluidized-bed unit is a convenient size, at least for Process A. Although this is probably not optimum, it was chosen to establish the basic production rate for the plant unit. The 24-kg/hour unit concept was carried over to those processes that do not employ fluidized beds. A 1000 MT/year facility was visualized as consisting of six 24-kg/hour units. No credit was taken for the fact that some equipment, notably tanks, might be common to the six units with a resultant saving. However, this potential economy is probably offset by the fact that to provide for flexibility of operation, a fully designed plant would probably use more tanks than were included here.

In the process flow diagrams that follow, each block represents a function or piece of major equipment. The conditions of that step are noted in the block; pressure $\sim$1 atm unless otherwise noted. Also given in each block is the corresponding enthalpy change (+ endothermic, - exothermic) in kilocalories per 1.000 g-mole of silicon product. The compositions (g-moles) of reactants and intermediates are given in parentheses beside arrows corresponding to the process streams.

It will be noted that the listing of major equipment items does not correspond exactly to the process flow diagram in some cases; this was due to changes in thinking during the evaluation. Revising the process flow sheets did not appear to be justified.

Process A, Fluidized-Bed Zinc Reduction of $SiCl_4$

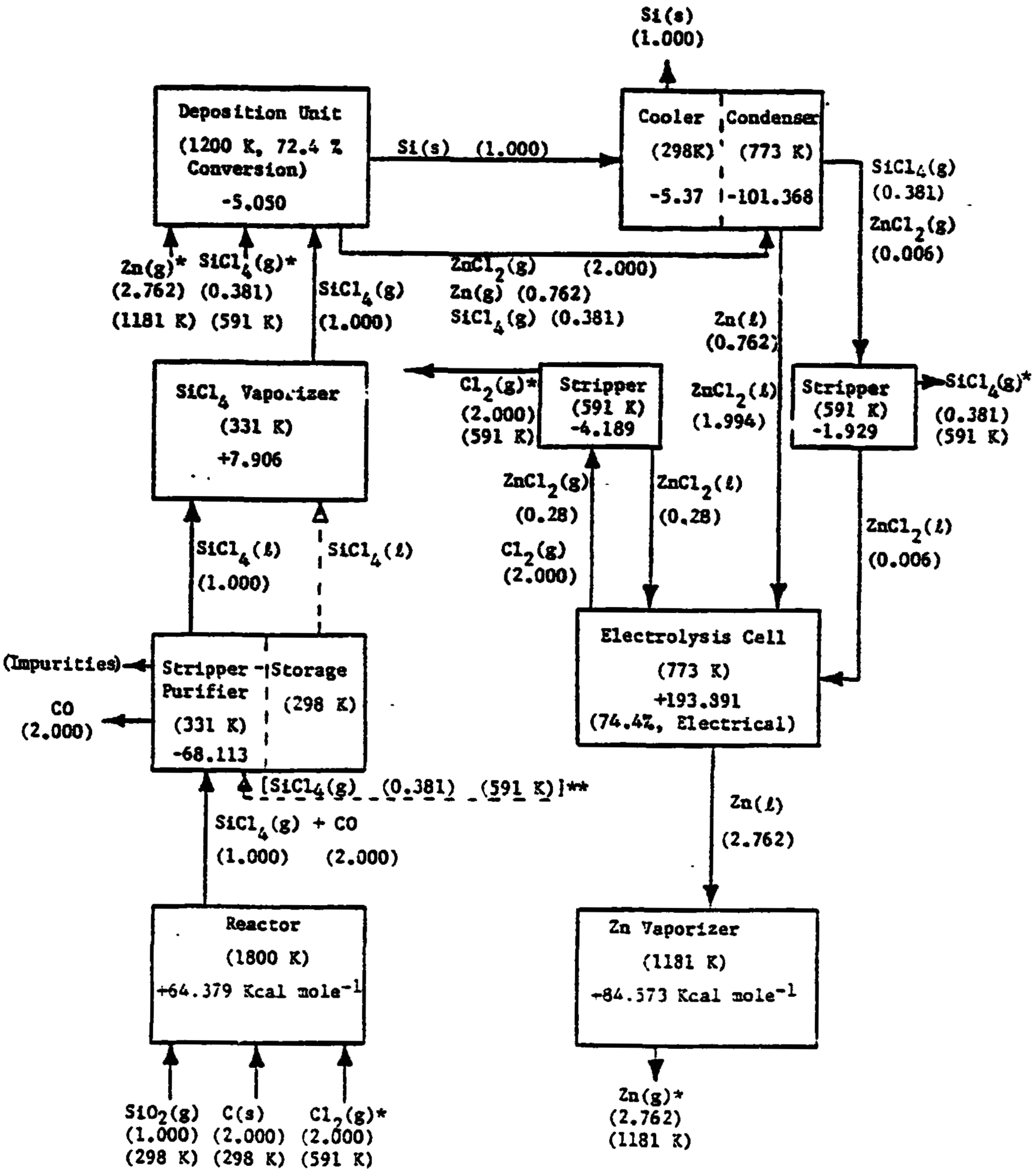
Figure 1 is the flow diagram for the zinc reduction of $SiCl_4$ in a fluidized bed of seed particles. Cost estimates are given in Tables 2, 3, and 4.

As noted above, although this process calls for generating the required $SiCl_4$ by treating SiO_2 + carbon mixtures with recycled by-product chlorine, the product cost was calculated by treating the $SiCl_4$ as a materials cost with a 20 percent credit for on-site preparation.

It should also be noted that two options for recycling the unreacted $SiCl_4$ are shown in Figure 1. In the economic analysis, this material was recycled to purification rather than directly to deposition.

By-product $ZnCl_2$ is most conveniently recycled by fused salt electrolysis at 500 C, which conserves energy. The cost of the electrolytic cells was based on the experience of Threlfall(16); however, it was later learned that the U.S. Bureau of Mines at Reno, Nevada, has been developing the $ZnCl_2$ electrolysis(17), and that work has been adopted as a guide for future reference.

The constraints that have prompted consideration of this single zinc-reduction process option are discussed in Section C of this report.



* Recycled material.

** Recycle route adopted in cost analysis.

FIGURE 1. PROCESS A FLOW SHEET
Zinc Reduction of Silicon Tetrachloride

TABLE 2. MAJOR EQUIPMENT COST, PROCESS A 24 kg/HOUR UNIT

Item	Function	Duty	Size	Cost, dollars
Vaporizer	$SiCl_4$ Vaporization	2.68E4* BTU/hour	45 ft^2	$ 4,000
Distillation Unit	$SiCl_4$ Purification	200.5 kg/hour $SiCl_4$	20 ft x 12 in. dia.	19,400
Deposition Unit	$SiCl_4$ Reduction	24 kg/hour Si	1.23 ft^2 (15 in. dia.)	29,400
Cooler/Condenser	Condenser Zn, $ZnCl_2$	34.37E4 BTU/hour	1076 ft^2	24,500
Electrolysis Cell	Zn Recovery	111.7 kg/hour Zn	5 x 6-electrode Threlfall cells	213,400
Vaporizer	Vaporize Zn	28.67E4 BTU/hour	240 ft^2	15,600
Stripper 1	Strip $ZnCl_2$ from Cl_2	1.42E4 BTU/hour	60 ft^2	4,400
Stripper 2	Strip $ZnCl_2$ from $SiCl_4$	0.64E4 BTU/hour	26 ft^2	2,900
Tank	$SiCl_4$ Storage	8 hours	200 gal	5,800
Heat Exchanger	Waste Heat Disposal	22.79E4 BTU/hour		2,600
			24 kg/hour unit total	$ 322,000
			x 6 = 1000 MT/year total	$1,932,000

* 2.68E4 = 2.68 x 10^4

TABLE 3. MATERIALS AND ENERGY COSTS, PROCESS A

Item	Conditions	Cost, $/kg Si
Zinc	10 percent loss or cost balanced recovery	$0.40
$SiCl_4$	90 percent utilization, 20 percent onsite manufacturing credit	2.19
	Total, materials	$2.59
Electrical, 90 percent utilization, 11.17 kwhr/kg		$0.335

TABLE 4. MANPOWER UNIT BREAKDOWN AND COST, PROCESS A 1000 MT/YEAR SILICON

Unit Operation	Number of Operators	
Deposition	16	
Zinc Electrolysis	20	
Distillation	16	
Raw Material Handling	8	(semi-skilled)
Product Handling	8	(semi-skilled)
	68*	(divided into four crews)

Equivalent manpower hourly rate of $416.80

Operating Labor Cost/year = $892,790
($416.80/hour x 2142 hours/year)

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* Fifty-two skilled operators at $6.60/hour; 16 semi-skilled operators at $4.60/hour.

Process B, Thermal Decomposition of SiI_4 Product from Metallurgical-Grade Silicon

Figure 2 covers Process B, the thermal decomposition of SiI_4 made from metallurgical-grade silicon. This is the conventional iodide silicon process as investigated by BCL(14) and carried to the prototype stage by Mallinckrodt, Inc. A compressor has been added to the process to permit condensation of I_2/SiI_4 for recycle as liquid rather than solid.

It will be noted that the major penalty on this process is the high cost of radiant energy lost from the "filaments" in the deposition step. In arriving at a projected energy loss for this factor, 25 kwhr kg^{-1} estimated process energy was subtracted from the 375 kwh kg^{-1} total reported(9) to be characteristic of the present Siemens Process production of silicon from trichlorosilane. It was then assumed that 45 percent could be saved by suitable external heat reflection $\left[\left(\frac{900\ K}{1300\ K}\right)^4 = 23 \text{ percent}\right]$ and by mutual heat reflection (22 percent) from a "forest" of filaments such as used in a titanium pilot plant deposition unit at BCL(14). Despite this projected saving, Process B would still require 190 kwh kg^{-1} solely to maintain the deposition surface temperature.

Process C, Thermal Decomposition of SiI_4 Produced by Iodination of SiO_2-Carbon Mixtures

The thermal decomposition of SiI_4 produced by iodination of SiO_2-carbon mixtures is shown in Figure 3. This process differs from Process B in the equipment and increased manpower needed to iodinate SiO_2-carbon mixtures. In analyzing the economics of this option, it was hoped that the lowered cost of SiO_2 and carbon relative to metallurgical-grade silicon would result in a net saving. Unfortunately, the efficiency of the iodination reaction

$$SiO_2 + 2I_2 + 2C = SiI_4 + 2CO \quad ,$$

found to be 20 percent at best, is too low to achieve that goal. The large iodine recycle load is defeating.

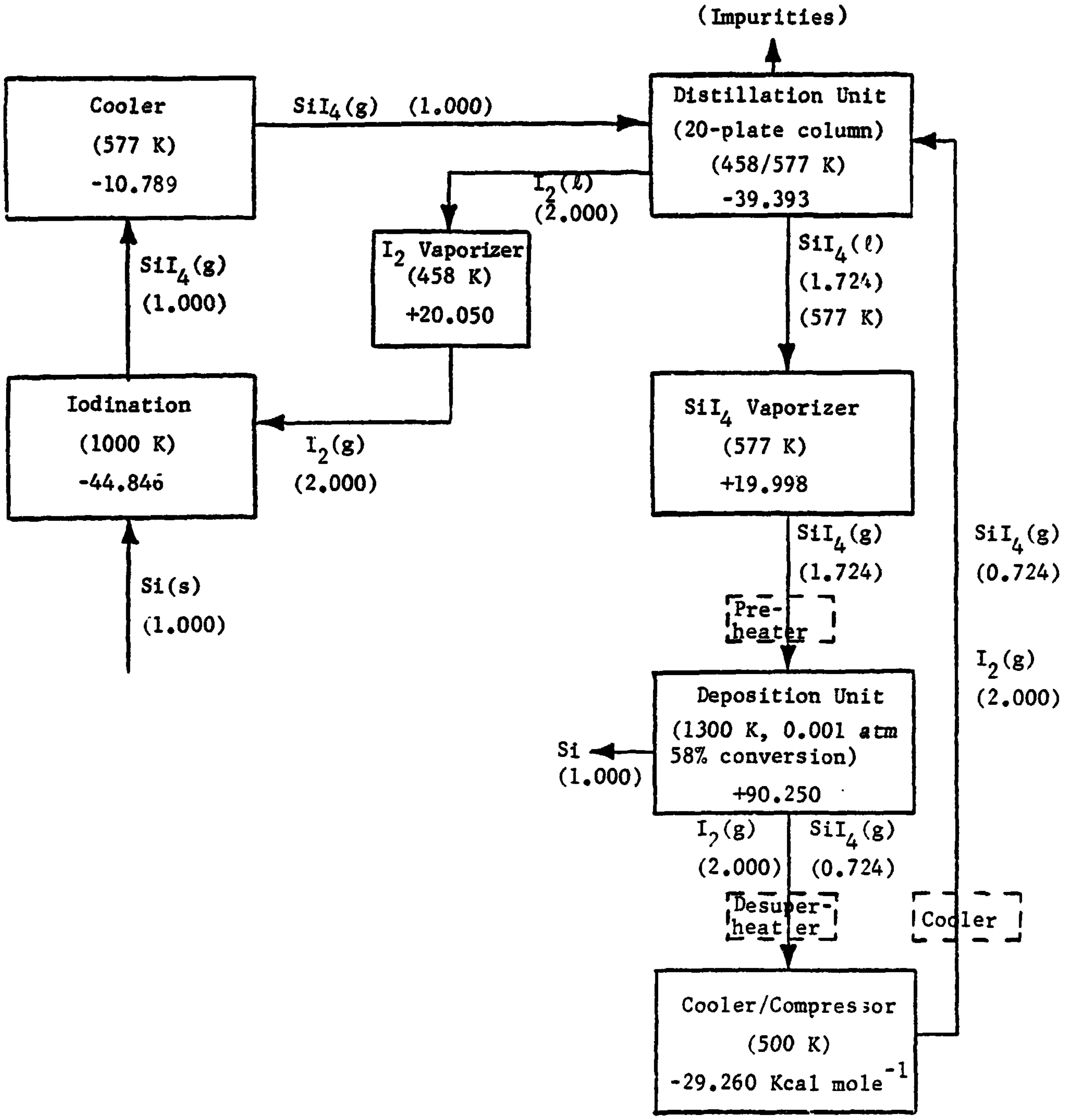

FIGURE 2. PROCESS B FLOW SHEET

Thermal Decomposition of SiI_4 Produced from Metallurgical-Grade Silicon

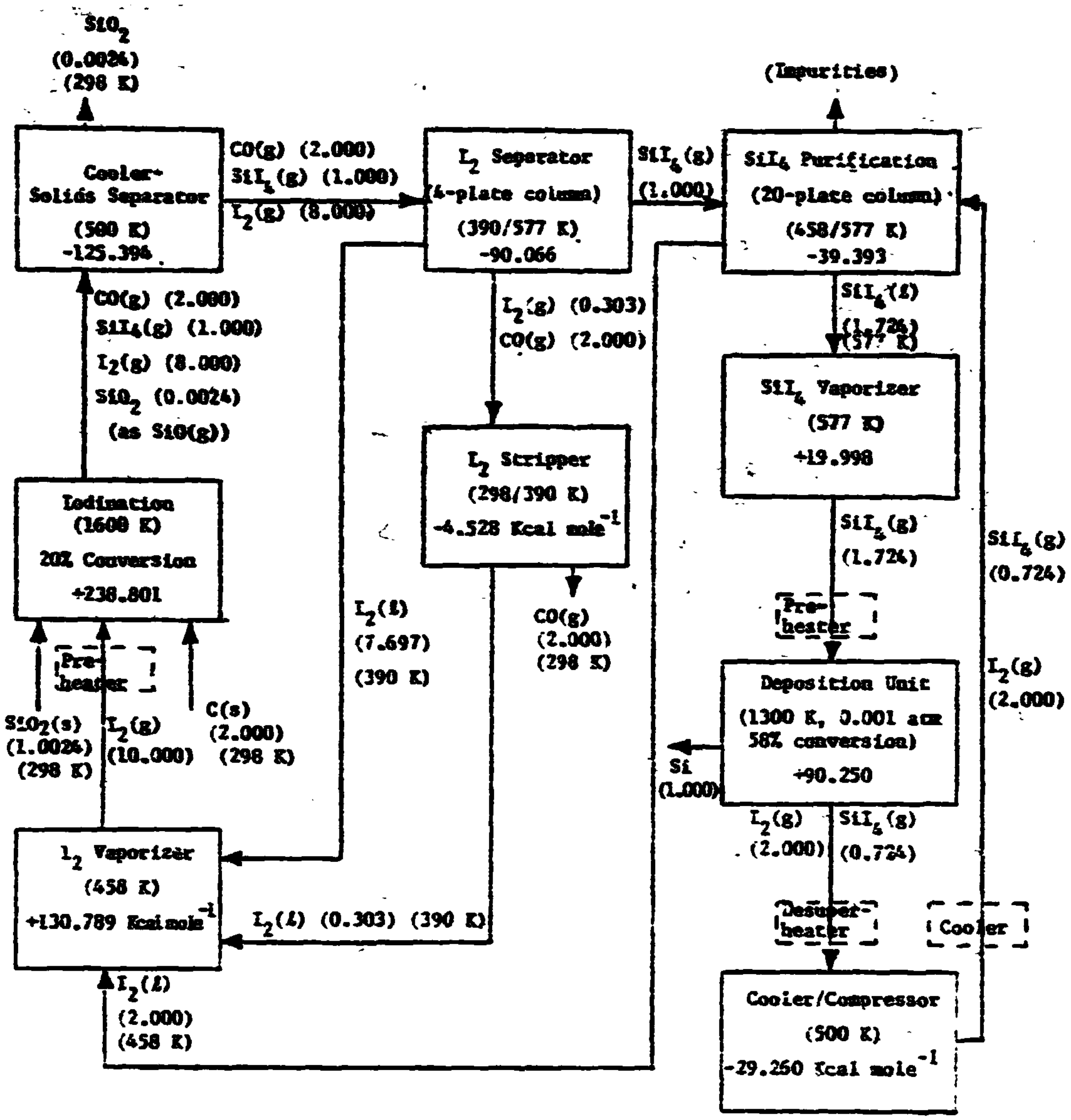

FIGURE 3. PROCESS C FLOW SHEET

Thermal Decomposition of SiI$_4$ Produced by Iodination of SiO$_2$/Carbon Mixtures

Experimental and theoretical work on the iodination of SiO_2 mixtures that resulted in the choice of the 20 percent conversion figure is discussed separately later.

Process D, Hydrogen Reduction of SiI_4 in a Fluidized Bed, Dry HI Recycle

An attractive option (Process D, Figure 4) for the production of silicon from SiI_4 is hydrogen reduction of the latter in a fluidized-bed reactor to avoid the large cost of the low pressure deposition cycle and to take advantage of the continuous process potential*. The HI by-product can be recycled by low-temperature condensation. However, this condensation is complicated by the high vapor pressure of solid HI, 0.46 atm at the melting point, -51 C. The dew point of HI in the deposition by-product for the representative condition chosen is 194 K (-79 C) and to condense out most of the HI at atmospheric pressure requires a scraper condenser operating at, say, -153 C. This mechanical condenser and the associated refrigeration accounts for about half of the capital investment. Pressurizing the HI + H_2 by-product to allow condensation of the HI as a liquid at 3 C above its melting point (i.e., at -48 C) alleviates the problem only slightly. Compression to 10 atm permits condensation of only 37 percent of the HI, and a pressure of 60 atm is necessary for 90 percent condensation. The option of operating this section of the plant at high pressures is discussed below in the comparison of process costs.

The other major cost items are the scraper condenser, necessary to remove SiI_4 as condensed solid at two points, and the fluidized-bed reactor(s) which, because of the lower efficiency and large volumes of excess hydrogen, require seven times the cross sectional area required in Process A. Operating manpower costs are correspondingly higher.

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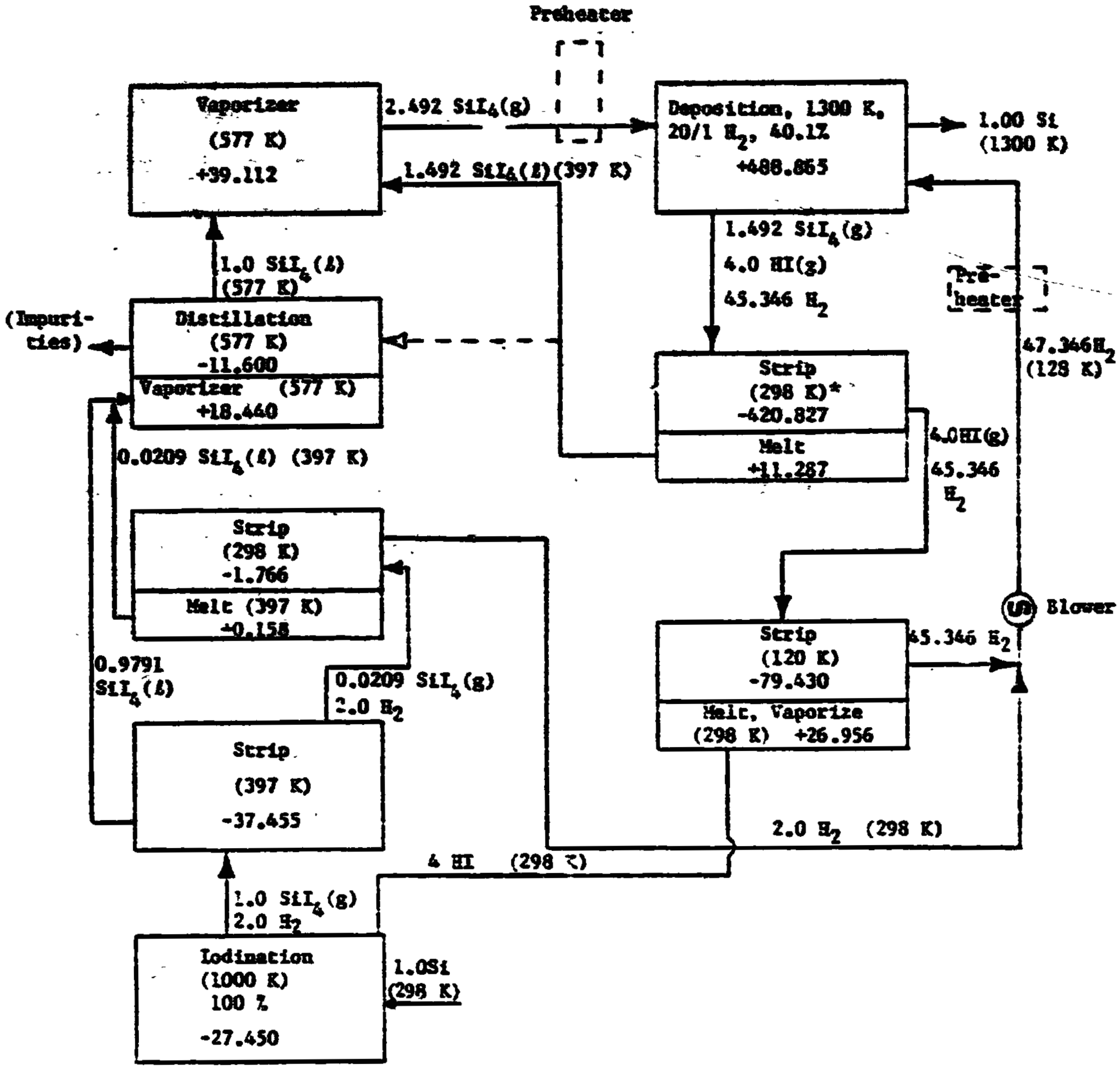
* Elimination of the large radiant energy loss of the "hot-wire" reactors is another advantage.



* Probably broken into 2 stages, 1st stripping out 0.994 moles $SiI_4(l)$ at 397 K, 2nd, residual 0.498 $SiI_4(s)$ moles at 298 K.

FIGURE 4. PROCESS D FLOW SHEET

Fluidized-Bed Hydrogen Reduction of SiI_4, Dry HI Recycle

Process E, Fluidized-Bed Hydrogen Reduction of SiI_4 with Wet-Process Iodine Recycle

As the condensation of the reaction product HI was such a problem in Process D, the possibility of scrubbing the HI from the H_2 process gas and recovering the iodine by wet chemistry was explored in Process E, as described in Figure 5.

Process F, Fluidized-Bed Hydrogen Reduction of SiI_4 with Recirculation of Unseparated HI/H_2

Although the wet-process iodine recovery in Process E avoids some of the high capital investment for dry HI recycle in Process D, this saving is more than offset by the $0.20/pound cost of recovering iodine by the wet process. It thus becomes of interest to examine the cost of a process in which the HI and H_2 are not separated and the less efficient iodination of silicon and deposition of silicon from the purified SiI_4 are accepted. Since the iodination and decomposition efficiencies are interdependent, it was necessary to calculate the process stream compositions by successive approximations which yielded the results shown in Figure 6. Owing to the lower efficiencies and lower concentrations of reactants in the feed streams, the sizes of the processing units are increased.

Processes A Through F Cost Summary

The fixed capital investments for Processes A through F are given in Table 5 and the product cost calculations are given in Table 6.

Table 7 and Figure 7 summarize the process cost estimates in terms of materials, utilities, capital-related, labor-related, and "other" costs. Process A, the zinc reduction of $SiCl_4$ shows lowest cost in all categories. "Improvements" (Processes C through F) on the basic "hot-wire" iodide process (B) led to higher costs as economies in one area were more than offset by increased costs in others.

