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SECOND QUARTERLY PROGRESS REPORT

Covering the Period December 15, 1975 to March 31, 1976

on

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

JPL Contract 954339

Silicon Material Task
Low-Cost Silicon Solar Array Project

to

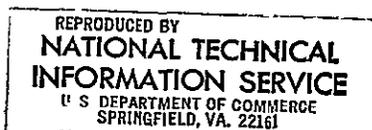
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by

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ABSTRACT

Plant construction costs and manufacturing costs have been estimated for the production of solar-grade silicon by the reduction of silicon tetrachloride in a fluidized bed of seed particles, and several modifications of the iodide process using either thermal decomposition on heated filaments (rods) or hydrogen reduction in a fluidized bed of seed particles. The objective was to evaluate the economics of the zinc reduction process and to determine whether any of the potential economies in the modifications of the iodide process would make it competitive in spite of the high relative cost of recycled iodine in the process intermediate.

The estimated cost of the zinc reduction process, $\$9.12 \text{ Kg}^{-1}$ silicon is within the target of $\$10.00 \text{ Kg}^{-1}$; however, none of the modifications of the iodide processes yielded costs below $\$20 \text{ Kg}^{-1} \text{ Si}$. Although

optimization of one of the iodide process modifications should bring the cost to below \$20 Kg⁻¹ Si, it would not be possible to reduce the cost to below that of the zinc reduction product.

Energy consumption data for the zinc reduction process and each of the iodide process options are given and all appear to be acceptable from the standpoint of energy pay back.

Information is presented on the experimental zinc reduction of SiCl₄ and electrolytic recovery of zinc from ZnCl₂. All of the experimental work performed thus far has supported the initial assumption as to technical feasibility of producing semiconductor silicon by the zinc reduction or iodide processes proposed.

The results of a more thorough thermodynamic evaluation of the iodination of silicon oxide/carbon mixtures are presented which explain apparent inconsistencies in an earlier cursory examination of the system.

INTRODUCTION

This is the Second Quarterly Report covering the work for JPL-ERDA at Battelle's Columbus Laboratories on the Evaluation of Selected Chemical Processes for Production of Low-Cost Silicon.

Two basic processes are being evaluated which have been demonstrated commercially to yield semiconductor grade silicon in the past but are currently not in use. These are the zinc reduction of silicon tetrachloride (DuPont) and the thermal decomposition (or hydrogen reduction) of silicon tetraiodide (Mallinckrodt). The objective of the current program is to evaluate potential process improvements to determine whether they can be effective in bringing the cost of the product to below \$10 kg⁻¹, and the process energy consumption to reasonable values in terms of payback time for photovoltaic arrays employing the product.

Results of thermodynamic evaluation of the processes were presented in the First Quarterly Report together with experimental data supporting the thermodynamic predictions and demonstrating the feasibility of several process options from the technical standpoint.

PROGRESS THIS QUARTER

The major effort during the second quarter of this program has been the estimation of plant construction and manufacturing costs for the fluidized bed reduction of silicon tetrachloride and several modifications of the iodide process involving either thermal dissociation or the hydrogen reduction of SiI₄ for the deposition of silicon.

The main body of the report relates to (1) description of the processes being evaluated, (2) identification of the bases for evaluation, (3) presentation of the results, and (4) recommendations for future work. Included in the Appendix to this report are sections on (1) experimental work done for verification of the assumptions and reaction rate data used in the process evaluation, and (2) summary of thermodynamic calculations on the iodination of SiO₂/C mixtures which explain the apparently inconsistent reaction yields obtained previously for a few sets of reaction conditions.

Outline of Processes Evaluated

Eight process options (to be referred to henceforth as "processes") determined to be technically feasible were considered for economic evaluation 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 "metallurgical grade" silicon from SiO_2 + carbon, preparation of SiI_4 by iodination of the metallurgical grade silicon, 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 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 hydrogen followed by wet processing (chlorination + 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 without separation
- Process G. Same as (D) except that SiI_4 is prepared by iodination of SiO_2 /carbon mixtures with HI

Process H. Direct iodination (with I_2) of SiO_2 /carbon mixtures with reduction and recycle as in (E) (wet process).

The reason that only one zinc reduction process has been chosen for evaluation lies in the facts that (1) the exothermic nature of the zinc reduction of $SiCl_4$ tends toward an unsatisfactory product form in all but the fluidized-bed reactor and (2) electrolysis appears to be the only logical approach to zinc recycle, the use of aluminum or magnesium (both electrolysis products) as reductants for $ZnCl_2$ offers no advantage, to say nothing of the prospect of contamination of the zinc by these elements. It will be noted that a potential iodide process variation has been omitted in the above, i.e., direct iodination of SiO_2 /carbon mixtures with the unseparated H_2 /HI by-product of the fluidized-bed hydrogen reduction of SiI_4 (parallel of Process F). This variation is not feasible because of the large increase in gas flow (e.g., 20-fold relative to Process F) through the iodination reactor, and further decrease of the reaction efficiency (already low, e.g., < 10 percent of HI undiluted with H_2).

Process G was eliminated from competition prior to detailed economic evaluation because of the low efficiency of iodination of SiO_2 /carbon mixtures with HF, as noted parenthetically above. Process H can be evaluated by the direct comparison of the results for Processes B, C, and E.

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

- (1) The fluidized-bed deposition reactor has the advantage of permitting continuous handling of the silicon product, it has the disadvantage in the iodide process of requiring excess hydrogen for reasonable efficiency. Operation of the fluidized-bed under reduced pressure is possible, but considered economically impractical for this application.

- (2) Direct halogenation of SiO_2 + carbon mixtures in place of metallurgical grade silicon offers the possible economy of avoiding that step. The advantage is clear for the preparation of SiCl_4 (Process A) where the chlorination efficiency is high, 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 byproduct, 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 requirements of 3000 metric tons per year of silicon would be produced at three sites with a capacity of 1000 metric tons per 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^{-1} of silicon (80 percent on stream). 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 Process A reactor to 15 inches in diameter and to proceed from that as a reference. Additional scaleup economies may be considered later.

Approach to Economic Evaluation

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

- (1) Determination of feasible pressure/temperature/composition ranges for operation of the candidate processes; this has been done by thermodynamic

calculations and experimental verifications as reviewed in the First Quarterly Report

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

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.

Sources of Data and Information

Thermodynamics

Estimates of the equilibrium efficiencies and the enthalpy requirements of the various process steps were made with Battelle's computer program EQUICA based on data primarily, from Hunt and Sirtl^(1,2) and the JANAF tables⁽³⁾. Most of the results are included in graphical form in the First Quarterly Report.

Cost Estimation Method

The cost estimation method used in the present program is that of Peters and Timmerhaus⁽⁴⁾. In the absence of data or estimates on items other than raw materials, labor, and major equipment, the recommendations of Reference 4 as to the factors to be employed in arriving at the final costs were used with appropriate shading based on judgments as to the complexity and difficulties of the processes being evaluated here, relative to those described in Reference 4.

Cost Data

Except for the major equipment items treated separately below, cost estimates were based on the graphical data of References 4, 5, and 6.

Although it is recognized that the various processes when fully designed would employ many types of equipment, the assumption was made that the relative costs of the processes could be ascertained by some simplifying assumptions. Accordingly, all heat transfer units, such as vaporizers, condensers, reboilers, coolers, and preheaters were assumed to be shell and tube heat exchangers with stainless steel tubes in the case of Process A, and with Hastelloy B tubes in the case of the iodide processes. To account for the Hastelloy, the stated^(*) cost for a given capacity (tube surface area) was doubled. The same was done for blowers. Fluidized bed reactors and halogenation units were assumed to be ceramic- or graphite-lined metal shells. Refrigeration equipment for 0° F was taken directly from the graphs.

* Reference (4) and (5) graphs.

Cost Indexing

The Cost indices given in Table 1 were used in the present calculations.

TABLE 1. INDICES FOR COST CALCULATIONS

Index or Reference	Year	Index	Multiplication Factor*
Chemical Engineering (CE) Cost Index (base 1957-59 = 100)			
CE Plant Construction Index	1975	179.4	1.00
CE Equipment Index	1975	191.6	1.00
CE Construction Labor Index	1975	166.7	1.00
Reference 4, Peters and Timmerhaus			
CE Plant Construction Index	1967	109.1	1.64
CE Construction Labor Index	1967	(127)**	1.31
Reference 5, Aries and Newton			
CE Plant Construction Index	1954	86.1	2.08
Reference 6, Winfield and Dryden			
CE Plant Construction Index	1962	102.0	1.76
BCL Titanium Pilot Plant Experience	1957	100	1.79

* Factor by which cost data from referenced sources is multiplied to bring cost to 1975.

** Obtained with reference to Figure 4-3, Reference 4.

Actually, the 1975 index of 179.4 was used in the detailed costing of equipment from References 4 and 5 and the BCL work. However, it was realized later that the equipment index of 191.6 would better represent the inflation factor for the items involved. Accordingly, the final equipment cost totals were raised by $\frac{191.6}{179.4} = 1.068$.

Fluidized-Bed Reactors

On the basis of experience with the experimental zinc reduction of SiCl_4 reactor* and other fluidized-bed reactors at BCL involving halide reactions, a 15-inch-diameter reactor with particles in the 300-600 μ range should have a capacity of 24 kg Si hr^{-1} . This is adopted as the reference reactor for Process A of the present work, six reactors providing the 1000 kg yr^{-1} output at a single site.

The size of the fluidized bed reactors for Processes B through F were scaled from this reference reactor as explained below under "Simplifying Assumptions". Estimates of the cost of the reference reactor were made on the basis of past experience with similar reactors and checked by a paper study of the cost of assembling a reactor of the type and size envisioned.

* For example, Run 90-23 with 149 x 210 μm particle size in a 2-in. experimental reactor produced 77g hr^{-1} silicon on the seed particles. If a seed particle size range were adopted which had a minimum size of 350 μm , it should be possible to increase the reactant throughput of this system by $(\frac{350}{149})^2$ (= 5.52). This same rate in a 15-in. reactor should give $\approx 24 \text{ kg hr}^{-1}$ ($\frac{77}{1000} \times 5.52 \times [\frac{15}{2}]^2$).

Halogenation Reactors

Size and cost of the halogenation reactors (packed bed) were based on experience with a 15-inch diameter furnace which was operated for 2 years at BCL for the iodination of titanium carbonitride to form titanium tetraiodide. The relative sizes of halogation reactors for the various processes were based on the same extrapolation as that adopted for the fluidized beds and explained under "Simplifying Assumptions".

Scraper Condensers, Iodine/Iodide Compressor, and Distillation Columns

The size and cost of scraper condensers for the condensation and recycle of solid iodine and silicon iodide were based on information from the large pilot plant operated at BCL for the preparation of titanium by thermal dissociation of titanium tetraiodide. Similarly the requirements and cost of a centrifugal compressor for compressing the low-pressure exhaust from the deposition cycle in Processes B and C were based on a similar unit ($\approx 1/3$ the size for Processes B and C) used in the titanium plant to maintain the pressure differential in the system. The size of distillation columns required were estimated by reference to similar units on the iodide titanium pilot plant and a smaller installation for iodide process silicon. Costs were obtained from references 4 and 5. Reboilers and condensers were assumed to be shell and tube heat exchangers whose costs were obtained from References 4 and 5.

"Hot-wire" Deposition Unit

The requirements and cost of the "hot-wire" deposition unit for Processes B & C were based on experience with a similar unit on the iodide

titanium pilot plant. The extrapolated Volume of the Process B, C reactors (1000 ft³) relative to the titanium pilot plant reactor (factor of 3) is also consistent with the fact that 1 kg hr⁻¹ of silicon from SiHCl₃ is reported for a 2 to 3-hairpin unit 3 ft in diameter by 6 ft long. A proportional volume scale-up from the latter leads to a volume requirement of 1018 ft³ for the Process B, C reactors. Radiation losses from resistively heated "filaments" (rods) in the deposition unit were estimated from experience with the titanium pilot plant and reported power costs for present manufacture of silicon from trichlorosilane.

Refrigeration, -280 F

The estimated unit cost, and power requirements for the refrigeration of the HI condenser in Process D were obtained from Mr. J. Kronholz of the York Company in Cleveland, Ohio.

Electrolytic Recovery of Zinc

The characteristics and structural requirements of a large electrolytic cell for the recovery of zinc from liquid zinc chloride were taken from a paper by Threlfall.⁽⁷⁾

Five units of the size described by Threlfall would be required for each of the six 24 kg hr⁻¹ reference systems at the 1000 MT yr⁻¹ production site.

The cost of the individual units was estimated by "construction" on paper of the equipment visualized. Additional guidance on the electrolysis power sources and the manpower requirements was obtained from an analysis by Meisel⁽⁸⁾ of the wet electrolytic recovery of zinc.

Wet Recovery of I₂

The cost of wet recovery of I₂, \$0.20 lb⁻¹, was based on an estimate made for the same process in the iodide titanium pilot plant work. The reasonableness of this estimate was confirmed in a telephone conversation of 3/10/76 with Dr. Vernon Stenger (retired) of Dow Chemical Company, Midland, Michigan, where this recovery process is used.

Materials and Power Costs

Table 2 gives the January 1975 materials costs used in the calculations, together with sources of the information.

The estimated cost of electric power of $\$0.03 \text{ kwh}^{-1}$ used in the calculations was obtained from a representative of the Columbus and Southern Electric Company, Columbus, Ohio. This represents the cost of electric power from coal mined in southern Ohio and should be typical of current power costs most places in the United States except in areas supplied by hydroelectric power.

Manpower Costs

The construction labor rates given by Peters (Reference 4) for 1966 were used in estimating the operating cost of all the process options. It is recognized that construction workers' rates are probably higher than that typically received by chemical plant operators, but since the construction workers' rate was available and its use afforded a conservative approach, it was adopted for this evaluation. These rates were adjusted (see Table 1) to January 1975 by using the cost index given in Peters to determine the labor rate in 1957, and then, using the Chemical Engineering Cost Index, to correct these rates to January, 1975. Both unskilled and skilled labor rates were used. Each unit operation for each of the process options was reviewed and assigned skilled and unskilled operators depending on its complexity. The labor rates (1975) employed in this cost analysis were

Skilled operator	-	$\$6.60 \text{ hr}^{-1}$
Unskilled operator	-	$\$4.60 \text{ hr}^{-1}$

Simplifying Assumptions

Opportunities were sought to minimize the task of cost estimation for the six processes, on the bases that (1) the similarity of the processes in many respects justified some simplifying assumptions, and (2) errors

TABLE 2. MATERIALS COSTS, JANUARY 1975

Material	Lot Size	Cost	Reference
Silicon (metallurgical grade)	Tonnage	\$1.00 Kg ⁻¹	(9)
SiO ₂ - 99.5% 325 mesh	Carload	\$0.0125 lb ⁻¹	(10)
Carbon, pet. coke	Tonnage	\$0.01 lb ⁻¹	(11)
Hydrogen	Piped under fence	\$0.96 lb ⁻¹ (\$0.50/100 SCF)	(12)
Iodine, crude	Drum	\$2.59 lb ⁻¹	(10)
SiCl ₄ , tech.	Drum	\$0.185 lb ⁻¹	(10)
Zinc chloride*	Granules, 100 lb.	\$0.34 lb ⁻¹	(10)
Chlorine*	Tanks	\$0.08 lb ⁻¹	(10)
Zinc	Prime Western tonnage	\$0.392 lb ⁻¹	(13)

* Not consumed in process as evaluated, but listed here for use in consideration of possible credit.

introduced by the simplifying assumptions would be small relative to differences in the major cost factors that were considered. The simplifying assumptions are noted and discussed in the following section.

General Assumptions

Although the formation of SiCl_4 by the chlorination of SiO_2 + carbon is visualized for Process A, the cost calculations are based on starting with SiCl_4 at market price, taking a small credit for onsite production. No such credit is taken for the metallurgical grade silicon for the other processes because the arc furnace for present production is 4 to 5 times that required for on-site silicon preparation at the 1000 MT yr^{-1} level and on-site preparation may not be economical. However, a single large arc furnace might supply the three sites with the combined $3000^+ \text{ MT yr}^{-1}$ requirement at a cost less than present market values. It should be noted here that although the cost calculations are based on starting with SiCl_4 in Process A and metallurgical grade silicon in the other Process, energy calculations for the overall processes include the production of these intermediates.

Reaction Efficiency

In every case it was assumed that the reaction involved could be carried out at the thermodynamically predicted efficiency. This was done to avoid repetition, on a reduced efficiency basis, of energy balance calculations that had already been completed on the prior basis when the economic analysis was initiated. The adoption of thermodynamically predicted reaction efficiencies for the iodide processes (B-F) is fully justified since experimental efficiencies in excess of those thermodynamically predicted have been consistently obtained, as discussed in the First Quarterly and subsequent monthly reports. The effect of this across-the-board assumption is to give a slight edge to the zinc reduction process (A). The magnitude of this bias will be discussed after the results have been presented.

Capacity of Halogenation Reactor
and Fluidized Bed Reactors

As noted above, a 15-inch diameter fluidized bed reactor was chosen for the 24 kg hr^{-1} reference conditions. The corresponding gas flow conditions are 200.4 kg hr^{-1} of SiCl_4 and 154.3 kg hr^{-1} of zinc (stoichiometric ratio) at a bed temperature of 1200 K. The sizes of fluidized reactors required for the other processes were scaled from the reference condition on two bases.

- (1) The linear gas velocity (i.e. temperature-corrected volumetric throughput) for equivalent fluidization is inversely proportional to the square root of the molecular weight and
- (2) The linear gas velocity for equivalent fluidization is inversely proportional to gas viscosity (equivalent to basing the correlation on Stoke's law).

Both correlations have been used at BCL with success and it is not certain which would be the better for this application. The difference is not large, however. For example the cross sectional area required for the hydrogen reduction of SiI_4 in Process E is 6.98 times that of the reference reactor by the first correlation and 7.15 times that of the reference reactor by the second. Accordingly, the average of the sizes predicted by the two correlations was used for Processes B-F.

