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THIRTEENTH QUARTERLY PROGRESS REPORT
Covering the Period October 1 to December 31, 1978

on

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

JPL Contract 954339

Silicon Material Task
Low-Cost Solar Array Project

to

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY

by

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

February 15, 1979

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES (Continued)

TABLE

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ABSTRACT

Refinements of the design of the 50 MT/year Experimental Process System Development Unit (EPSDU) have been made and competitive bids have been received from mechanical, electrical, and structural contractors. Bids on most of the equipment have been received and cataloged. Emergency procedures have been defined to counter a variety of contingencies disclosed in operations and safety reviews.

Work is being continued with the fluidized-bed model to define conditions under which useful segregation of large particles can be obtained. Experimental work with an electrolytic cell for zinc chloride disclosed no significant increase in power efficiency by steps taken to increase electrolyte circulation.

On the basis of materials compatibility and permeability tests, 310 stainless steel was chosen for the shell of the fluidized-bed reactor and SiC-coated graphite for the liner.

Experiments on the volatility of lead, iron, and cadmium at the ppm level in zinc at its boiling point are being continued with provisions being made to withdraw molten samples so as to avoid segregation on freezing, believed to be the cause of earlier discrepancies.

INTRODUCTION

This Thirteenth Quarterly Report is the second of the Phase III effort at Battelle's Columbus Laboratories (BCL) for DOE/JPL on the Evaluation of Selected Processes for the Production of Low-Cost Silicon. Phase III is directed toward the construction and operation of a 50 MT Si/year Experimental Process System Development Unit (EPSDU)* for the production of granular semiconductor-grade silicon by the zinc vapor reduction of silicon tetrachloride in a fluidized bed of seed particles.

During this report period, in addition to the EPSDU-oriented work, supportive activities have been carried out that will facilitate timely and trouble-free progress in establishing the EPSDU once the authorization to initiate construction is given.

Consistent with the format used in the past, this report is divided into two sections, the first dealing with the actual design and costing of the EPSDU, and the second, with the concurrent experimental support program.

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* The designation of the 50 MT/year facility was changed to "Experimental Process System Development Facility" (EPSDU) in Unilateral Modification No. 15 (July 19, 1978) of the contract for this work, No. 954339. However, the old term "Experimental Process Facility" (EPF) was continued in use through the Eleventh/Twelfth Quarterly Report and the Final Report on Phases I and II of the Program, DOE/JPL 954339, dated July 9, 1978, and issued in January, 1979. The new term will be used in this and subsequent reports.

DESIGN OF THE EXPERIMENTAL PROCESS SYSTEM DEVELOPMENT UNIT (EPSDU)

The design of the EPSDU was completed at Raphael Katzen Associates International, Inc. (RKAII), with the cooperation of BCL personnel. No basic changes have been made in the design since those discussed in the Eleventh/Twelfth Quarterly Report. Refinements have included:

(1) Silicon tetrachloride purification system
   (a) Storage tanks TK1 and TK2 reinstrumented to operate at gas-purge pressure (<1/2 psig) instead of purification-system pressure (10 psig) for increased safety
   (b) By-pass circuits provided on pumps to permit operation under more variable load situations

(2) Reactor
   (a) Tap closure design modified to simplify assembly
   (b) Sight port and silicon seed values redesigned to improve performance
   (c) Support structure modified to simplify installation and removal
   (d) Distributor plate redesigned to simplify and enlarge zinc inlet annulus
   (e) Shell to be fabricated by rolling 3/16-inch plate instead of using pipe, to facilitate delivery and lessen size restriction
   (f) Preferred liner candidate changed from sintered SiC to SiC-coated graphite because of the probability of improved silicon product purity and decreased permeability

(3) Reactor furnace
   (a) Reactor furnace modified to include two 20 kw and three 10 kw individually controlled heated zones to enhance reactor temperature control

(b) Design voltage changed from 220-volt to 440-volt service to be compatible with a centralized power control