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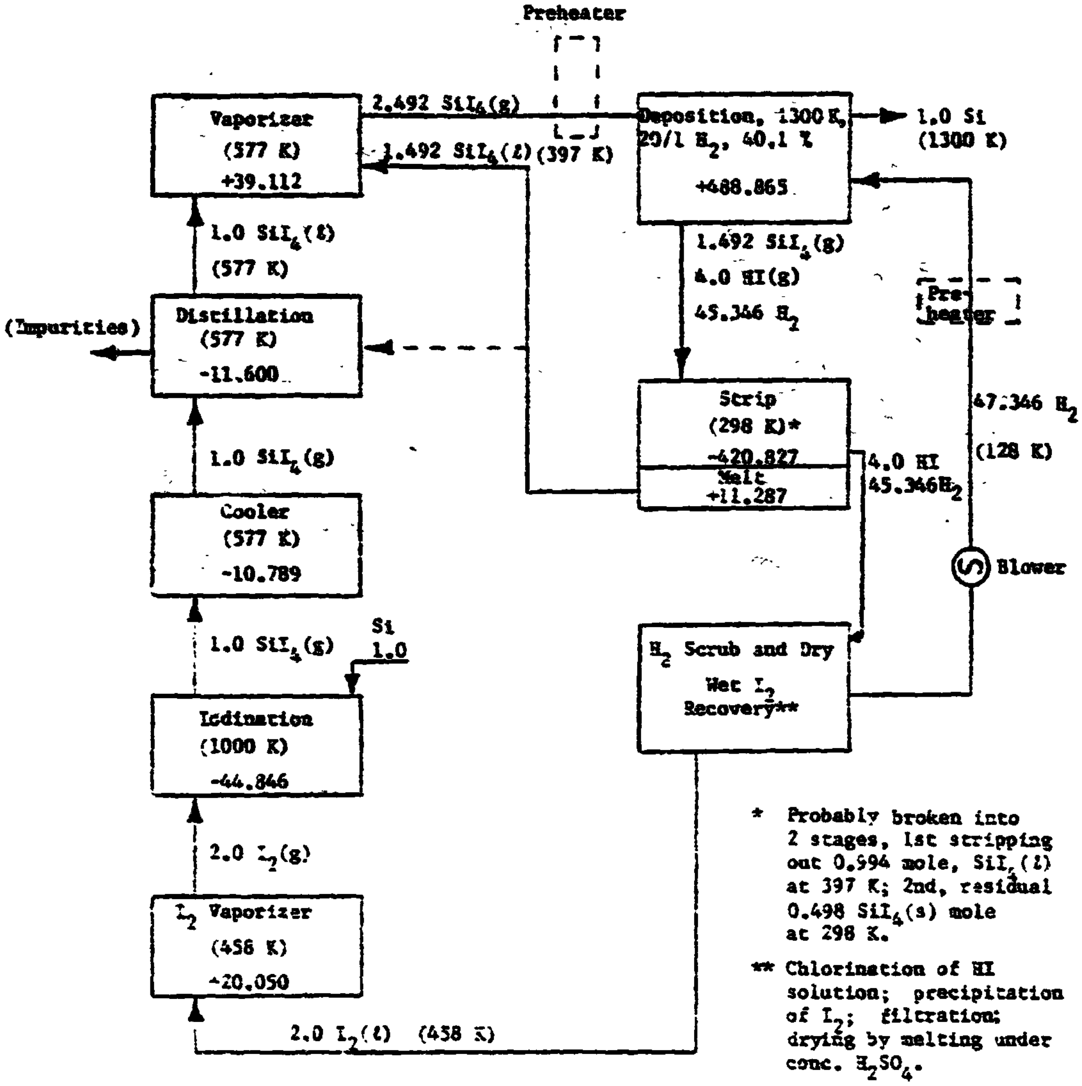
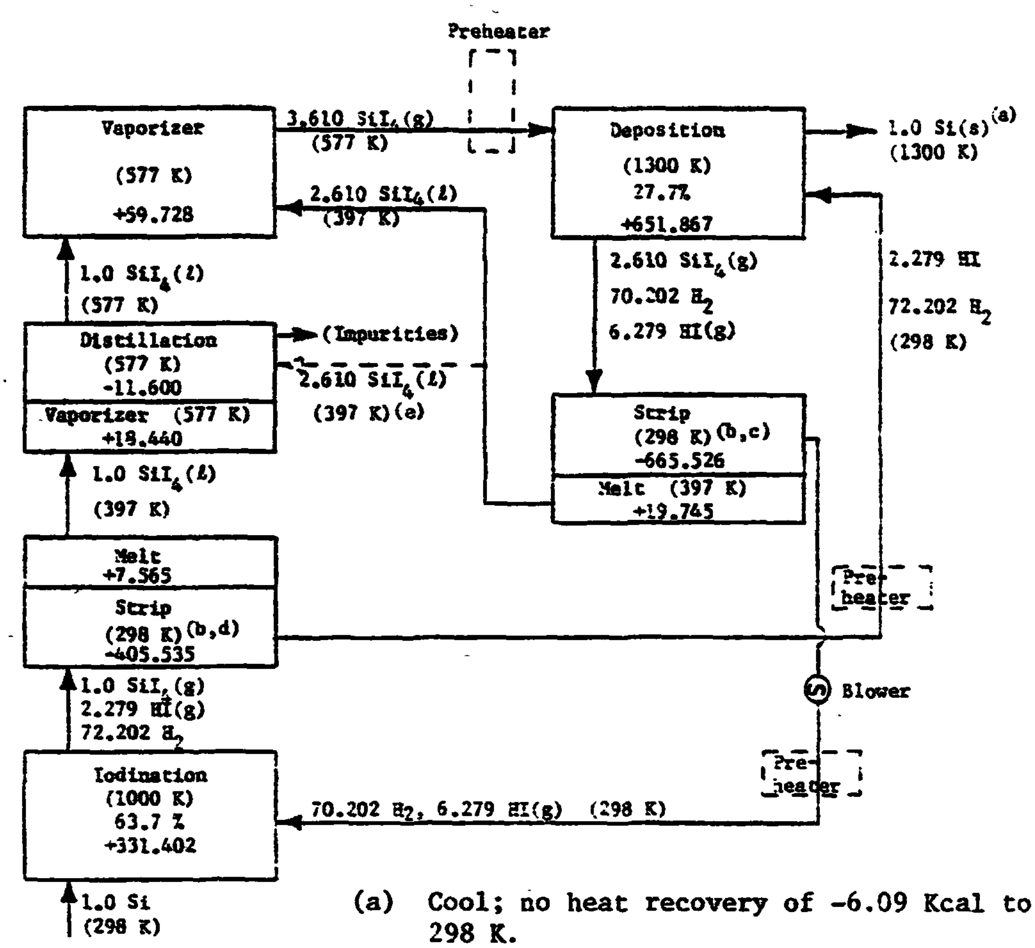


* Probably broken into 2 stages, 1st stripping out 0.994 mole, $SiI_4(\ell)$ at 397 K; 2nd, residual 0.498 $SiI_4(s)$ mole at 298 K.

** Chlorination of HI solution; precipitation of I_2; filtration; drying by melting under conc. H_2SO_4.

FIGURE 5. PROCESS E FLOW SHEET

Fluidized-Bed Hydrogen Reduction of SiI_4, Wet-Process I_2 Recycle



(a) Cool; no heat recovery of -6.09 Kcal to 298 K.

(b) Neglect 0.001 mole SiI_4 that escapes stripper at 298 K.

(c) Would probably be done in two stages; 1.838 mole SiI_4 condensing as liquid at 397 K (mp) leaving 0.772 mole to be stripped as solid at 298 K.

(d) If broken into two stages, 0.752 mole SiI_4 would escape the 397 K (mp) condenser, i.e., 0.248 mole condenses at 397 K.

(e) Recycle route adopted in cost analysis.

FIGURE 6. PROCESS F FLOW SHEET

Fluidized-Bed Hydrogen Reduction of SiI_4 With Recirculation of Unseparated H_2/HI

TABLE 5. FIXED CAPITAL INVESTMENT
1000 MT/YEAR SILICON

Cost Item		Process A	Process B	Process C	Process D	Process E	Process F
Direct Cost (D)							
Purchased equipment (E)		$1,932,000	$ 4,488,000	$ 6,180,000	$11,808,000	$ 5,166,000	$11,622,000
Installation of E	40 percent of E	772,800	2,019,600*	2,781,000*	4,723,000	2,066,400	4,684,800
Instrumentation (Installed)	25 percent of E	483,000	1,122,000	1,545,000	2,952,000	1,291,500	2,905,500
Piping (Installed)	60 percent of E	1,159,200	2,692,800	3,708,000	7,084,800	3,099,600	6,973,200
Electrical (Installed)	15 percent of E	289,800	673,200	927,000	1,771,200	774,900	1,743,300
Buildings and Services	47 percent of E	908,040	2,109,360	2,904,600	5,549,760	2,428,020	5,462,340
Yard Improvements	10 percent of E	193,200	448,800	618,000	1,180,800	516,600	1,162,200
Service Facilities	40 percent of E	772,800	1,795,200	2,472,000	4,723,000	2,066,400	4,684,800
Land	6 percent of E	115,920	269,280	370,800	708,480	309,960	697,320
TOTAL DIRECT COST		$6,626,760	$15,618,240	$21,506,400	$40,501,440	$17,719,380	$39,861,460
Indirect Cost (I)							
Engineering and Supervision	15 percent of E	$ 289,800	$ 673,200	$ 927,000	$ 1,771,200	$ 774,900	$ 1,743,300
Construction Expenses	14 percent of E	270,480	628,320	865,200	1,653,120	723,240	1,627,080
TOTAL D AND I		$7,187,040	$16,919,760	$23,298,600	$43,925,760	$19,217,520	$43,233,840
Contractor's Fee	10 percent of D and I	$ 718,680	$ 1,692,000	$ 2,329,860	$ 4,392,600	$ 1,921,740	$ 4,323,360
Contingency	10 percent of D and I	$ 718,680	$ 1,692,000	$ 2,329,860	$ 4,392,600	$ 1,921,740	$ 4,323,360
Fixed Capital Investment, 1000 MT/year		$8,624,400	$20,303,760	$27,958,320	$52,710,960	$23,061,000	$51,880,560

* 45 percent of E.

TABLE 6. PRODUCT COSTS

Cost Item		Process A	Process B	Process C	Process D	Process E	Process F
<u>Manufacturing Cost</u>							
1. Direct Production Cost							
a. Materials		$2,590,000(a)	$ 2,860,000(b)	$ 3,842,000(c)	$ 3,330,000(b)	$11,300,000(b)	$ 4,240,000(b)
b. Operating labor		892,790	1,045,300	1,124,120	1,141,260	1,036,730	1,310,900
c. Supervisory and clerical	15 percent of b	133,920	156,800	168,620	171,190	155,500	196,635
d. Utilities		335,000	5,924,000	6;409,000	1,019,000	483,000	850,000
e. Maintenance and repairs	10 percent of fixed capital	862,440	2,030,380	2,795,830	5,271,100	2,306,100	5,188,060
f. Operating supplies	15 percent of e	129,370	304,560	419,370	790,660	345,920	778,210
g. Laboratory charges	15 percent of b	133,920	156,800	168,620	171,190	155,500	196,635
h. Patents and royalties	4 percent of product cost	364,660	826,270	1,022,190	1,161,770	1,001,400	1,199,590
2. Fixed Charges							
a. Depreciation	10 percent of fixed capital	$ 862,440	$ 2,030,380	$ 2,795,830	$ 5,271,080	$ 2,306,100	$ 5,188,060
b. Local taxes	2 percent of fixed capital	172,490	406,080	559,170	1,054,220	461,220	1,037,610
c. Insurance	1 percent of fixed capital	86,240	203,040	279,580	527,110	230,610	518,810
d. Interest	6 percent of dixed capital	517,460	1,218,230	1,677,500	3,162,650	1,383,668	3,112,830
3. Plant Overhead	60 percent of (1b + 1c + 1e)	$1,133,490	$ 1,939,490	$ 2,453,140	$ 3,950,120	$ 2,099,800	$ 4,017,360
<u>General Expenses</u>							
1. Administration	50 percent of 1b	$ 446,400	$ 522,650	$ 562,060	$ 570,630	$ 518,360	$ 655,450
2. Distribution	2 percent of product cost	182,330	413,140	511,100	580,880	500,700	599,790
3. Research and Development	3 percent of product cost	273,490	619,700	766,640	871,320	751,040	899,690
<u>Total Product Cost</u>		$9,116,460	$20,656,820	$25,554,770	$29,044,180	$25,034,840	$29,989,630
1. Product Cost, per kg Si		$9.12	$20.65	$25.55	$29.04	$25.03	$29.99

(a) Includes all cost (operating and capital investment) for $SiCl_4$ used.

(b) Includes all cost (operating and capital investment) for the recovery of iodine scrap by the wet process.

(c) Includes all cost (operating and capital investment) for the recovery of scrap and recycled iodine by the wet process.

TABLE 7. ESTIMATED COST BREAKDOWN, PROCESSES A THROUGH F, DOLLARS PER kg SILICON

Item	Process A	Process B	Process C	Process D	Process E	Process F
Materials	$2.59	$ 2.86	$ 3.84	$ 3.33	$11.30	$ 4.24
Utilities(a)	0.34	5.92	6.41	1.02	0.48	0.85
Capital-related(b)	3.15	7.41	10.20	19.24	8.42	18.94
Labor-related	2.22	2.60	2.80	2.84	2.58	3.26
Others(c)	0.82	1.86	2.30	2.61	2.25	2.70
TOTAL	$9.12	$20.65	$25.55	$29.04	$25.03	$29.99

(a) Electrical only, see text.

(b) Includes labor portion of maintenance cost based on capital.

(c) Patents and royalties, 4 percent of total; distribution, 2 percent of total; research and development, 3 percent of total

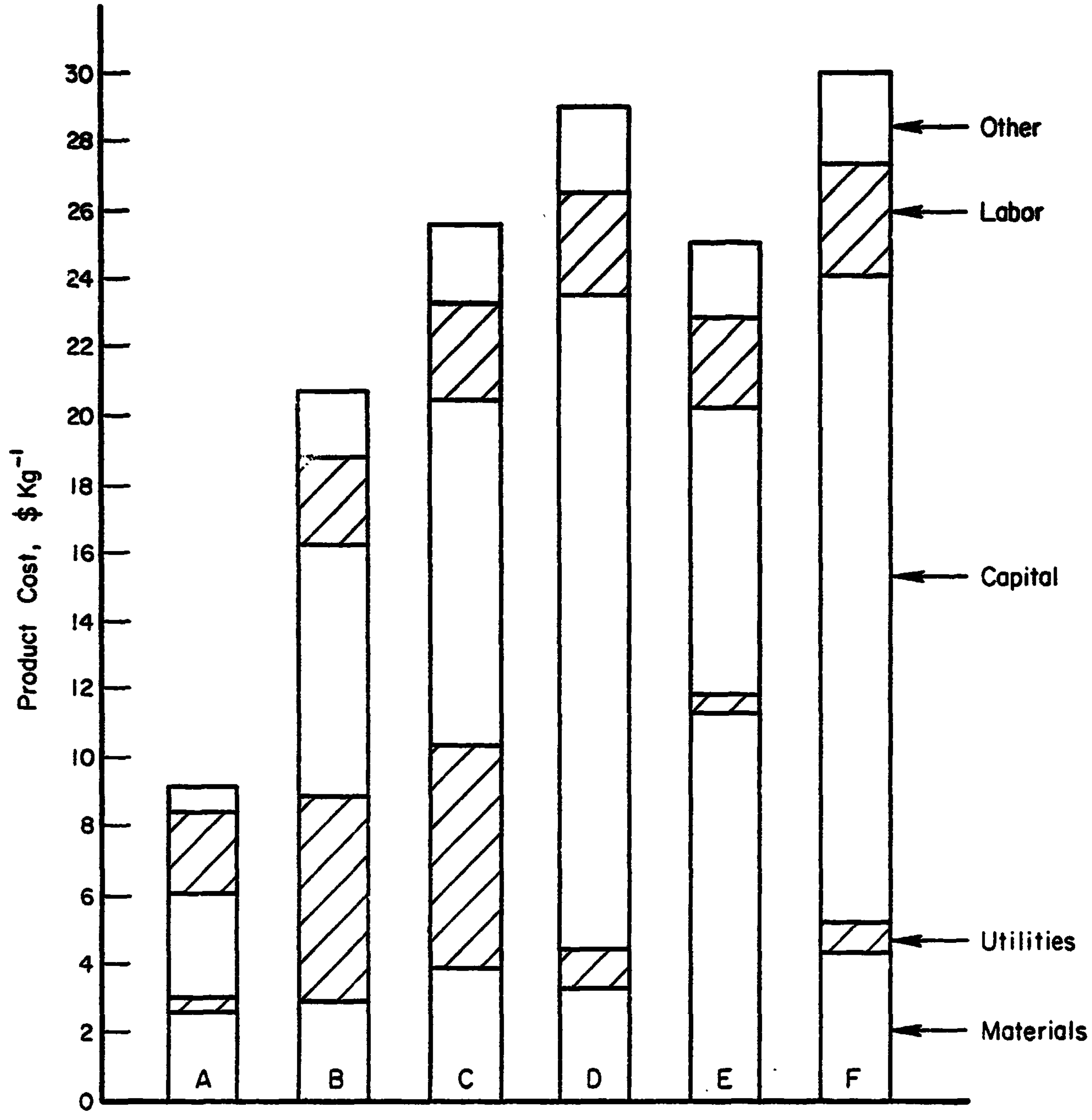


FIGURE 7. PRODUCT COST BREAKDOWN, PROCESSES A THROUGH F

The most promising approach for reducing the cost of the iodide processes would be via optimizing the recycle of the HI by-product of Process D by pressurized condensation, whereby it may well be possible to beat the $20.65/kg cost of the "hot wire" process (B). However, Process D optimized in that way can never be less expensive than Process A, as even if the cost of HI recycle were zero (equivalent to subtracting the wet process recycle cost from the product cost in Process E), the net cost would be $15.70/kg of silicon ($25.03 - $9.33), which exceeds the $9.12/kg cost of Process A by 70 percent.

In making the above cost estimates, it was recognized that a more detailed engineering design of the processes would disclose needs for additional minor items of process equipment that would result in higher costs, presumably by a small fraction of the major cost items already identified. On the other hand, opportunities for economies should be also recognized which may well offset the cost of added equipment. It should also be pointed out that considerable uncertainty exists in the cost of electrolytic zinc recovery for Process A which will not be fully resolved until a prototype plant is operated. If this cost can be made less than that assumed, a significant decrease in the cost of the product will be obtained because of the appreciable fraction of the total cost represented by the electrolytic zinc recovery operation.

Although some uncertainty exists in the absolute validity of the above cost estimates, their relative values indicate a clear choice of Process A over the iodide process variations. The product cost estimate for Process A which fell below the $10/kg LSA target and the short energy payback time (discussed in the next section) gave the incentive for continued development of this zinc reduction process. The decision to proceed with that development was further justified by an independent economic analysis of Process A by Lamar University(18) which led to an estimated product cost of $9.63/kg. The 22 percent higher capital equipment cost estimate by Lamar was partially offset by a 41 percent lower labor requirement.

Development of the zinc reduction of silicon tetrachloride on seed particles in a fluidized bed to yield a free flowing granular product is discussed in Section C of this report.

Energy Consumption

There exists an as yet undetermined limit to the energy consumption that can be tolerated for a process producing silicon for solar cell use. That is, the energy consumed in materials production must be a small fraction of that produced by the cell during its lifetime. Table 8 gives the energy consumption estimated for the candidate Processes A through F. The values shown were obtained by adding the energy costs of producing or reclaiming certain raw materials to the process energies given in the corresponding tables for the individual processes.

Although it is recognized that some of the process energy may be other than electrical, the calculations are based on units of kwh electrical, since that is the form of energy to be credited to the cell operation as a photovoltaic device.

The last column gives the energy payback time in months for a reference cell:

> 0.0254-cm thick producing 0.1 kw/m^2 in 1825 hr/yr operation, allowing for 20 percent loss of silicon during cell manufacture, i.e., 20.5 kwh/(mo Kg).

These results show that none of the processes can be ruled out on the basis of energy consumption, although the "hot wire" processes (B and C) have high energy burdens which may be prohibitive when cell and array manufacturing energy requirements are added. The zinc reduction of silicon tetrachloride (Process A) is among the lowest of the others in terms of energy burden with a payback time of only 2.2 months (see revised estimate, page 108).

Experimental Hydrogen Reduction of SiI_4

To confirm the feasibility of the fluidized-bed hydrogen reduction of SiI_4, two experimental runs were made in a 50-mm fluidized-bed reactor similar to that to be described in Section C of this report (Figure 12). The conditions and results for the run which proceeded without operational problems are given in Table 9.

TABLE 8. PROCESS ENERGY COST, kwh/kg SILICON

Process	Material	Added, kwh/kg	Basis*	Requirement from Process Tabulation, kwh/kg	Total Energy, kwh/kg	Reference Cell Payback Time, months
A	Zn	2.30	(a)			
	$SiCl_4$	32.53	(b)	11.17	46.00	2.2
B	Met.-grade Si	16.26	(c)			
	I_2	2.74	(d)	197.5	216.50	10.6
C	Carbon	--	(e)			
	SiO_2	--	(e)			
	I_2	2.97	(f)	213.6	216.57	10.6
D	Met.-grade Si	16.26	(c)			
	I_2	2.61	(g)			
	H_2	2.10	(h)	16.0	36.97	1.8
E	Met.-grade Si	16.26	(c)			
	I_2	25.69	(i)			
	H_2	2.10	(h)	16.0	60.05	2.9
F	Met.-grade Si	16.26	(c)			
	I_2	2.80	(j)			
	H_2	3.3	(k)	28.3	50.66	2.5

* See next page for footnotes.

Footnotes to Table 8

(a) 1.02 pounds zinc reprocessed (exclusive of in-plant recycle) per kg silicon at 2.25 kwh/pound(19).

(b) 13.34 pounds $SiCl_4$/kg silicon, at energy requirement of contained chlorine [1.65 kwh/pound(20)], x 1.77 for other requirements, total = 2.44 kwh/pound $SiCl_4$.

(c) 1.17 kg/kg silicon at 11.39 kwh/kg(21).

(d) 4.73 pounds I_2 reprocessed (esclusive of in-plant recycle) per kg silicon at energy cost for chlorine used in wet chlorination at 80 percent utilization efficiency; 0.58 kwh/pound I_2.

(e) No data readily available; minor energy cost not included.

(f) 5.12 pounds I_2 reprocessed per kg silicon; see (d).

(g) 4.50 pounds I_2 reprocessed per kg silicon; see (d).

(h) 0.07 pound H_2 consumed per kg silicon; at 30 kwh/pound H_2 calculated on basis of cell potential of 2v(22) and assumed 80 percent current efficiency.

(i) 44.3 pounds I_2 reprocessed per kg silicon; see (d).

(j) 4.83 pounds I_2 reprocessed per kg silicon; see (d).

(k) 0.11 pound H_2 used per kg silicon; see (h).

(l) External zinc recovery of 0.46 kg zinc/kg silicon assumed to be 40 percent efficient as in-plant recycle.

TABLE 9. DATA ON THE PREPARATION OF SILICON BY THE FLUIDIZED-BED HYDROGEN REDUCTION OF SiI_4

Reactor diameter	50 mm
Bed	328 g of 425 to 590 μm
Bed temperature	1050 C
Preheater temperature	400 C
SiI_4 vaporizer temperature	172 to 187 C
H_2/SiI_4 mole ratio	32
Run time	40 minutes
Silicon deposited	12 g
Overall efficiency	66 percent
Efficiency from thermodynamic calculations(3)	56 percent

These results confirmed those obtained earlier at BCL(14) in an open-tube reactor where the experimentally determined SiI_4 reduction efficiency was consistently above that predicted thermodynamically on the basis of Reference (3). Adjustments of the values for the estimated thermodynamic properties of $SiI_2(g)$, $SiH_2I_2(g)$, and $SiHI_3(g)$ may accommodate the discrepancy. However, no effort was made to accomplish this other than to determine that the difference could not be accounted for by any reasonable adjustments of the $SiI_2(g)$ estimates alone.

Experimental Iodination of SiO_2 + C Mixtures

One of the potential economies in the iodide process was to form the SiI_4 feed material by iodination of SiO_2-plus-carbon mixtures (Process C) rather than metallurgical-grade silicon. It was thus necessary to know something of the efficiency of that reaction. Accordingly, mixtures of iodine vapor, of from 16 to 65 percent in an argon gas carrier, were passed through a 25-cm packed bed of ground and pressed SiO_2-plus-carbon pellets containing stoichiometric quantities of carbon, and 50 and 100 percent excesses of carbon, at 1523 C. Efficiencies of conversion of iodine to SiI_4 of from 16 to 32 percent were observed to correlate poorly with conditions. A detailed thermodynamic analysis in the Second Quarterly Report$^{(1)}$ revealed that because of the competing reactions

$$SiO_2 + 2C + 2I_2 = 2CO + SiI_4$$

and

$$SiO_2 + 3C = 2CO + SiC$$

and the variation of equilibrium composition with the solid phases present (see Figure 8), it would not be possible to calculate the expected conversion. The question as to whether the addition of hydrogen would aid the conversion was answered in the negative as can be seed from the figure.

A nominal conversion efficiency of 20 percent was adopted in calculating the costs of Process C.