It was assumed that the packed bed halogenation reactors followed the same correlation as the fluidized bed reactors in terms of permissible throughput for a given size.

Heat Transfer Coefficients

Calculation of heat transfer coefficients for the conditions appropriate to each of the roughly 50 units employed in Processes A-F could not be justified. Therefore, characteristic heat transfer coefficients were estimated for the predominant conditions involved in the candidate processes. These estimates were based on past pilot plant experience and information from Perry⁽¹⁴⁾. The characteristic process conditions are:

- (1) Process gases high (>90 %) in hydrogen, for which a value of $70 \text{ BTU hr}^{-1} \text{ ft}^{-2} \text{ F}^{-1}$ was adopted.
- (2) High molecular weight hydrogen-free gases or vapors, for which a value of $3 \text{ BTU hr}^{-1} \text{ ft}^{-2} \text{ F}^{-1}$ was adopted.
- (3) High molecular weight vapors condensing as a solid in a scraper condenser, for which the value of $3 \text{ BTU hr}^{-1} \text{ ft}^{-2} \text{ F}^{-1}$ was adopted on the basis of data from a similar unit in the titanium pilot plant.
- (4) High molecular weight material being vaporized from its liquid; for which a value of $30 \text{ BTU hr}^{-1} \text{ ft}^{-2} \text{ F}^{-1}$ was adopted.

In the case of noncondensable/condensable systems in which the condensable is condensed as a liquid, the heat transfer coefficient for the liquid film was considered to be so high that the noncondensable gas coefficient was limiting, thus, $70 \text{ BTU hr}^{-1} \text{ ft}^{-2} \text{ F}^{-1}$ as in No. 1 above was used.

Process waste heat disposal was handled collectively using a heat transfer coefficient of $300 \text{ BTU hr}^{-1} \text{ ft}^{-2} \text{ F}^{-1}$. Cooled recirculated water would be used in those cases justified by heat load.

With the fixed coefficients of Items 1-4 above, it was only necessary to estimate the available Δt for each process step and combine this with the heat duty and the appropriate coefficient to obtain the required surface area for that unit. The corresponding equipment cost was obtained from References 4 and 5 as noted above.

Distillation

Pending availability of data for the purity requirements of solar cell silicon, it was assumed that 20-plate column having H.E.T.P. of 1 ft per plate with a reflux ratio of unity would suffice, if on first passage through the column, 10% of the silicon halide is removed, 5% as tops and 5% as bottoms. The permissible boiling rate, well short of flooding was based on experience from the iodide titanium plant and information from Reference 14,

and the columns were sized accordingly. Although the sizes of the columns were adjusted in accordance with differences in the recycle load from process to process, no adjustment was made from the 5% tops and 5% bottoms removal on first pass, on the assumption that the major purification would be required on first pass. Cost data were taken from References 4 and 5 for packed towers with suitable additions being made for reboilers and condensers (shell and tube).

Zinc Recycle (Process A)

On paper, the recovery of zinc by electrolysis of the molten zinc chloride appeared to be the simplest approach. However, after exposure to the attractive, $\$0.13 \text{ Kg}^{-1}$ zinc ($\$0.60 \text{ Kg}^{-1} \text{ Si}$), recovery cost substantiated in detail for the aqueous process described in Reference 8, some consideration was given to the potential of the aqueous route to zinc recycle in Process A. Although that option may merit study in the future, it was concluded tentatively that two advantages of the molten chloride process may offset possible economies of recycling the zinc by the aqueous route:

1. Conservation of process heat
2. Avoidance of introduction of moisture or oxides into the zinc cycle.

Accordingly, the nonaqueous route was adopted for the cost calculations.

It will be noted from the cost data of Table 2 that the cost of zinc chloride, 0.34 lb^{-1} , is about 50% higher than the cost of the contained zinc and chlorine. Thus, if the market conditions were right, one might consider taking credit for the zinc chloride as a marketable by-product rather than recycling it. No effort was made to pursue this option in terms of investigating the size of the present market for zinc chloride relative to the anticipated output of the Process A plant, and the more conservative approach of accepting the cost of recycle was adopted.

Capital Investment in Iodine

To bypass the estimation of total iodine inventory and its cost as a pseudo-capital-investment item, it was assumed that the original cost of

the iodine inventory could be eventually recovered without loss* by virtue of its being upgraded in the process.

Utilities Cost

Although it is recognized that utilities other than electrical will be required, these requirements are small relative to the electrical requirements and have not been estimated. Inclusion of these and other such minor cost items would not be expected to alter the final process ratings, although their inclusion would be mandatory in subsequent cost calculations on the surviving process.

Although it may be possible to use other than electrical heating in some steps of the candidate processes, the simplifying assumption was adopted that all energy requirements are to be supplied electrically.

Process Heat Recovery

In both the dollar and energy economy calculations it was assumed that one-half of the exothermic heat from process steps involving temperatures above 1000 F (≈ 800 K) could be recovered to offset endothermic requirements. However, no detailed study was made as to just where such economies could be effected. It has been a general rule-of-thumb that the cost of equipment for the recycle of <1000 F process heat is such as to make it uneconomical. The quest for energy conservation would justify reconsideration of this question in the future; however, the relative status of all processes but those involving the hot wire unit (large radiation losses) should not be affected by this basis for estimating the process heat recovery potential. As an expedient, the actual cost of the heat disposal equipment for each process was based on a single shell and tube exchanger using the intermediate heat transfer coefficient of $300 \text{ BTU hr}^{-1} \text{ ft}^{-2} \text{ F}^{-1}$, as discussed earlier in the "Heat Transfer Coefficient" section, and assuming a $150 \text{ F } \Delta t$ in all cases. The equipment cost were derived from information given in Peters⁽⁴⁾. Where justified by the heat load, cooling equipment with recirculated water was included in the cost.

* A profit might actually be realized; however, no credit was taken.

Manpower Requirements

Manpower requirements were based on information given in Peters⁽⁴⁾ relating the number of operators per major process step versus plant size. In Peters, chart curves are given representing three types of plants: (1) batch, (2) average, and (3) highly automated processes. The individual unit operations of the anticipated silicon plants are so varied in nature that they are best judged individually as to the category which applies rather than assigning one of the three types to the entire plant. For an ≈ 4 ton day⁻¹ (1000 MT yr⁻¹) plant, the number of operators per unit operation are (1) automated - 16, (2) average - 23, and (3) batch - 35. The number of operators provided for each major process step was based on a judgment of its ranking between automated and batch. In some cases, the operation was not considered to fall precisely under one of these categories and so an intermediate number of operators was assigned. The operating personnel are divided into four crews each working 42 hrs wk⁻¹ and 51 wks yr⁻¹ (eight holidays). Obviously, during vacations each man must be replaced so no adjustment for vacation is required.

Flow Chart Simplification

To simplify the flow charts, reaction products such as SiCl₂(g) and SiI₂(g), SiH₂I₂(g,l), and SiHI₃(g,l) were not included. SiCl₂ and SiI₂ formed at equilibrium would be expected to back react with ZnCl₂ or unreacted I₂, respectively on cooling. SiH₂I₂ and SiHI₃ were assumed to behave as SiI₄, although a detailed plant design would have to consider the differences. The calculated reaction efficiencies did take all of these species into consideration (plus monatomic iodine).

Results of Economic Evaluation

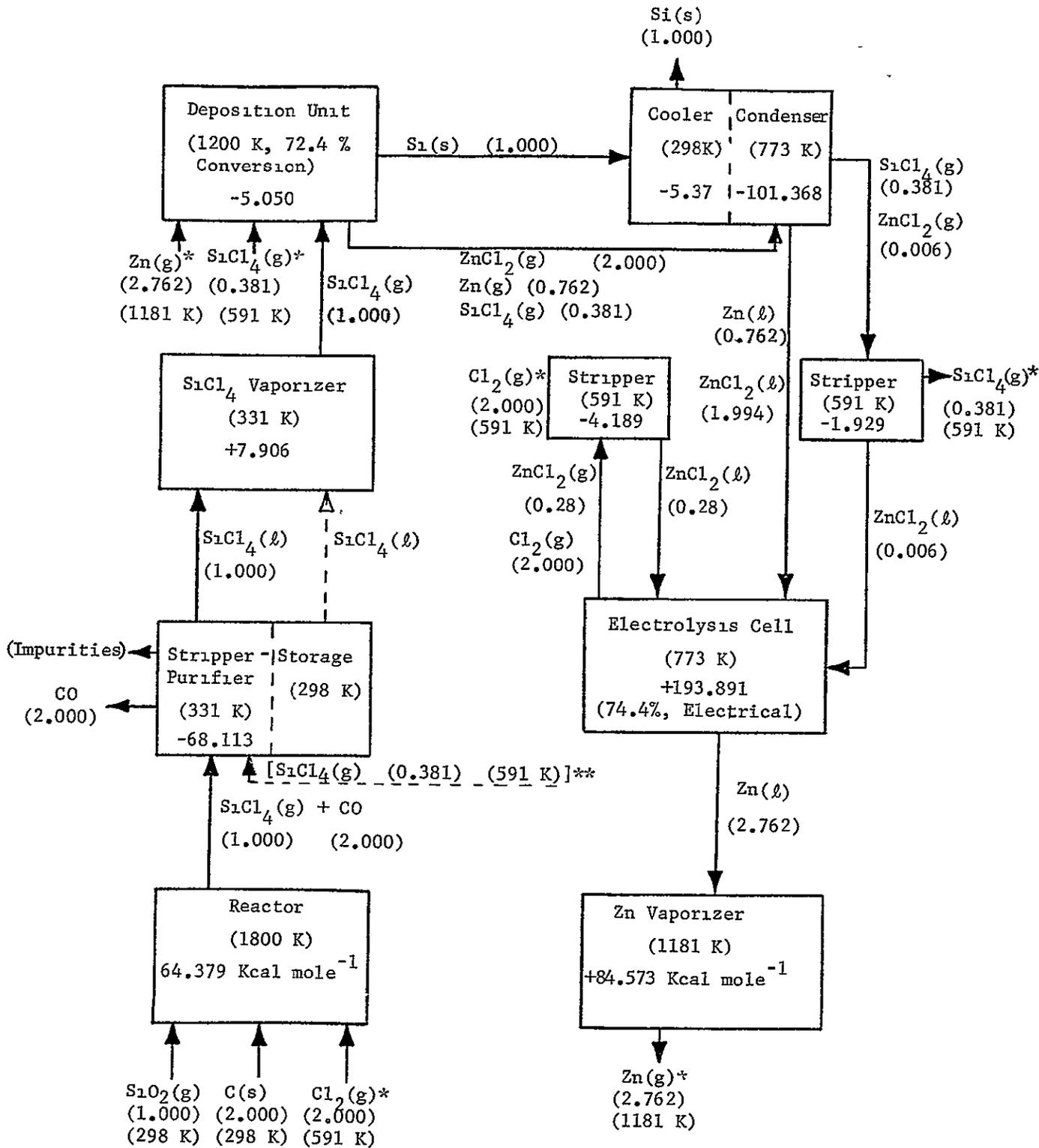
In this section there are presented for each of Processes A-F in turn, process flow diagrams, followed by data on (1) costs of major items of equipment, (2) materials costs, (3) utilities costs, (4) manpower costs, (5) fixed capital investment costs, and (6) final estimated product costs. These are followed by a statement relative to the overall energy requirement for the subject process. Following that is a discussion of the reasons for the cost differentials, and the possible effects of alternative assumptions on the process ratings. Finally a recommendation is made as to the course of future work.

It should be noted that in the following information on the individual processes, more process units appear in the lists of major equipment items than show in the flow sheets. This reflects the fact that the flow sheets are primarily related to process functions (although some breakdown is indicated). Where several units are involved in a given function or where the recycle route is altered, appropriate distribution of the enthalpy changes is made.

Process A

Figure 1 is the mass and energy flow sheet for the zinc reduction of silicon tetrachloride (Process A). In this flow sheet and subsequent ones for the other processes, the number of moles of each reactant entering a process step is given with its temperature. Reaction products or unconverted reactants leaving a process step are assumed to leave at the temperature given in the box corresponding to that step, if not otherwise indicated. The figures given in the boxes are the enthalpy changes (+ = endothermic, - = exothermic) for that particular step in units of Kcal per gram mole of silicon produced. Recycle streams are adjusted to reflect conversion efficiencies of less than 100 per cent in a given step.

It should be noted that although the original flow diagram (solid lines) shows the recycle of unreduced SiCl_4 without purification, it was later decided for the purpose of cost analysis, to recycle the unreduced SiCl_4 to the distillation column (dashed line). It should also be noted that,



* Recycled material
 ** Recycle route adopted in cost analysis

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

although some of the endothermic enthalpy requirements might be supplied by other than electrical energy, 74.4 per cent of the electrolysis requirement is in the free energy term and must be supplied as low-voltage D.C. Several of the cells required for the 1000 MT yr⁻¹ installation might well be placed in series to cut down on bus bar size.

Table 3 gives the function size, and cost, of the large equipment items for the Process A reference installation (24 kg hr⁻¹). It is recognized that equipment in contact with liquid and gaseous zinc presents certain problems with materials of construction which have not been analyzed in detail. These estimates are based in part on the costs of stainless steel shell and tube exchangers to which the cost of units in other materials of construction should be proportional if not equal.

Table 4 gives the materials and electrical energy costs associated with Process A. In estimating the cost of recycled material for Process A and subsequent processes, a percentage loss was estimated, representing the sum of (1) material actually lost, and (2) material recovered at a cost equal to that of purchase. As pointed out above, although the actual plant would start out with SiO₂ and carbon, the cost estimate for Process A is based on the cost of purchased SiCl₄ less 20% for economies of on-site production. A 90% utilization factor was introduced to account for loss or cost balanced recovery of material taken from the top and bottom of the distillation step, containing impurities. Electrical costs were obtained by summing the enthalpy changes in the flow diagram as described under "Simplifying Assumptions" and applying a 90% utilization factor to account for heat loss.

Table 5 shows the manpower unit breakdown and cost for Process A. The reference factor of 16 operators per unit was used for most of the operations in Process A since the anticipated plant was considered to be highly automated. The one exception was the zinc electrolysis unit which was considered to be intermediate between automated and average. Although listed separately, the raw material and product handling were considered to be one unit operation.

Tables 6 and 7 give the Fixed Capital Investment and Product Costs.

TABLE 3. MAJOR EQUIPMENT COST, PROCESS A

Item	Function	Duty	Size	Cost \$
Vaporizer	SiCl ₄ Vaporization	2.68E4* BTU hr ⁻¹	45 ft ²	3,700
Distillation Unit	SiCl ₄ Purification	200.5 Kg hr ⁻¹ SiCl ₄	20 ft x 12 in. dia.	18,200
Deposition Unit	SiCl ₄ Reduction	24 Kg hr ⁻¹ Si	1.23 ft ² (15 in. dia.)	27,500
Cooler/Condenser	Condenser Zn, ZnCl ₂	34.37E4 BTU hr ⁻¹	1076 ft ²	22,900
Electrolysis Cell	Zn Recovery	111.7 Kg hr ⁻¹ Zn	5 x 6-electrode Threlfall cells	200,000
Vaporizer	Vaporize Zn	28.67E4 BTU hr ⁻¹	240 ft ²	14,600
Stripper 1	Strip ZnCl ₂ from Cl ₂	1.42E4 BTU hr ⁻¹	60 ft ²	4,100
Stripper 2	Strip ZnCl ₂ from SiCl ₄	0.64E4 BTU hr ⁻¹	26 ft ²	2,700
Tank	SiCl ₄ Storage	8 hr	200 gal	5,400
Heat Exchanger	Waste Heat Disposal	22.79E4 BTU hr ⁻¹		2,400
			Sub total	\$301,500
			Total after index adjustment**	\$322,000

* 2.68E4 = 2.68 x 10⁴

** See "Cost Indexing"

TABLE 4. MATERIALS AND ENERGY COSTS, PROCESS A

Item	Conditions	Cost, \$ Kg ⁻¹ Si
Zinc	10% loss or cost balanced recovery	\$0.40
SiCl ₄	90% utilization, 20% onsite manufacturing credit	<u>2.19</u>
	Total, Materials	\$2.59
Electrical	90% utilization, 11.17 kwhr Kg ⁻¹	\$0.335

TABLE 5. MANPOWER UNIT BREAKDOWN AND COST, PROCESS A
(6 x 24 Kg/hr⁻¹ Si)

Unit Operation	No. Operators
Deposition	16
Zinc Electrolysis	20
Distillation	16
Raw Material Handling	8 (unskilled)
Product Handling	<u>8 (unskilled)</u>
	66* (divided into 4 crews)

* 52 Skilled operators at \$6.60 hr⁻¹ (Equivalent manpower
hourly rate of \$416.80)

* 16 Unskilled operators at \$4.60 hr⁻¹

Operating Labor Cost yr⁻¹ = \$892,790 (\$416.80 hr⁻¹ x 2142 hrs yr⁻¹)

TABLE 6 . FIXED CAPITAL INVESTMENT, PROCESS A

A. Direct Cost (D)		
1. Purchased equipment - E		\$ 322,000
2. Installation of E	40 percent of E	128,800
3. Instrumentation (Installed)	25 percent of E	80,500
4. Piping (Installed)	60 percent of E	193,200
5. Electrical (Installed)	15 percent of E	48,300
6. Buildings and Services	47 percent of E	151,340
7. Yard Improvements	10 percent of E	32,200
8. Service Facilities	40 percent of E	128,800
9. Land	6 percent of E	<u>19,320</u>
TOTAL DIRECT COST		\$1,104,460
B. Indirect Cost (I)		
1. Engineering and Supervision	15 percent of E	\$ 48,300
2. Construction Expenses	14 percent of E	<u>45,080</u>
TOTAL D & I		\$1,197,840
C. Contractor's Fee	10 percent of D & I	\$ 119,780
D. Contingency	10 percent of D & I	<u>119,780</u>
E. Fixed Capital Investment - 24 Kg hr ⁻¹		\$1,437,400
	- 1000 MT yr ⁻¹ (24 Kg hr ⁻¹ x 6)	\$8,624,400

TABLE 7. PRODUCT COSTS, PROCESS A

A. Manufacturing Cost

1. Direct Production Cost

a. Materials		\$2,590,000 ^a
b. Operating labor		892,790
c. Supervisory and clerical	15 percent of b	133,920
d. Utilities		335,000
e. Maintenance and repairs	10 percent of fixed capital	862,440
f. Operating supplies	15 percent of e	129,370
g. Laboratory charges	15 percent of b	133,920
h. Patents and royalties	4 percent of product cost	364,660

2. Fixed Charges

a. Depreciation	10 percent fixed capital	\$ 862,440
b. Local taxes	2 percent fixed capital	172,490
c. Insurance	1 percent fixed capital	86,240
d. Interest	6 percent fixed capital	517,460

3. Plant Overhead	60 percent of (1b + 1c + 1e)	\$1,133,490
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B. General Expenses

1. Administration	50 percent of 1b	\$ 446,400
2. Distribution	2 percent of product cost	182,330
3. Research and Development	3 percent of product cost	<u>273,490</u>

C. Total Product Cost

1. Product Cost, per kg S ₁		\$9,116,440
		\$9.12

*Includes all cost (operating and capital investment) for SiCl₄ used.