(4) Reactor Condenser

(a) Therminol "66" (liquid at ambient temperatures) substituted for "88" (solid at ambient temperatures) to eliminate the need for a heat-up system, in view of the fact that the condenser has been redesigned to operate at 350 C instead of 500 C

(5) Zinc and zinc chloride storage tanks

(a) Design details of inlet, purge, instrumentation feed-through modified to assure more positive seal and simplify construction

(6) Electrolytic cell

(a) Design modified to accept Glassrock sheet in place of a castable insulation to minimize a potential contamination and improve resistance to chlorine

(b) Zinc outlet redesigned to overcome anticipated operational problems

(c) Use of water-cooled electrical bus system adopted to simplify installation and repair

(7) Zinc vaporizer

(a) Design modified to include bottom inlet, top outlet, and baffles to improve operability

(b) Zinc control valve between vaporizer and zinc storage attached to vaporizer support to enhance operation and facilitate shut-down

(8) Chlorine supply altered significantly upon recommendations of the BCL safety group

(9) Selected equipment added and duplicated as indicated by an emergency analysis involving loss of

power, cooling water, or instrument air, and

events such as fire, flood, and tornado.

In addition to the above-specified modifications, numerous small details have been altered as required to accommodate problems with material availability, materials compatibility, and equipment assembly, and to account for identifiable potential operational problems.

EPSDU Model

As part of the design activity, two models of the EPSDU have been made, one primarily for display purposes, consisting of only the Reactor/Recovery section of the facility (Figures 6 and 7 of the Eleventh/Twelfth Quarterly Report), and the other, a 1/16 scale model of the entire facility. The latter, delivered to BCL in November, 1978, was constructed (1) to facilitate the layout and piping phases of the design, (2) to aid construction contractors in cost estimation, and (3) to serve as reference during construction. Figures 1 through 4 show four views of the model.

Bid Procurement

Specifications for all items of individual equipment have been sent out for bids and replies have been received from most of the vendors and catalogued. It is too early to refine the equipment cost estimate. However, many bids are falling close to the estimates made originally. As soon as all bids have been received, a new estimate of total equipment cost will be made.

The tabulation below shows the contractor bids received for construction of the EPSDU.

Bids received from three each of mechanical contractors and electrical contractors came within 17 percent of the average for each group. Bids from the three structural/concrete contractors agreed to within 3 percent of the average. If the next lowest of the four electrical contractor's bids is added to the lowest bids of the other contractors, the total is very

FIGURE 1. SILICON TETRACHLORIDE STORAGE AND PURIFICATION

Tanks for storage of purified and crude $SiCl_4$ are shown in the center, upper level, with a tank for emergency $SiCl_4$ storage below. Part of the system for purifying $SiCl_4$ by distillation is shown on the left.

FIGURE 2. FLUIDIZED-BED REACTORS

The two vertical fluidized-bed reactors are shown left of center. The one on the right is enclosed by a (transparent) furnace and is provided with a product-withdrawal tank below. The reactor on the left has been stripped for maintenance. The zinc vaporizers are shown to the right and left just behind the product-withdrawal tank. The $SiCl_4$ vaporizer is located to the left and just behind the 6-foot model person in the right foreground.

FIGURE 3. RECOVERY-RECYCLE SECTION

The vertical condensers for $ZnCl_2$ are shown at the highest point above and to the left of the $ZnCl_2$ storage tank in the center. Below the $ZnCl_2$ storage tank are the electrolytic cells which feed the zinc storage tank at the lowest level. In this view, the fluidized-bed reactors are in the rear just left of center.