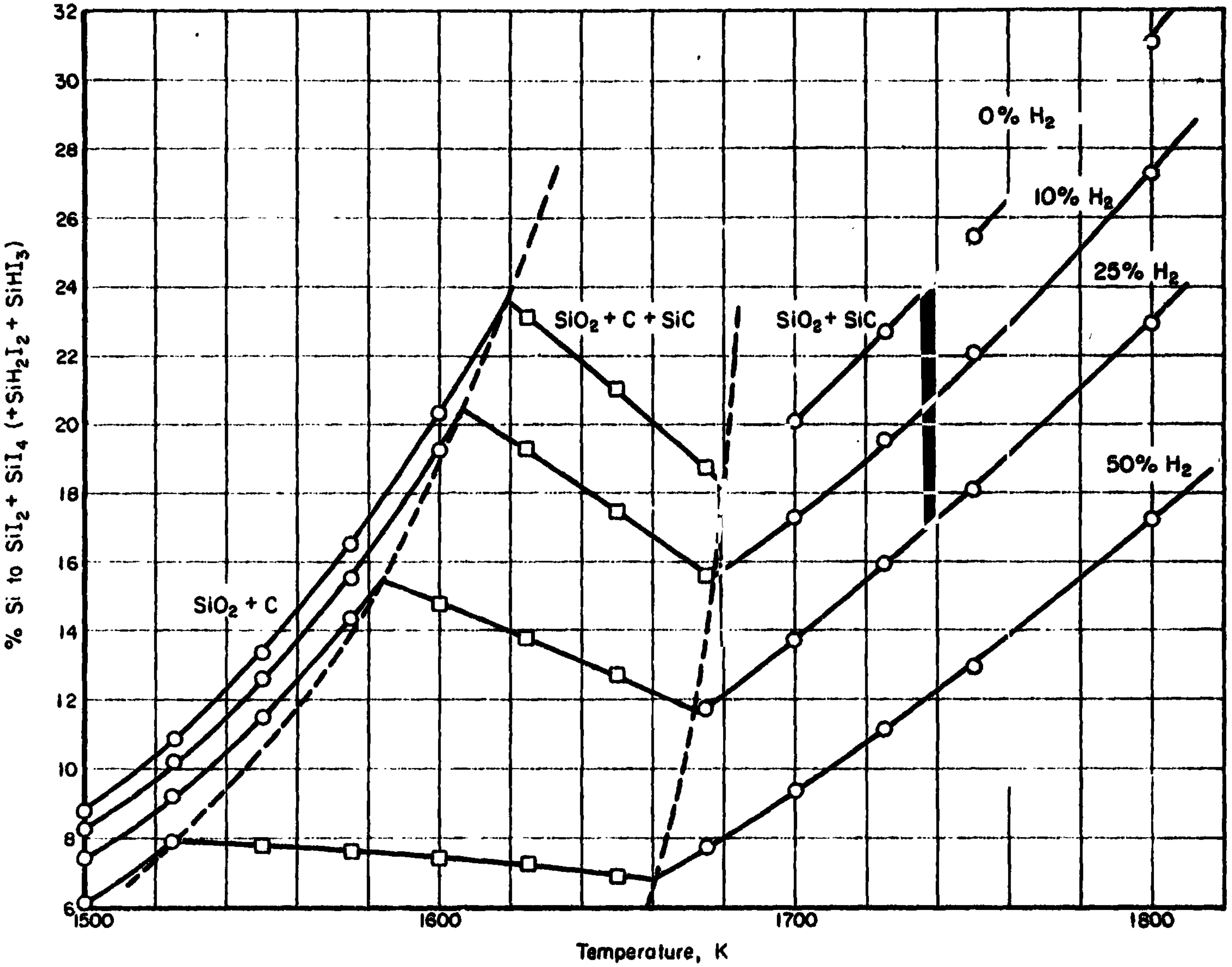


FIGURE 8. IODINATION OF SILICON OXIDE-CARBON MIXTURES

(Equilibrium conversion as functions of temperature and percent H_2 added to $I_2(g)$, showing region of stability of solid phases starting with stoichiometric C/SiO_2 ratio = 2/1)

C. ZINC REDUCTION PROCESS DEVELOPMENT

In the early days of the semiconductor silicon industry, DuPont produced silicon by the batchwise zinc reduction of $SiCl_4$ having the characteristics given in Table 10.

TABLE 10. SPECIFICATIONS FOR DUPONT SILICON(23)

	Grade I	Grade II	Grade III	Solar Cell Grade
Boron Content (ppb)*	1	1 to 3	6 to 11	—
Minimum Resistivity for Top 60 Percent of Crystal (ohm cm)				
"P" Type	100	50	25	—
"N" Type	25	15	5	0.5

* Calculated from resistivity of float-zoned bar cut from Czochralski crystal.

This material was of variable quality, and although contacts with DuPont have not resulted in more definitive information on minority carrier lifetime, etc., it is understood that solar cells with efficiencies of 10 to 12 percent were made.

The standard DuPont product was a mass of dendrites, difficult to handle in further processing. Recognizing the limitations of the process, DuPont briefly experimented with the fluidized-bed approach. In the example given in their patent(24), essentially stoichiometric quantites of zinc and $SiCl_4$, vapors were passed through a ∿10-cm-deep bed of 250- to 590-μm silicon particles at 900 C. About 21 percent of the silicon fed as $SiCl_4$

was deposited on the particles with an equal amount of silicon fines being collected with the reaction product.

With improvements in fluidized-bed technology since that time, it was believed possible to improve the yield of silicon on the seed particles and to take advantage of the potential for continuous operation provided by the fluidized bed, which should lead to increased uniformity of product.

The discussions immediately following include the theoretical and experimental work that has gone into assessing the technical feasibility of the process.

Thermodynamic Analysis

Fortunately, the reaction temperature level of interest is high enough that reaction kinetics does not appear to be controlling, and the silicon yield is practically thermodynamically and supply limited.

The thermodynamic data given in Table 11 were used to calculate the equilibrium conversion efficiencies for the reaction

$$2Zn(g) + SiCl_4(g) = Si(s) + 2ZnCl_2(g,\ell)$$

under several conditions. It was determined that $ZnCl(g)$ and $Zn_2Cl_4(g)$ were insignificant species, although $SiCl_2(g)$ was included in the analysis. Where the effect of using hydrogen as a diluent was explored, the species $H_2(g)$, $SiH_2Cl_2(g)$, $SiHCl_3(g)$, and $HCl(g)$ were added.

Based on the results of the thermodynamic calculations, Figure 9 shows the decrease in efficiency with increasing temperature to be expected from the exothermic nature of the reduction reaction. The decreased efficiency effected by dilution with inert gas for this reaction which has a net decrease in molar volume is also reflected.

The effect of hydrogen dilution is also shown in Figure 9. Although a "reducing agent", hydrogen is less effective than zinc, and the net effect is an actual reduction of conversion efficiency due to the formation of the chlorosilanes $SiHCl_3$ and SiH_2Cl_2 at lower temperatures.

A clear limitation on the operating range is indicated by the appearance, at the inflection, of $ZnCl_2(\ell)$ as a condensed phase below 727 C. Operating in this range for higher efficiency (assuming that kinetic limitations would not set in) is attractive but impractical, as the accumulation of liquid $ZnCl_2$ in the bed would result in agglomeration of the bed particles.

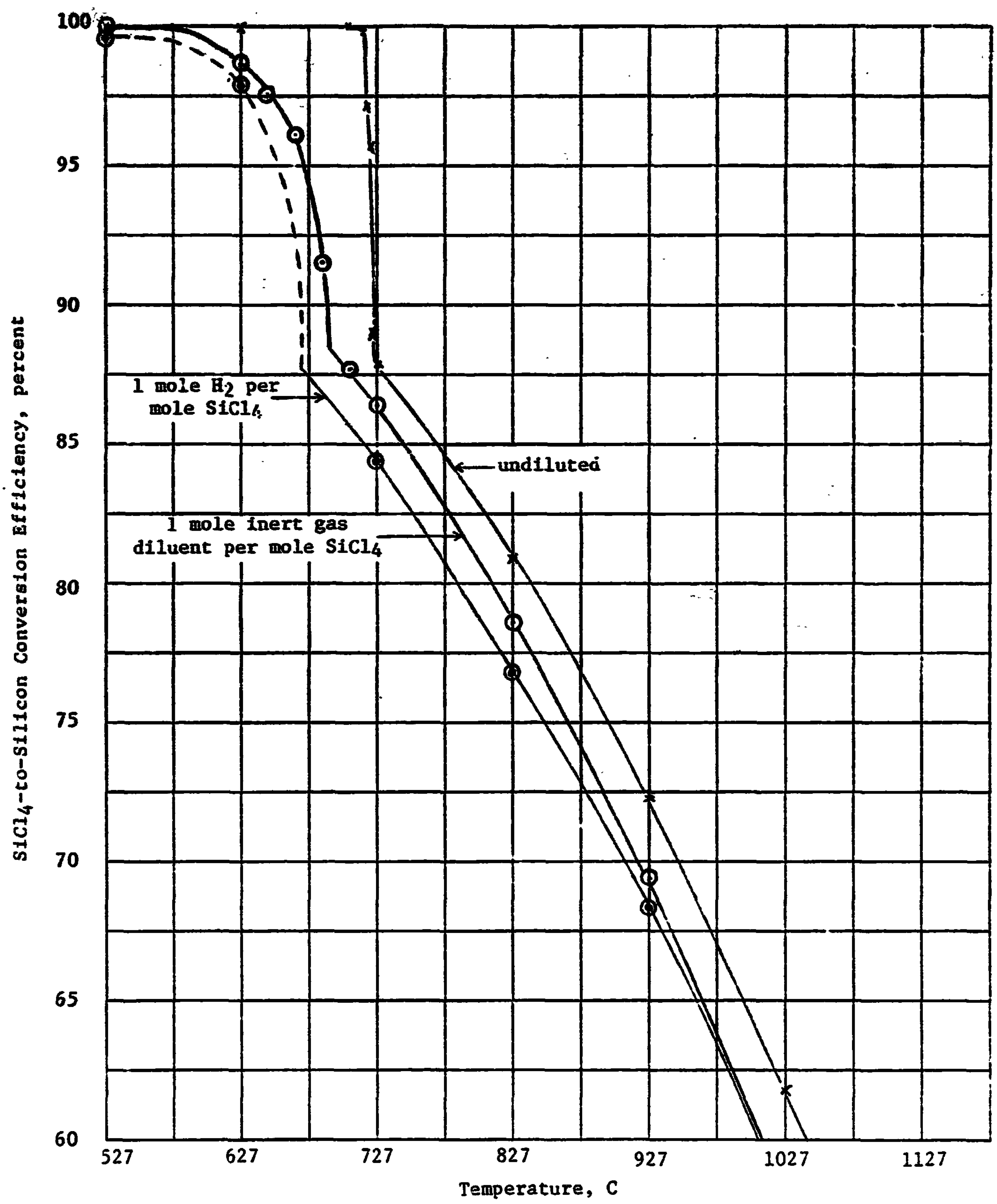


FIGURE 9. CONVERSION EFFICIENCY, $2Zn + SiCl_4 = 2ZnCl_2 + Si$, 1 atm

TABLE 11. THERMODYNAMIC PROPERTIES OF $ZnCl_2$

Quantity		Reference
For $ZnCl_2$:		
ΔH°_{298}	-99200 cal $mole^{-1}$	(25)
S_{298}	26.64 e.u. $mole^{-1}$	(25)
ΔH_m	2450 cal $mole^{-1}$	(26)
Tm	591 K	(26)
$C_p(s)$	14.5 + 0.0055 T cal $mole^{-1}$ deg^{-1}	(26)
$C_p(\ell)$	24.1 cal $mole^{-1}$ deg^{-1}	(26)
ΔH_v	28500 cal $mole^{-1}$	(27,28)
T_B	1005 K	(27,28)
$C_p(g)$	14 cal $mole^{-1}$ deg^{-1}	(estimated as per Reference 29)
For Zn, Cl_2 S_T, G°_T	Various	(30)

Another and potentially more serious limitation exists at the entrance end of the reactor, that is, the dew point of the unreacted zinc, 908 C for 1 atm and correspondingly higher for higher pressures. Not only would the condensation of liquid zinc in the bed lead to its agglomeration and loss of fluidization, but it has been shown that very fine silicon whiskers nucleate on the liquid zinc surface and are entrained in the fluidizing gas and lost to the seed particles, or if generated in sufficient quantity, can form a porous mass in the reactor outlet and obstruct the flow.

With the above limitations in mind, it was decided to adopt 1200 K (927 C) as the nominal operating temperature, where the equilibrium efficiency is 72 percent for the undiluted gas.

Later in the work the concept of a graded bed temperature was adopted, whereby the upper part of the bed, in which the dew point of the partially reacted zinc was lower, could be cooled somewhat to gain efficiency. This option obviously becomes more feasible with increasing bed-height-to-diameter ratio.

Figure 10 shows the relatively small effect of dilution on conversion efficiency and Figure 11 shows the effect of stoichiometry of the feed gas on the efficiency of conversion of zinc to $ZnCl_2$ and $SiCl_4$ to silicon. The expected increased efficiency of conversion of one reactant in an excess of the other is evident. That the zinc and $SiCl_4$ conversion efficiencies are not equal at 2/1 stoichiometry lies in the fact that whereas the zinc is constrained to form $ZnCl_2$, $SiCl_4$ can form Si(s) or $SiCl_2$(g), the fraction of the latter increasing with temperature (e.g., 1 percent of the $SiCl_x$ at 827 C and 4 percent of the $SiCl_x$ at 927 C).

Effect of Stoichiometry on Product Cost

Because of the difference, in principle, of the cost of recycling unreacted zinc and unreacted $SiCl_4$, it became of interest to analyze the cost of off-stoichiometry operation, which should show a minimum on one side or the other. Details of the approach are given in the Third Quarterly Progress Report(1). However, it involves basically adjusting the sizes of all of the process units affected by a change in stoichiometry and adding or subtracting a proportionate amount to the cost of the product, using the values for 2/1 stoichiometry as reference. The reactant conversion efficiencies used in the calculations for Zn/$SiCl_4$ mole ratios of from 0.8 to 5 were those predicted thermodynamically.

Table 12 gives the results for the capital-, energy-, and materials-related costs. The labor-related costs were assumed not to change significantly.

Two conclusions can be drawn from the data of Table 12.

(1) No marked economic advantage exists in operating at a Zn/$SiCl_4$ ratio of other than 2/1; the savings gained by increased efficiency in utilization of one reactant

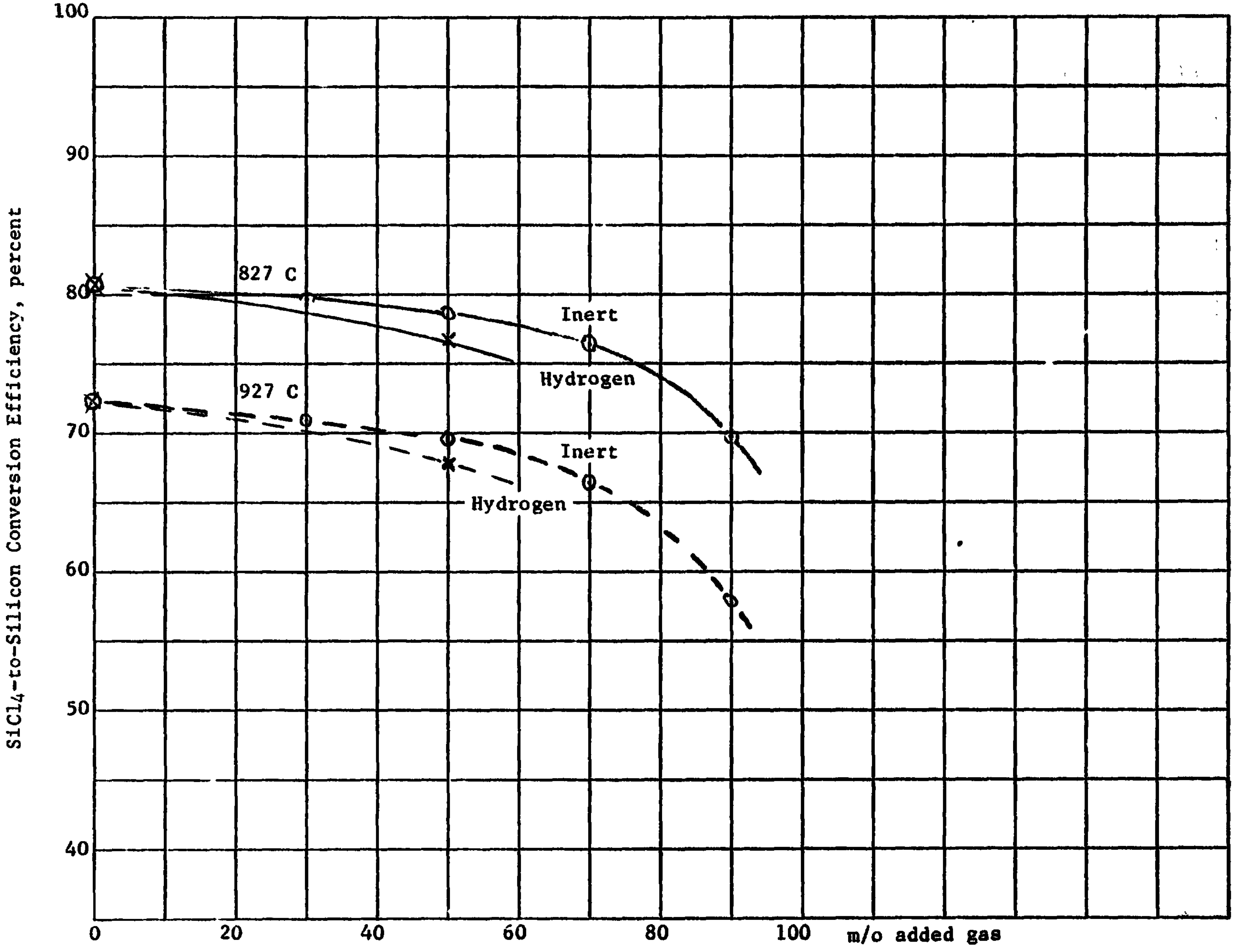


FIGURE 10. EFFICIENCY VERSUS DILUTION OF $SiCl_4$ WITH INERT GAS (o) AND HYDROGEN (x), 1 atm

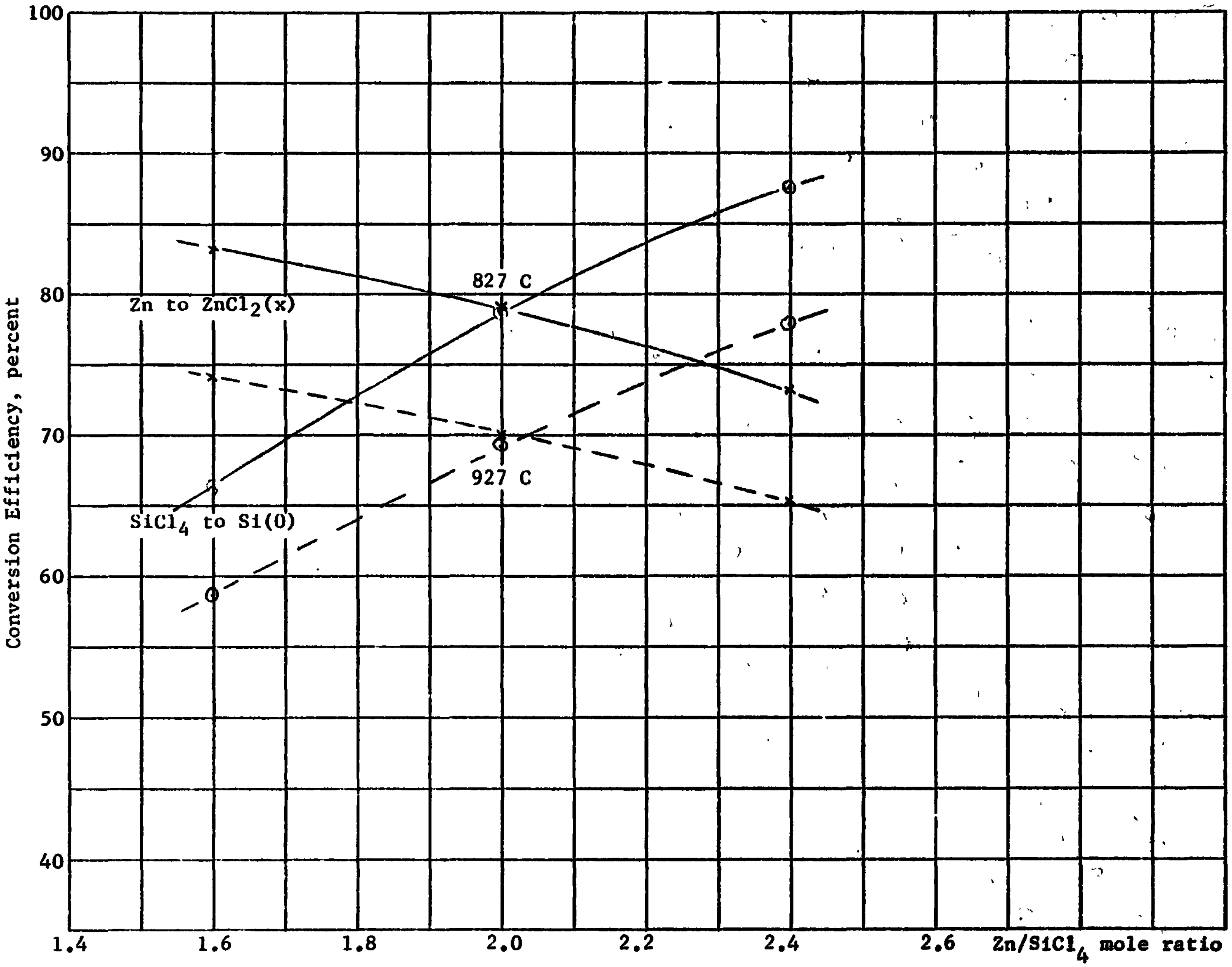


FIGURE 11. EFFICIENCY VERSUS STOICHIOMETRY IN Zn REDUCTION OF $SiCl_4$ (DILUTED 1/1 WITH INERT GAS

TABLE 12. ADDED COST (DOLLARS PER kg SILICON) OF OFF-STOICHIOMETRY OPERATION FOR FLUIDIZED-BED ZINC REDUCTION OF SILICON TETRACHLORIDE AT 1200 K, 1 atm

Mole Ratio $Zn/SiCl_4$	Zinc Equipment	$SiCl_4$ Equipment	Fluidized Bed	Zinc Materials	Zinc Energy	$SiCl_4$ Materials	$SiCl_4$ Energy	Total
0.80	-0.035	0.171	0.051	-0.049	-0.012	0.283	0.074	0.483
1.00	-0.031	0.117	0.031	-0.044	-0.011	0.171	0.048	0.281
1.20	-0.027	0.080	0.018	-0.038	-0.010	0.112	0.031	0.166
1.40	-0.021	0.051	0.009	-0.030	-0.007	0.070	0.020	0.092
1.60	-0.015	0.028	0.004	-0.022	-0.006	0.039	0.011	0.039
1.80	-0.008	0.014	0.001	-0.010	-0.003	0.018	0.005	0.017
2.00	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2.22	0.009	-0.011	0.001	0.016	0.004	-0.014	-0.004	0.001
2.50	0.028	-0.022	0.004	0.040	0.010	-0.027	-0.008	0.025
2.86	0.051	-0.030	0.012	0.076	0.019	-0.036	-0.010	0.082
3.33	0.088	-0.036	0.025	0.132	0.033	-0.044	-0.012	0.186
4.00	0.139	-0.042	0.046	0.216	0.055	-0.051	-0.014	0.349
5.00	0.213	-0.045	0.080	0.352	0.089	-0.054	-0.015	0.620

are roughly balanced by the cost of decreased efficiency in utilization of the other.

(2) The added cost of operating with as much as 43 percent excess of either reactant ($Zn/SiCl_4$ ratios between 1.4 and 2.86) is less than \$0.10/kg silicon.

Actually, when the data of the last column of Table 12 are plotted as a function of $Zn/SiCl_4$ ratio, a minimum is observed at $Zn/SiCl_4 \sim 2.1$; however, the corresponding cost saving of ∿\$0.002/kg silicon is insignificant.

Although the prospect of appreciable cost savings in off-stoichiometry operation does not exist, the second of the above conclusions is significant in two respects.

(1) Strict control of stoichiometry is not mandatory from an economic standpoint.

(2) If any advantages in kinetics or in the form or purity of the product were to accrue from operation at $Zn/SiCl_4$ ratios $\neq 2/1$, it is possible that they might be obtained at relatively low cost, depending upon the degree of departure from stoichiometry required.

Experimental Fluidized-Bed Zinc Reduction of $SiCl_4$

During the course of this program, nearly 100 experimental runs were made in which silicon tetrachloride was reduced with zinc in small fluidized-bed reactors of various designs and under various conditions. Runs to prepare material for product quality evaluation were made under a nominal set of conditions that yielded no conclusions other than confirmation of previous results.

In all cases, fused quartz was the material of construction. The reactor diameter, ∿50 mm, was chosen as a compromise between the desire to limit the consumption of feed materials and the size of associated feeding equipment and facilitation of the fabrication, in fused quartz, of the bed support designs that would provide for the various options of reactant introduction and bed dynamics desired.

The run time in the initial equipment was limited by the capacity of the zinc feed and zinc chloride condensation systems. A "miniplant" constructed later provided for increased capacity as well as for transfer of the condensed zinc chloride to an experimental electrolytic cell.

Rather than to summarize all of the data, this section of the report is organized with reference to various subjects of interest and the related conclusions drawn. In each case, reference to the Quarterly Report is given in which more details can be found.