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Process B

Figure 2 and Tables 8 through 12 give the input and results for Process B, thermal decomposition of SiI_4 produced by direct iodination of metallurgical grade silicon. This is the conventional iodide silicon process as investigated by BCL for Mallinckrodt Inc., with the addition of a compressor 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 to be characteristic of the present production from trichlorosilane. It was then assumed that 45% could be saved by suitable external heat reflection $\left(\left[\frac{900^\circ\text{K}}{1300^\circ\text{K}} \right]^4 = 23\% \right)$ and by mutual heat reflection (22%) from a "forest" of filaments such as used in the titanium pilot plant deposition unit. Despite this projected saving, Process B would still require 190 Kwh Kg^{-1} solely to maintain the deposition surface temperature.

In the manpower unit breakdown and costs shown in Table 9 for Process B, the unit operations were considered to vary from automated to intermediate between average and batch. The hot-wire deposition unit operated at reduced pressure was judged to be the least automated.

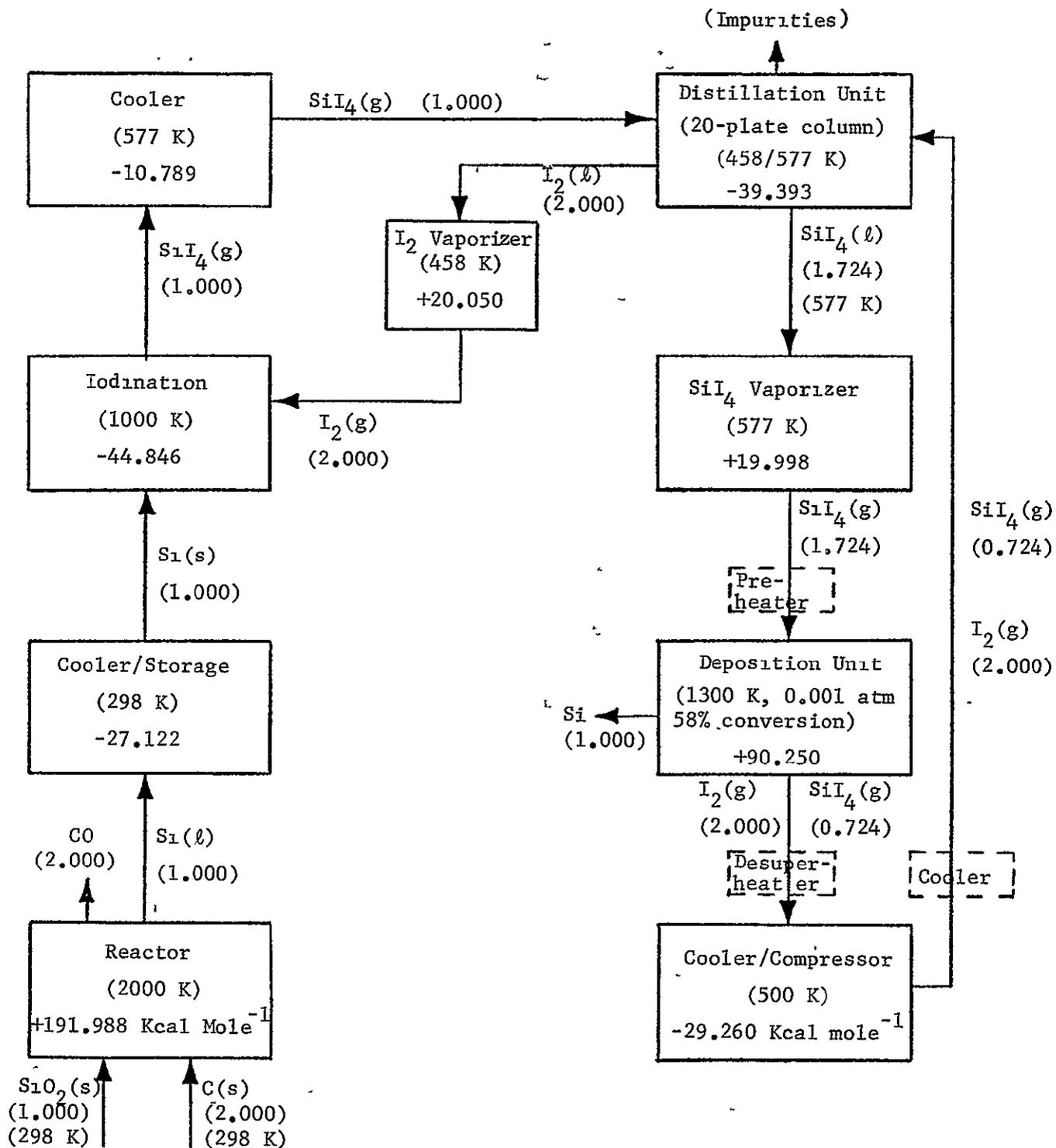


FIGURE 2. PROCESS B FLOW SHEET
 Thermal Decomposition of SiI_4
 Produced from Metallurgical Grade Silicon

TABLE 8. MAJOR EQUIPMENT, PROCESS B
(24 Kg hr⁻¹ Si)

Item	Function	Duty	Size	Cost
Vaporizer	Vaporize I ₂	433.7 Kg hr ⁻¹ , 6.80 E4 BTU hr ⁻¹	113 ft ²	\$ 12,500
Reactor	Iodinate Si	457.7 Kg hr ⁻¹ SiI ₄	0.56 ft ²	21,200
Cooler	Cool. iodination product	3.66 E4 BTU hr ⁻¹	64 ft ²	9,200
Distillation Unit	Purify SiI ₄	789.1 Kg hr ⁻¹ SiI ₄ + 433.7 Kg hr ⁻¹ recycled I ₂	20 ft x 17 in dia	64,700
Vaporizer	Vaporize SiI ₄	6.78 E4 BTU hr ⁻¹	113 ft ²	12,500
Preheater	Preheat SiI ₄	15.30 E4 BTU hr ⁻¹	350 ft ²	24,400
Deposition Unit	Deposit Si	24 Kg hr ⁻¹ Si	1000 ft ³	300,000*
Desuperheater	Cool byproduct	9.92 E4 BTU hr ⁻¹	92 ft ²	11,600
Compressor	Compress I ₂ /SiI ₄	765.1 Kg hr ⁻¹ I ₂ + SiI ₄	41.5 hp	200,000
Cooler	Remove heat of compression	6.33 E4 BTU hr ⁻¹	422 ft ²	20,800
Heat Exchanger	Waste heat disposal	38.31 E4 BTU hr ⁻¹		3,000
Vacuum System (including oil reclaiming)	Prime compressor			20,000**
			Subtotal	\$700,400
			Total after index adjustment	\$748,000

† Includes electrical equipment

* "Top of the head" estimate, no data

TABLE 9. MATERIALS AND ENERGY COSTS, PROCESS B

Item	Conditions	Cost, \$ Kg ⁻¹ Si
Metallurgical grade Si	85% utilization	\$1.17
I ₂	Wet recovery of 5% tops + 5% bottoms from distillation @ \$0.20 lb ⁻¹	0.80
I ₂	Loss or cost-balanced recovery of recycle load, 6.896 = atomic ratio I/Si	<u>0.89</u>
	Total, Materials	\$2.86
Electrical	Other than radiation loss in deposition, 90% utilization, 7.47 Kwh Kg ⁻¹	0.224
Electrical	Radiant loss in deposition, 190 Kwh Kg ⁻¹	<u>5.700</u>
	Total Electrical	\$5.924

TABLE 10. MANPOWER UNIT BREAKDOWN AND COST, PROCESS B
(6 x 24 Kg hr⁻¹ S₁)

Unit Operation	No. Operators
Iodination	20
Distillation	16
Deposition	28 (4 unskilled)
Raw Material Handling	8 (unskilled)
Product Handling	8 (unskilled)
	80* (divided into 4 crews)
*60 Skilled Operators at \$6.60 hr ⁻¹	(Equivalent Manpower
*20 Unskilled Operators at \$4.60 hr ⁻¹	hourly rate of \$488)
Operating Labor Cost =	\$1,045,300 (\$488 hr ⁻¹ x 2142 hr yr ⁻¹)

TABLE 11. FIXED CAPITAL INVESTMENT, PROCESS B

A. Direct Cost (D)		
1. Purchased equipment - E		\$ 748,000
2. Installation of E	45 percent of E	336,600
3. Instrumentation (Installed)	25 percent of E	187,000
4. Piping (Installed)	60 percent of E	448,800
5. Electrical (Installed)	15 percent of E	112,200
6. Buildings and Services	47 percent of E	351,560
7. Yard Improvements	10 percent of E	74,800
8. Service Facilities	40 percent of E	299,200
9. Land	6 percent of E	<u>44,880</u>
	TOTAL DIRECT COST	\$2,603,040
B. Indirect Cost (I)		
1. Engineering and Supervision	15 percent of E	\$ 112,200
2. Construction Expenses	14 percent of E	<u>104,720</u>
	TOTAL D & I	\$2,819,960
C. Contractor's Fee	10 percent of D & I	\$ 282,000
D. Contingency	10 percent of D & I	<u>282,000</u>
E. Fixed Capital Investment - 24 Kg hr ⁻¹		\$3,383,960
	- 1000 MT yr ⁻¹ (24 Kg hr ⁻¹ x 6)	\$20,303,760

TABLE 12. PRODUCT COSTS, PROCESS B

A. Manufacturing Cost		
1. Direct Production Cost		
a. Materials		\$2,860,000*
b. Operating labor		1,045,300
c. Supervisory and clerical	15 percent of b,	156,800
d. Utilities		5,924,000
e. Maintenance and repairs	10 percent of fixed capital	2,030,380
f. Operating supplies	15 percent of e	304,560
g. Laboratory charges	15 percent of b	156,800
h. Patents and royalties	4 percent of product cost	826,270
2. Fixed Charges		
a. Depreciation	10 percent fixed capital	\$2,030,380
b. Local taxes	2 percent fixed capital	406,080
c. Insurance	1 percent fixed capital	203,040
d. Interest	6 percent fixed capital	1,218,230
3. Plant Overhead	60 percent of (1b + 1c + 1e)	1,939,490
B. General Expenses		
1. Administration	50 percent of 1b	\$ 522,650
2. Distribution	2 percent of product cost	413,140
3. Research and Development	3 percent of product cost	619,700
C. Total Product Cost		\$20,656,820
1. Product Cost, per kg		\$20.65

* Includes all cost (operating and capital investment) for the recovery of iodine by the wet process, and the preparation of MG silicon used.

Process C

It was hoped that production of SiI_4 for the iodide decomposition by the direct iodination of SiO_2 plus carbon would result in a net savings over the cost of iodinating $\$1.00 \text{ Kg}^{-1}$ metallurgical grade silicon. Unfortunately, in contrast to the corresponding TiI_4 production, efficiency is low, requiring a large I_2 recycle load and a net increased cost, as shown in the following Figure and Tables for Process C.

As noted in the Appendix of this report, the phase stability ranges in the $\text{SiO}_2 + \text{C}$ iodination system are quite involved, making it difficult to predict yields other than by operation of a large-scale iodination unit. It may be possible that attaining 20 percent iodination efficiencies will require temperatures $> 1600 \text{ K}$.

As in Process B, the number of operators on the deposition unit was increased to 28. In addition, only 16 operators were assigned to operate both the I_2 separation and SiI_4 distillation columns instead of 16 each since these operations should be well automated. The number of operators assigned to the iodination and raw materials handling was increased relative to Process B because this process involved the iodination of $\text{SiO}_2 + \text{carbon}$ instead of metallurgical grade silicon.

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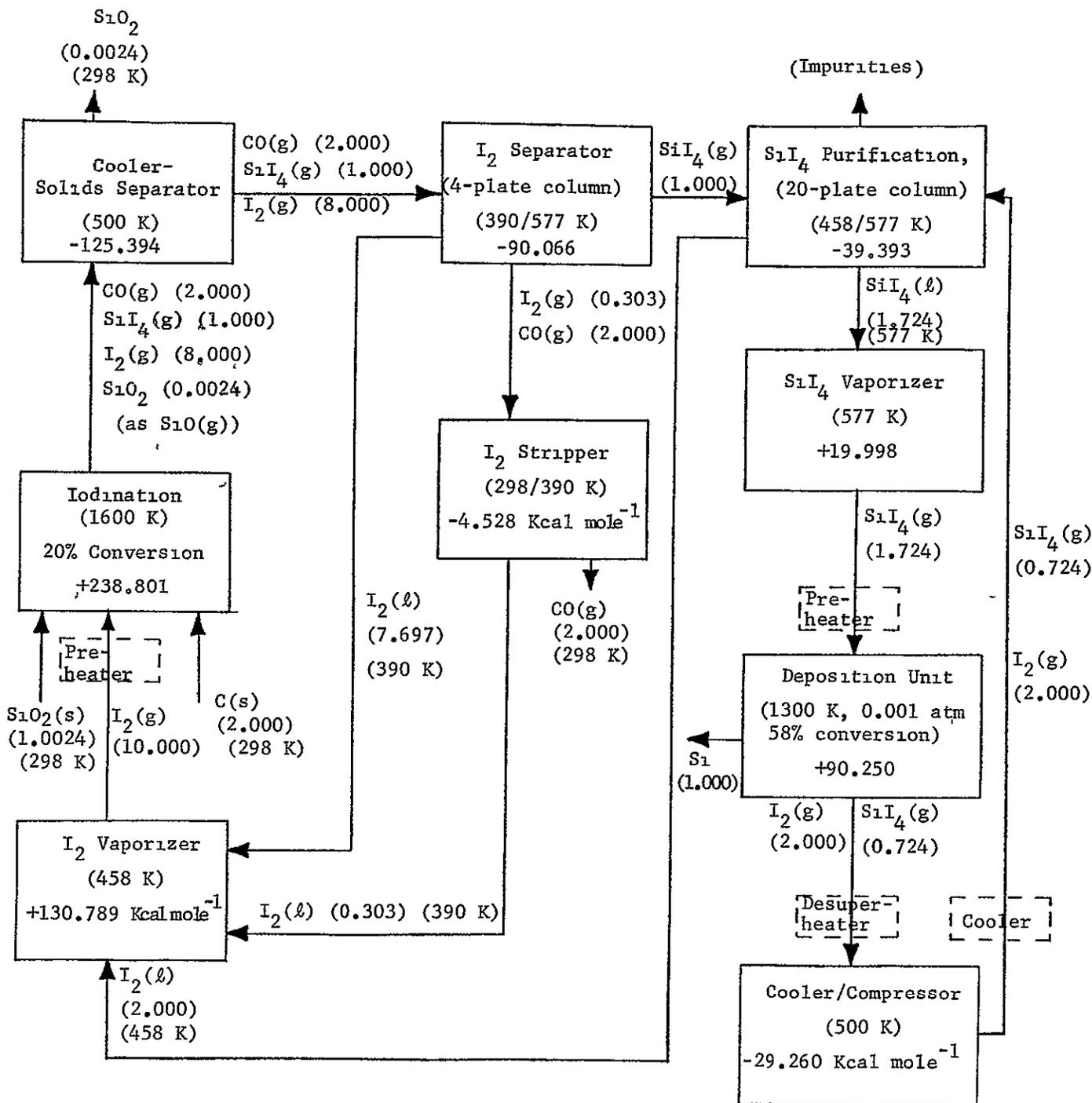


FIGURE 3. PROCESS C FLOW SHEET

Thermal Decomposition of SiI₄ Produced
by Iodination of SiO₂/Carbon Mixtures

TABLE 13. MAJOR EQUIPMENT COSTS, PROCESS
(C, 24 Kg/hr⁻¹ Si)

Unit	Function	Duty	Size	Cost *
Vaporizer	I ₂ Vaporization	37.53E4 BTU hr ⁻¹	625 ft ²	\$ 33,000
Preheater	Preheat I ₂	16.54E4 BTU hr ⁻¹	298 ft ²	20,800
Reactor	Iodinate SiO ₂ /C	457.7 Kg/hr ⁻¹ SiI ₄	503 ft ²	103,000
Cooler	Cool iodination product	73.04E4 BTU hr ⁻¹	529 ft ²	29,100
Distillation Unit	Separate I ₂	1735 Kg/hr ⁻¹ I ₂	10 ft x 10-in dia.,	58,200
Scaper Condenser	Strip I ₂ from CO	1.54E4 BTU hr ⁻¹	111 ft ²	79,500
Refrigerator (0°F)	Cool scraper condenser	1.54E4 BTU hr ⁻¹	1.3 ton	6,200
Distillation Unit	Purify SiI ₄	789.1 Kg/hr ⁻¹ SiI ₄		
		+433.7 Kg/hr ⁻¹ recycled I ₂	20 ft x 17 in.	41,500
Vaporizer	Vaporize SiI ₄	6.78E4 BTU hr ⁻¹	113 ft ²	12,500
Preheater	Preheat SiI ₄	15.30E4 BTU hr ⁻¹	350 ft ²	24,900
Deposition Unit	Deposit Si	24 Kg/hr ⁻¹ Si	1,000 ft ³	300,000
Desuperheater	Cool byproduct	9.92E4 BTU hr ⁻¹	92 ft ²	11,600
Compressor	Compress I ₂ /SiI ₄	765.1 Kg/hr ⁻¹ I ₂ +SiI ₄	41.5 hp	200,000
Cooler	Remove heat of compression	6.33E4 BTU hr ⁻¹	422 ft ²	20,200
Heat Exchanger	Waste heat dissipation	67.07E4 BTU hr ⁻¹		3,600
Vacuum System (including oil reclaiming)	Prime compressor			<u>20,000*</u>
			Subtotal	\$ 964,100
			Total after index adjustment	\$1,030,000

* "Top-of-the-head estimate", no data.