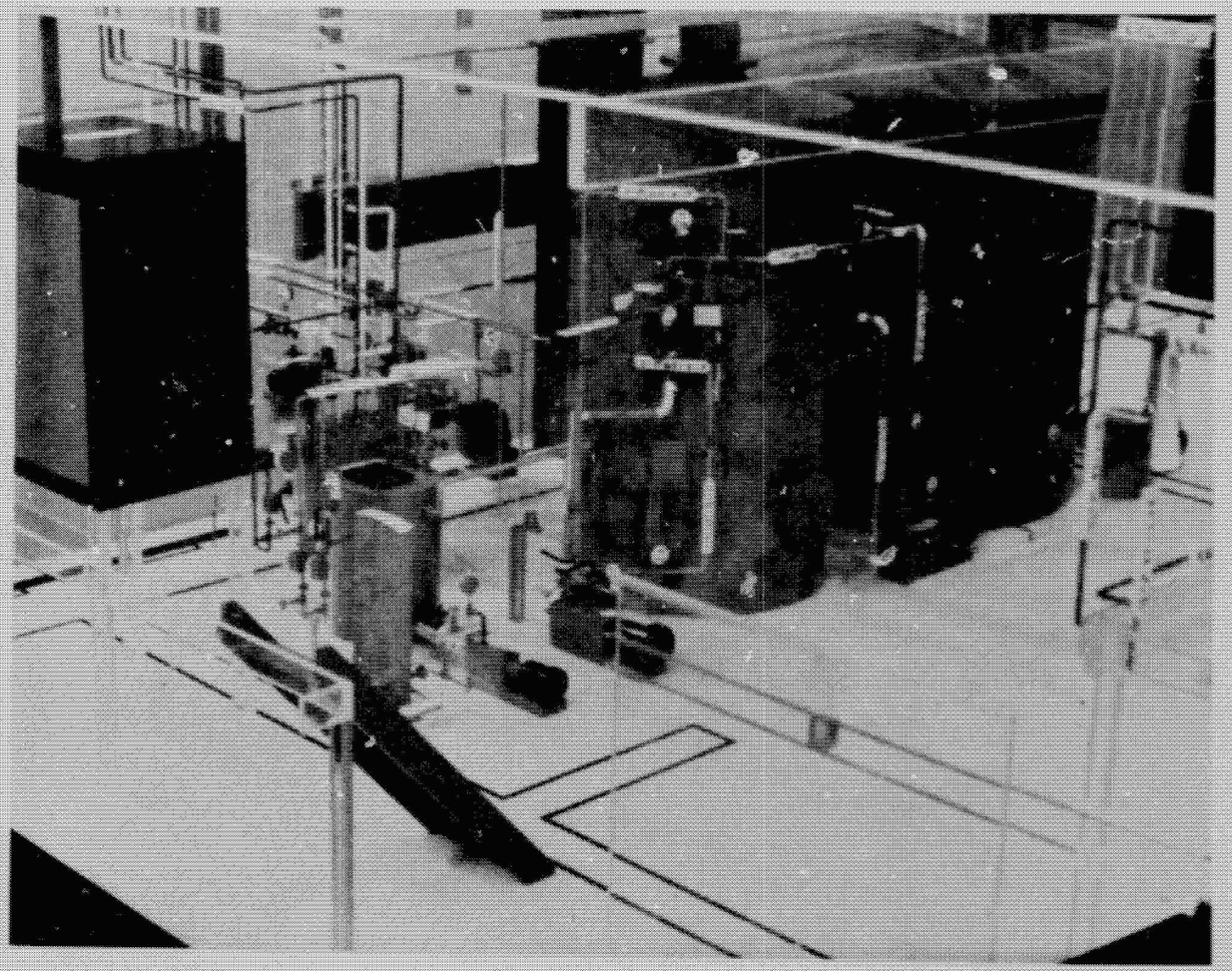

FIGURE 4. WASTE DISPOSAL AREA

The large tank in the center is the vent gas scrubber with the equipment for neutralizing chlorine and $SiCl_4$ shown on the left. The large tank at the right rear is for the storage of sodium hypochlorite formed by the chlorine neutralization. The power supply for the electrolytic cells is shown at the extreme left.

close (within a few thousand dollars) of the construction cost used at the end of Phase II of this program in arriving at the estimated total cost of 1.6×10^6 for the EPSDU.