Solid Versus Gaseous Zinc Feed

Because of the difficulty of boiling zinc and feeding it at a controlled rate to a fluidized bed, the possibility of metering solid zinc granules to the fluidized bed from above was explored. Favorable results with feeding solid volatile reactants directly to fluidized beds had been experienced at BCL in the coating of nuclear fuel particles; vaporization occurs within the fluidized bed and the CVD reaction ensues. Accordingly, a reactor of the design shown in Figure 12a was used to test the concept, with results given in the First Quarterly Report(1). The solid zinc granules used were of ∿550-μm diameter. From ∿120 to ∿237 g of 210 x 297-μm silicon seed particles were used as the fluidized bed. Despite variations of the temperature between 750 C and 1000 C and the $Zn/SiCl_4$ ratio from 0.6 to 4 (stoichiometry = 2), no silicon was deposited on the seed particles. Rather, a mass of silicon needles, from 100 to 1000 μm long and 0.2 to 0.4 μm across, was formed downstream of the bed; the higher the bed temperature, the farther downstream, suggesting that the needle formation resulted from heterogeneous reaction on condensed zinc droplets. While it is true that some needles may have formed on the zinc particles introduced into the bed, those needles were probably elutriated and carried downstream.

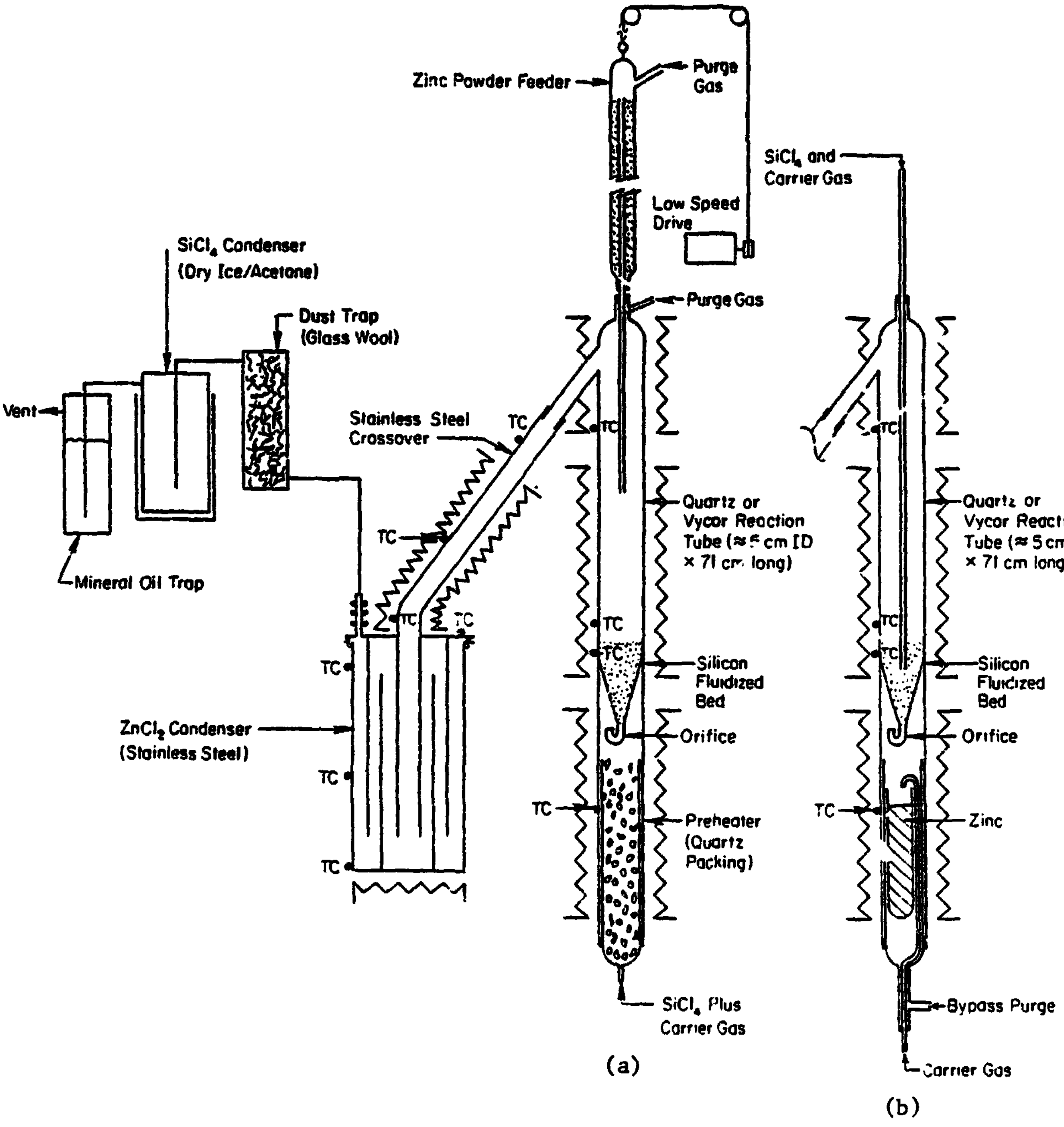


FIGURE 12. SCHEMATIC DIAGRAM OF UNIT FOR THE PREPARATION OF SILICON BY THE ZINC REDUCTION OF SiCl$_4$

(a) SOLID ZINC FEED
(b) VAPOR ZINC FEED

By contrast, when zinc was fed as the vapor at temperatures of from 900 to 1027 C in the apparatus of Figure 12b, and Zn/$SiCl_4$ ratios from 0.55 to 1.8 in ∿70 m/o diluent gas, over 96 percent of the silicon produced was collected as dense material on the seed particles. $SiCl_4$ conversion efficiencies in the range of 12 to 40 percent were obtained, corresponding to from 60 to 100 percent of those expected thermodynamically under any given condition. The predicted ineffectiveness of hydrogen as an added reductant was confirmed.

Accordingly, the concept of using a solid zinc feed was abandoned in favor of the vapor feed technique.

Use of Diluent or Carrier Gas

Although in many CVD reactions an inert carrier gas is used for convenience in transporting materials, it is recognized that to obtain the highest possible production rate from a fluidized-bed reactor where the throughput is limited by potential elutriation of the bed particles, the reactants should be undiluted. However, in the present case, with most of the reaction products constituted of condensible materials, a diluent gas (argon or hydrogen) was used initially to avoid potential problems with decreased pressure due to condensation of reaction products. Hence, early deposition rates were from 10 to 40 grams of silicon per hour in a 5-cm-diameter fluidized bed. In later work such as that described in the Fifth/Sixth and Seventh Quarterly Progress Reports(1), in which the diluent was decreased to a few percent* (typically 3 to 4 percent), much higher rates (above 300 g/hour) were obtainable than would have been the case with normal concentrations of diluent or carrier gas.

Not only does the increased production rate per unit cross section of the fluidized bed demand the minimization of diluent content, but the cost of the latter, if discarded, or of its recycle if reclaimed, is an important factor in demanding minimum use.

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* Some noncondensible gas is necessary to allow the system to "breathe".

Fluidized-Bed Dynamics

In any chemical vapor deposition reaction leading to the growth of particles in a fluidized bed, it is essential that the particles be kept in motion relative to each other, otherwise the points of contact can be bridged by deposited material, leading to agglomeration. Further, a layer of stagnant particles exposed to the reactant gases will become coated with reaction product. To avoid stagnation, the bed action must be vigorous. However, it is also desirable to expose all particles to the same reaction conditions on the average and to limit access of the reactant gas to the wall of the fluidized bed. The latter objectives may be met by using the proper combination of particle size, gas flow, and design of the reactant inlet system and associated bed support plate. A net flow of particles up the center area and downward along the reactor wall is desirable, similar to the particle motion in a spouted bed but without the continuous dilute phase along the axis of the inlet and general absence of gas bubbles that characterize the latter. The presence of a relatively dense descending layer of particles along the walls is desirable to minimize contact of the reactants with the wall and thus prevent, or at least minimize, "wall deposition". Such particle movement requires that the reactant inlet(s) be located away from the wall of the reactor, and that the wall in the vicinity of the distributor plate be sloped inward toward the reactant inlet(s).

Frequently a cone-bottom reactor is used, which is convenient for deposition from one reactant or for a reaction where a second reactant can be introduced through a dip tube (Figure 12b). In a larger reactor, it is preferable to bring both reactants in from the bottom; however, it was found early in the present work that providing adjacent inlets for the zinc and $SiCl_4$ vapors at the apex of a cone-bottom reactor, such as shown in Figure 13, Design B, was not satisfactory because of silicon deposition in the cone area.

A more satisfactory design was that shown in Figure 13, Design A, with a hemispherical bottom and multiple inlets; however, with the zinc vapor fed through the outside inlets and $SiCl_4$ through the center, deposition of silicon on the reactor wall was still a problem, and unless conditions

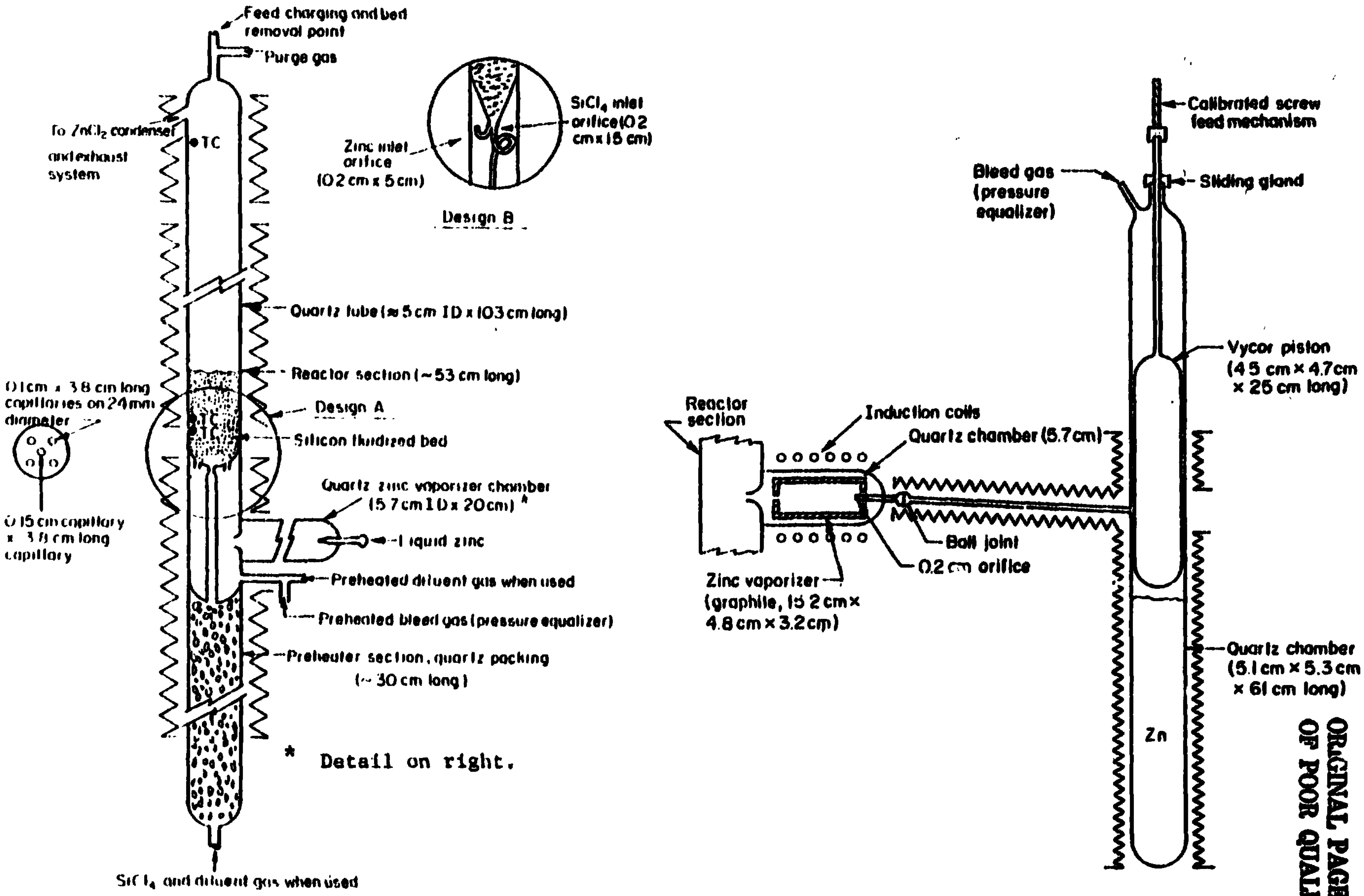

FIGURE 13. SCHEMATIC DIAGRAM OF FLUIDIZED-BED REACTOR FOR THE PREPARATION OF SILICON BY THE ZINC (VAPOR FEED) REDUCTION OF $SiCl_4$

(The zinc feed system is shown on the right) were "right" (a combination of parameters not well defined), tubes of agglomerated particles coated with silicon were observed to grow upward through the bed as extensions of one or more of the zinc vapor inlets. The most satisfactory design, and that finally adopted [Fifth/Sixth Quarterly Report(1)], was to bring the zinc in from the center inlet and the $SiCl_4$ from the outer inlets.

It had been consistently observed that deposition occurred preferentially in the areas of high zinc concentration. This behavior can be rationalized on the basis that for the reaction

$$SiCl_4(g) + 2Zn(g) = Si(s) + 2ZnCl_2(g) \quad ,$$

kinetic expressions might be expected to involve a squared term in the concentration of zinc.

With the zinc vapor introduced in the center, deposition of silicon on the wall was limited in most runs to the area above the fluidizing bed, indicating that with deeper beds attainable in scaled-up reactors, reduction of the fraction of silicon deposited on the wall might be obtained beyond that expected merely from the decrease of the ratio of wall area per unit bed height to cross sectional area as the bed diameter is increased.

Other important aspects of particle dynamics in fluidized-bed deposition on seed particles are (1) particle growth and (2) discharge of product. In the present case, it is intended that seed particles be prepared initially from semiconductor-grade silicon, and eventually from the recycled product, by crushing, screening, and leaching. (Information on this operation is given in the Product Quality Section of this report.) It is desirable that the seed content of the product be minimized for two reasons:

(1) To minimize the contribution of impurities from the seed

(2) To minimize the cost of producing seed.

Although an economic optimum obviously exists, the seed content of the product chosen for process design purposes is 5 percent, corresponding to a ratio of deposited material to seed of 19 and an average increase in particle diameter, in a batchwise operation, by a factor of 2.7. In actual practice at a constant bed inventory and with seed particles fed semicontinuously at a prescribed fraction of the production rate, the product will show a characteristic size distribution after the system has reached a steady state(31). In theory, with the violent mixing that is characteristic of the level of fluidization required, a finite number of particles on the tail of the distribution curve could grow to very large size; however, in practice, with particle withdrawal at the bottom, appreciable segregation occurs apparently in the vicinity of the high velocity incoming gas jets where the terminal velocity of the larger particles is not reached*, but where the smaller particles are blown back into the bed mixture, with the larger ones left behind.

This behavior has been demonstrated with a mixture of sand containing glass balls of about ten times the diameter of the sand particles amounting to less than 0.1 percent of the total bed weight. Under normal fluidization, the rate of ball discharge was about twice that of the sand discharge.

Although it is expected to be less of a problem in the larger experimental facility, condensation of zinc on the product (as semicontinuously withdrawn from the tube at the bottom of the bed) was observed in the "mini-plant"**. In the extreme, condensation of zinc or $ZnCl_2$ has been observed to plug the withdrawal tube. Proper operation of the product withdrawal system depends upon balancing the purge gas flow in the exit line so that pressure surges in the reactor do not drive the zinc or $ZnCl_2$ vapor down the withdrawal tube to where the temperature of the tube and its contents is below the dew point of the vapor. This requires a balance of purge rate. It is obvious that the product should be withdrawn slowly and as nearly continuously as possible. Surges of product result in displacement of the vapor in the interstices. High rates of purge are beneficial in limiting penetration of vapor into the

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* To prevent discharge into the reactant inlet system, the velocity in the gas inlet proper must obviously exceed the terminal velocity of the largest particles.

** Approximately 5-cm-diameter experimental unit.

withdrawal tube as the pressure at the bottom of the bed fluctuates. However, cooling of the exit tube increases with increasing purge, driving the zone at the dew point of the vapor closer to the reactor and making it more accessible to condensation during pressure surges. Clearly, a balance must be struck.

After a number of alternatives were considered in the light of the above factors, distributor plates of various design were tested in a full-scale mock-up using sand as the particles and air as the fluidizing gas. In this work, described in the Ninth and Tenth Quarterly Reports(1), the design shown in Figure 14 gaves the most acceptable bed action as judged from visual observation and from slow-motion pictures, and with minor modifications in dimensions, has been adopted for the design of the experimental facility.

Figure 15 is a typical sequence of frames from the motion pictures, showing first a collapsed bed, gradually expanding bed with breaking of the bubble through the top of the expanded bed, and finally return of the bed to the collapsed condition. At the scale shown, it is obviously not possible to discern the predominant motion of the particles downward along the walls in the bottom section of the bed that is readily observed visually.

Rate and Efficiency of Silicon Production

As discussed above in part, the rate of silicon production to be expected from the zinc reduction appears to be limited by the thermodynamic equilibrium and the rate of feed of reactants to the fluidized bed. The permissible throughput is a function of the particle size and particle size distribution. The major product is a dense deposit of silicon on the seed particles; however, two co-products must be considered, (1) silicon deposited on the wall and (2) that formed as finely divided particles that escape the bed. For most economical operation, the yield of the major product must be maximized and the throughput also maximized.

With these as the major objectives, a large number of experimental runs were made in 5-cm-diameter clear quartz reactors of various design,

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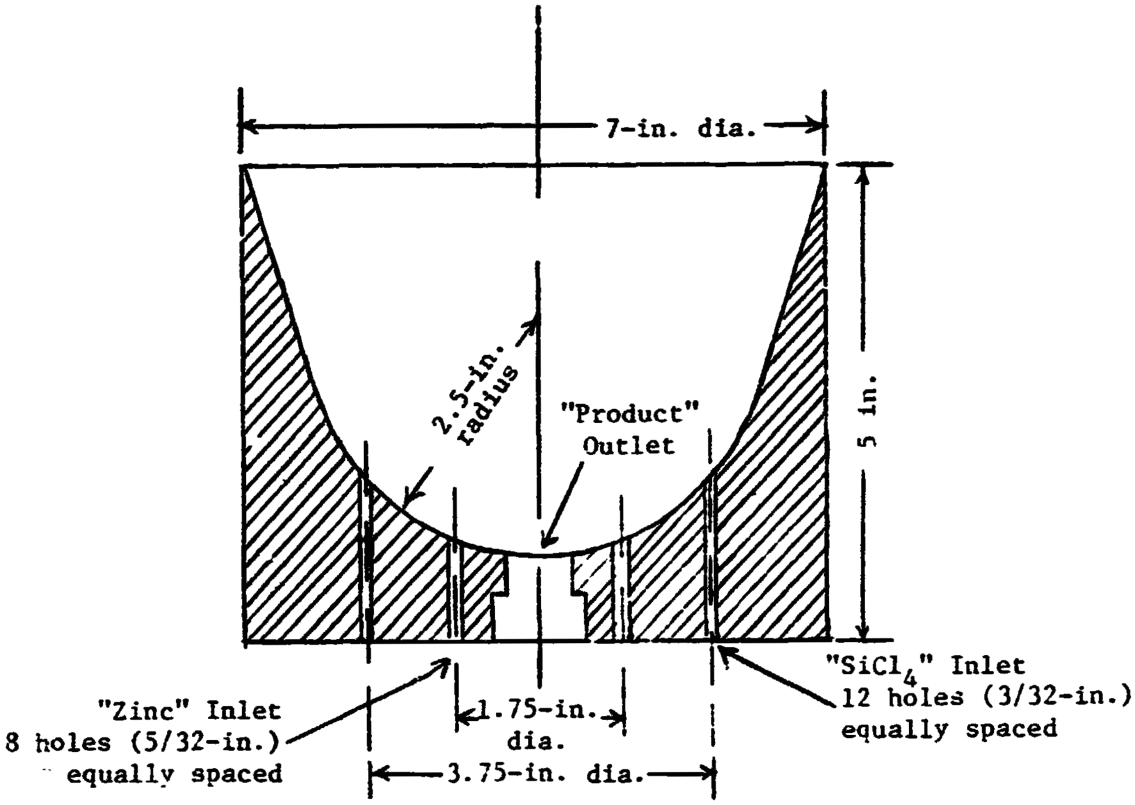

FIGURE 14. DIAGRAM OF ROUND-BOTTOM DISTRIBUTOR USED IN MODEL STUDIES

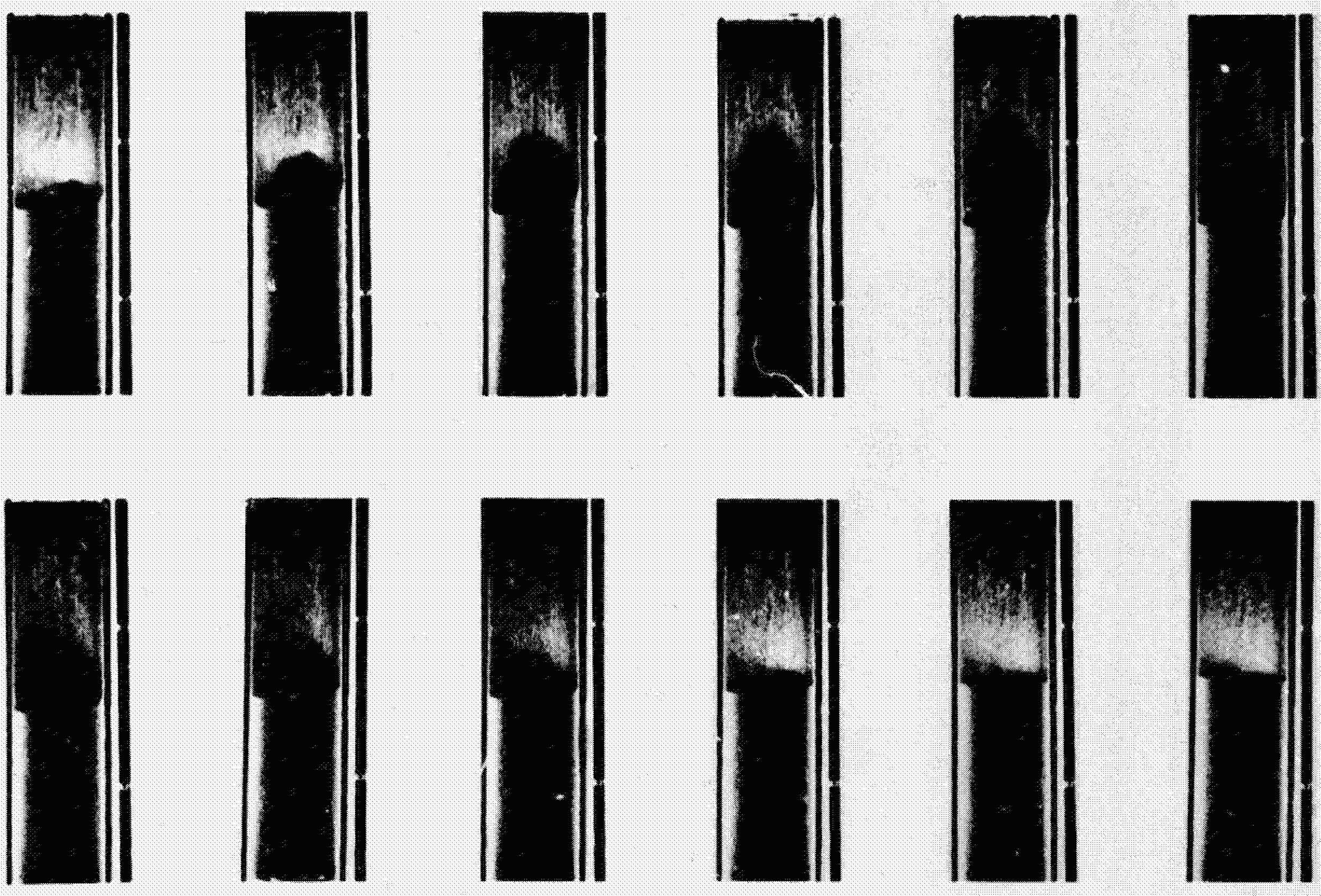

FIGURE 15. TYPICAL SEQUENCE FROM MOTION PICTURES OF THE FLUIDIZED BED MOCK UP (see Figure 14) (time interval = 0.375 second)

some of which have been already shown as Figures 12 and 13. The bulk of this work appears in the first seven of the Quarterly Progress Reports(1).

Rather than to review all of this work, the major conclusions will be summarized with appropriate references given to the supporting data. As in any work of this type, considerable effort went into solving operational problems with the experimental equipment. That work will not be discussed except as it relates to certain design features of the 50 MT/year facility, e.g., vaporization of zinc. Such topics will be considered individually in later sections of this report.

Effect of Reactant Throughput and Particle Size

By going to a reactor outlet design which minimized inertial loss* of bed material to the exit line, and by using a graded-temperature bed (to be discussed later), the highest rate of deposition obtained was 344 g/hour on the seed particles in the 5-cm-diameter reactor (Run No. 64), which (on an area basis) scales directly to 25 MT/year (80 percent on stream) in the 6.5-inch-diameter reactors that form the basis for the 50 MT/year facility design. It is believed that the deeper beds in the larger units may lead to efficiencies** exceeding the 62 percent observed in Run 64. However, if the thermodynamically calculated efficiencies are valid, there may be limited room for improvement, as the conversion efficiencies of $SiCl_4$ to silicon (bed + wall + "dust") were consistently in the range of ~85 to 95 percent of theoretical.