TABLE 14. MATERIALS AND ENERGY COSTS, PROCESS C

Items	Condition	Cost, \$Kg ⁻¹ Si
Carbon	80% utilization	0.023
SiO ₂	80% utilization	0.074
I ₂	Wet recovery of 5% tops + 5% bottoms from distillation column at \$0.20 lb ⁻¹	0.797
I ₂	Loss or cost-balanced recovery of 0.5% of recycle load. 22.896 = atom ratio I/Si	<u>2.948</u>
	Total Materials	\$3.84
Electrical	Other than radiation loss in deposition, 90% utilization, 23.62 Kwh Kg ⁻¹	0.708
Electrical	Radiation loss in deposition, 190 Kwh Kg ⁻¹	<u>5.700</u>
	Total Electrical	\$6.41

TABLE 15. MANPOWER BREAKDOWN AND COST, PROCESS C
(6 x 24 Kg/hr⁻¹ Si)

Unit Operation	No. Operators
Iodination	24
I ₂ Separation	16
SiI ₄ Purification	
Deposition	28 (4 unskilled)
Raw Material Handling	12 (unskilled)
Product Handling	<u>8</u> (unskilled)
	88 *(divided into 4 crews)

* 60 Skilled operators at \$6.60 hr⁻¹

* 28 Unskilled operators at \$4.60 hr⁻¹ (Equivalent manpower hourly rate of \$524.80)

Operating Labor cost yr⁻¹ = \$1,124,120 (\$524.80 hr⁻¹ x 2.42 hr yr⁻¹)

TABLE 16. FIXED CAPITAL INVESTMENT, PROCESS C

A. Direct Cost (D)		
1. Purchased equipment - E		\$1,030,000
2. Installation of E	45 percent of E	463,500
3. Instrumentation (Installed)	25 percent of E	257,500
4. Piping (Installed)	60 percent of E	618,000
5. Electrical (Installed)	15 percent of E	154,500
6. Buildings and Services	47 percent of E	484,100
7. Yard Improvements	10 percent of E	103,000
8. Service Facilities	40 percent of E	412,000
9. Land	6 percent of E	<u>61,800</u>
	TOTAL DIRECT COST	\$3,584,400
B. Indirect Cost (I)		
1. Engineering and Supervision	15 percent of E	\$ 154,500
2. Construction Expenses	14 percent of E	<u>144,200</u>
	TOTAL D & I	\$3,883,100
C. Contractor's Fee	10 percent of D & I	\$ 388,310
D. Contingency	10 percent of D & I	<u>388,310</u>
E. Fixed Capital Investment - 24 Kg hr ⁻¹		\$4,659,720
	1000 MT yr ⁻¹ (24 Kg hr ⁻¹ x 6)	\$27,958,320

TABLE 17. PRODUCT COSTS, PROCESS C

A. Manufacturing Cost		
1. Direct Production Cost		
a. Materials		\$3,842,000*
b. Operating labor		1,124,120
c. Supervisory and clerical	15 percent of b	168,620
d. Utilities		6,409,000
e. Maintenance and repairs	10 percent of fixed capital	2,795,830
f. Operating supplies	15 percent of e	419,370
g. Laboratory charges	15 percent of b	168,620
h. Patents and royalties	4 percent of product cost	1,022,190
2. Fixed Charges		
a. Depreciation	10 percent fixed capital	\$ 2,795,830
b. Local taxes	2 percent fixed capital	559,170
c. Insurance	1 percent fixed capital	279,580
d. Interest	6 percent fixed capital	1,677,500
3. Plant Overhead	60 percent of (1b + 1c + 1e)	\$ 2,453,140
B. General Expenses		
1. Administration	50 percent of 1b	\$ 562,060
2. Distribution	2 percent of product cost	511,100
3. Research and Development	3 percent of product cost	766,640
C. Total Product Cost		\$25,554,770
1. Product Cost, per kg		\$25.55

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

Process D

An attractive option (Process D) 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. It should be noted that the dew point of HI in the deposition by-product for the representative condition chosen is 194°K (-79°C) and the melting point is 222 K (-51°C). Therefore, the HI is condensed as a solid, requiring a scraper condenser (the option of compressing the H_2/HI to allow condensation above the melting point is discussed later). The data and results for Process D are given in Figure 4 and Tables 18-22.

The manpower loading assigned to the process was the same as that of Process B except for the scraper condenser and fluidized bed deposition units. The three scraper condensers required were allocated 16 operators or 4 per crew. This was based on the experience of operating this type of condenser. In the case of the deposition units, 20 operators were employed. This is a larger number than was assigned to the fluidized bed unit in Process A but a greater cross sectional area is required for this Process. An even larger number of operators would have been required if a direct extrapolation of the Process A unit were used. However, it is a reasonable assumption that to be economically practical, a fewer number of larger reactors must be used.

TABLE 18. MAJOR EQUIPMENT COST, PROCESS D
(24 Kg/hr⁻¹Si)

Items	Function	Duty	Size	Cost, \$
Reactor	Iodination of Si	457.7 Kg/hr ⁻¹ SiI ₄	1.01 ft ²	\$27,000
Stripper	Strip SiI ₄ as liquid from H ₂	12.70E4 BTU hr ⁻¹	23 ft ²	5,000
Scraper Condenser	Strip SiI ₄ as solid from H ₂	0.60E4 BTU hr ⁻¹	224 ft ²	15,650
Refrigerator (0°F)	Cool scraper condenser	0.60E4 BTU hr ⁻¹	0.5 ton	2,400
Distillation Unit	Purify SiI ₄	457.7 KgSiI ₄ hr ⁻¹	20 ft x 14 in dia.	37,500
Vaporizer	Vaporize SiI ₄	13.26E4 BTU hr ⁻¹	221 ft ²	17,400
Preheater	Preheat SiI ₄ to 800 K	4.8E4 BTU hr ⁻¹	160 ft ²	15,400
Preheater	Preheat H ₂ to 800 K	75.5E4 BTU hr ⁻¹	36 ft ²	7,100
Fluidized bed(s)	Deposit Si	24 Kg/hr ⁻¹	8.71 ft ²	220,500
Stripper	Strip SiI ₄ as liquid from H ₂ mixture	128.18E4 BTU hr ⁻¹	45 ft ²	7,500
Scraper Condenser	Strip SiI ₄ as solid from H ₂ mixture	14.49E4 BTU hr ⁻¹	543 ft ²	400,000
Refrigerator (0°F)	Cool scraper condenser	14.49E4 BTU hr ⁻¹	12 ton	18,000
Intercooler	Cool H ₂ + HI to dew pt.	11.70E4 BTU hr ⁻¹	35.6 ft ²	6,600
Scraper Condenser	Condense HI as solid	15.22E4 BTU hr ⁻¹	750 ft ²	500,000
Refrigerator (-280 F)	Cool scraper condenser and intercooler	26.92E4 BTU hr ⁻¹	22.4 ton	540,000
Blower (10 psi)	Circulate H ₂	47.35 moles H ₂ /mole Si	582 cfm	16,700
Heat Exchanger	Waste heat disposal	113.8E4 BTU hr ⁻¹		6,100
		Subtotal		\$1,842,850
		Total after index adjustment		\$1,968,000

TABLE 19. MATERIALS AND ENERGY COST, PROCESS D

Item	Condition	Cost \$Kg ⁻¹ Si
Metallurgical grade Silicon	85% Utilization	1.17
I ₂	Wet recovery of 5% tops and 5% bottoms from distillation @ \$0.20 lb ⁻¹	0.80
I ₂	Loss or cost-balanced recovery of 0.5% of recycle load, 9.968 = atomic ratio I/Si	1.29
H ₂	1% loss of recycled H ₂ , 47.35 moles H ₂ /Mole S ₁	<u>0.07</u>
	Total Materials	\$3.33
Electrical	Other than refrigeration, 15.26 Kwh Kg ⁻¹	
	0°F Refrigeration, 12 ton (24 Kg Si) ⁻¹ at \$0.05 ton ⁻¹ hr ⁻¹ Kg ⁻¹	0.025
	-280°F Refrigeration, 418 Kwh (24 Kg Si) ⁻¹ at \$0.03 Kwh	<u>0.540</u>
	Total electrical	\$1.02

TABLE 20. MANPOWER UNIT BREAKDOWN AND COST, PROCESS D
(6 x 24 Kg hr⁻¹ S₁)

Unit Operation	No. Operators
Iodination	20
Distillation	16
Deposition	20
Scraper Condensers (3)	16 (8 unskilled)
Raw Material Handling	8 (unskilled)
Product Handling	8 (unskilled)
	88* (Divided into 4 crews)
*64 Skilled Operators at \$6.60 hr ⁻¹	(Equivalent to manpower hourly rate of \$532.80)
*24 Unskilled Operators at \$4.60 hr ⁻¹	
Operating Labor Cost yr ⁻¹ = \$1,141,260	(\$532.80 hr ⁻¹ x 2142 hrs yr ⁻¹)

TABLE 21. FIXED CAPITAL INVESTMENT, PROCESS D

A. Direct Cost (D)		
1. Purchased equipment - E		\$1,968,000
2. Installation of E	40 percent of E	787,200
3. Instrumentation (Installed)	25 percent of E	492,000
4. Piping (Installed)	60 percent of E	1,180,800
5. Electrical (Installed)	15 percent of E	295,200
6. Buildings and Services	47 percent of E	924,960
7. Yard Improvements	10 percent of E	196,800
8. Service Facilities	40 percent of E	787,200
9. Land	6 percent of E	<u>118,080</u>
	TOTAL DIRECT COST	\$6,750,240
B. Indirect Cost (I)		
1. Engineering and Supervision	15 percent of E	\$ 295,200
2. Construction Expenses	14 percent of E	<u>275,520</u>
	TOTAL D & I	\$7,320,960
C. Contractor's Fee	10 percent of D & I	\$ 732,100
D. Contingency	10 percent of D & I	<u>732,100</u>
E. Fixed Capital Investment - 24 Kg hr ⁻¹		\$8,785,140
	1000 MT yr ⁻¹ (24 Kg hr ⁻¹ x 6)	\$52,710,840

TABLE 22. PRODUCT COSTS, PROCESS D

A. Manufacturing Cost		
1. Direct Production Cost		
a. Materials		\$3,330,000*
b. Operating labor		1,141,260
c. Supervisory and clerical	15 percent of b	171,190
d. Utilities		1,019,000
e. Maintenance and repairs	10 percent of fixed capital	5,271,080
f. Operating supplies	15 percent of e	790,660
g. Laboratory charges	15 percent of b	171,190
h. Patents and royalties	4 percent of product cost	1,161,770
2. Fixed Charges		
a. Depreciation	10 percent fixed capital	\$5,271,080
b. Local taxes	2 percent fixed capital	1,054,220
c. Insurance	1 percent fixed capital	527,110
d. Interest	6 percent fixed capital	3,162,650
3. Plant Overhead	60 percent of (1b + 1c + 1e)	\$3,950,120
B. General Expenses		
1. Administration	50 percent of 1b	\$ 570,630
2. Distribution	2 percent of product cost	580,880
3. Research and Development	3 percent of product cost	<u>871,320</u>
C. Total Product Cost		\$29,044,160
1. Product Cost, per kg		\$29.04

* Includes all cost (operating and capital investment) for the recovery of iodine by the wet process and the preparation of metallurgical grade silicon.

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Process E

Process E involves the hydrogen reduction of SiI_4 in a fluidized bed followed by wet-process iodine recovery for recycle. It is otherwise closely related to Process D, except that the iodination of silicon is with I_2 rather than HI. Figure 5 is the flow sheet and Tables 23-27 give the data and results.

In terms of manpower requirements, this process is similar to Process D. Accordingly, the same number of operators was assigned to most of the operations - the scraper condenser being the only exception. Even though only one scraper is involved in Process E as opposed to 3 in Process D, its size, overall complexity, and associated equipment prompted the assignment of 8 operators (2 per crew).

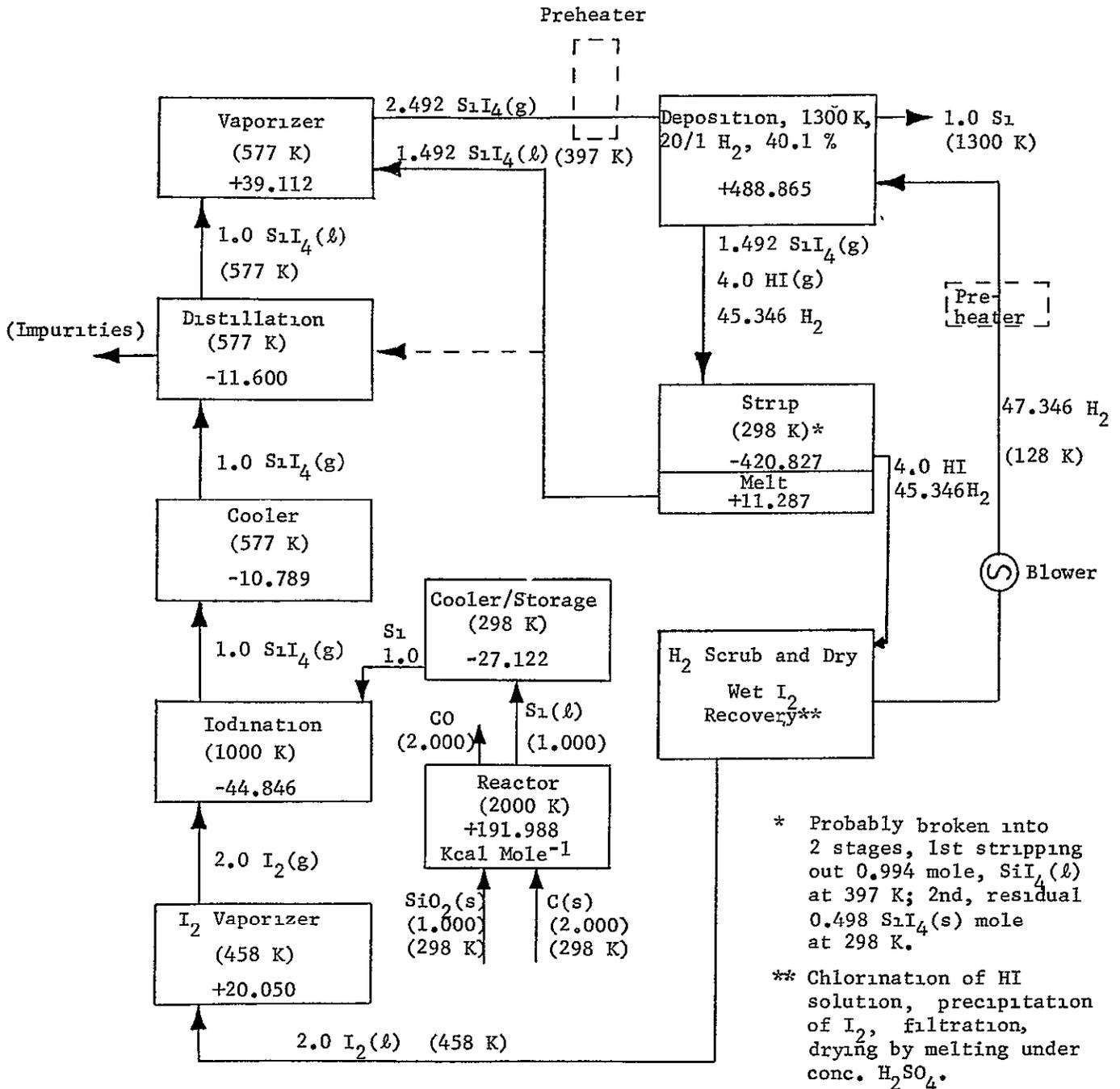


FIGURE 5. PROCESS E FLOW SHEET
Hydrogen Reduction of SiI_4
Wet-Process I_2 Recovery

TABLE 23. MAJOR EQUIPMENT COST, PROCESS E
(24 Kg hr⁻¹ Si)

Item	Function	Duty	Size	Cost, \$
Vaporizer	Vaporize I ₂	433.7 Kg hr ⁻¹ 6.8E4 BTU hr ⁻¹	113 ft ²	\$ 12,500
Reactor	Iodinate Si	457.7 Kg hr ⁻¹ SiI ₄	0.56 ft ²	21,200
Cooler	Cool SiI ₄	3.66E4 BTU hr ⁻¹	64 ft ²	9,200
Distillation Unit	Purify SiI ₄	457.7 Kg hr ⁻¹ SiI ₄	20 ft x 14 in. dia.	37,500
Vaporizer	Vaporize SiI ₄	13.26E4 BTU hr ⁻¹	221 ft ²	17,400
Preheater	Preheat SiI ₄ to 800 K	4.8E4 BTU hr ⁻¹	160 ft ²	15,400
Preheater	Preheat H ₂ to 800 K	75.5E4 BTU hr ⁻¹	36 ft ²	7,100
Fluidize bed(s)	Deposit Si	24 Kg hr ⁻¹ Si	8.71 ft ²	220,500
Stripper	Strip SiI ₄ as liquid from H ₂ mixture	128.18E4 BTU hr ⁻¹	45 ft ²	7,500
Scraper Condenser	Strip SiI ₄ as solid from H ₂ mixture	14.49E4 BTU hr ⁻¹	543 ft ²	400,000
Refrigerator(0°F)	Cool scraper condenser	14.49E4 BTU hr ⁻¹	12, Ton	18,000
Dryer	Dry H ₂	47.35 moles H ₂ /mole Si	582 cfm	20,000*
Blower (10 psi)	Circulate H ₂	47.35 mole H ₂ /mole Si	582 cfm	16,200
Heat Exchanger	Waste heat disposal	80.78E4 BTU hr ⁻¹		3,900
			Sub total	\$806,400
			Total after index adjustment	\$861,000

* "Top-of-the-head estimate", no data.