	Bid	Administrative* and Equipment Purchase
Mechanical		
Contractor A	$192,159	3.85 percent
Contractor B	190,000	5.0 percent
Contractor C	245,000	10.0 percent
Electrical		
Contractor A	$ 92,560**	
Contractor B	213,364	
Contractor C	250,600	
Contractor D	288,841	
Structural/Concrete		
Contractor A	$ 57,000	
Contractor B	58,400	
Contractor C	60,800	

As an expedient with the current Phase III, the managerial approach adopted initially assumed that BCL personnel would purchase the equipment and act as the general contractor dealing with each type of contractor individually during the plant construction. This approach would be expected to (1) provide a total cost estimate in the shortest time, (2) result in the lowest total cost because of the add-on costs charged by a contractor to buy equipment and handle the other contractors, but (3) present the most uncertainty in cost, scheduling, and possibly quality of workmanship.

The approach outlined above did provide the cost information required quickly. However, after receiving the mechanical contractor bid of only 3.85 percent fee and considering the advantage of the mechanical

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* Fraction of equipment and other contractor cost that would be charged if they had the responsibility of purchasing equipment and administering other contractors.

** This bid is considered suspect and must be reviewed with the contractor for a misinterpretation before being considered a valid bid.

contractor's acting as a general contractor, it was decided that this approach to construction management would be by far the best with respect to minimization of potential problem areas, and probably cost.

Safety Review

A safety review, by the BCL Safety Office, of the design and planned operation of the EPSDU is underway. In addition, the project personnel have examined the effect of loss of power, of cooling water, and of instrument air on each unit operation, as well as of inoperability of critical pieces of equipment due to mechanical failure.

In general, it was concluded that instrument air and cooling water supplies must be maintained during an orderly shut-down. Instrument air can be provided by an emergency compressed air supply in the form of cylinders or a gasoline-powered air compressor. Another possibility would be to use nitrogen from the plant's cryogenic supply. Provisions will be made to quickly connect to city water in the event of failure of the process water supply (recirculated well-water) used for cooling.

It was tentatively decided that it was too expsneive (and unnecessary) to provide the capability to operate the entire plant in the event of a power failure, but that selected pieces of equipment would be critical in an orderly shut-down, such as the waste treatment system, a portion of the Therminol system, and the sump pump for moving $SiCl_4$ to emergency storage. It was estimated that the required equipment could be handled by a 75-KVA diesel-powered generator. Furthermore, it was decided that only the primary scrubber recirculation, NaOH transfer pump, and sump pump need be paralleled to provide their functions in the event of a mechanical failure.

Other minor safety or emergency procedures were also identified.

Conformance With EPA Regulations

EPA forms for approval to operate were completed, but will not be filed until the date for initiating EPSDU construction is set.

EXPERIMENTAL SUPPORT PROGRAM

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

(1) Fluidized bed modelling

(2) Zinc chloride electrolysis

(3) Materials compatibility

(4) Vaporization of zinc.

These subjects will be discussed in turn.

Fluidized Bed Modelling

Full-scale* modelling of the fluidized-bed reactor was continued in an effort to define the conditions under which segregation of particles and preferential withdrawal would occur to the extent that would prevent the growth of a few large particles to where they might block the particle-withdrawal tube. It should be noted that this question becomes academic if the entire bed is withdrawn and screened frequently enough to arrest growth of the large particles. Total bed withdrawal is planned prior to removal by chlorination of the silicon wall deposit, nominally once a week. If it is not necessary to remove the wall deposit that frequently, limitation of large-particle growth might then determine the cycle. However, as it is most economical to maximize on-stream time, the prospect of automatically limiting the particle growth by preferential discharge of large particles rather than by total bed withdrawal is of interest.

In early work with a flat-plate gas distributor (page 51 of Phase I/II Final Report**), segretation of large particles*** was observed

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* Diameter = 7 inches corresponding to that of one of the two 25 MT/year fluidized-bed reactors in the 50 MT/year EPSDU.