The above-referenced result was obtained with a seed bed of 149 x 297 μm particles which increased in volume and bed depth by 96 percent during the run, i.e., from an L/D of 3.5 to 7.

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* As distinguished from loss by elutriation.

** Fraction of silicon fed as silicon chloride that is collected on the seed particles.

Subsequent runs (Nos. 69, 72, 78) with a 30 percent deeper starting bed on the average and with larger particles, 279 x 590 μm corresponding to a net decrease in starting bed area of to ∿33 percent of that used in the reference run (No. 64) noted above, the fraction of silicon product collected on the seed particles decreased to about 93 percent of that observed earlier, as the result of a ∿60 percent increase in the amount of finely divided silicon carried downstream, i.e., from ∿8 percent to ∿14 percent. Another run with a shallower bed of the larger particles (equivalent to ∿18 percent of the surface area of the reference run) resulted in even lower efficiency of collection of silicon on the bed particles.

The variation of efficiency with bed area discussed above and the fact that in early runs on the program (Nos. 8, 9, 11, 13) with the reactants diluted with 70 percent inert gas, the recovery of the product silicon on the bed particles was greatest, is consistent with the anticipated competition of heterogeneous deposition with gas-phase nucleation and growth. Clearly the production of gas-phase nucleated material must be minimized for greatest economy and operability. A target of 2 percent of the silicon product as silicon dust has been established for the experimental facility with the probability that the system can accommodate considerably more.

Not only is the specific surface area of the bed important in its potential for limiting silicon dust formation, but in affecting the efficiency of deposition on the seed particles and limiting deposition on the reactor wall (assuming equal radial growth rate on all surfaces). These factors favor the use of small particles. However, permissible throughput decreases with particle size. Thus there will be an optimum bed particle size distribution as determined by initial seed size and the ratio of seed rate to production rate. These factors have not yet been established.

Fortunately the effect on overall efficiency of wall deposits will rapidly decrease with reactor scale up to where periodic chlorination of the accumulated material can be used to keep it in check. By contrast, gas-phase nucleation of solids is a volume phenomenon and unless a mechanism is available for capture of once-nucleated particles in a deeper bed of the same fluidization characteristics, such particles will be elutriated from the bed. Thus their formation must be controlled regardless of reactor size.

Before leaving the subject of product collection efficiency and the relation to it of gas-phase nucleation, it should be noted that part, if not all, of the gas-phase nucleation observed may be due to misting of the zinc. The three-body collision reaction

$$2Zn(g) + SiCl_4(g) = Si(g) + 2ZnCl_2(g)$$

or the sequence

$$Zn(g) + SiCl_4(g) = SiCl_2(g) + ZnCl_2(g)$$
$$Zn(g) + SiCl_2(g) = Si(g) + ZnCl_2(g)$$

should both be less rapid than

$$2Zn(\ell) + SiCl_4(ads) = Si(s) + 2ZCl_2(g) \quad .$$

Further, it has been demonstrated that silicon growth in a $SiCl_4$ atmosphere is rapid on zinc droplets. Accordingly, the presence of zinc mist in the vapor should lead to silicon dust formation. Such zinc mist could be entrained by the zinc vaporization, or could result from condensation on cooling by insufficiently preheated $SiCl_4$ or product-outlet purge gas. In this connection, it should be recognized that the amount of zinc condensation in the gas phase required to give the observed behavior would be miniscule. A 0.01-μm zinc nucleus for each 1-μm silicon particle would have required condensation of only 7.7E-6 percent of the zinc fed in a run from which an aspirated sample was taken. It is concluded that every effort should be made to avoid formation of zinc mist by condensation or by entrainment.

Zinc/Zinc Chloride Condensation

As indicated in the Thermodynamic Analysis section of this report (Figure 9), cooling of the reaction product tends to drive the reaction in the direction of generating more silicon (kinetics permitting). This effect was observed in the early work on the program to have occurred to the extent of plugging the exit line from the fluidized-bed reactor. For that reason, it is necessary to maintain the temperature of the exit line at or above the reactor temperature. Further, it may be expected that any zinc condensed in the presence of silicon tetrachloride would be coated with a thin film of silicon. It is believed that this effect accounted for the sluggish flow of zinc condensate in the reactor exit until this line was maintained at a temperature equal to or exceeding that of the top portion of the fluidized bed so that no zinc condensed.

The necessity for quenching the reaction by-product is shown by the calculations of Table 13 which predict equilibrium liquid zinc condensation from $\sim$800 C downward.

Experiments described in the Fifth/Sixth Quarterly Report(1) demonstrated the formation of silicon crystallites (as well as submicron gas-phase nucleated material) in the temperature range 730 to 930 C. Thus, if equilibrium by-product condensation were allowed to occur, ample opportunity would exist for reduction of residual $SiCl_4$ as predicted by the equilibrium conversion of Figure 9.

Electrolytic Recovery of Zinc From Zinc Chloride

As discussed above, the electrolytic cell has two functions:

(1) To recover zinc and chlorine from the zinc chloride by-product for recycle

(2) Chlorination of the particulate silicon that is suspended in the zinc chloride.

The first function has been demonstrated in the early work of Threlfall(16), Fray(32), and more recently by Haver, et al.(33), and Shanks,

TABLE 13. EQUILIBRIUM CONDENSATION OF ZINC AND ZINC CHLORIDE FROM BY-PRODUCT GAS CONTAINING 30.45 m/o Zn(g), 41.85 m/o $ZnCl_2$(g), 15.23 m/o $SiCl_4$(g), and 2.47 m/o INERT GAS

(Nominal 50 MT/year facility by-product composition)

T, C	Zinc Condensed cumulative percent	Zinc Chloride Condensed, cumulative percent
827	0	0
802	0 (∿ dew point)	0
777	34.45	0
752	56.49	0
727	70.90	0
702	80.40	0
677	86.45	0
652	96.98	86.65
627	98.34	92.70
602	99.01	95.88
577	99.44	97.68
552	99.64	98.68
527	99.82	99.26
502	99.87	99.62

et al.[(17)], of the Bureau of Mines. However, the by-product of the present process differs from the zinc chloride used in the published work in that it contains unreacted zinc and suspended silicon "dust". Thus it became of interest to verify the electrolysis of zinc chloride by-product and the chlorination of the contained silicon.

The experimental electrolytic cell as initially used with vertical electrodes is shown in Figure 16. However, to avoid loss of current efficiency due to rechlorination of deposited zinc, horizontal electrodes were later used and the cell was nickel plated to reduce corrosion by the evolved chlorine. Further, a syphon arrangement was substituted for the bottom-delivery valve which was subject to malfunction. In accordance with the Bureau of Mines practice, 50 m/o KCl was used in most runs to increase conductivity and to decrease $ZnCl_2$ volatility.

Table 14 summarizes the data obtained in selected runs from which the following conclusions could be drawn.

(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.

In Table 15 are listed pertinent data on the history and projections for $ZnCl_2$ electrolysis from which it can be concluded that a projected electrical energy requirement of about 2 kwh per pound of zinc electrolyzed appears to be reasonable.

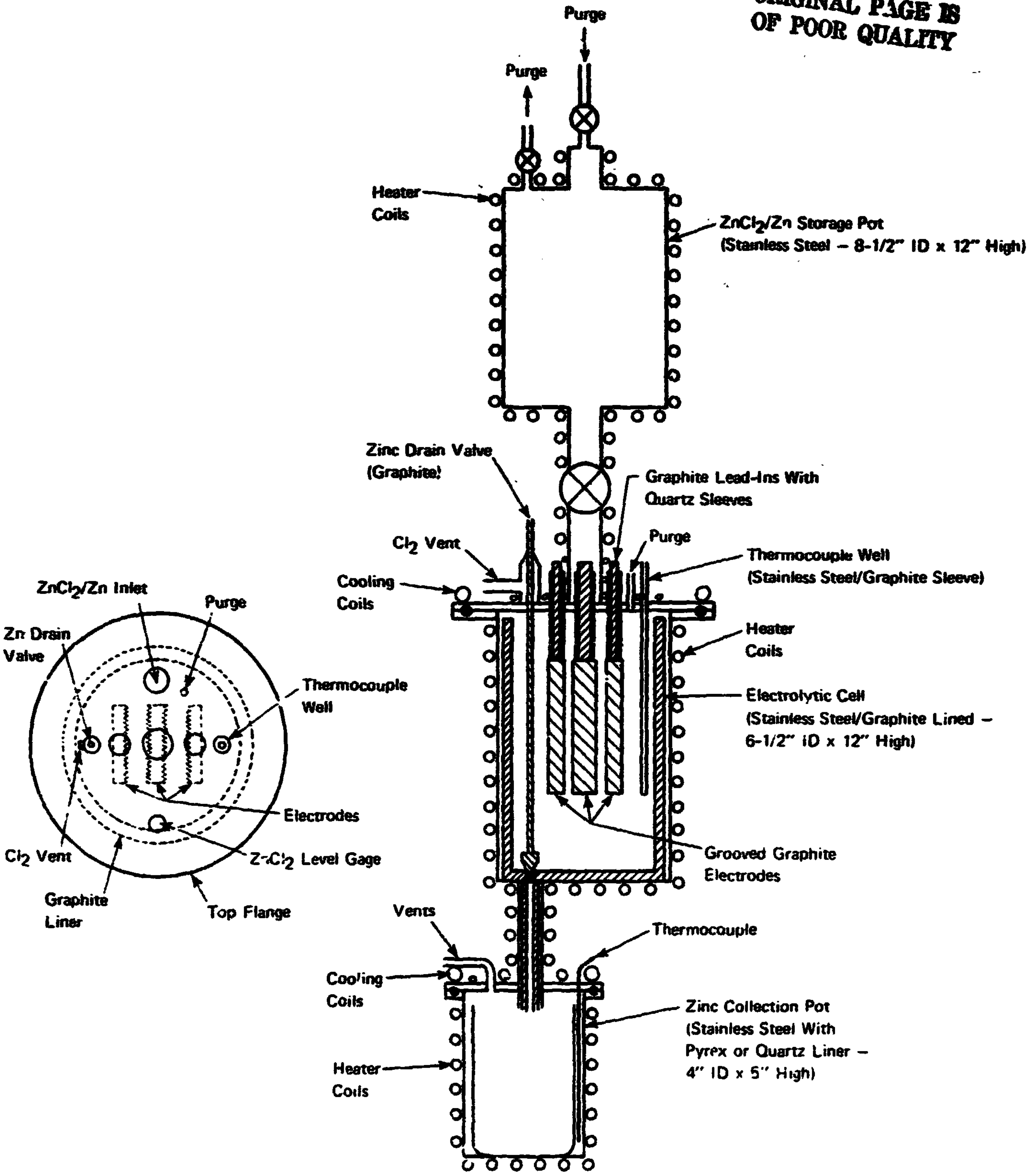

FIGURE 16. SCHEMATIC DIAGRAM OF EXPERIMENTAL ZINC CHLORIDE TO ZINC RECOVERY SYSTEM AS ORIGINALLY CONSTITUTED

(see text for modifications)

TABLE 14. SUMMARY OF EXPERIMENTAL ELECTROLYSIS(a) OF $ZnCl_2$ AT 500 C (SELECTED DATA)

Run	Cell Configuration	Feed	I amp	I amp/cm^2	V volts	Time, hours	CE,(b) percent	PE,(c) percent	kwh/lb	Remarks	Quarterly Report(1) Reference
A	Verticle electrodes	Miniplant condensate	∿140	0.8	∿15	45	80-108(d)	9-11	∿5.8	Low power efficiency due to high resistivity of $ZnCl_2$	7
B	Horizontal electrodes(17) ∿125 cm^2	Synthetic $ZnCl_2$; 50 m/o in KCl	100	0.8	5	21	76	22	2.5	Terminated by cell overflow due to electronic level indicator malfunction	8
C	Horizontal electrodes(17) ∿125 cm^2	Synthetic $ZnCl_2$; 50 m/o in KCl	100 150	0.8 1.2	5 8	30 6	61	17	3.4	Zinc non-coalescence presumably due to moisture in $ZnCl_2$	9
D	Horizontal electrodes(17) ∿125 cm	Synthetic $ZnCl_2$; 50 m/o in KCl	100	0.8	10	12	95	15	3.4	--	--
E	Horizontal electrodes(17) ∿125 cm^2	Miniplant condensate 50 m/o in KCl	100 115 150	0.8 0.9 1.2	∿9 10 12	5 10 12	87	13	4.5	Suspended Si dust chlorinated to $SiCl_4$ equivalent to 3.4 percent of miniplant product Si	10
F	Horizontal electrodes(17) ∿125 cm^2	Miniplant condensate 50 m/o in KCl	94	0.8	∿9	95	95	16	∿3.5	Except for power supply malfunction run essentially trouble-free	--

(a) Re-examination of data resulted in selected values which may differ from those given in Quarterly Reports(1).

(b) Current efficiency.

(c) Power efficiency.

(d) Composition of feed uncertain.

TABLE 15. HISTORY AND PROJECTION OF $ZnCl_2$ ELECTROLYSIS

Reference	Type of Cell	Cathode Area, cm^2	Anode-Cathode Spacing, cm	Electrolyte	Current, amp	Current Density, amp/cm^2	Current Efficiency, percent	Voltage	Power Efficiency, percent	Energy, kwh/lb Zn
Threlfall(16)	45° "V" electrodes	33,000	?	$ZnCl_2$	6,500	0.2	89	4.6	29	2.0
Fray(32)	horizontal electrodes	14.5	2.5	50 m/o $ZnCl_2$ 50 m/o KCl	10	0.7	95	3.5	41	1.4
Bureau of Mines(33)	horizontal electrodes	26	2.5	40 m/o $ZnCl_2$ 60 m/o KCl	85	3.3	96	6.2	24	2.4
Bureau of Mines(17)	horizontal electrodes	1,032	1.3	38 m/o $ZnCl_2$ 31 m/o NaCl 31 m/o KCl	1,500	1.45	95 minimum	6.7	23	2.5
Bureau of Mines Projected(34)	horizontal electrodes	26,000	(?)	(?)	50,000	1.9	95 (assumed)	4	36	1.6

Zinc Vaporization

Although zinc is sufficiently volatile to be feasible as a reductant in the present process, the boiling temperature (908 C at 1 atm, 918 C at 1.1 atm, and 927 C at 1.2 atm) is high enough so that the prospect of monitoring flow rate by pressure drop across a sonic orifice is not attractive. This would require operating the boiler at pressures appreciably above 2 atm, i.e., at boiling temperatures above 980 C

The use of a flash vaporizer with a metered stream of liquid zinc was explored as an alternative. This arrangement had been used successfully in the miniplant, as pictured in Figure 13, with the vaporizer temperature at 1350 C. Although this flash vaporizer was marginally satisfactory on a small scale with quartz equipment, the prospect of scaling it up by a factor of 10 to provide the 1/2 kg of zinc per minute required for each of the two 25 MT/year reactors of the projected 50 MT/year facility appeared to be formidable. In attempting to decrease the temperature of the flash vaporizer, it was found that the inventory of zinc in the vaporizer would have to be undesirably large, resulting in a hysteresis in zinc vapor flow following a change in the liquid feed rate. Although the heat-transfer coefficient from graphite (the preferred liner material) to boiling zinc was found to be high (450 BTU/hour·ft^2·F), zinc does not wet graphite, and a thick film (representing a significant inventory) is present on the heat-transfer surface. Details of the types of "flash" vaporizers considered theoretically and experimentally are given in the Seventh, Eighth, and Ninth Quarterly Reports(1).

As none of the vaporizer designs considered were attractive, induction coupling of energy directly to the liquid zinc was explored. If the thermal capacity of the vaporizer and the degree of superheating can be minimized in a direct induction-coupled system, it should be possible to control the rate of vaporization by the energy input with a minimum of hysteresis.

The Tenth Quarterly Report describes an experiment in which boiling rates of 1/2 and 1 pound per minute of zinc* were readily maintained in a horizontal vaporizer consisting of a quartz tube 57 mm in diameter and 30 cm in length. To aid in initial heating of the vaporizer (into which liquid zinc was metered) as well as to reduce the inventory and to decrease misting, the cross section of the tube was filled with 1/4- to 3/8-inch graphite chips. No attempt was made to control the rate of vaporization by energy input except to raise the energy input to the point that the vaporization rate (as measured by weighing the condensed zinc continuously) was equal to the liquid feed rate (as metered by displacement).

Subsequent contacts with Lepel, Inc., makers of the induction heating equipment, confirmed the feasibility of controlling the vaporization rate by energy input. Lepel engineers are also considering the feasibility of sensing the zinc inventory in the vaporizer by its induction coupling characteristics. Although that method of control may be desirable, it has been determined that the zinc level can be readily sensed by a simple electric contact consisting of a sheathed tungsten wire. Even if an impedance-based sensor were to be used, an electrical contact indicator should probably be incorporated as a backup.

Product Quality

As mentioned earlier, the feasibility of preparing semiconductor-grade silicon by the zinc reduction of silicon tetrachloride has been demonstrated by DuPont, although improved uniformity of product appeared to be desirable and is thought to be attainable through the semicontinuous operation of this program. Most of the work with the miniplant has related to study of the process, in which case seed beds of crushed metallurgical-grade silicon were used for reasons of economy. However, several runs were made with seed of semiconductor-grade silicon crushed, leached and dried, and with semiconductor-grade silicon tetrachloride as the feed material. The zinc

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* The 1 pound per minute being about that required by one of the 25 MT/year units of the 50 MT/year facility.

was distilled zinc obtained in ingot form from Belmont S&R, Inc. The zinc ingots were cleaned after machining by degreasing.

A total of 6.1 kg of product for quality evaluation has been forwarded to JPL. Some of this was as the product of single runs with seed contents ranging from 30 to 50 percent. However, late in the program, a series of runs was made in which the product served as the seed for subsequent runs. In this way seed contents as low as 5.6 percent were obtained. Table 16 summarizes the geneology and disposition of this material.

In some of the runs made in the miniplant for quality-evaluation purposes, the product was recovered after the bed had been purged (at operating temperature) to remove zinc vapor. Despite this precaution, some zinc condensate was observed on some of the particles. In other runs where a semicontinuous product withdrawal system was used, zinc condensation occurred briefly in the particle withdrawal tube as discussed under the section of this report on Particle Dynamics.

The actual zinc content of the granular silicon sent to JPL for evaluation is uncertain, spark source mass spectrometric analyses having ranged from 140 to 3000 ppmw. A series of experiments is being run to determine (1) what part of the zinc is on the surface (e.g., as condensate), (2) what part has been entrapped in the growing granules, and (3) what part can be removed by a simple heat treatment. Further, JPL has submitted samples for neutron activation analysis as will be discussed below.

The problem with analysis of as-produced particles by the spark source mass spectrometer is that only one or a few particles are "seen" in the analysis. As the particle-to-particle composition uniformity should be good during the growth process, one particle should be representative of the entire bed. However, in the matter of zinc condensed on the outer surface considerable inhomogeniety might be expected.

With the objective of eliminating contamination of surface-condensed zinc and whatever occluded zinc that might diffuse to the surface in vacuum heat treatment, the products of Runs Nos. 97 and 98 were heated for 1 hour at 920 C in an evacuated quartz tube before shipment to JPL. In the course of this heat treatment, No. 97 lost 1090 ppm of zinc and No. 98, 1280 ppm.

TABLE 16. GENEOLOGY AND DISPOSITION OF QUALITY EVALUATION PRODUCTS

				Disposition				
							Recycled	
Run No.	Initial Bed Weight, g	Final Bed Weight, g	Seed Content, percent	To JPL, g	Reserve,[a] g	Residue,[b] g	Weight, g	To Run No.
91	458[c]	743	61.6	--	57	---	371	92
							313	94
92	371	687	33.3	--	---	---	500	93
							187	94
93	500	738	22.6	722	10	6	---	--
94	500	1024	24.9	--	3	21	500	95
							500	96
95	500	847	14.7	829	10	8	---	--
96	500	1039	12.0	--	10	12	511	97
							506	98
97	511	1102	5.6	1000	99	3	---	--
98	506	817.5	7.4	750	63.7	3.8	---	--

(a) Free flowing material, retained at BCL.

(b) Contaminated with zinc on withdrawal (see text), retained at BCL.

(c) 105- x 149 μm semiconductor-grade silicon seed.

With the possibility of surface contamination obviated, residual zinc detected in subsequent analyses of these samples would thus be attributable to the bulk material.

Because of high volatility, it has not been possible to dope silicon with zinc in the work at Westinghouse/Dow Corning(35) and at Monsanto(36). Thus, in any solar cell-forming process that involves melting silicon, residual zinc is expected to be evolved and a few thousand ppm may not be detrimental in the product fed to that melting step. To determine the loss of zinc on fusion of the silicon, two products, one high and one low in zinc, were melted and held molten at ∿1440 C for 1 hour in vacuum and in a stream of gettered argon. The results are given in Table 17.

TABLE 17. REMOVAL OF ZINC FROM SILICON ON FUSION IN ARGON AND VACUUM
(1 hour, ∿1440 C, sample weight 2.5 g)

Treatment	Zinc in Silicon, ppmw (atomic absorption)	
	Run 50 Product	Run 97 Product
None	180 (as-produced)	1500 (after 920 C vacuum heat treatment of solid)
Vacuum, 1 hour	50	10
Argon, 50 cc/minute	<30	<6

The 3 ℓ of argon that was passed over the 2.5-g silicon sample is more than sufficient to account for removal of zinc from the 1500 to 6 ppm level by the most conservative assumptions. The reasons for the discrepancies between the results of the argon purge and the vacuum treatment (which should be more effective) may be related to the presence of an oxide or nitride film on the silicon, which although of insufficient thickness to be visible, would be expected to constitute and effective diffusion barrier for zinc removal

at the surface. The effective purity of the argon may have been higher than that of the vacuum.

It is evident that the zinc content of the product can be reduced to the ppm level or below by fusion of the silicon. Whether or not zinc removal is necessary remains to be determined. It is possible that the zinc content can be adequately reduced by heat treatment short of fusion.

The reason for the large difference in occluded zinc content between the products of Runs 50 and 97 is probably significant and will be studied.

Except for the question of contamination by surface-condensed zinc (which is removable by leaching or vacuum heat treatment), the analysis for zinc is under control as indicated by the data of Table 18. Neutron activation and atomic absorption appear to give the most reliable analysis; however, the accuracy of the mass spectrometric analysis could undoubtedly be improved by the use of standards.

TABLE 18. COMPARATIVE ANALYTICAL RESULTS, ppmw, FOR ZINC IN SILICON

Analytical Method	Sample 97	Sample 98
Spark-source spectrometer, BCL	3000	2000
Atomic absorption, BCL	1500	--
Neutron activation, LLL(37)		
from decay of $_{30}Zn^{65}$, $t_{1/2}$ = 250 d	1480 ± 12	1519 ± 12
from decay of $_{30}Zn^{69}$, $t_{1/2}$ = 13.8 h	1469 ± 12	1517 ± 12

Comparison of mass spectrometric (SSMS) and neutron activation (NA) analyses for other elements is made in Table 19.

For those elements not listed as "<" (inconclusive) the SSMS analyses are reasonably consistent with the NA analyses for Zn and Sb but not for Na and W.

TABLE 19. COMPARATIVE ANALYSES OF SILICON PRODUCTS, ppmw

Element	Run 97		Run 98	
	SSMS(a)	NA(b)	SSMS(a)	NA(b)
Na	4	0.0004 ± 0.0003	20	0.002 ± 0.0017
Cr	<3	(0.3 ± 0.3)(c)	<3	(0.2 ± 0.2)(c)
Fe	<3	(5 ± 5)	<3	(3.6 ± 3.6)
Ni	<5	(25 ± 25)	<1	(26 ± 26)
Co	<3	---	<3	0.024 ± 0.006
Cu	<7	4.4 ± 0.5	<7	1.4 ± 0.3
Zn(d)	3000	1480 ± 12	2000	1519 ± 12
Zn(e)	3000	1469 ± 12	2000	1517 ± 11
Ga	<1	0.009 ± 0.007	<1	0.009 ± 0.008
As	<0.1	0.043 ± 0.003	<0.1	0.035 ± 0.002
Zr(f)	<1	(12 ± 12)	<2	(12 ± 12)
Zr(g)	<1	(3.5 ± 3.5)	<2	(3.4 ± 3.4)
Mo	<1	(0.7 ± 0.7)	<1	(0.6 ± 0.6)
Ag	<2	2.4 ± 0.1	<1	0.85 ± 0.08
Sb(h)	4	3.10 ± 0.02	2	0.810 ± 0.007
Sb(i)	4	2.96 ± 0.04	2	0.83 ± 0.03
La	<0.1	0.0047 ± 0.0003	<0.1	0.0040 ± 0.0004
Ta	<2	0.025 ± 0.005	<6	0.411 ± 0.009
W	0.4	0.016 ± 0.003	0.4	0.023 ± 0.002
Au	<0.1	0.0008 ± 0.0004	<0.2	0.0005 ± 0.0001

(a) SSMS = spark source mass spectrometer, BCL.
(b) NA = neutron activation, LLL(37)
(c) Parenthetical values indicate that nuclide was not detected above background.
(d) NA via Zn^{65}.
(e) NA via Zn^{69}.
(f) NA via Zr^{95}.
(g) NA via Zr^{97}.
(h) NA via Sb^{122}.
(i) NA via Sb^{124}.

The sodium in the SSMS analysis is believed to come from the high-purity graphite used to form an electrode of the silicon granules by compaction, or from contamination. The reason for the difference in tungsten values is not clear.