TABLE 24. MATERIALS AND ENERGY COST, PROCESS E

Item	Condition	Cost, \$ Kg ⁻¹ Si
Metallurgical Grade Silicon	85% utilization	1.17
I ₂	Wet recovery of 5% tops and 5% bottoms from distillation at \$0.20 lb ⁻¹	0.80
I ₂	Wet processing of HI byproduct at \$0.20 lb ⁻¹ I ₂	7.97
I ₂	Loss or cost-balanced recovery of 0.5% of recycle load, 9.968 = atomic ratio I/Si	1.29
H ₂	1% loss of recycled H ₂ , 47.35 moles H ₂ /mole Si	0.07
Total Materials		\$11.30
Electrical	Other than refrigeration, 90% utilization, 15.26 Kwh Kg ⁻¹	\$ 0.458
Electrical	0° F refrigeration, 12 ton (24 Kg Si) ⁻¹ at \$0.05 ton ⁻¹ hr ⁻¹ Kg ⁻¹	0.025
Total Electrical		\$ 0.48

TABLE 25. MANPOWER UNIT BREAKDOWN AND COST, PROCESS E
(6 x 24 Kg hr⁻¹ Si)

Unit Operation	No. Operators
Iodination	20
Distillation	16
Deposition	20
Scraper Condenser	8
Raw Material Handling	8
Product Handling	8
	80* (divided into 4 crews)
* 86 Skilled Operators at \$6.60 hr ⁻¹	
* 22 Unskilled Operators at \$4.60 hr ⁻¹	Equivalent to manpower hourly rate of \$488
Operating Labor cost yr ⁻¹ = \$1,045,300 (\$488 hr ⁻¹ x 2142 hrs yr ⁻¹)	

TABLE 26. FIXED CAPITAL INVESTMENT, PROCESS E

A. Direct Cost (D)		
1. Purchased equipment - E		\$ 861,000
2. Installation of E	40 percent of E	344,400
3. Instrumentation (Installed)	25 percent of E	215,250
4. Piping (Installed)	60 percent of E	516,600
5. Electrical (Installed)	15 percent of E	129,150
6. Buildings and Services	47 percent of E	404,670
7. Yard Improvements	10 percent of E	86,100
8. Service Facilities	40 percent of E	344,400
9. Land	6 percent of E	<u>51,660</u>
TOTAL DIRECT COST		\$2,953,230
B. Indirect Cost (I)		
1. Engineering and Supervision	15 percent of E	\$ 129,150
2. Construction Expenses	14 percent of E	<u>120,540</u>
TOTAL D & I		\$3,202,920
C. Contractor's Fee	10 percent of D & I	\$ 320,290
D. Contingency	10 percent of D & I	<u>320,290</u>
E. Fixed Capital Investment - 24 Kg hr ⁻¹		\$3,843,500
	- 1000 MT yr ⁻¹ (24 Kg hr ⁻¹ x 6)	\$23,061,000

TABLE 27. PRODUCT COSTS, PROCESS E

A. Manufacturing Cost		
1. Direct Production Cost		
a. Materials		\$11,300,000*
b. Operating labor		1,045,300
c. Supervisory and clerical	15 percent of b	156,800
d. Utilities		483,000
e. Maintenance and repairs	10 percent of fixed capital	2,306,100
f. Operating supplies	15 percent of e	345,920
g. Laboratory charges	15 percent of b	156,800
h. Patents and royalties	4 percent of product cost	1,002,330
2. Fixed Charges		
a. Depreciation	10 percent fixed capital	\$2,306,100
b. Local taxes	2 percent fixed capital	461,220
c. Insurance	1 percent fixed capital	230,610
d. Interest	6 percent fixed capital	1,383,660
3. Plant Overhead	60 percent of (1b + 1c + 1e)	\$2,104,920
B. General Expenses		
1. Administration	50 percent of 1b	\$ 522,650
2. Distribution	2 percent of product cost	501,170
3. Research and Development	3 percent of product cost	<u>751,750</u>
C. Total Product Cost		\$25,058,330
1. Product Cost, per kg		\$25.06

* Includes all cost (operating and capital investment) for the recovery of iodine by the wet process and the preparation of metallurgical grade silicon.

Process F

Although the wet-process iodine recovery avoids some of the high capital investment in HI recycle by condensation, this saving is more than offset by the $\$0.20 \text{ lb}^{-1}$ cost of I_2 recovery. Accordingly, Process F was investigated to determine the magnitude of the penalty involved in recirculation of the H_2/HI mixture without separation of the HI. To be practical, this option would not only have to have a cost advantage, but it would be necessary that shunting the hydrogen stream into the iodination section and bypassing the distillation column with part of the iodination product (noncondensibles in $\text{H}_2 + \text{HI}$) would not result in prohibitive contamination. This analysis treats only the economic factors involved.

In process F, the iodination and deposition efficiencies are interdependent. Accordingly, the generalized flow diagram shown in Figure 6 was prepared. A deposition efficiency (E) of 50% and an iodination efficiency (e) of 50% were assumed initially and substituted in the equation for the deposition product composition which was used in calculating a new value of the equilibrium iodination efficiency (e) by means of the computer program EQUICA. This result was then used to obtain a new value of E for the deposition byproduct, etc. After 16 iterations stable values of $e = 63.7 \pm 0.1\%$ for the iodination efficiency and $E = 27.7 \pm 0.1\%$ for the deposition efficiency were obtained. These values were chosen for the cost analysis based on the flow diagram of Figure 7. Data and results are given in Tables 28-32.

The need for a larger iodination unit and deposition reactor area than required in the other processes prompted the increased number of operators assigned to these two operations in Process E. Experience indicates that only 16 operators (4 per crew) should be required to monitor two condensers even though they are relatively large.

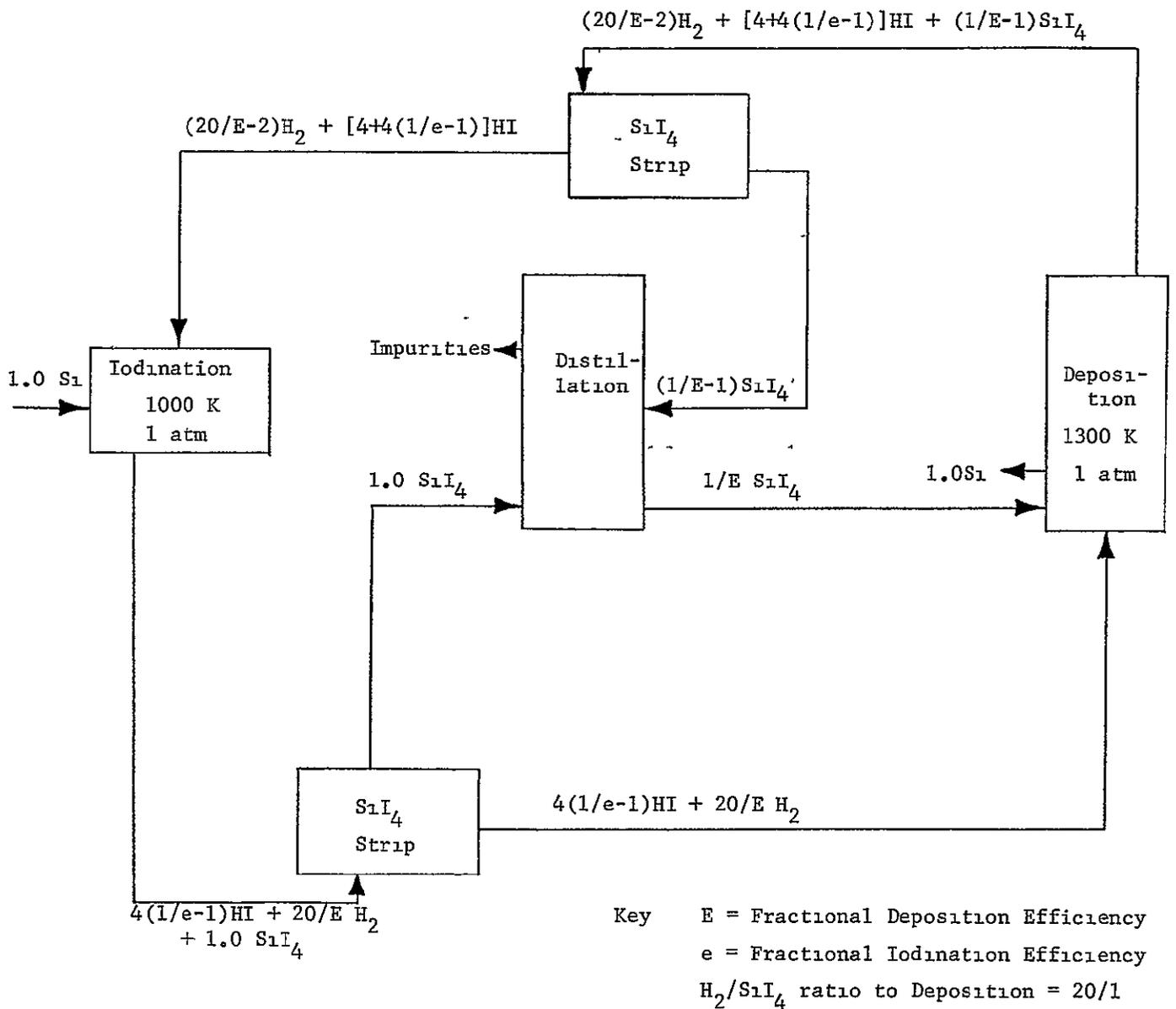


FIGURE 6. GENERALIZED FLOW DIAGRAM FOR RECIRCULATION OF UNSEPARATED H_2+HI , PROCESS F

TABLE 28. MAJOR EQUIPMENT COST, PROCESS F
(24 Kg hr⁻¹ Si)

Item	Function	Duty	Size	Cost
Reactor	Iodination of Si	457.7 Kg hr ⁻¹ SiI ₄	8.7 ft ²	62,000
Stripper	Remove SiI ₄ as liquid from H ₂ /HI	115.60 E4 BTU hr ⁻¹	60.8 ft ²	87,000
Scraper Condenser	Remove SiI ₄ as liquid from H ₂ /HI	21.86 E4 BTU hr ⁻¹	819 ft ²	570,000
Refrigerator (0°F)	Cool scraper condenser	21.86 E4 BTU hr ⁻¹	18.2 ton	26,200
Distillation Unit	Purify SiI ₄	1652 Kg hr ⁻¹ SiI ₄	20 ft x 16 in dia	40,200
Vaporizer	Vaporize SiI ₄	20.25 E4 BTU hr ⁻¹	337 ft ²	23,200
Preheater	Preheat SiI ₄ to 800K	6.96 E4 BTU hr ⁻¹	231 ft ²	17,000
Preheater	Preheat H ₂ + HI to 800K	88.82 E4 BTU hr ⁻¹	56.1 ft ²	8,300
Fluidized bed(s)	Deposit Si	24 Kg hr ⁻¹ Si	12.9 ft ²	315,000
Stripper	Remove SiI ₄ as liquid from H ₂ /HI	203.15 E4 BTU hr ⁻¹	71.4 ft ²	9,600
Scraper Condenser	Remove SiI ₄ as solid from H ₂ /HI	22.46 E4 BTU hr ⁻¹	840 ft ²	590,000
Refrigeration (0°F)	Cool scraper condenser	22.46 E4 BTU hr ⁻¹	18.7 ton	26,900
Preheater	Preheat H ₂ + HI	127.88 E4 BTU hr ⁻¹	58 ft ²	8,800
Blower (10 psi)	Circulate H ₂ + HI	76.5 moles/mole Si	940 cfm	22,900
Heat Exchanger	Waste heat disposal	185.30 E4 BTU hr ⁻¹		6,400
Subtotal				\$1,813,500
Total after index adjustment				\$1,937,000

TABLE 29. MATERIALS AND ENERGY COST, PROCESS F

Item	Condition	Cost, \$Kg ⁻¹ Si
Metallurgical grade Silicon	85% Utilization	1.17
I ₂	Wet recovery of 5% tops and 5% bottoms from distillation	0.80
I ₂	Loss or cost-balanced recovery of 0.5% of recycle load, 16.719 = atomic ratio I/Si	2.16
H ₂	1% loss of recycle load, 72.2 moles H ₂ /mole H ₂	<u>0.11</u>
	Total Materials	\$4.24
Electrical	Other than refrigeration, 25.97 Kwh Kg ⁻¹ Si (90% utilization)	0.778
	0° F refrigeration, 36.9 ton (24 Kg Si) ⁻¹ at \$0.05 ton ⁻¹ hr ⁻¹ Kg ⁻¹	<u>0.077</u>
	Total Electrical	\$0.85

TABLE 30. MANPOWER UNIT BREAKDOWN AND COST, PROCESS F
(6 x 24 Kg hr⁻¹ S₁)

Unit Operation	No. Operators
Iodination	24
Distillation	16
Deposition	28
Scraper Condensers	16 (8 unskilled)
Raw Material Handling	8 (unskilled)
Product Handling	8 (unskilled)
	100* (divided into 4 crews)
* 76 Skilled Operators at \$6.60 hr ⁻¹	(Equivalent manpower
* 24 Unskilled Operators at \$4.60 hr ⁻¹	hourly rate of \$612)
Operating Labor Cost yr ⁻¹ = \$1,541,380	(\$612 hr ⁻¹ x 2142 hr yr ⁻¹)

TABLE 31. FIXED CAPITAL INVESTMENT, PROCESS F

A. Direct Cost (D)		
1. Purchased equipment - E		\$1,937,000
2. Installation of E	40 percent of E	774,800
3. Instrumentation (Installed)	25 percent of E	484,250
4. Piping (Installed)	60 percent of E	1,162,200
5. Electrical (Installed)	15 percent of E	290,550
6. Buildings and Services	47 percent of E	910,390
7. Yard Improvements	10 percent of E	193,700
8. Service Facilities	40 percent of E	774,800
9. Land	6 percent of E	<u>116,220</u>
TOTAL DIRECT COST		\$6,643,910
B. Indirect Cost (I)		
1. Engineering and Supervision	15 percent of E	\$ 290,550
2. Construction Expenses	14 percent of E	<u>271,180</u>
TOTAL D & I		\$7,205,640
C. Contractor's Fee	10 percent of D & I	\$ 720,560
D. Contingency	10 percent of D & I	<u>720,560</u>
E. Fixed Capital Investment - 24 Kg hr ⁻¹		\$8,646,760
	- 1000 MT yr ⁻¹ (24 Kg hr ⁻¹ x 6)	\$51,880,560

TABLE 32. PRODUCT COSTS, PROCESS F

A. Manufacturing Cost		
1. Direct Production Cost		
a. Materials		\$4,240,000*
b. Operating labor		1,310,900
c. Supervisory and clerical	15 percent of b	196,635
d. Utilities		850,000
e. Maintenance and repairs	10 percent of fixed capital	5,188,060
f. Operating supplies	15 percent of e	778,210
g. Laboratory charges	15 percent of b	196,635
h. Patents and royalties	4 percent of product cost	1,199,590
2. Fixed Charges		
a. Depreciation	10 percent fixed capital	\$5,188,060
b. Local taxes	2 percent fixed capital	1,037,610
c. Insurance	1 percent fixed capital	518,810
d. Interest	6 percent fixed capital	3,112,830
3. Plant Overhead	60 percent of (1b + 1c + 1e)	\$4,017,360
B. General Expenses		
1. Administration	50 percent of 1b	\$ 655,450
2. Distribution	2 percent of product cost	599,790
3. Research and Development	3 percent of product cost	<u>899,690</u>
C. Total Product Cost		\$29,989,630
1. Product Cost, per kg		\$29.99

* Includes all cost (operating and capital investment) for the recovery of iodine by the wet process and the preparation of metallurgical grade silicon.

DISCUSSION

Cost Analysis

In the course of this process cost analysis, an effort was made to be conservative in the costing of individual process units and in assigning manpower loads. It is believed that this conservative approach will compensate for the cost of items overlooked in the analysis. For example, a small cost item for pelletizing the SiO_2/C mixture should have been added for Process C. However, the addition of this or similar omitted items should not alter the basic conclusions.

Figure 8 and Table 33 summarize the product costs estimated for Processes A-F. Labor-related costs have been consolidated as have capital-related costs. "Other" costs include patents and royalties, distribution, and research and development. It is clear that the fluidized bed zinc reduction of SiCl_4 (Process A), at an estimated cost of $\$9.12 \text{ Kg}^{-1}$, is the most economical process. Costs in all the individual cost categories shown in Table 33 are lowest for this process.

The hot wire iodide process starting with the iodination of metallurgical grade silicon (Process B) appears to be the most economical of the iodide processes at $\$20.65 \text{ Kg}^{-1} \text{ Si}$; however, the high power costs and large capital equipment costs prevent its being competitive with the fluidized bed zinc reduction of SiCl_4 . All of the potential improvements in the basic iodide process led to higher costs, as increased economies in one area of Processes C-F were more than offset by increased costs in another area.

Substituting the iodination of low cost SiO_2/C mixtures for the iodination of metallurgical grade silicon increased the capital cost because of the low efficiency of the iodination step. The increased anticipated loss or cost-balanced recovery of iodine due to the increased iodine recycle load results in a net increase in materials cost rather than a decrease.

The fluidized bed hydrogen reduction of silicon tetraiodide would be attractive relative to the "hot wire" process (B) if there were a good way to recycle the HI byproduct. Recycle by low temperature condensation (Process D) involves a large capital investment. Pressurizing the $\text{H}_2 + \text{HI}$

byproduct to 10 atm does not help much, in that a large fraction would still have to be condensed as a solid. There undoubtedly exists an optimum in saving on scraper condenser and refrigeration costs, as the pressure in the HI + H₂ recycle stream is increased or as residual HI is tolerated in

TABLE 33. ESTIMATED COST BREAKDOWN, PROCESSES A-F, \$Kg⁻¹ S₁

Item	Process					
	A	B	C	D	E	F
Materials	\$2.59	\$ 2.86	\$ 3.84	\$ 3.33	\$11.30	\$ 4.24
Utilities	0.34	5.92	6.41	1.02	0.48	0.85
Capital-related	3.15	7.41	10.20	19.24	8.42	18.94
Labor-related	2.22	2.60	2.80	2.84	2.60	3.26
Others**	<u>0.82</u>	<u>1.86</u>	<u>2.30</u>	<u>2.61</u>	<u>2.25</u>	<u>2.70</u>
Total	\$9.12	\$20.65	\$25.55	\$29.04	\$25.05	\$29.99

* Electrical only, see text.

** Patents and Royalties, 4% of total, Distribution, 2% of total, Research and Development, 3% of total.

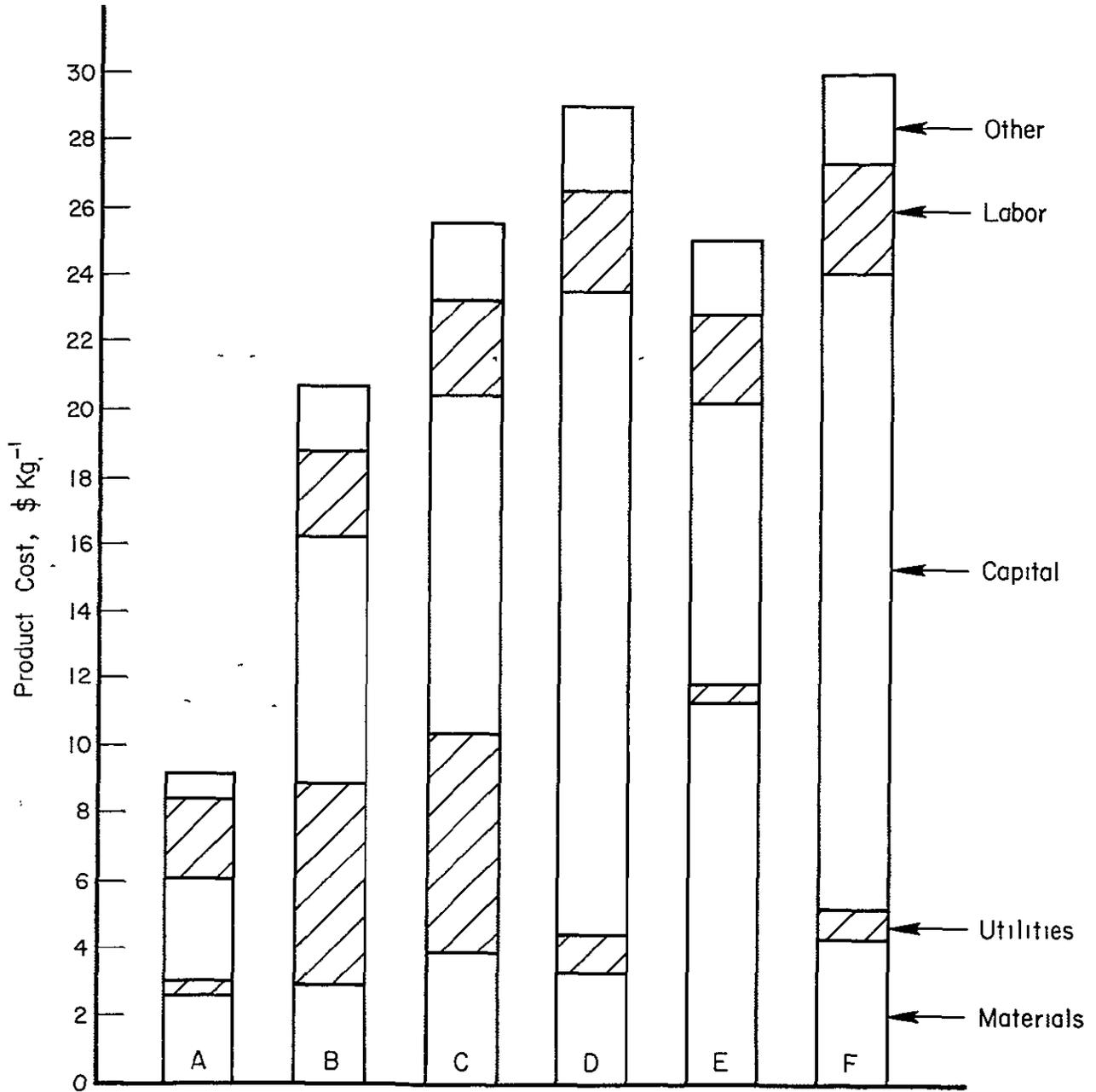


FIGURE 8. PRODUCT COST BREAKDOWN, PROCESSES A-F

the H_2 recycled to the deposition unit. Recycling the HI by scrubbing and wet-process I_2 recovery (Process E) loses out because of the high cost of the wet recovery operation.

Recycling the HI/ H_2 byproduct without separation of the HI (Process F) results in higher capital costs related to the larger units required to handle the increased volumes of gases at lower conversion efficiencies.

It will be recalled that Process G (hydrogen reduction of SiI_4 with iodination of SiO_2/C mixtures with the HI byproduct) was eliminated from the step-wise analysis by virtue of its low (<10%) iodination efficiency. Process H, (same as Process G but with the more efficient iodination with I_2 from wet recovery from HI) is also out of contention, because as pointed out above in the comparison of Processes B and C, iodination of SiO_2/C mixtures is actually more expensive than iodinating metallurgical grade Si, not less expensive, so no saving would be realized to offset the increased cost of wet recovery.

The most promising approach for improving the iodide process would be to optimize the recycle of the HI byproduct of Process D relative to pressurized condensation. However, even if the recycle cost were zero (equivalent to subtracting the wet process recycle cost from the Process E product cost), one would still have a product cost of $\$25.05 - \$11.30 = \$13.75 \text{ Kg}^{-1} \text{ Si}$.

The cost of Process D can probably be reduced below that of the "hot-wire" iodide process (B) by optimization, but it cannot be less than that of the zinc reduction of $SiCl_4$ (Process A).

It should be reemphasized that because of the conservative approach adopted in this initial analysis, the product cost of the zinc reduction might well be considerably less than the preliminary estimate (\$9.12). There are several known areas which if reevaluated might result in a product cost reduction. The first is the somewhat arbitrary adoption of the 15-in diameter fluidized bed size. In view of the exothermic nature of the zinc reduction of $SiCl_4$, a large diameter reactor might be used which could decrease capital investment and operating costs. A second area which would be reconsidered before designing a pilot plant would be the recovery of the zinc from zinc chloride. In the article by Meisel⁽⁸⁾ the total operating

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cost (exclusive of equipment depreciation) was given as $\approx \$0.13 \text{ Kg}^{-1} \text{ Zn}$. If one attempts to adjust this to account for only the cell room operation, the cost of electrolytic zinc recovery is reduced to the $\$0.07$ to $\$0.08^*$ Kg^{-1} range. In Process A an operating cost of roughly $\$0.27 \text{ Kg}^{-1}$ zinc recovery is calculated on essentially the same bases. This difference would appear to be larger than can be attributed to the differences in the aqueous and fused salt operations and would suggest the desirability of reevaluating the estimates for the molten salt recovery or possibly adoption of the aqueous process. A savings of $\$0.20 \text{ Kg}^{-1}$ zinc in recycle costs would result in a cost reduction of about $\$0.90 \text{ Kg}^{-1}$ silicon.

A third area which could be reviewed would be the maintenance and repairs cost of $\$862,440 \text{ yr}^{-1}$. This would seem excessive for this type of plant if it were not for the uncertainty at this time of the electrolytic cell requirements.

The point of the above discussion is to make the reader aware that there are obvious uncertainties in the factors which were used in the zinc reduction product cost estimate which, if properly resolved, would support the conclusion that a real potential exists for reduction of the product cost below the $\approx \$9 \text{ Kg}^{-1}$ estimated.

Energy Consumption

There exists an 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 34 gives the energy consumption estimated for the candidate processes A-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 process.

* Cost adjusted to reflect power cost of $\$0.03 \text{ Kwh}^{-1}$ instead of $\$0.008 \text{ Kwh}^{-1}$ used by Meisel⁽⁸⁾.

TABLE 34. PROCESS ENERGY COST, Kwh Kg⁻¹ Si

Process	Material	Added Cost Kwh Kg ⁻¹ Si	Basis*	Cost from Process Tabulation	Total Energy Cost, Kwh Kg ⁻¹	Reference Cell Payback Time, mo.
A	Zn	2.30 ⁽¹⁾	a	-	-	-
	Si-Cl 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

* For footnotes, see next page.

Footnotes to Table 34

- a. 1.02 lb Zn reprocessed (exclusive of in-plant recycle) per Kg Si at 2.25 Kwh lb⁻¹(8)
- b. 11.83 lb Kg⁻¹ Si, at 4 x energy cost of contained chlorine (1.65 Kwh lb⁻¹(15)), doubled for other costs, total = 2.75 Kwh lb⁻¹.
- c. 1.17 Kg Kg⁻¹ Si @ 11.39 Kwh Kg⁻¹(16).
- d. 4.73 lb I₂ reprocessed (exclusive of in-plant recycle) per Kg Si at energy cost for chlorine used in wet chlorination at 80% utilization efficiency, 0.58 Kwh lb⁻¹ I₂.
- e. No data readily available, not included.
- f. 5.12 lb I₂ reprocessed per Kg Si, see d.
- g. 4.50 lb I₂ reprocessed per Kg Si; see d.
- h. 0.07 lb H₂ consumed per Kg Si, @ 30 Kwh lb⁻¹ H₂ calculated on basis of cell potential of 2v⁽¹⁷⁾ and assumed 80% current efficiency.
- i. 44.3 lb I₂ reprocessed per Kg Si; see d.
- j. 4.83 lb I₂ reprocessed per Kg Si; see d.
- k. 0.11 lb H₂ used per Kg Si, see h.
- l. External Zn recovery of 0.46 Kg Zn Kg⁻¹ Si assumed to be 40% as efficient as in-plant recycle.

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 for 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^{-1} operation, allowing for 20% loss of silicon during cell manufacture, i.e., $20.5 \text{ Kwh mo}^{-1} \text{ Kg}^{-1}$.

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. 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.

RECOMMENDATIONS

In the light of the results of the foregoing analysis, it is recommended that no further work be done at this time with the iodide process(es), and that the effort be concentrated on building and operating a "miniplant" based on the fluidized bed zinc reduction of SiCl_4 to verify process operability and product quality and to obtain further engineering information to permit a more accurate product cost estimate.

It is recommended that for economy of construction and operation, the size of the "miniplant" be limited to that corresponding to a 2-inch diameter fluidized bed reactor for the reduction step. Deposition runs in a 2-inch reactor during the month of February, 1976 yielded silicon at rates of up to 83 g/hr on 180μ seed particles. Use of 400μ seed particles would permit increasing the throughput by $\left(\frac{400}{180}\right)^2$, which extrapolates to a production rate of $>400 \text{ g Si hr}^{-1}$. It is anticipated that the yields will be improved. However, even though yields are not improved, the capacity of a 2-in reactor should be more than adequate to obtain process data and to supply JPL with kilogram quantities of the product for evaluation.

REFERENCES

- (1) L. P. Hunt and E. Sirtl, "A Thorough Thermodynamic Evaluation of the Silicon-Hydrogen-Chlorine System", J. Electrochem. Soc., 119, (12) 1741 (1972).
- (2) L. P. Hunt and E. Sirtl, "The Equilibrium Behavior of the Silicon-Hydrogen-Bromine and Silicon-Hydrogen-Iodine Systems", J. Electrochem. Soc., 120 (6), 806-811 (1973).
- (3) D. R. Stull, et al., JANAF Thermochemical Tables, Dow Chemical Corporation, Midland, Michigan.
- (4) M. S. Peters and D. K. Timmerhaus, "Plant Design and Economics for Chemical Engineers", Second Edition, McGraw-Hill, Inc., New York, New York (1968).
- (5) R. S. Aries and R. D. Newton, "Chemical Engineering Cost Estimation", McGraw-Hill, Inc., New York, New York (1955).
- (6) Michael D. Winfield and Charles F. Dryden, "Chemical Engineering Costs", Dept. of Chemical Engineering, Ohio State University (621-1) (1962).
- (7) R. Threlfall, "The Electrolysis of Molten Zinc Chloride", Journal of the Society of Chemical Industry, Trans. 48, 210-223 (1929).
- (8) G. M. Meisel, "New Generation Zinc Plants, Design Features and Effects on Costs", Journal of Metals, 26 (8), 25-32 (Aug., 1974).—
- (9) Personal Communication with L. Hunt, Dow Corning Corp., Hemlock, Mich.
- (10) Chemical Marketing Reporter, Jan. 6, 1975.
- (11) L. P. Hunt, "Low Cost Processes for Integrated Solar Arrays", Second Quarterly Progress Report to N.S.F. (RANN) under U. of Pennsylvania Grant No. GI-29729, October 1974.
- (12) Personal Communication with G. F. Wakefield, Texas Instruments, Inc., Dallas, Texas.
- (13) Lead & Zinc Statistics, Volume XVI, No. 1, Jan. 1976, Monthly Bulletin of the International Lead and Zinc Study Group.
- (14) J. H. Perry, Chemical Engineers Handbook, Fourth Edition, McGraw Hill, New York (1963).
- (15) "Industrial Engineering Study of Industrial Chemicals", Intl. Res. & Development Corp. to U.S. Dept. Commerce and F.E.A., August 30, 1974.
- (16) W. T. Fairchild, Trans. Met. Soc. AIME, Paper No. A70-36 (1970).
- (17) E. R. Riegel "Industrial Chemistry", Reinhold, New York, N.Y. (1949).

APPENDIX A

EXPERIMENTAL SUPPORT

During this Second Quarterly Report period, the main objective of the experimental support work has continued to be the generation of operational data of value in judging the relative merits of the process options and the validation of the thermodynamic predictions. The two processes being evaluated in this program, zinc reductions of SiCl_4 and hydrogen reduction or thermal dissociation of SiI_4 , will be discussed separately below.

Zinc Reduction of SiCl_4

Three areas of the overall zinc reduction process received experimental attention this quarter; (1) fluidized bed deposition, (2) zinc recovery from molten ZnCl_2 by nonaqueous electrolysis, and (3) condensing and flow characteristics of Zn/ZnCl_2 mixtures.

Deposition of Silicon

The fluidized bed approach, general operating procedure, and equipment used during this quarter were presented and discussed in detail in the First Quarterly Report and will not be repeated. All the effort this period was concentrated on the introduction of zinc as a vapor rather than as a solid. Although addition of zinc as a solid is attractive from an operational point of view, the experimental results last quarter indicated the silicon product form to be needlelike and unacceptable.

Three basic methods of operating the fluidized-bed reactor in the zinc reduction process were explored: (1) the use of hydrogen as a diluent gas, (2) the use of an inert gas at ~50% dilution, and (3) the use of essentially no gas diluent (>90% SiCl_4 and zinc). In each case, the object was to increase reactor capacity by improved yield and/or reactant throughput.

As discussed in the First Quarterly Report, it is not expected from thermodynamic predictions that conversion efficiencies in the zinc reduction

of SiCl_4 would be improved by the use of hydrogen as a diluent at temperatures <1300 K. This work was continued and the results confirmed that experimental conversion efficiencies were no better than those predicted thermodynamically. The best of the hydrogen dilution experiment (32283-70-20) gave an efficiency of 21 percent and was operated under conditions for which thermodynamics would predict 30 percent conversion. The data for this run and other selected zinc reduction experiments were given in Table A-1. All hydrogen experiments conducted shared the same operational difficulty to varying extents, i.e., a lower-than-planned zinc vapor rate because of the cooling effect of the hydrogen carrier gas even after a preheater was installed in the hydrogen line. However, the information desired on the effect of hydrogen was obtained without completely eliminating this problem.

Most of the experiments made thus far have involved the use of diluent gasses considerably in excess of 50 percent. This was an expedient as far as fluidized bed operation is concerned, but severely penalizes the potential capacity of a given size of equipment by limiting the reactant throughput and resulting in a lower thermodynamic conversion efficiency. However, at dilutions below ≈ 50 percent, thermodynamics predicts much less effect on the efficiency: e.g., an increase from 70 to 72 percent between 50 and 0 percent inert/ SiCl_4 dilution at 1200 K and a stoichiometric Zn/ SiCl_4 mole ratio. Accordingly, a few experiments were made using lower dilution.

The best of the experiments performed at lower dilutions (No. 80-22) 1300 K, 1.95 Zn/ SiCl_4 mole ratio 54% argon dilution in SiCl_4 + argon resulted in an overall conversion efficiency of 60 percent (see Table A-1). A conversion of ~ 57 percent would be predicted thermodynamically for a deposition made under these conditions. These results give additional justification for assuming that >75 percent of the silicon formed in a fluidized-bed zinc-reduction system can be collected in a useful form. However, in this experiment the silicon production rate was only 29g hr^{-1} . This could be improved by using larger seed particles which would permit higher gas throughput (increase roughly proportional to the square of the ratio of the particle diameters). This could result in an increase in the rate to $100 - 200\text{g hr}^{-1}$ since a seed particle with an average size of only $180\ \mu\text{m}$ was used.