For what it is worth, the SSMS analyses show 0.02 ppmw (0.06 ppma) boron in the products of Runs 97 and 98. However, because of the possibility of contamination as in the case of sodium, confirmation by other methods or comparison with uncontaminated standards is necessary before these values can be taken seriously.

The significance of the elements for which the neutron activation analysis appears to give meaningful results will be studied as additional data are obtained.

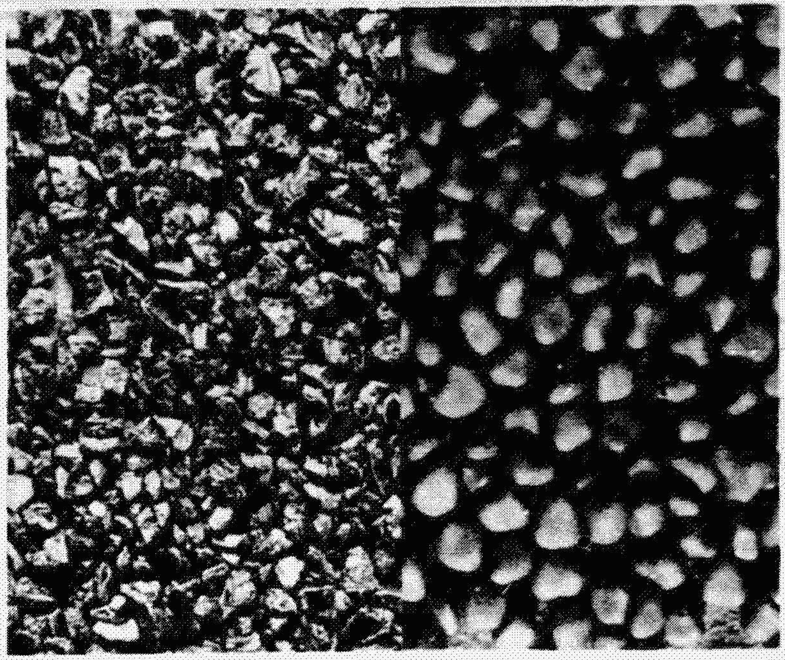
In terms of bulk properties, the granular product is free flowing, with the particles becoming more nearly spherical as shown in Figure 17 which compares the product of Run 64 containing about 50 percent residual seed with that of Run 97 containing 5.6 percent residual seed.

The density of the as-produced particles approaches theoretical as indicated by the density measurements shown in Table 20.

TABLE 20. DENSITY OF SILICON PRODUCT*

Material	Particle Size, μm	Density, g/cm^3
Silicon	---	2.33 (theoretical)
Run No. 97 Product (5.6 percent seed)	400-600	2.325
	Corrected (-0.3 percent) for assumed 1500 ppmw Zn	2.320
	Density, percent of theoretical	99.6

* Pycnometric density (xylene) measured with granular material.



4225VD 13X 3484VD 13X

Run 64 Product
∿50 percent seed

Run 97 Product
5.6 percent seed

FIGURE 17. COMPARISON OF AS-PRODUCED PARTICLES INDICATING INCREASED SPHERICITY WITH DECREASED SEED CONTENT

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The near-theoretical density of the product is evident from the scanning electron micrograph of a fractured particle from Run No. 36 (Figure 18), in which very few voids are seen. The deposited silicon appears between the two markers.

A new scanning electron micrograph is being installed at BCL with which much higher resolution will be available than was available for taking the micrograph of Figure 18. It will be of interest to see if porosity at a higher level of dispersion can be detected. A mottled appearance developed on etching a polished particle cross section suggests that possibility.

Seed Preparation

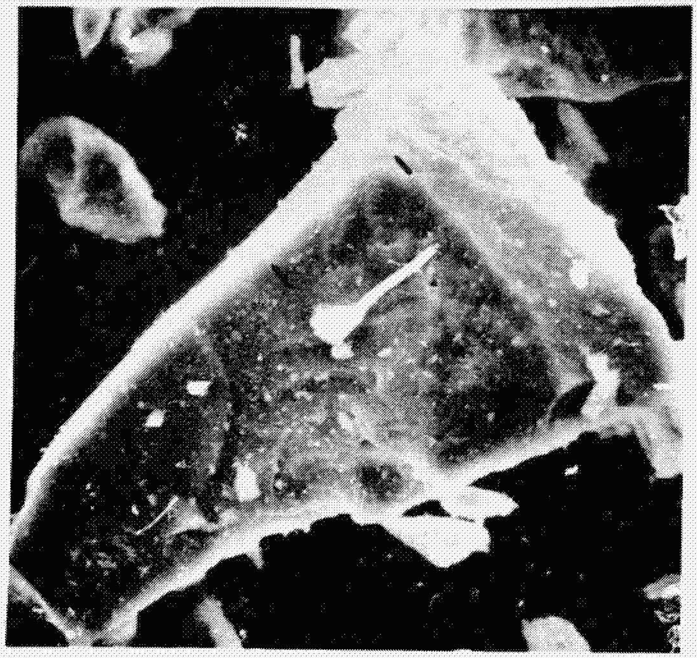
To provide seed material for the runs to produce quality-evaluation samples, semiconductor-grade silicon was crushed in a hammer mill*, yielding about 50 percent in the desired particle size range of 149 to 420 µm.

Screening the seed was done on stainless steel screens with the solder seams and brass rims coated with epoxy to prevent contamination from those materials. Following screening, the seed was treated for 24 hours in HF and 24 hours in 50 percent HF-H_2SO_4 with intermittent agitation, and then washed with deionized water and dried.

Spark-source mass spectrometric analyses of the milled and leached material were compared to those of the semiconductor-grade starting material. For all elements analyzed (74), the leached material was as good or better than the starting material.

---

* Dedicated hammer mill.



2951VD 1000X

FIGURE 18. SCANNING ELECTRON MICROGRAPH OF FRACTURED PARTICLE FROM RUN 36 SHOWING ABSENCE OF APPRECIABLE POROSITY IN COATING BETWEEN MARKERS

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D. 50 METRIC TON PER YEAR EXPERIMENTAL FACILITY

For purposes of large-scale feasibility study and refinement of cost estimates, the design of a 50 MT/year facility was initiated. Contingent upon continued favorable indications of technical and economic feasibility, building, debugging, and operating the facility at BCL are contemplated as Phases III, IV, and V, respectively, of the present program.

Several objectives would be served:

(1) Confirmation of technical feasibility
(2) Confirmation of economic feasibility
(3) Refinement of design
(4) Demonstration and refinement of operation
(5) Provision of larger quantities of representative product to aid in meeting the materials requirements of the LSA and other programs
(6) Provision of a base for the transfer of technology to commercial interests.

Three organizations have cooperated in formulating the design of the 50 MT/year facility. The $SiCl_4$ purification system was the primary responsibility of Pace Engineers, Inc. (Pace), of Houston, Texas; the remainder of the more conventional aspects of the design was handled by Raphael Katzen Associates International, Inc. (RKAII), of Cincinnati, Ohio; and the less conventional aspects of the design and its overall integration were handled by BCL in cooperation with RKAII.

As the full design, submitted to JPL in early April, 1978, for their consideration, represents a large package, it is difficult to report in detail without reproducing the package. The design package is referred to as Reference 38.

Accordingly, a few of the most significant drawings are reproduced here with explanatory notes so that the current status of the program may be appreciated by the reader. It is recognized that the drawings contain some detail that may not be legible at the scale used here; however, they are believed to be sufficiently informative for the present purpose. In the interest of continuity, some of the material cited earlier in this report is repeated.

50 MT/Year Si Facility Design

In general, the process provides for mixing purified silicon tetrachloride and zinc vapor in the lower part of a fluidized bed of silicon seed particles on which the reaction product accumulates as a relatively dense and adherent deposit. The by-product zinc chloride vapor and unreacted zinc vapor are condensed and routed to electrolytic cells for recovery and recycle of the zinc. The unreacted silicon tetrachloride is recycled to the purification unit. In a production plant, the chlorine from the zinc chloride electrolysis would be used to produce the make-up silicon tetrachloride by reaction with metallurgical-grade silicon or with silicon carbide; however, in the experimental facility, it was deemed prudent to bypass this step, since silicon tetrachloride is readily available at a reasonable cost. Further, when the chlorination step is eventually undertaken for minimizing overall cost, the design can be based on well-established practice, which needs no verification in the experimental facility considered here. Accordingly, the chlorine from the electrolytic cells is converted to sodium hypochlorite for use locally in treating sewage plant effluent. The chlorine-to-hypochlorite conversion system is integrated in the waste treatment section of the facility with a system for neutralizing and disposing of the waste silicon tetrachloride from the purification system.

Table 21 lists the major design parameters of the 50 MT/year Si experimental facility. It is to be noted that two 25 MT/year fluidized-bed units nominally of 6.5-inch ID are used for flexibility and as a reasonable scale-up from the 2-inch ID reactor used in the miniplant. Although the nominal design is for 6.5-inch (16.5-cm) diameter, final choice will probably be for somewhat larger, e.g., 7-inch (17.8-cm) diameter. The capacity of

TABLE 21. DESIGN PARAMETERS - 50 MT/YEAR SILICON EXPERIMENTAL FACILITY

• On-stream factor	80 percent
• $Zn/SiCl_4$ stoichiometry	2/1
• Reaction temperature	927 C (1700 F)
• Operation pressure	∿1 atm above fluidized bed
• Conversion of $SiCl_4$	63 percent per pass
• Production rate	7.20 kg/hour (15.87 lb/hour) (16.8 g/hour/cm^2 cross section)
• Seed requirement (5 percent)	0.36 kg/hour (0.79 lb/hour)
• Fluidized-bed reactors (two)	16.5-cm (6.5-inch) diameter
• $SiCl_4$ purification by distillation	92 percent center cut
• Zinc recycle by electrolysis	Six 5000- to 6000-amp cells
• Zinc recovery	95 percent
• Cl_2 disposal	Conversion to NaOCl

each unit, 3.6 kg/hour, is a direct scale-up on an area basis from the 340 g/hour production level attained in the miniplant unit. The 63 percent $SiCl_4$ conversion per pass is a projection of miniplant experience; however, the seed requirements (5 percent of production) and the zinc recovery (95 percent) estimates are somewhat arbitrary at this point and subject to modification by experience.

As the initial basis of design, RKAII and Pace were provided with materials and energy flow sheets of the type shown in Table 22. The version given in Table 22 was the last revision (October 20, 1977) in that format. Subsequent changes were made via the design package(38) as it progressed. A major difference between Table 22 and the final design was the substitution of NaOH neutralization of the waste SiCl for the $Ca(OH)_2$ neutralization which was thought at the time to be more economical. Integrating the $SiCl_4$ waste disposal and chlorine to hypochlorite improves the overall design. Other less fundamental changes from the October 20, 1977, version were made as the design proceeded, and are reflected in the discussion that follows.

In the discussion that follows, the process is divided into three sections -- Feed Preparation, Reaction and Recovery, and Waste Treatment.

Feed Preparation

Figure 19 shows the feed preparation section of the facility, with process flow rates tabulated at upper left. Silicon tetrachloride of the approximate analysis given in Table 23 is received in 40,000-pound tank trucks. This material is purified by distillation in two columns (light-end and heavy-end) with intermediate surge tank (T101 in the figure). A 92-percent center cut is taken, with 4 percent each of tops and bottoms going to waste. The purified product from the top of the heavy-ends column goes to a feed tank that supplies each of the $SiCl_4$ boilers for the two 25 MT/year Si fluidized-bed units. As shown in Figure 19, the pure $SiCl_4$ storage tank is compartmentalized (tentatively in six sections) to permit independent qualification of lots of $SiCl_4$ before committing them to use. Nitrogen is provided to allow the various units to breathe to a vent system, the $SiCl_4$

TABLE 22. MATERIAL AND ENERGY FLOW SHEET (ENGLISH UNITS)
50 MT/YEAR SILICON FACILITY (Revised 10/20/77)

[← → = materials in or out; (ℓ) = liquid phase]

		Input						Output						Process Heat	
Unit		Material	T, F	lb mole hr^{-1} x 10^2	lb hr^{-1}	ft^3(gal) hr^{-1}	Viscosity, cp	Material	T, F	lb mole hr^{-1} x 10^2	lb hr^{-1}	ft^3(gal) hr^{-1}	Viscosity, cp	Btu hr^{-1}	Kw
A1	Pure $SiCl_4$ Tank Capacity 5 day 19588.8 1,564.80 gal	$SiCl_4$(ℓ)	77	96.060	163.24	(13.040)	0.45	$SiCl_4$(ℓ)	77	96.060	163.24	(13.040)	0.45	0.0	0.0
A2†	$SiCl_4$ Boiler (1.7 atm) Capacity 8 hrs 1306.0 lb 104.4 gal	$SiCl_4$(ℓ)	77	96.060	163.24	(13.040)	0.45	$SiCl_4$(ℓ)	164.5	1.884	3.20	(0.274)	0.3		
								$SiCl_4$(g)	164.5	94.176	160.04	252.6	0.012	14031.2	4.12
A3†	Fluidized Bed Reactor	$SiCl_4$(g)	164.5	94.176	160.04	252.6	0.012	Si prod.	1701	59.336	16.66	0.1116			
		→ Inert	77	5.652		22.16	0.019	Si wall	1701	1.694	0.48	0.0028			→
		Zn (g)	1701	188.350	123.14	2415.2	0.085	Si dust	1701	1.128	0.32	0.0022			
		→ Si seed	77	2.826	0.80	0.0052	∞	Inert	1701	5.652					
								$SiCl_4$(g)	1701	34.846	59.22				
								Zn (g)	1701	69.688	45.54	3609.6	0.046	1830.2	0.54
								$ZnCl_2$ (g)	1701	118.662	161.74				
A4†	Zn Hopper	→ Zn (s)	77	5.934*	3.88*	0.0084*		Zn (s)	77	5.934*	3.88*	0.0084*		0.0	0.0
A5†	Zinc Molten Storage Capacity 2 days 5910.8 lb 108.8 gal	Zn (ℓ)	932	112.726	73.70	(1.358)	3.(.987)	Zn (ℓ)	932	188.350*	123.14*	(2.266)*	3(0.987)	528.6*	0.154*
		Zn (ℓ)	932	69.688	45.56	(0.840)	3.(.987)								
		Zn (s)	77	5.934*	3.88*	0.0084*	∞								
A7†	Zinc vaporizer (1.23 atm)	Zn (ℓ)	932	188.350	123.14	(2.266)	3(.987)	Zn (g)	1701	188.350	123.14	2415.2	0.085	104,128.8	30.50
A8†	Silicon Cooler	Si prod.	1701	59.336	16.66	0.1116		Si prod.	77	59.336	16.66	0.1116		-5735.0	-1.68 →
A10†	Zn/$ZnCl_2$ Condenser	Si dust	1701	1.128	0.32	0.0022		Si dust	932	1.128	0.32	0.0022			
		Zn (g)	1701	69.688	45.56			Zn (ℓ)	932	69.688	45.54	(0.840)	3(.987)		
		$ZnCl_2$(g)	1701	118.662	161.74			$ZnCl_2$(ℓ)	932	118.662	161.74	(7.972)*	~1		
		$SiCl_4$(g)	1701	34.846	59.22	3609.6	0.046	$ZnCl_2$(g)	621	1.186	1.64				
		Inert (g)	1701	5.652				$SiCl_4$(g)	621	34.846	59.22	329.0	0.021	-126,367.2*	-37.00*
		$ZnCl_2$(ℓ)	621	1.186*	1.62	(0.080)*	~1	Inert (g)	621	5.652					
A11†	$ZnCl_2$ stripper Cool cycle	$SiCl_4$(g)	621	34.846	59.22			$ZnCl_2$(s)	171	1.186	1.64				
		$ZnCl_2$(g)	621	1.186	1.62	329.2	0.021	$SiCl_4$(g)	171	34.846	59.22	186.4	0.013	-4,075.4	-1.20
		Inert (g)	621	5.652				Inert (g)	171	5.652					
		Si(s)	621	1.128	0.32	0.0022		Si(s)	171	1.128	0.32	0.0022			
A12†	$ZnCl_2$ stripper Melt cycle	$ZnCl_2$(s)	171	1.186*	1.62*			$ZnCl_2$(ℓ)	621	1.186*	1.64*	(0.080)*	~1	173.0*	0.050*
		Si(s)	171	1.128*	0.32*	0.0022		Si(s)	621	1.128*	0.32*	0.0022*			
A13	$SiCl_4$ recycle condenser	$SiCl_4$(g)	171	34.846	59.22	186.4	0.013	$SiCl_4$(ℓ)	32	34.220	58.16	(4.554)	0.51		
		Inert	171	5.652				$SiCl_4$(g)	32	0.626	1.06	22.6	0.018	-6,401.0	-1.88 →
								Inert (g)	32	5.652					→
A14†	$SiCl_4$ Preheater	$SiCl_4$(g)	164.5	94.176	160.04	252.6	0.012	$SiCl_4$(g)	1701	94.176	160.0	874.2	0.036	35,752.0	10.47
														(included in A3 heat)	

* Average of intermittent operation.

† Total of duplicate units.

TABLE 22. (Continued)

Unit	Input Material	Input T, F	Input lb mole $hr^{-1} \times 10^2$	Input lb hr^{-1}	Input ft^3(gal) hr^{-1}	Input Viscosity, cp	Output Material	Output T, F	Output lb mole $hr^{-1} \times 10^2$	Output lb hr^{-1}	Output ft^3(gal) hr^{-1}	Output Viscosity, cp	Process Heat Btu hr^{-1}	Process Heat Kw
B1† Electrolysis Feed Tank Capacity 2 days														
Si dust 15.4 lb 0.1 ft^3	Si dust	932	1.128	0.32	0.0022		Si dust	932	1.128	0.32	0.0022			
$Zn(\ell)$ 2186.8 lb 40.4 gal	$Zn(\ell)$	932	69.688	45.54	(0.840)	3(0.987)	$Zn(\ell)$	932	69.688	45.54	(0.840)	3(0.987)		
$ZnCl_2(\ell)$ 7685.8 lb 378.8 gal	$ZnCl_2(\ell)$	932	117.474	160.12	(7.894)	~1	$ZnCl_2(\ell)$	932	117.474	160.14	(7.894)	~1	0.0	0.0
B2†† Electrolysis Cell	Si dust	932	1.128	0.32	0.0022		$Zn(\ell)$(recyc)	932	112.726	73.72	(1.358)	3(0.987)		
	$ZnCl_2(\ell)$	932	118.662	161.74	(7.972)	~1	$Zn(\ell)$(loss)	932	5.934	3.88	(0.072)	3(0.987)		→
	$ZnCl_2(\ell)$	621	1.344	1.83	(0.090)	~1	$SiCl_4(g)$	932	1.128	1.94			203,654.2	59.64ΔH
							$Cl_2(g)$	932	116.404	82.54	1208.4	0.032	(154,121.6)	(45.14 ΔG=-nFE)
							$ZnCl_2(g)$	932	1.344	1.86				
B3 $ZnCl_2$ Stripper Cool cycle	$Cl_2(g)$	932	116.404	82.56	1208.4	0.032	$Cl_2(g)$	77	116.404	82.54				→
	$ZnCl_2(g)$	932	1.344	1.86			$SiCl_4(g)$	77	1.128	1.92	460.6	0.014		→
	$SiCl_4(g)$	932	1.128	1.92			$ZnCl_2(s)$	77	1.344	1.86			-9,841.4	-2.88
B4 $ZnCl_2$ Stripper Melt cycle	$ZnCl_2(s)$	77	1.344*	1.86*			$ZnCl_2(\ell)$	621	1.344*	1.86	(0.090)*	~1	189.0*	0.054*
C1 $SiCl_4$ Storage Capacity = 18 days 50,000 lb 4,000 gal	$SiCl_4(\ell)$	77	68.150	115.80	(9.252)	0.45	$SiCl_4(\ell)$	77	68.150	115.80	(9.252)	0.45	0.0	0.0
C2 $SiCl_4$ Reserve Capacity = 2 days	$SiCl_4(\ell)$	77	68.150	115.80	(9.252)	0.45								
8503.6 lb	$SiCl_4(\ell)$	32	34.220	58.16	(4.554)	0.41								
679.6 gal	$SiCl_4(\ell)$	164.5	1.882	3.20	(0.274)	0.3	$SiCl_4(\ell)$	77	104.252	177.16	(14.160)	0.45	437.2	0.12
C3 $SiCl_4$ Purification	$SiCl_4(\ell)$	77	104.252	177.16	(14.160)	0.45	$SiCl_4(\ell)$	77	96.060	163.24	(13.040)	0.45		
							$SiCl_4(\ell)$waste	77	8.192	13.92	(1.114)	0.45	to be determined →	
C4 $SiCl_4$ Emergency Storage Capacity, [illegible]	$SiCl_4(\ell)$	77	--	--	--	--	Energy balance:					total of steps =	172,550	50.54
												products - reactants =	172,582	

Materials and Energy Balance for Cl_2-Handling System, $SiCl_4/Cl_2$ Waste, Wall Deposit Chlorination

Unit	Input Material	Input T, F	Input lb mole $hr^{-1} \times 10^2$	Input lb hr^{-1}	Input ft^3(gal) hr^{-1}	Input Viscosity, cp	Output Material	Output T, F	Output lb mole $hr^{-1} \times 10^2$	Output lb hr^{-1}	Output ft^3(gal) hr^{-1}	Output Viscosity, cp	Process Heat Btu hr^{-1}	Process Heat Kw
D1** $SiCl_4$ Waste Holding Tank Capacity = 1 week 2795.5 lb 223.3 gal	$SiCl_4(\ell)$	77	8.192	13.92			$SiCl_4(\ell)$	77	9.792	16.64	(1.329)	0.45		
	$SiCl_4(\ell)$	32	1.600	2.72										

---

* Average of intermittent operation.

** Hourly rate of D units to be divided by (chlorination time/silicon production time) to get real-time rates during chlorination; D1-D4 must also be adjusted to production versus chlorination real time values.

† Total of duplicate units.

†† Total of six units.

TABLE 22. (Continued)

Unit	Input: Material	T, F	lb mole hr^{-1} x 10^2	lb hr^{-1}	ft^3(gal) hr^{-1}	Viscosity, cp	Output: Material	T, F	lb mole hr^{-1} x 10^2	lb hr^{-1}	ft^3(gal) hr^{-1}	Viscosity, cp	Process Heat: BTU hr^{-1}	Kw
D2** $Ca(OH)_2$ Slurry Tank	$Ca(OH)_2$(s)	77	21.870	16.21			$Ca(OH)_2$(s)	77	21.870	16.21				
	H_2O(ℓ)	77	y (to be determined)				H_2O(ℓ)	77	y (to be determined)					
D3** $SiCl_4$ Waste Processing	$SiCl_4$(ℓ)	77	9.792	16.64			SiO_2	77	10.512	5.32				
	$SiCl_4$(g)	32	0.626	1.06			$CaCl_2$	77	21.446	23.81				
	$SiCl_4$(g)	32	0.092	0.16		Slurry	$Ca(OCl)_2$	77	0.424	0.61				
	Inert(g)	32	5.652				H_2O	77	21.870+y	3.94+0.18016y				
	Cl_2(g)	32	0.846	0.60			Inert(g)	77	5.652					
	$Ca(OH)_2$	77	21.870	16.21										
	H_2O(ℓ)	77	y	0.18016y										
D4 Waste Storage Tank Capacity = 2 weeks	SiO_2	77	10.512	6.32			SiO_2	77	10.512	6.32				
	$CaCl_2$	77	21.446	23.81			$CaCl_2$	77	21.446	23.81				
	$Ca(OCl)_2$	77	0.424	0.61			$Ca(OCl)_2$	77	0.424	0.61				
	H_2O	77	21.870+y	3.94+0.18016y			H_2O	77	21.870+y	3.94+0.8016y				
E5, E6 Caustic/Hypochlorite Reactor/Storage 8684 gal/wk 19% NaOH 9925 gal/wk 14% NaOCl	Cl_2(g)	77	116.40	82.55			Na_2SiO_3	77	1.13	1.38			-51,676	-15.11
	$SiCl_4$(g)	77	1.13	1.92			NaCl	77	120.92	70.69			(Cl_2+NaOH soln. only)	
	NaOH	77	251.94	100.80		Soln.	NaOCl	77	116.40	86.67				
	H_2O	77	2385.36	429.75			NaOH	77	12.37	4.95				
							H_2O	77	2505.15	451.33				
E7 Caustic Cooler (Refrig.)	E5, E6 Contents	77	to be determined				E5, E6 Contents	40	to be determined					
F1 Reactor Wall Deposit Chlorination	Si(s)	?***	1.694				$SiCl_4$(g)	?***	1.694					
	Cl_2(g)	77	4.232				Cl_2(g)	?***	0.846					
	Zn	?***	z (neglected in Zn + Cl_2 balance)				$ZnCl_2$(g)	?***	z (neglected in Zn + Cl_2 balance)					
F3 $SiCl_4$/$ZnCl_2$ Condenser	$SiCl_4$(g)	?***	1.694				$SiCl_4$(ℓ)	32	1.600					
	Cl_2(g)	?***	0.846				$SiCl_4$(g)	32	0.094					
	$ZnCl_2$(g)	?***	z (neglected in Zn + Cl_2 balance)				Cl_2(g)	32	0.846					
							$ZnCl_2$(s)	32	z (neglected in Zn + Cl_2 balance)					
F4 Cl_2 Supply Capacity = 2 weeks 1007.50 lb 17.62 gal	Cl_2(ℓ)	77	4.232*	3.00*	(0.112)*		Cl_2(g)	77	4.232*	3.00*	16.570*			

* Average of intermittent operation.