TABLE A-1. SUMMARY OF DATA FOR SELECTED EXPERIMENTS ON
 THE PREPARATION OF SILICON BY THE ZINC
 VAPOR REDUCTION OF SiCl_4 ^(a)

Run No.	70-20	80-22	80-23
Reaction Temperature °K	1300	1300	1200
Run Time, min	60	47	46
Reactant Composition m/o			
Zn	22.7	47.5	66.9
SiCl_4	36.0	24.3	28.6
Diluent gas	43.1 (H_2)	28.1 (Ar)	4.4 (Ar)
Total gas flow Moles hr^{-1}	9	9.6	14.9
Mole Ratio Zn/ SiCl_4	0.63	1.95	2.34
Total Silicon Deposited grams hr^{-1}	20.6	39.4	83.2
% Silicon on Bed	74	73	92%
Total Silicon Efficiency ^(b) (TD)	23	60	59
Thermodynamic Efficiency (TDE), %	30	57	65
TD % of TDE	76%	105	91

(a) 280 to 288g of 149 x 210 μm silicon seed used in all experiments.

(b) Based on silicon available in SiCl_4 used.

Such a production rate in a 2-in-ID reactor is not particularly attractive from a scale up point of view and as originally anticipated a system employing essentially no diluent gas probably will be required to achieve the economic goals of this project. Since the use of a nondiluent system presented more critical design problems than a diluent system, the latter was scheduled for the initial work to expedite obtaining operational data on the process to quickly establish technical feasibility or confirm reliability of the thermodynamic predictions. After this was achieved the experimental effort was directed towards the feeding of essentially 100 percent reactants.

A series of experiments were performed this quarter in which essentially no diluent was used. Data for these experiments are given in Table A-1. The fluidized bed reactor used previously was modified so that both reactants could be introduced into the bottom of the fluidized bed without the use of a carrier gas as shown in Figure A-1. This was accomplished by employing a conical bed support and one centered inlet orifice surrounded by four smaller orifices, spaced roughly midway between the center inlet and the reactor wall. The center inlet was isolated from the outer inlets and connected to a SiCl_4 flash vaporizer located external to the reactor tube. The outer inlets were connected to a zinc boiler also located external to the reactor. The SiCl_4 flow was effectively controlled by a liquid SiCl_4 flow meter/valve system. However, the zinc flow rate was controlled by power input (Zn rate/power input determined experimentally). A rough on-stream guide to the flow was provided by the pressure drop obtained across the inlet orifices.

Three experiments with the equipment described above indicated that the fluidized-bed system could be operated with essentially no non-condensable carrier gas flow. The best experiment (No. 90-23, see Table A-1) gave an overall silicon efficiency of 59 percent which is ≈ 91 percent of that predicted thermodynamically (65 percent). This represents 83 g hr^{-1} of silicon in a 2-inch system using a seed particle with an average size range of 149 to 210 μm .

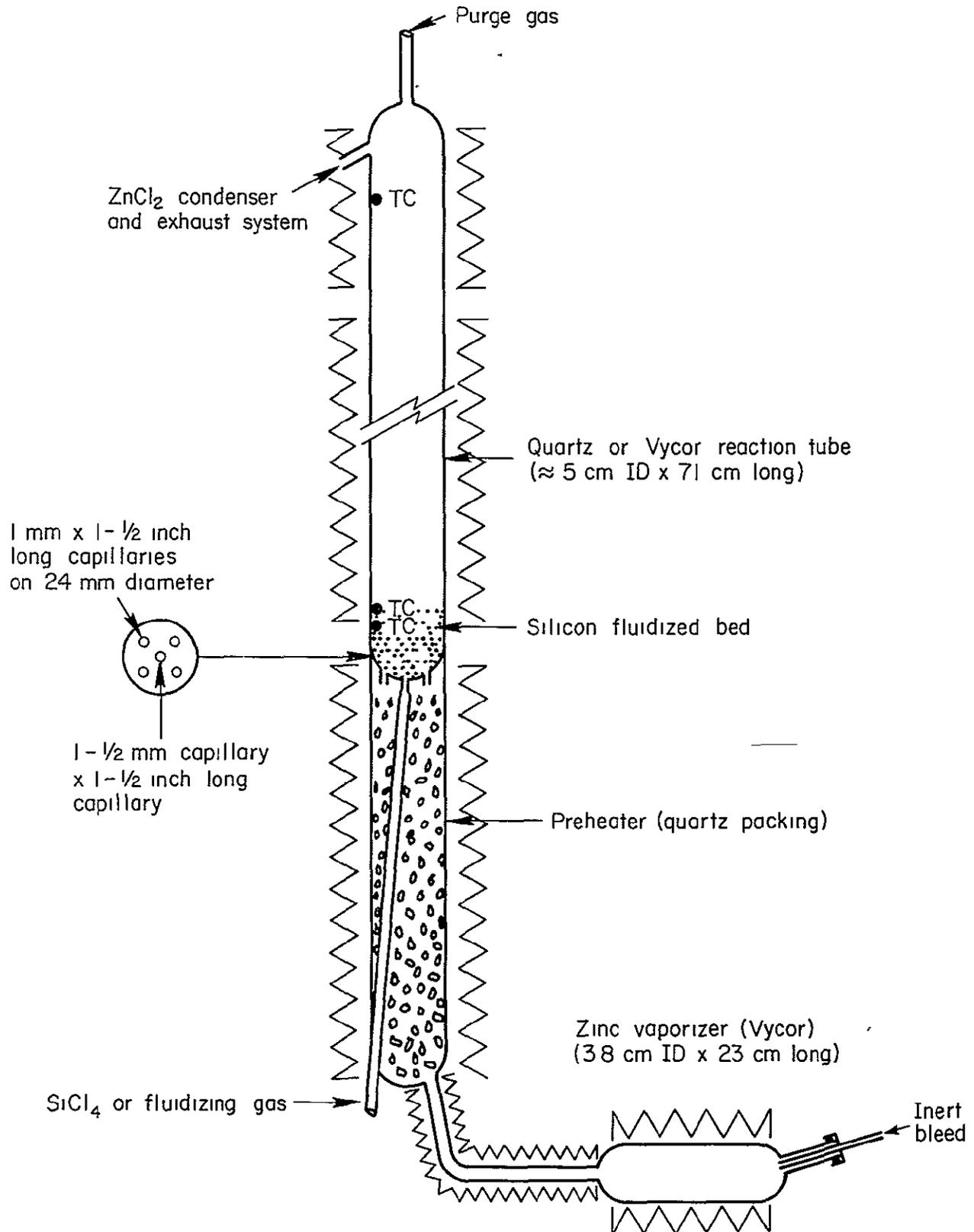


FIGURE A-1. SCHEMATIC DIAGRAM OF REACTOR FOR THE PREPARATION OF SILICON BY THE ZINC (VAPOR FEED) REDUCTION OF SiCl₄

Of this silicon 77 g hr^{-1} was collected on the seed bed, representing 92 percent of the silicon formed. Seed particles of a minimum size of $>350 \text{ }\mu\text{m}$ have been used in systems of this size, which would extrapolate to higher permissible gas flow with anticipated production rates of $>400 \text{ g hr}^{-1}$ without assuming any further improvement in yield efficiency. This production rate should be sufficient to accomplish the goals of the "miniplant" in the recommended next phase of this program.

Electrolysis of Molten Zinc Chloride

Early in the program it was tentatively concluded that a molten ZnCl_2 electrolysis process developed by Threlfall⁽⁷⁾ would be suitable for the recovery of zinc required by the zinc reduction process. Recently a detailed analysis by Meisel⁽⁸⁾ of an aqueous electrolysis system for zinc recovery from ZnSO_4 suggests that this conclusion should be reviewed before a decision is made on a final plant design. However, it still appears that having to cool the ZnCl_2 to essentially room temperature and remelt the zinc formed, as required by the use of the aqueous process, offsets the additional cost associated with operating a molten salt cell (if indeed there are significant cost differences).

If it was deemed necessary to determine if a cell of the general type developed by Threlfall, would operate satisfactorily with a $\text{Zn}/\text{ZnCl}_2/\text{Si}$ mixture considered representative of a typical condensate from the zinc reduction of SiCl_4 . In Threlfall's work, a high purity ZnCl_2 was used.

The electrolysis unit shown in Figure A-2 was constructed for the present work. This cell consisted of a Type 304 stainless steel container (≈ 5 inches in diameter by 6 inches high) with a Pyrex liner ($\approx 1000 \text{ cm}^3$ capacity). Two grooved graphite electrodes isolated from each other and the metal container were introduced through the top. The cell had an opening in the top for venting chlorine, vaporized ZnCl_2 , and SiCl_4 (if any) into appropriate trapping equipment. Provisions were made for heating the ZnCl_2 initially; however, no additional heat was required after the salt was up to temperature and electrolysis had been initiated. A silicon rectifier power supply was used. The cell was operated at $\approx 500 \text{ C}$, ≈ 36 amperes, and ≈ 10 volts. Two experimental runs were made with the results given in Table A-2.

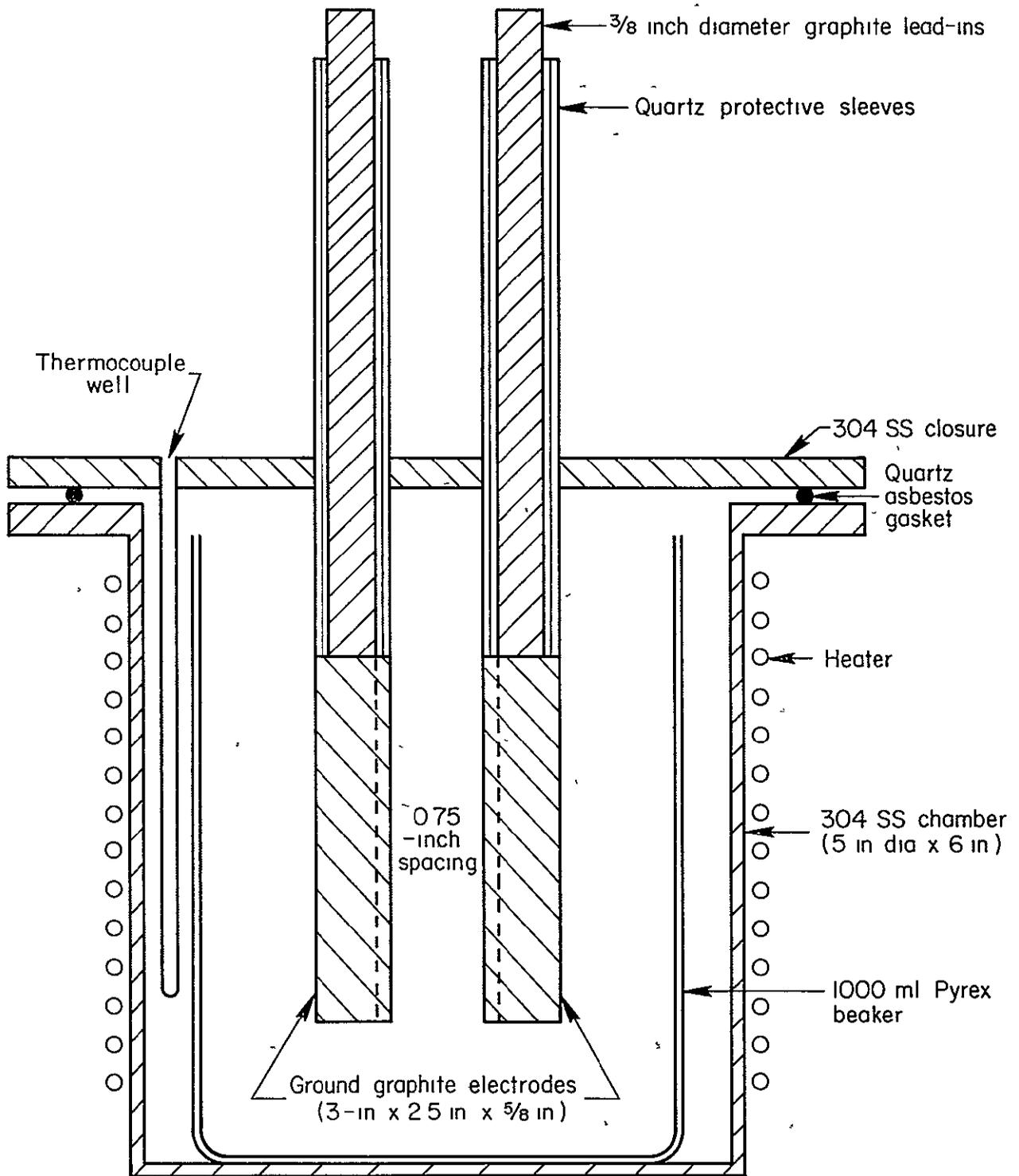


FIGURE A-2. SCHEMATIC DIAGRAM OF ELECTROLYTIC CELL FOR RECOVERY OF ZINC FROM MOLTEN ZINC CHLORIDE

TABLE A-2. SELECTED DATA ON ELECTROLYSIS OF MOLTEN $ZnCl_2$

Run No.	32-1	35-2
Cell temperature °C	496-526	480-530
Salt composition	100% $ZnCl_2$	77.9% $ZnCl_2$ 17.3% Zn 4.8% Si
Voltage	10 to 10	9.4 to 15.7
Current, amp.	30 to 42	24 to 36
Time, min	70	120
Zinc produced, g	36.5	57.2
Current efficiency, %	70	67

In the first experiment, $ZnCl_2$ was used, and in the second a mixture of $ZnCl_2$, zinc powder, and silicon powder (77.9 percent $ZnCl_2$, 17.3 percent Zn, 4.8 percent Si), considered to be representative of a possible condensate from the zinc reduction of $SiCl_4$, was evaluated. Essentially, no difficulty was encountered in either experiment. As indicated above, the temperature of the $ZnCl_2$ was maintained without external heating at the current/voltage conditions given, which limited the current that could be employed. Even in this crudely designed cell, electrolyzed zinc current efficiencies of 70 percent were obtained. As a result of this work, it was concluded that the information generated earlier by Threlfall⁽⁷⁾ on the electrolysis of pure $ZnCl_2$ is suitable for use in making the "choice of process".

Condensate Flow

A key factor in the zinc-reduction process is the recycle of the unreacted zinc and recovery of the zinc from the zinc chloride. In order for this to be accomplished effectively, the product of a 500 C condenser, designed to collect the major portion of the zinc and zinc chloride leaving the deposition chamber, must flow freely from this condenser to the electrolytic cell used to recover the zinc.

An experiment was designed to evaluate the flow properties of the Zn/ZnCl₂ condensate. A 2.5 cm ID x 50 cm-long tube was mounted slightly inclined. A temperature gradient from 900 to 185 C was maintained over the length of this tube with the lowest end being the coolest. At the higher end SiCl₄ was reacted with zinc vapor. This system was operated until a product was visible at the lower cooler end. The tube was then cooled and examined. It could be easily noted that the Zn/ZnCl₂ condensate had flowed down the tube into a zone roughly estimated to be in the 200 to 300 C temperature range. This would indicate that no difficulty should be encountered with the flow properties of this condensate.

Hydrogen Reduction Or Thermal Dissociation of SiI_4

Experimental work on the iodide process was continued this quarter in two areas. (1) Deposition of silicon by hydrogen reduction of SiI_4 and (2) Iodination of C/SiO_2 mixtures to form SiI_4 . The latter is a continuation of the work initiated in this area last quarter, but the former is a new area in which exploration was considered necessary.

Deposition of Silicon by Hydrogen Reduction of SiI_4

Previous work at Battelle had demonstrated that silicon of acceptable semiconductor grade could be prepared in a hot wire or a hot wall deposition unit by either the thermal dissociation or hydrogen reduction process. However, no fluidized bed experience was gained with either of these systems. Since the fluidized-bed approach was considered to be economically attractive, it was deemed advisable to explore its use with a hydrogen reduction system. The thermal dissociation system must be carried out at reduced pressure to achieve practical conversion efficiencies. Accordingly, since fluidized bed operations are not well suited to reduced pressure operation, they were not considered for use in this application.

The reactor employed in the zinc reduction work was modified as shown in Figure A-3 for use in the hydrogen reduction of SiI_4 experiments. As can be seen in Figure A-3 the modification consisted mainly of installing a SiI_4 vaporizer for introducing this material into the bottom of the fluidized bed along with the desired amount of hydrogen. Only two hydrogen reduction experiments were made in this equipment. The data for the run free of operational problems (No. 87-21) are given in Table A-3.

These results reinforce those obtained in a previous program which indicated that actual conversion efficiencies in the hydrogen reduction of SiI_4 systems can be expected to be somewhat greater than those predicted thermodynamically. These results also verify that hydrogen reduction of the iodide can be handled in a fluidized bed without any apparent difficulty.

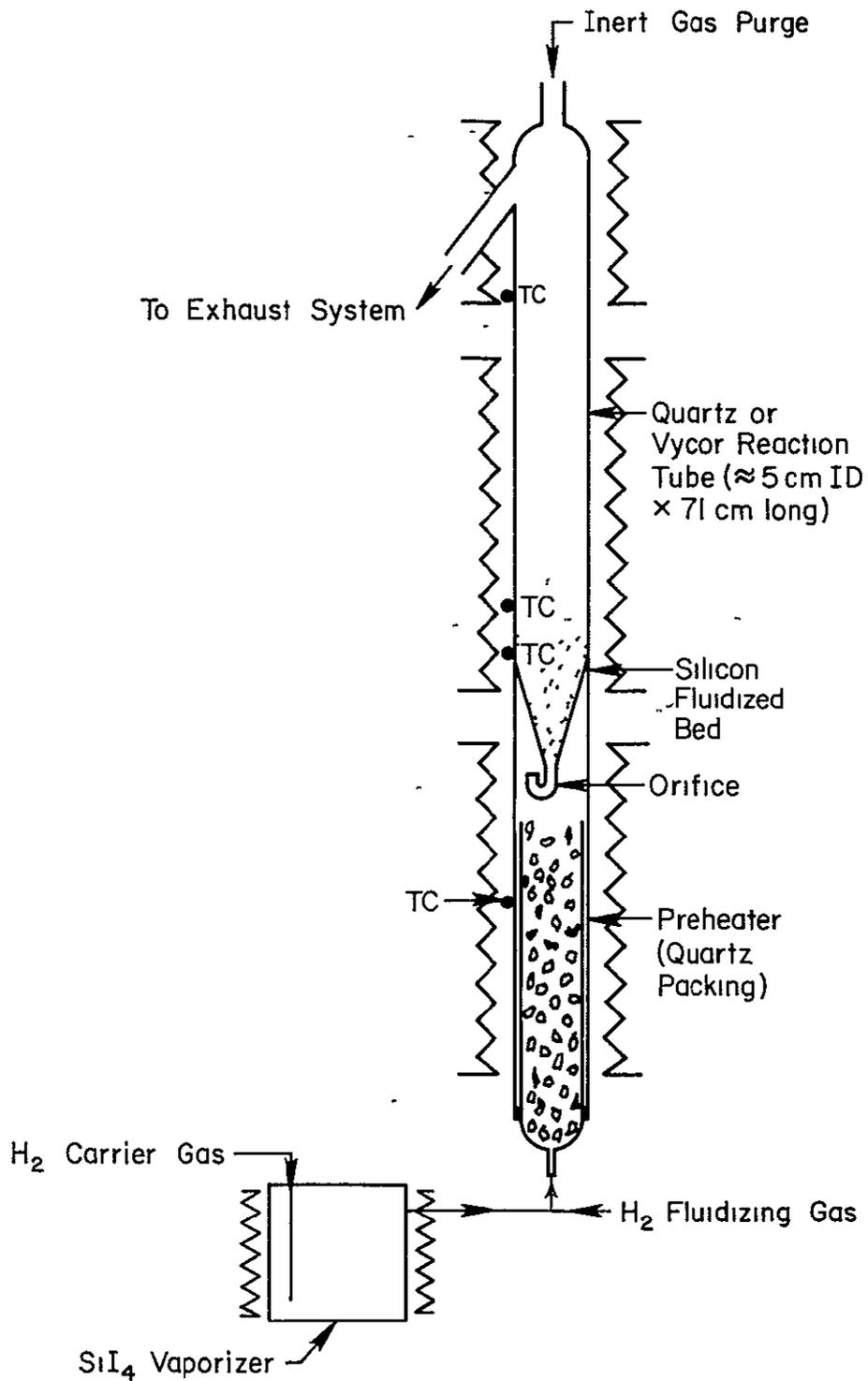


FIGURE A-3. SCHEMATIC DIAGRAM OF REACTOR FOR THE PREPARATION OF SILICON BY THE HYDROGEN REDUCTION OF SiI_4 IN A FLUIDIZED BED

TABLE A-3. DATA ON THE PREPARATION OF SILICON
BY THE HYDROGEN REDUCTION OF SiI_4

Run No.	87-2I
Bed temperature	1323K
Preheater temperature	673K
SiI_4 vaporizer temperature	445 to 460K
H_2/SiI_4 mole ratio	32
Run time	40 min.
Si deposited	12g
Overall efficiency	66%
Efficiency interpolated from prior thermodynamic calculations	56%

Iodination of $\text{SiO}_2 + \text{C}$ to Form SiI_4

Experimental work was continued this quarter on the formation of SiI_4 by the iodination of $\text{SiO}_2 + \text{C}$ mixtures. The purpose of this additional work was to (1) explore variations of selected operating parameters and (2) eliminate operational problems experienced in the earlier work which decreased the reliability of the earlier results. In the previous work the dilution and SiI_4 vaporization rates were not as constant throughout the experiments as desired. In addition, it was deemed desirable to evaluate lower iodine flow rates and $\text{SiO}_2/\text{carbon}$ mixtures containing a larger amount of carbon than had been used previously. The data for the iodination runs are given in Table A-4.

TABLE A-4. SELECTED DATA FOR IODINATION
OF SiO_2 + CARBON

Run No.	14-7	18-8
Reaction temp. K	1800	1800
Run time, min.	130	158
I_2 , g	200.0	200.0
Argon, liters	130	15.8
C/ SiO_2 mixture, % carbon	29	44
SiI_4 , g	34.3	51.1
I_2 converted, % ^(b)	16.2	24.2
Thermodynamic prediction of I_2 converted, %	(a)	(a)

(a) Cannot be reliably predicted--see Appendix B.

(b) Based on quantity of SiI_4 collected.

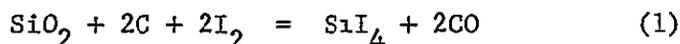
These results confirmed the conclusion that iodine conversion efficiencies of no more than 30 percent can be expected from this system even at temperatures as high as 1800 K. This relatively low efficiency coupled with the high temperature and costly iodine separation/recycle makes this system much less attractive than the iodination of metallurgical-grade silicon.

APPENDIX B

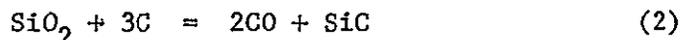
Thermodynamics of the I₂-SiO₂-C System

In the initial thermodynamic study of the iodination of SiO₂ + C mixtures, the data (Table 10 of the First Quarterly Report) showed inflections which did not seem consistent with the simple appearance of SiC as the carbon-containing solid phase at 1700 K and above. Further study of the system revealed four ranges of solid phase stability with four different temperature dependencies of equilibrium iodination conversion efficiency, and a fifth range of non-equilibrium conversion. This complexity makes it difficult to relate the results of simple iodination experiments to thermodynamic predictions.

The complexity of this system results from the competing reactions:



and



The key to understanding the thermodynamic behavior of the system lies in the equilibrium partial pressure of CO (CO₂ is a minor species at these temperatures). In Figure B-1, the solid line shows the partial pressure of CO over the system where the three solid phases SiO₂ + C + SiC coexist. This CO partial pressure is fixed by temperature according to Reaction 2 above and is independent of Reaction 1. At temperatures above 1785 K the CO partial pressure exceeds 1 atm, and in a system operating under 1 atm ambient pressure, Reaction 2 will proceed spontaneously, limited in rate only by solid-solid diffusion kinetics. Under these conditions the efficiency of the concurrent Reaction 1 cannot be predicted on the basis of thermodynamics. This is the range (fifth) of non-equilibrium conversion efficiency mentioned above.

Where the partial pressure of CO of Reaction 2 lies below 1 atm (T < 1785K), Reaction 2 will proceed (at 1 atm of I₂ fed) only as rapidly as it is displaced by I₂ or SiI₄ from Reaction 1. At temperatures below ≈ 1620 K, the partial pressure of CO from Reaction 1 (dashed line, Figure B-1) exceeds that of Reaction 2 and the formation of SiC is suppressed, that is

B-2

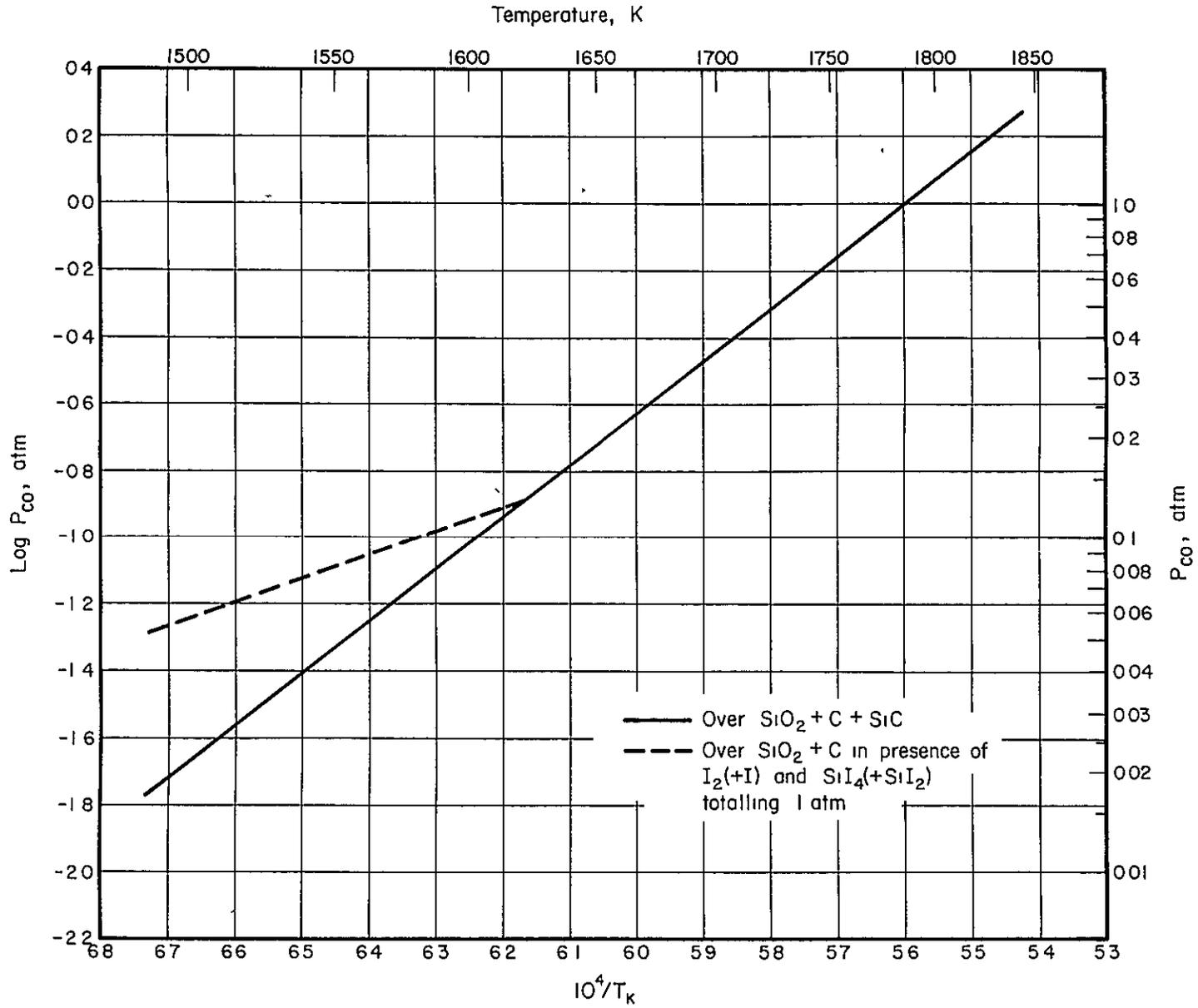
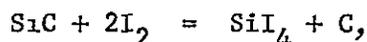


FIGURE B-1. EQUILIBRIUM CO PRESSURE VS. TEMPERATURE

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SiC is not formed. This is the first of the four equilibrium ranges mentioned above, i.e. where SiO₂ and C are the solid phases and the evolution of CO (plus small quantities of CO₂) is stoichiometrically related to the conversion of SiO₂ to SiI₄ (assuming SiI₂(g) produced at equilibrium reacts with unreacted I₂ downstream).

Above 1620 K, one enters the second equilibrium range, where SiO₂, C, and SiC are the solid phases present. Iodination in this regime continues until carbon is consumed in forming the SiC. At this point SiO₂ and SiC are the solid phases (third range) and the iodination proceeds under new equilibrium conditions until SiO₂ is consumed (assuming enough carbon is available), whereupon the system enters the fourth range where SiC is iodinated without the evolution of CO according to



leaving a residue of carbon. If the carbon supply (as SiC) were limited relative to SiO₂, iodination in the third range would cease when the SiC in the presence of SiO₂ was consumed, SiO₂ would be the residue, and the fourth region (iodination of SiC above) would not be entered.

Table B-1 shows, for example, the amounts of SiI₄ formed in the iodination at 1750 K of 4.13 moles of SiO₂ and 11.73 moles of carbon in the second, third, and fourth ranges, showing the efficiency of iodine conversion and the mole ratio of CO (+CO₂) to SiI₄ in the reaction products at each stage, and the weighted average conversion efficiency for the overall reaction.

The weighted average efficiency of the 1750 K reaction, 24.6%, compares with a predicted 20.3% at 1600 K in the first range of equilibrium where no SiC is formed. Thus, little is gained in equilibrium conversion by going to 1750 K, to say nothing of the complexity of the reaction. However, preliminary experimental data indicate that the reaction may be kinetically limited at 1600 K. Despite the uncertainty, this condition was chosen for the energy and mass flow calculation of Process C.

Figure B-2 shows the effect of hydrogen addition on the iodination of SiO₂-C mixtures in the first (SiO₂+C), second (SiO₂+C+SiC) and third (SiO₂+SiC) equilibrium ranges. Note that 50% H₂ addition is the equivalent

TABLE B-1. IODINATION AT 1 ATM OF 4.13 MOLES SiO₂ + 11.73 MOLES C AT 1750 K THROUGH THE SECOND,²THIRD, AND FOURTH EQUILIBRIUM RANGES*

Range	Solid Phases	Product Moles SiI ₄ **	I ₂ Conversion Efficiency, %**	CO/SiI ₄ **
2	SiO ₂ , C, SiC	0.11	10.6	74
3	SiO ₂ , SiC	0.53	53.0	0.67
4	SiC (+C)	3.49	20.8	0
	Total	<u>4.13</u>	Wtd. avg. <u>24.6</u>	

* The formation of small amounts of SiO(g) and back reaction to SiO₂ (0.03 moles) in the reaction products is ignored in this tabulation.

** SiI₂(g) at equilibrium assumed to form SiI₄(g) with unreacted I₂ downstream.

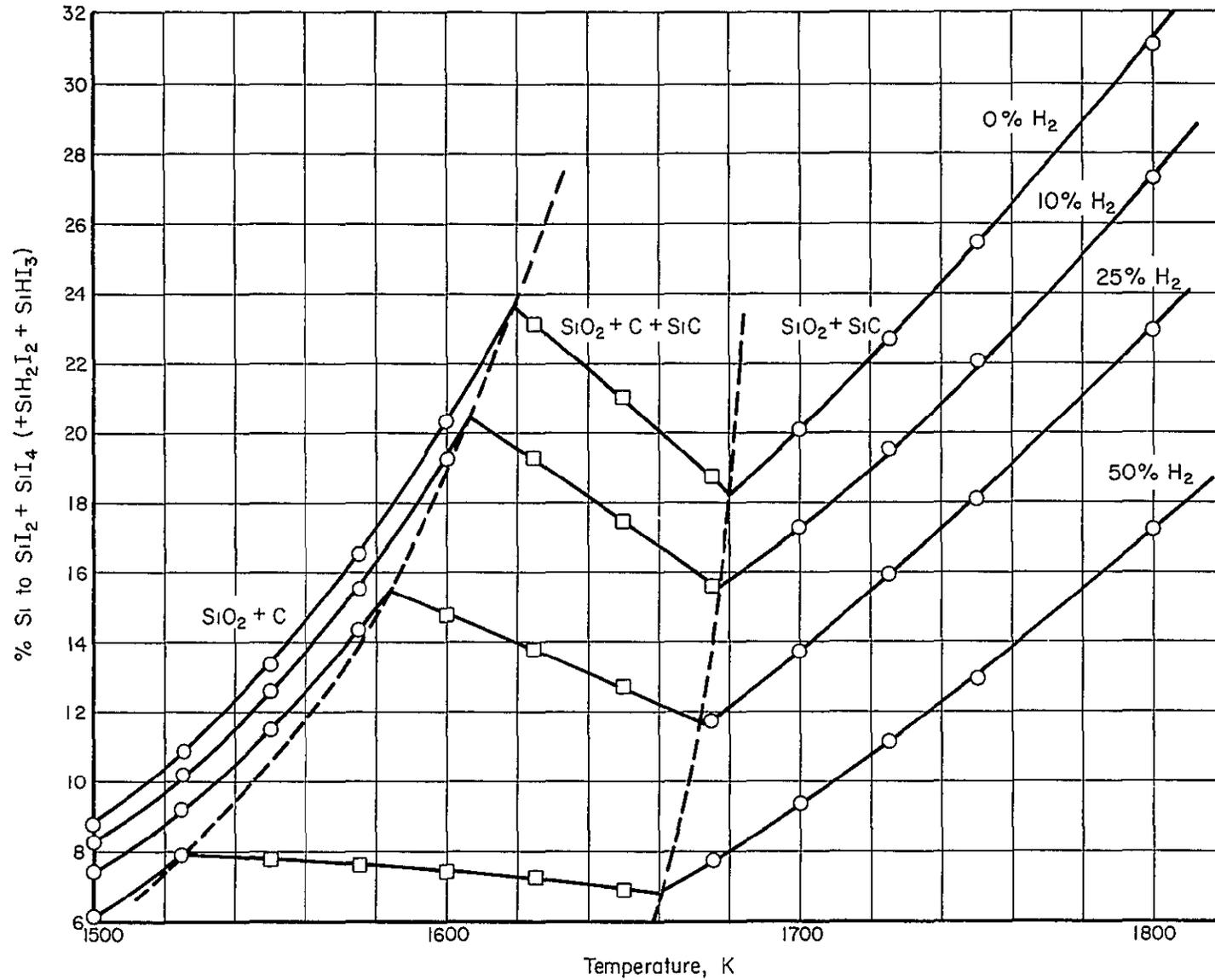


FIGURE B-2. IODINATION OF SILICON OXIDE-CARBON MIXTURES

(Equilibrium conversion as functions of temperature and percent H₂ added to I₂(g), showing region of stability of solid phases starting with stoichiometric C/SiO₂ ratio = 2/1)

C-2

of iodination with HI in place of I_2 . This condition corresponds to Process G. The inflections of equilibrium conversion as a function of temperature from one range to another are striking. Because of the complexity of this system, it is impossible to quantitatively check the thermodynamic predictions with a few simple iodination experiments, and the potential for use of the system is not sufficient to justify a detailed experimental study. The most that can be done is to show that the predictions are "in the ball park".