** See footnote, page 2.

*** To be determined.

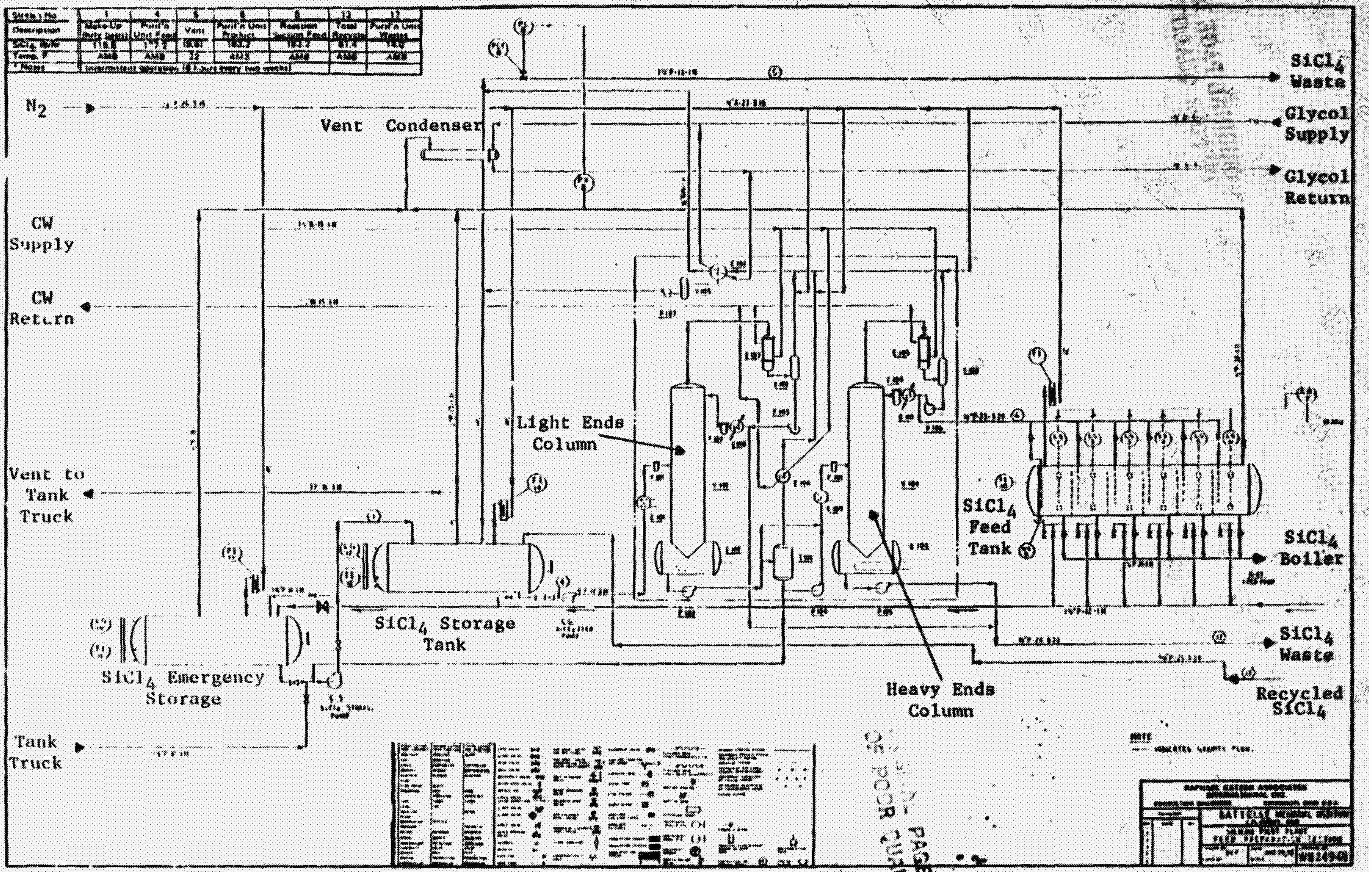

FIGURE 19. FEED PREPARATION

TABLE 23. $SiCl_4$ COMPOSITION

Compound or Element	Typical Analysis, as received(a)	Target Analysis, product, ppb
$SiCl_4$	98 percent (min)	balance
$(CH_3)_2SiCl_2$	$\sim$2 percent [max(b)]	---
$SiHCl_3$	0.X percent	---
B	3-10 ppb	1
P	0.5-5 ppb	2
As	0.2-1.5 ppb	<1
Fe	40-100 ppb	<1
Al	40 ppb	<1
Cu	1-5 ppb	<1
Ni	3 ppb	<1
Mn	1 ppb	---
Pb	ND	---
Sb	ND	---
Sn	ND	---
Ti	ND	---
V	ND	---

(a) Grade A160, Union Carbide Company, Sistersville, West Virginia.

(b) Controllable to lower levels by avoiding cross product contamination in loading and shipping.

condensate from which goes to waste. An emergency storage tank is provided so that the contents of units containing appreciable quantities of $SiCl_4$ can be conveniently drained if necessary. The individual compartments of the pure $SiCl_4$ feed tank can be drained to the $SiCl_4$ storage tank for repurification or to the $SiCl_4$ emergency storage tank as desired.

The feed preparation section is designed to operate at pressures of up to 60 psig.

Reaction and Recovery

Figure 20 shows the reaction and recovery section of the facility with process flow rates tabulated at upper left.

Purified $SiCl_4$ from the feed preparation section is held at constant level (pumped from storage) and constant pressure (power input-controlled) in the $SiCl_4$ boiler from where it is metered by gas-flow control into a preheater in the bottom section of the fluidized bed. Provision is made to introduce an inert gas at this point to purge the product withdrawal line. This addition will also avoid the problems inherent in systems containing all condensible vapors. A proportionate flow control provides for continuously bleeding part of the boiler contents to storage to prevent impurity build-up.

The $SiCl_4$ vapor entering the bed is met by an approximately stoichiometric* quantity of zinc vapor. The silicon product grows on silicon particles introduced as seed from the hopper shown atop the reactor adjacent to a sight port. The granular product is withdrawn from the bottom of the reactor at a rate equal to the production rate [controlled by maintenance of constant bed level (pressure-drop monitored)].

Provision is made to periodically chlorinate the fraction of the silicon that deposits on the fluidized bed wall so as not to have excessive build-up.

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* As noted earlier in this report (Table 12), calculations have shown no economic advantage in deviating from stoichiometry. Further, the incidence of gas-phase-nucleated silicon tends to be increased on the zinc-rich side.

The zinc/zinc chloride component of the by-product is condensed in a large condenser/heat exchanger (to be discussed later) and flows through an electrolysis feed tank into a bank of electrolysis cells (to be discussed later). In the design version shown in Figure 20, the $SiCl_4$/inert gas component of the by-product is passed through alternately cooled (for condensation) and heated (for melt-down) $ZnCl_2$ strippers, and then through a glycol-cooled condenser to remove $SiCl_4$ for recycle. A simplification of the design has since been made providing for use of a single $ZnCl_2$ stripper operating just above the melting point and which will allow the small amount of $ZnCl_2$ that escapes to condense (as a slurry) with the $SiCl_4$.

An organic heat exchange fluid, Therminol*, is used to maintain proper temperature levels for condensation in the large $Zn/ZnCl_2$ condenser and $ZnCl_2$ strippers, and for melt-down of the $ZnCl_2$ strippers.

Condensed zinc and $ZnCl_2$, containing small quantities of suspended silicon "dust"**, flows from the electrolysis feed tank (provided with a load cell for content monitoring) to one or more of the electrolytic cells (to be discussed later). The liquid zinc entering the electrolytic cells plus that produced by electrolysis of the $ZnCl_2$ is withdrawn to the zinc storage tank by an overflow system whose height is chosen to prevent overflow when the zinc has dropped to where (still above the submerged outlet) the head of $ZnCl_2$ (controlled via a level indicator) is insufficient to cause flow. Prevention of accumulation of impurities from the zinc is accomplished by periodic manual skimming of the zinc or $ZnCl_2$ content of the electrolytic cells. Zinc from the load-cell-monitored zinc storage tank is fed by gravity to a constant level tank that feeds the zinc vaporizer. The zinc vaporizer (to be discussed later) is induction heated, directly coupled to the zinc so that the vaporization rate can be controlled by power input. It is possible that the zinc inventory in the vaporizer can be monitored by the current-voltage relationship in the induction heater with the constant level device as back-up.

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* Monsanto Industrial Chemical Company.

** Gas-phase-nucleated silicon that does not accumulate on the seed particles.

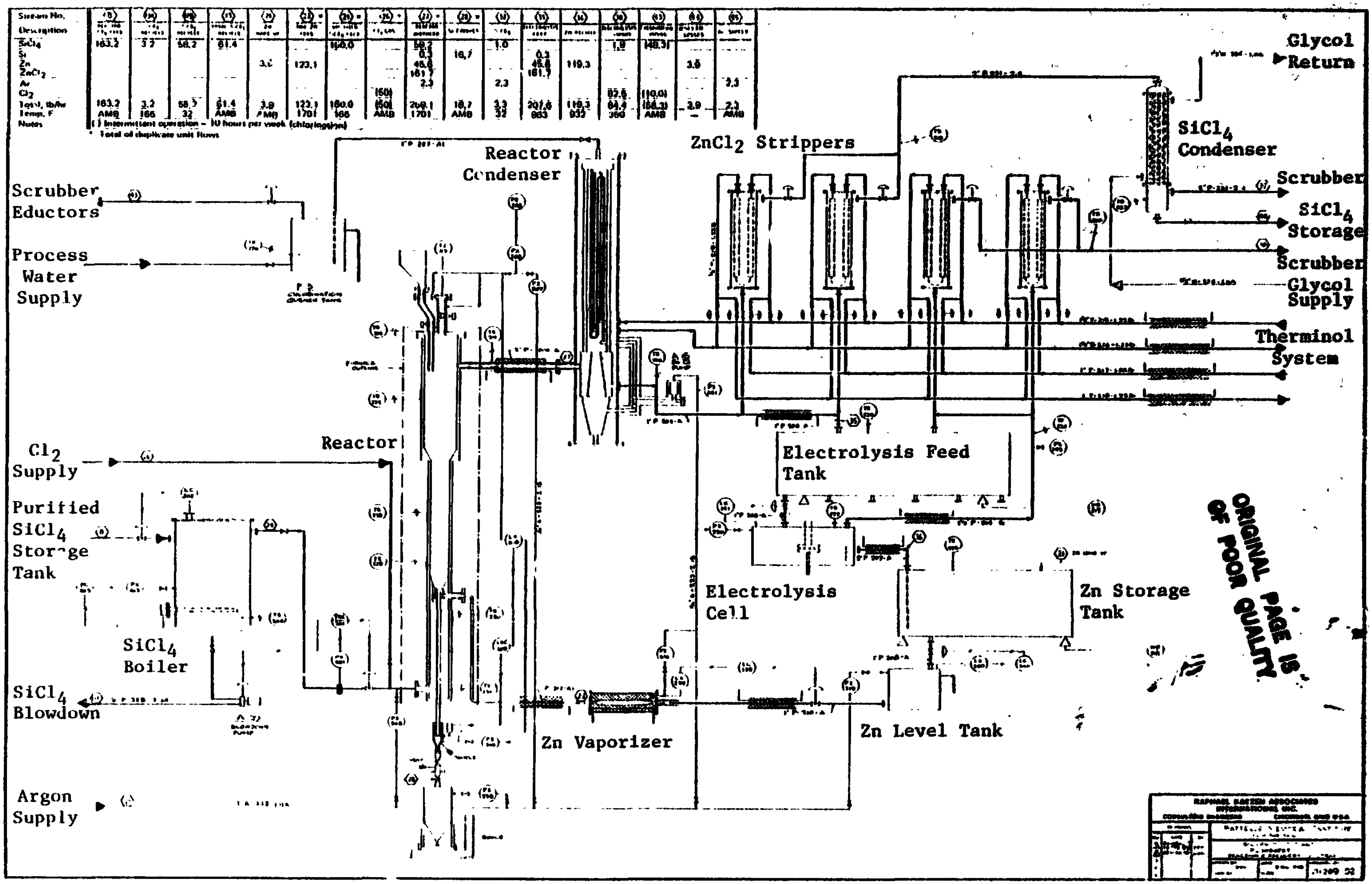

FIGURE 20. REACTION AND RECOVERY

Provisions are made for appropriate pressure equalization and venting of the reaction and recovery system.

Waste Treatment

The waste treatment section of the facility shown in Figure 21 has two primary functions: (1) to convert the chlorine from the electrolytic cells to hypochlorite that can be disposed of in local sewage treatment and (2) to neutralize and dilute the $SiCl_4$ waste (tops and bottoms from distillation and vented $SiCl_4$).

In removing the heat of reaction between chlorine and NaOH to form hypochlorite, air cooling of the hypochlorite has been combined with scrubbing of the air from the plant area in the large unit, E7, termed the Area/Vent Gas Scrubber. This scrubber is provided with two sets of perforated trays over which solution is recirculated in two respective loops. The bottom loop contains 1 percent NaOH* and the top loop, essentially 19 percent NaOH as it comes from the Caustic Storage Tank, E6. The solution in the bottom loop circulates across the trays and through one of two interchangeable** eductors (E8) where it meets and reacts with the chlorine from the electrolytic cells to form hypochlorite solution. The NaOH concentration in the lower loop is maintained at 1 percent by demanding overflow from the top (19 percent NaOH) loop. The net hypochlorite solution production is pumped out of the lower loop and into the Hypochlorite Storage Tank as controlled by a constant level device. A flow of outside and/or inside air through the Area/Vent Gas Scrubber cools the hypochlorite solution. Chlorine lost by volatilization from the lower trays is reabsorbed by the 19 percent NaOH in the upper loop. An exhaust blower, E9 ($\sim$10,000 cfm), in the scrubber exit is used to move the air through the trays.

Neutralization of the $SiCl_4$ wastes is taken care of in the system on the left of Figure 21. A solution of 2 percent NaOH circulates through the

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* Equivalent to 14 percent NaOCl.

** Duplicates provided to allow for cleaning of accumulated hydrated SiO_2 from $SiCl_4$ hydrolysis.

C-2

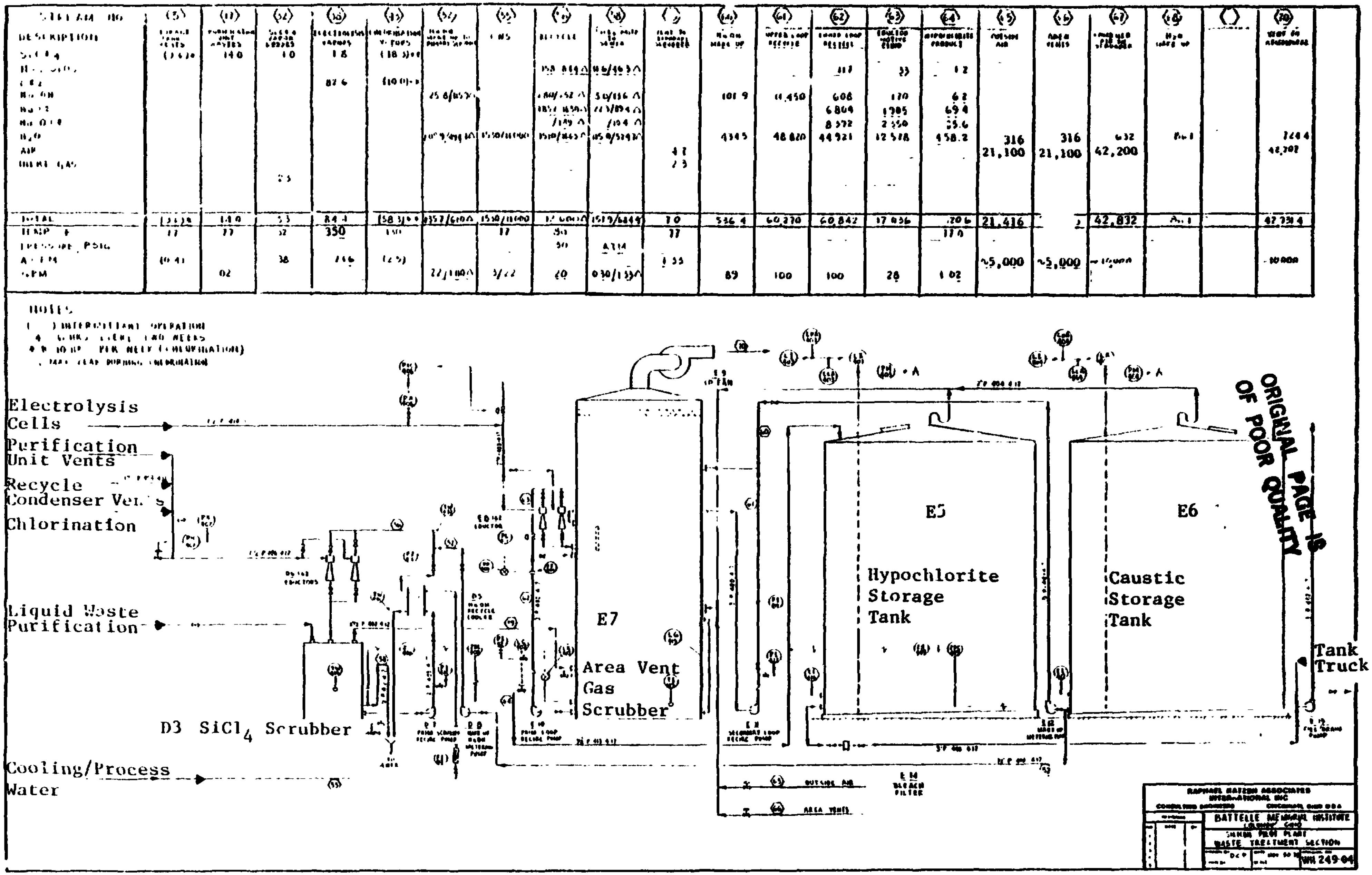


FIGURE 21. WASTE TREATMENT

C-2

$SiCl_4$ Scrubber, D3, where the liquid $SiCl_4$ wastes are neutralized. $SiCl_4$ vapors in the vent gases are fed to one of a pair of interchangeable eductors, D6, through which the 2 percent NaOH solution circulates as the motive fluid. The net discharge from the $SiCl_4$ scrubbing system ($\sim$0.3 gpm) overflows to the sewer. No environmental problems should be caused by this amount of material, particularly since it will be heavily diluted with cooling water (e.g., 10/1) from the rest of the facility.

The heat of the neutralization of the $SiCl_4$ is dissipated in a water-cooled exchanger, D5 (NaOH Recycle Cooler). The capacity of this exchanger is chosen to provide for the increased load during the periodic chlorination of silicon from the reactor walls.

Fluidized-Bed Reactor

Figure 22 shows the fluidized-bed reactor in greater detail than in Figure 20. $SiCl_4$ vapor enters at the bottom, is preheated in the graphite-granule-packed annulus, and enters the fluidized bed through outer ports in the round-bottom distributor plate. Zinc vapor at just above its boiling point (918 C at 1.1 atm) enters the bed through a ring of inner ports in the distributor plate.

The fluidized-bed reactor is constructed of silicon-carbide-coated graphite or solid silicon carbide, encased in a No. 310 stainless steel shell provided with bellows to accommodate thermal expansion differentials.

Changes in the positions of the $SiCl_4$ inlet and reaction product outlet relative to the fixed zinc vapor inlet and the connecting equipment are accommodated in the assembly sequence and by means of appropriate slip joints in non-critical positions.

The graphite is rendered impervious by appropriate coating to avoid deleterious exposure of the stainless steel shell to zinc vapor. Tungsten coating of the stainless steel is being studied as additional protection.

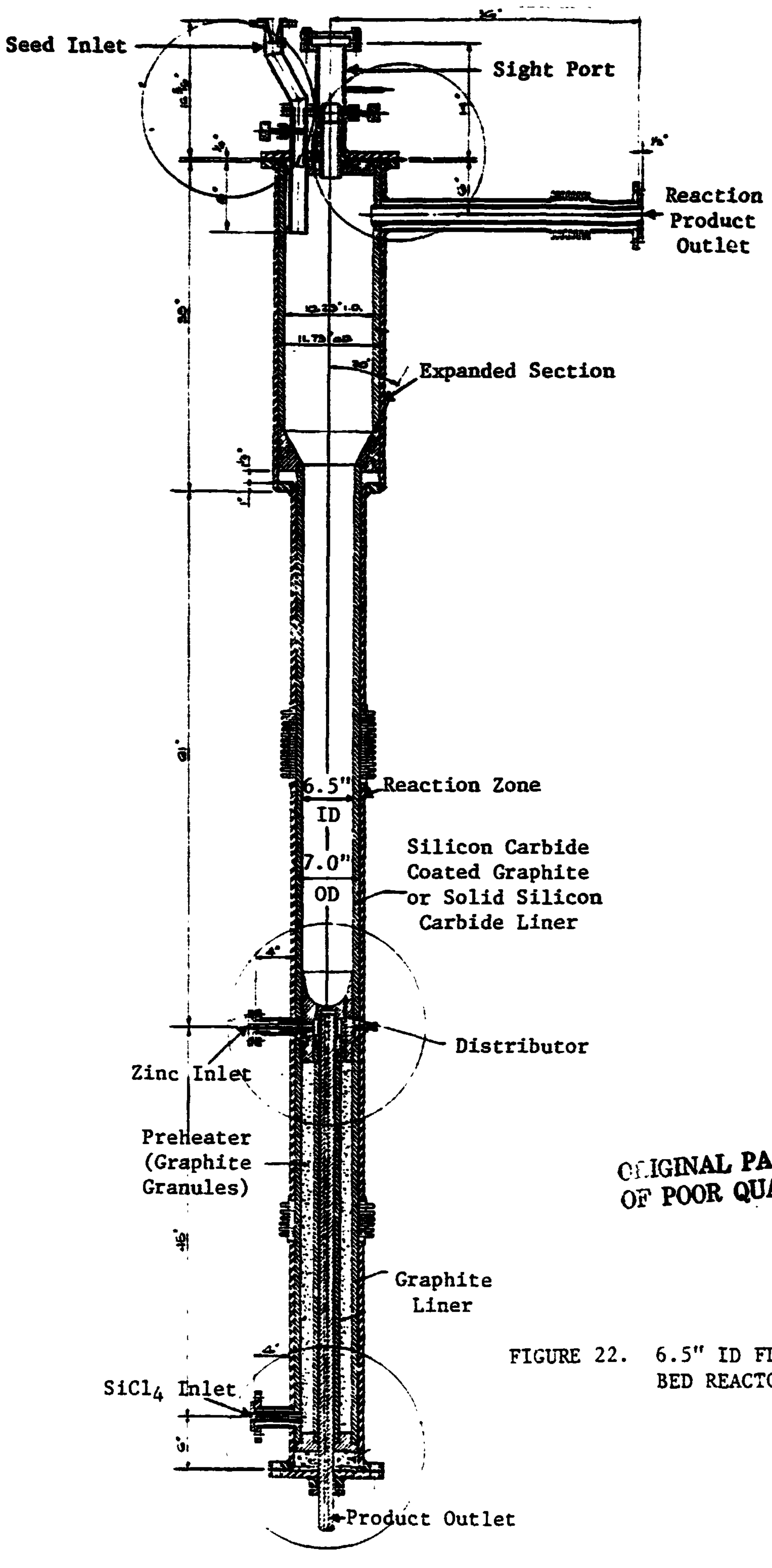


FIGURE 22. 6.5" ID FLUIDIZED-BED REACTOR

Zinc Vaporizer

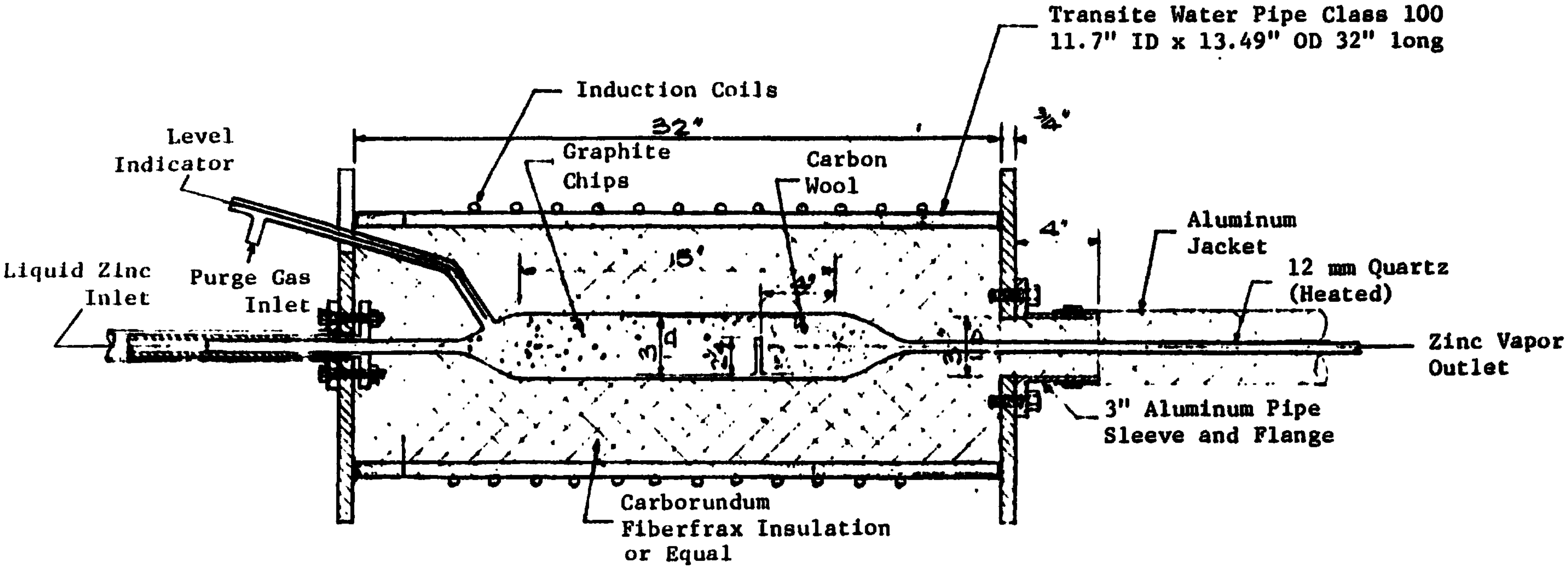
As discussed in an earlier section of this report, one of the more difficult aspects of the facility design has been the problem of supplying the high heat of vaporization of zinc while maintaining a limited zinc vaporizer inventory to minimize hysteresis in the vaporizer output response. To drive the heat of vaporization through graphite or silicon carbide requires bulky equipment, steep temperature gradients, and excessive zinc inventory. This problem has been solved by direct induction coupling to the zinc in a quartz vessel. The zinc vaporizer design (without blowdown, Figure 23) is patterned after the vaporizer tested experimentally.

The vaporizer is packed with graphite chips to facilitate heating before liquid zinc is added and to reduce the inventory of zinc in the vaporizer per unit effective volume. Carbon wool is contained in the compartment formed by a wier placed 4 inches from the exit end, to act as a demister for the zinc vapor. Entrained droplets of unvaporized zinc not only serve to carry over impurities, but they act as nucleation and growth sites for silicon needles and powders, which can escape deposition on the seed particles of the fluidized bed. The zinc vapor line is lagged with heaters until well inside the fluidized bed furnace, to prevent condensation of zinc.

It is planned that the zinc vaporization rate be controlled by power input, and although present plans call for constant level control based on electrical contact level sensing, it is possible that the liquid zinc inventory in the vaporizer can be sensed by the current-voltage relationship in the converter, and the latter used for control with the electrical contact retained as backup.

Zinc/Zinc Chloride Condenser

As indicated in the general description above, the reaction product consists of $ZnCl_2$ vapor, unreacted zinc and $SiCl_4$ vapor, a small amount of entrained gas-phase-nucleated silicon powder, and inert purge gas. The condenser, shown in two sectional views at right angles in Figure 24, provides



LONGITUDINAL SECTION
Scale 1/8" = 1"

FIGURE 23. ZINC VAPORIZER

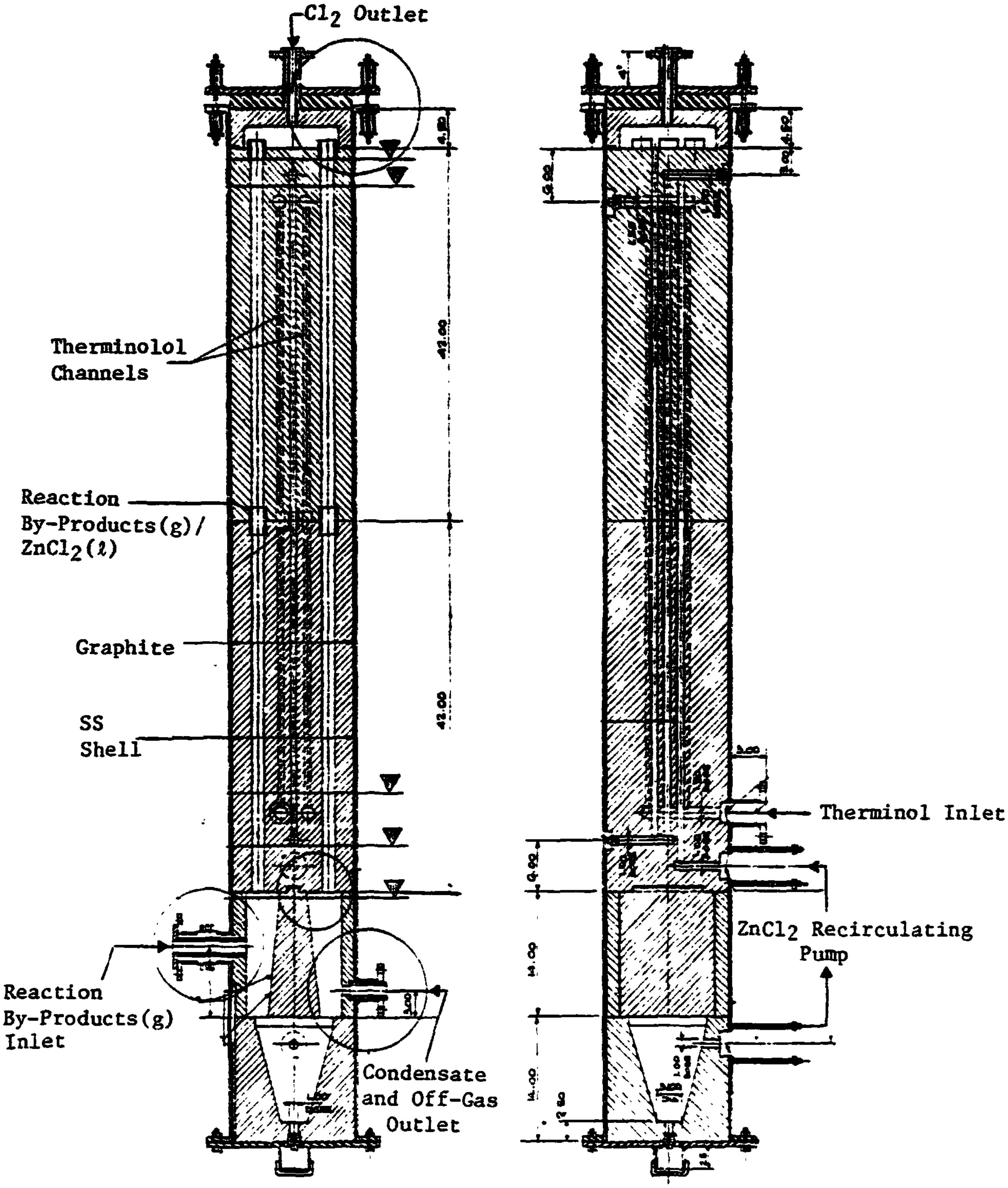


FIGURE 24. ZINC/$ZnCl_2$ CONDENSER

for recirculating the condensed zinc chloride to act as a fluid for wet-wall condensation. The reaction by-products enter the condenser at the lower left of the view on the left and are directed up the left-hand open channel and down the right by virtue of the seal made by the liquid $ZnCl_2$ in a pool at the bottom, at the level of the condensate outlet and above the bottom of the wedge-shaped barrier. Liquid $ZnCl_2$, taken from below the surface of the pool is cooled by circulation through the graphite block (see open channels on right-hand drawing). At the top of the block it overflows the barriers and wets the condenser surfaces.

Therminol 88, an organic heat exchange medium, is used to remove heat from the condenser to a separate Therminol heat-exchange system. Although as shown in Figure 24, the original plan was to have the Therminol in direct contact with the graphite block, relying on impregnation of the graphite to keep the Therminol out of the process stream, the decision has been made to use a metal shot heat-transfer layer between the graphite block and the metal wall and to confine the Therminol to the outside of the wall. Additional heat transfer by the same principle will be provided by a Therminol-cooled bayonet extending down the center of the graphite block.

Zinc condensation occurs between about 800 and 690 C and $ZnCl_2$ condensation from 690 to 565 C*. The gas leaving the condenser will be at about 510 C and is directed to the $ZnCl_2$ strippers (shown in Figure 20) for removal of the remainder of the $ZnCl_2$.

Electrolytic Cell

The cells for fused salt electrolysis recovery of zinc from the by-product $ZnCl_2$ are patterned after those being developed at the U.S. Bureau of Mines, Reno, Nevada,(17) for electrowinning zinc from sulfide ores. The present design is shown in Figure 25. Depending upon the current efficiency attainable, six 5000- to 6000-amp cells will be required for the 50 MT/year

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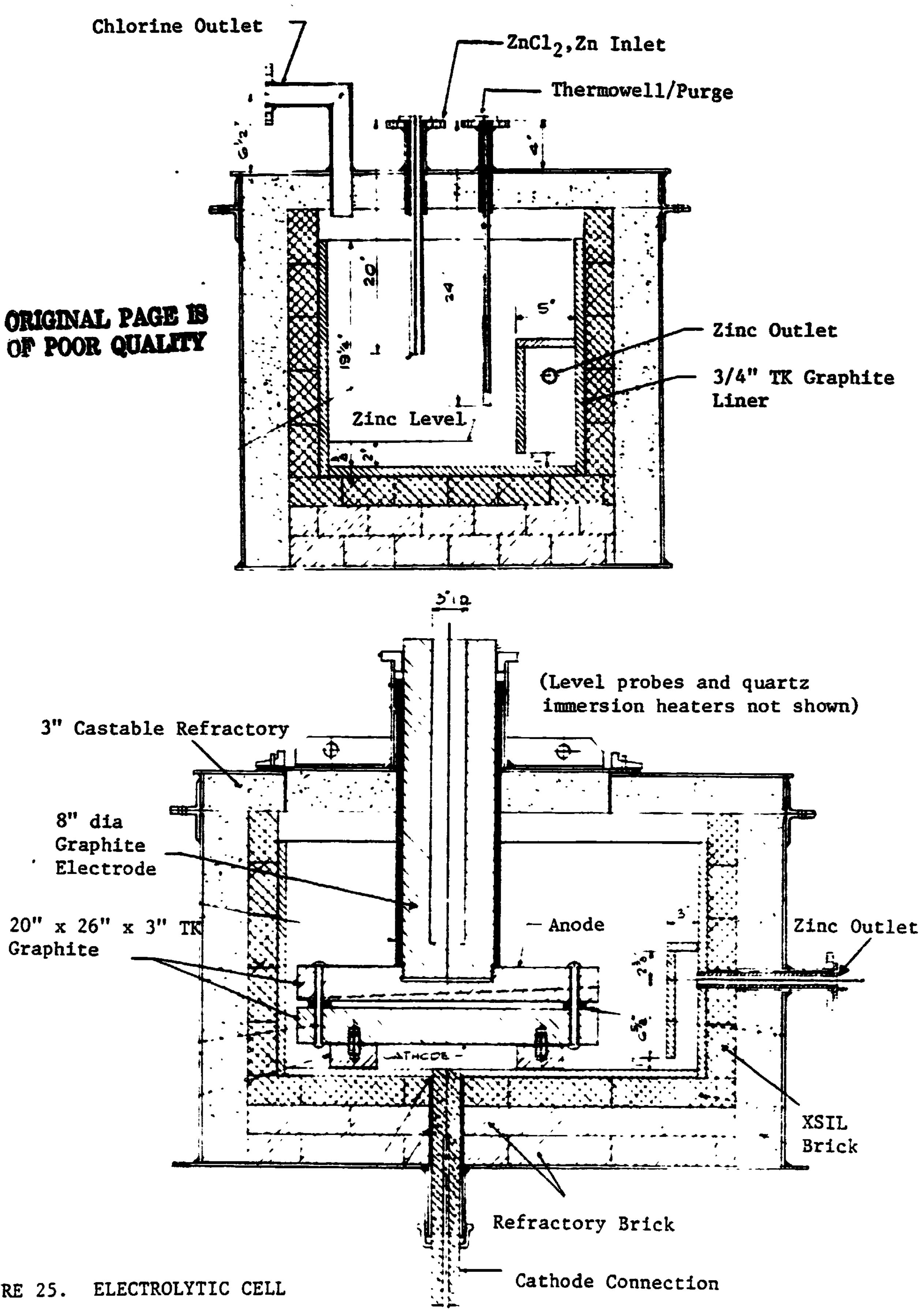
* The difference in these values from those of Table 13 results from use of different data in their calculation. The difference is not serious enough to force a choice.



(Level probes and quartz immersion heaters not shown)

FIGURE 25. ELECTROLYTIC CELL

Si facility. They are of "cold"-wall construction, graphite lined, with graphite electrodes. The cathode contacts the liquid zinc pool at the bottom of the cell which is connected to the current supply via a plug of frozen zinc extending through the cell wall (Shown at the bottom, but probably to be through the side). A cell voltage of 4 to 5 volts is anticipated at a current density of 10 to 12 amps/in.^{2}: Excess heat is removed through a heat exchanger (not shown) in the hollow anode. By means of electric contact level probes (of tungsten or graphite), not shown in the figure, upper and lower $ZnCl_2$ level limits are set to control the addition of $ZnCl_2$ to the cell. The zinc overflows automatically on balancing the hydrostatic head of the $ZnCl_2$ approximately at the $ZnCl_2$ lower level limit. Blockage of the zinc outlet and resulting excess accumulation of zinc in the cell would be indicated by a shorted cell as the zinc level reaches the anode.

The entire electrode assembly is removable through the cell roof to provide for ease of cell maintaince.

Plant Layout

Figure 26 shows the plan view of the facility, as designed to fit into an available building area at BCL. As the zinc and zinc chloride flow is by gravity*, the $Zn/ZnCl_2$ condenser, electrolysis feed tank, electrolytic cells, zinc storage tank, zinc level tank, and zinc vaporizer are on different levels. Accordingly, some of the associated units are not shown in the plan view of Figure 26 at the electrolytic cell level.

The layout is designed to permit ready access for $SiCl_4$ and NaOH delivery and for hypochlorite removal, and to minimize the length of connecting lines carrying zinc and zinc chloride.

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* Except for pumped recycle of liquid $ZnCl_2$ in the wet-wall $Zn/ZnCl_2$ condenser.

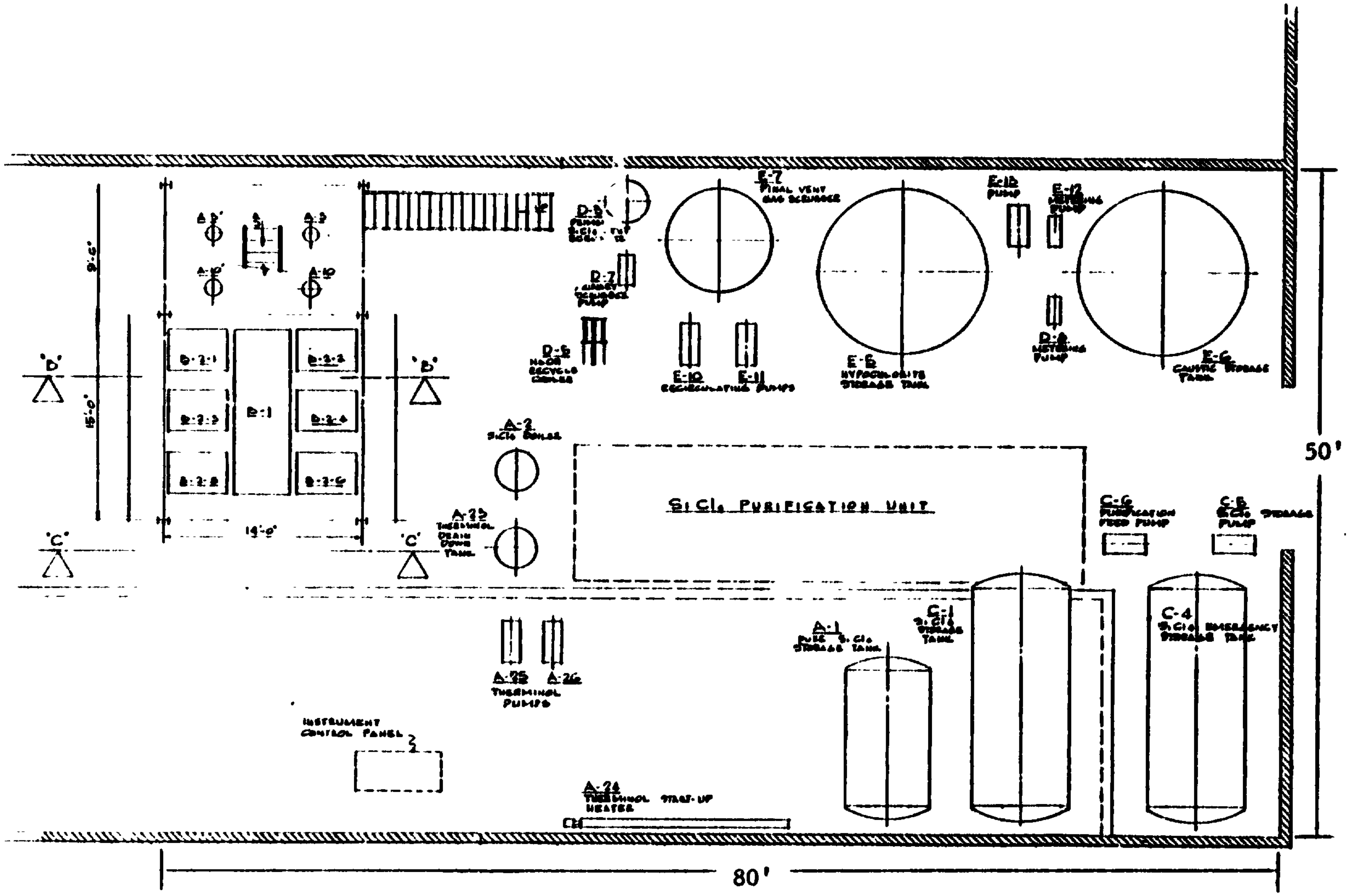

FIGURE 26. PLAN VIEW

Cost of Experimental Facility

It should be re-emphasized that many of the details and most of the specifications in the design package have been omitted in the above discussion which has been presented primarily for orientation. However, on the basis of a detailed summation of the vendor-estimated costs for equipment costs of the instrument package, and construction costs based on standard construction cost-estimating techniques, RKAII arrived at an initial cost estimate of \$1,536,000, of which \$266,500 for the $SiCl_4$ purification system was estimated independently by Pace. The overall cost estimate arrived at by RKAII includes all procurement, installation, management, and tax costs for constructing this facility in an existing building by a company building the facility for its own use. A contingency item of \$191,139 was included.

Because of differences in overhead, fee structure, and labor rates, the cost of building the facility at BCL would be higher; however, removal of the contingency item, credit of certain economies agreed upon by BCL and RKAII, and adjustment for the differences mentioned above led to a figure of \$1.5 million*, which was presented to JPL for budgetary purposes. This estimate is based on purchasing equipment from outside vendors, subcontracting a significant portion of the construction and installation to an outside contractor, BCL's involvement in construction and installation of nonconventional equipment, and overall management of the program by BCL personnel.

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* This facility construction cost, revised later to ∿\$1.6 million, does not include the cost of a concurrent design finalization and experimental support program.

E. 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

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

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 24 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 24. 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
C1	$SiCl_4$ Storage Tank 4,600 gal 7' D x 16' T/T	$ 7,000
C2	Not Used	
C3	$SiCl_4$ Purification Section	57,227
C4	$SiCl_4$ Emergency Storage Tank 4,600 gal 7' D x 16' T/T	7,000
C5	Purification Feed Pump 30 gpm 30' TDH 1.5 SG 1-1/2 hp	760
C6	$SiCl_4$ Feed (Metering) Pump 1/2 hp 13 pgh	1,100
C7	Not used	
C8	Vent Condenser 37 sq ft 2 pass on tube side 15° < in horizontal	1,300
	Refrigeration System 5T 10 hp	6,500
A1	Pure $SiCl_4$ Storage Tank 6' D x 10' T/T	6,000
A2	$SiCl_4$ Boiler 2.75' D x 3' T/T 4 kW, includes heater and controls	1,400
A3 A3′	Fluidized Bed Reactors	22,500
	Seed Addition Hopper	1,000
	Furnace 80 kW, includes all necessary controls	21,500
A4	Zinc Hopper	500
A5	Zinc Molten Storage Tank 20 kW, includes heaters and controls	17,600
A6 A6′	Zinc Level Tanks includes heaters and controls	$ 3,500
A7 A7′	Zinc Vaporizer includes power supply and temperature controls	15,000
A8 A8′	Silicon Product Coolers	800
A9 A9′	Silicon Collectors	300
A10 A10′	Zinc/$ZnCl_2$ Condensers	15,800
A11 A11′	$ZnCl_2$ Strippers	13,120
A12	Not used	
A13	$SiCl_4$ Condenser	1,700
A15 A15′	$ZnCl_2$ Circulating Pumps 2.4 gpm	1,500
A17	Therminol Cooler (Hot Circuit) 120,000 But/hr	1,900
A19	Therminol Cooler (Cold Circuit)	800
A20	$SiCl_4$ Boiler Blowdown Pump Automatic Control	1,700
A21	Therminol Cooler Blower 500 acfm, 8" WG, 1-1/2 hp	1,000
A22	Hot Circuit Head Tank 1.5' C x 3.75' T/T, includes heater and controls	800
A23	Therminol Draindown Tank 2.75' C x 3' T/T, includes heater and controls	1,100

(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 24. (Continued)

Item No.	Description	Estimated Item Cost
A24	Start-Up Heater 29 kW	$ 2,000
A25	Hot Circuit Pump	2,900
A26	Cold Circuit Pump	1,400
A27	$SiCl_4$ Feed Pump 1 gph @ 48' TDH	300
B1	Electrolysis Feed Tank 20 kW, includes heaters and controls	17,600
B2	Electrolysis Cells	9,700
A-F	Power Supply 160 kW	15,300
	Bus	7,600
B3	$ZnCl_2$ Strippers	4,480
B4	Not used	
C3	Not used	
C4	Chlorine Supply Tank	500
D1	Not used	
D2	Not used	
D3	Primary $SiCl_4$ Vent Scrubber 3' D x 4'4" T/T, flat bottom	1,000
D4	Not used	
D5	NaOH Recycle Cooler Plate and Frame Exchanger	5,100
D6 1&2	Eductor Penberthy Series 60 Size LL-1-1/2"	140
D7	Primary Scrubber Recirculation Pump; 20 gpm @ 125' TDH 2.5 hp	1,160
D8	Makeup NaOH Metering Pump 1/2 hp	$ 1,700
E1	Not Used	
E2	Not used	
E3	Not used	
E4	Not used	
E5	Not used	
E6	Caustic Storage Tank 12,000 gal capacity 12' D x 14'6" T/T	8,500
E7	Final Vent Gas Scrubber 7'6" D x 17'4" T/T four polypropylene trays Teflon mist eliminator	14,000
E8- 1&2	Eductor Penberthy Series 60 Size LL-2"	300
E9	ID Fan 10,000 acfm @ 15" WG 50 hp	6,800
E10	Primary Loop Recirculation Pump 100 gpm @ 100' TDH 8 hp	1,890
E11	Secondary Loop Recirculation Pump; 100 gpm @ 30' TDH 2 hp	1,820
E12	Makeup NaOH Metering Pump 54 gph 1/2 hp	1,700
E13	Fill/Drain Pump 100 gpm @ 30' TDH 2 hp	1,830
E14	Not used	

(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 amperes 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 25 gives the equipment costs, scaled as indicated above, for Cases I, II, and III for each of the six sections of the plant.

Table 26 gives the manpower breakdown and costs for the three cases.

The materials requirements given in Table 27 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 (relative use) = (relative size)$^{0.5}$. For simplification, the utility costs given in Table 28 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 area $\propto$ volume$^{2/3}$, i.e.,

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

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 25. 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
	$362,631	$3,468,953	$2,402,659	$1,695,576
			$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 26. MANPOWER BREAKDOWN AND COSTS[(a,b)]

	Manhours per Day					
	Case I		Case II		Case III	
Operation	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(5) number of operator hours/major process step.

(b) Labor rate based on Peters and Timmerhaus(5) adjusted to 1975 dollars:

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

TABLE 27. MATERIALS COST (1975 DOLLARS)

Material	Requirement per kg Si	Unit Cost, dollars	Cost/kg Si, dollars
$SiCl_4$	15.68 lb	0.135 x 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
			2.26

(a) Credit for on-site manufacture.

TABLE 28. 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 $Zn/ZnCl_2$ condenser.

(d) Exothermic reaction.

(e) Additional 3.8 kwh supplied by heat exchange with $Zn/ZnCl_2$ 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 29 gives the fixed capital investment costs for Cases I, II, and III based on Table 25.

Table 30, in the Lamar University format(18), gives the total product cost on the basis of Tables 26, 27, 28, and 29. It can be seen from the data of Table 30 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 30 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 28 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 31 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 kwh/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/m^2 over 1825 hours/year.

TABLE 29. 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 30. 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 percent materials)	1.55	1.07	0.76
6. Operation Supplies, 20 percent of 1.5	0.31	0.22	0.15
7. Laboratory Charge, 15 percent 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 30. (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	0.29	0.23	0.19
6. Total Cost of Product, 4A + 5	\$11.21	\$8.71	\$7.35
		(\$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 31. ENERGY REQUIREMENTS, kwh/kg Si

Item	Basis	Energy Requirement, kwh/kg Si
Process	Table 28	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
		71.27

(a) Reference (22).

(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(34).

(d) Reference (39).

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 $ZnCl_2$ electrolysis step, of including the energy requirements of the make-up zinc and the caustic used to neutralize the waste $SiCl_4$ and Cl_2 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.

F. CONCLUSION

In view of the favorable indications of technical feasibility, economic feasibility, and reasonable energy payback time of the process, it is recommended that the construction and operation of the 50 MT/year experimental facility be initiated.

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