** Final Report for Phases I and II, DOE/JPL 954339-78/11, July 9, 1978.

*** Particles (~5000 μm) having about 10 times the diameter of the remainder (99.9 w/o) of the particles of the bed.

at the bottom of the bed. Thus, preferential discharge could be anticipated. However, in experiments with the round-bottom distributor (Figure 14 of the Final Report), little if any segregation of ∿5000 μm balls was obtained. The difference is believed to relate to the increased bed activity in the inlet region that is characteristic of the round-bottom design. It should be noted that in both designs, a minimum of bed activity must be maintained at any point to prevent agglomeration and bridging. Apparently at some level of bed activity higher than that minimum, the segregation tendency in the area of the gas inlets can be erased.

During the next report period, modelling experiments will be made with "large" particles ranging from 8000 μm to 10,000 μm in a hypothetical steady-state bed (200 to 1000 μm), to determine whether a range of conditions exists in which useful segregation of the large particles can be obtained.

Zinc Chloride Electrolysis

Experiments with a cell for the experimental electrolysis of liquid $ZnCl_2$ have been described in the Phase I/II Final Report and in Quarterly Reports of this series. Electrolysis of the $ZnCl_2$ by-product of the "miniplant"* to yield zinc and chlorine for recycle, and to chlorinate the by-product gas-phase-nucleated silicon from the fluidized-bed reactor was demonstrated. However, although runs with current efficiencies of the expected 95 percent were made, the current efficiency sometimes fell short, and the power efficiency, around 20 percent, was consistently below the ∿36 percent obtained by the Bureau of Mines in a small cell and projected for their 50,000-amp cell.

In an effort to learn more about the system and to raise the power efficiency if possible, a more flexible closed cell was designed in which the entire electrode assembly is brought in from the cell cover so that it can be immersed in the 55 m/o $ZnCl_2$-45 m/o KCl electrolyte contained

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* Containing (e.g.) 7 percent of residual elemental zinc and 3 percent of finely divided <1 μm silicon.

in a 1000-cc Pyrex beaker. No more than 20 percent of the $ZnCl_2$ is electrolyzed during any run so that the $ZnCl_2$ concentration does not drop below 49 m/o. As shown by the work at the Bureau of Mines[1] (Figure 5), this change should have little effect on the results.

Aside from the fact that the Bureau of Mines experimental cell in which the data of Figure 5 were taken was an open cell, the major difference in the cell being used in the present work is the larger electrodes (8.9- versus 3.8-cm diameter) for which the removal of chlorine from the electrode area would be more difficult and shielding of the anode by chlorine gas bubbles potentially more or a problem. The graphite electrodes in the present cell are 8.8-cm diameter near-horizontal plates, leaving 0.6 cm clearance at the container wall. Rather than to complicate the cell cover design by using massive electrodes, graphite rods of convenient size are used to make the connections to the anode and cathode. The claculated IR drop in these leads (e.g., 2 V at 45 amp) is subtracted from the measured cell voltage in determining the power efficiency of the cell.

Six experiments with electrodes of different configuration and spacing are summarized in Table 1. The major objective of these experiments was to explore the effect of enhanced chlorine removal and electrolyte circulation on the power efficiency of the cell. Although a number of changes in electrode design were made, the effects of the changes on the initially improved, ∿30 percent, power efficiency were so small (in most cases 1 to 2 percent) as to possibly be within experimental error and make difficult the correlation of any real but minor effect.

Although one might attempt to draw a conclusion from a comparison of the results of Runs 2 and 3 regarding the effect of slotting the inclined electrodes, the presence of other variables clouds the picture. Although the slotting should decrease gas-bubble shielding of the anode by facilitating the removal of chlorine, increasing the current density acts in the opposite direction. The temperature difference may also have an effect [expected 5 relative percent decrease in power efficiency[1]]. Further, the low current efficiency in Run 2 is hard to explain in the light of prior and subsequent experiments in which current efficiencies

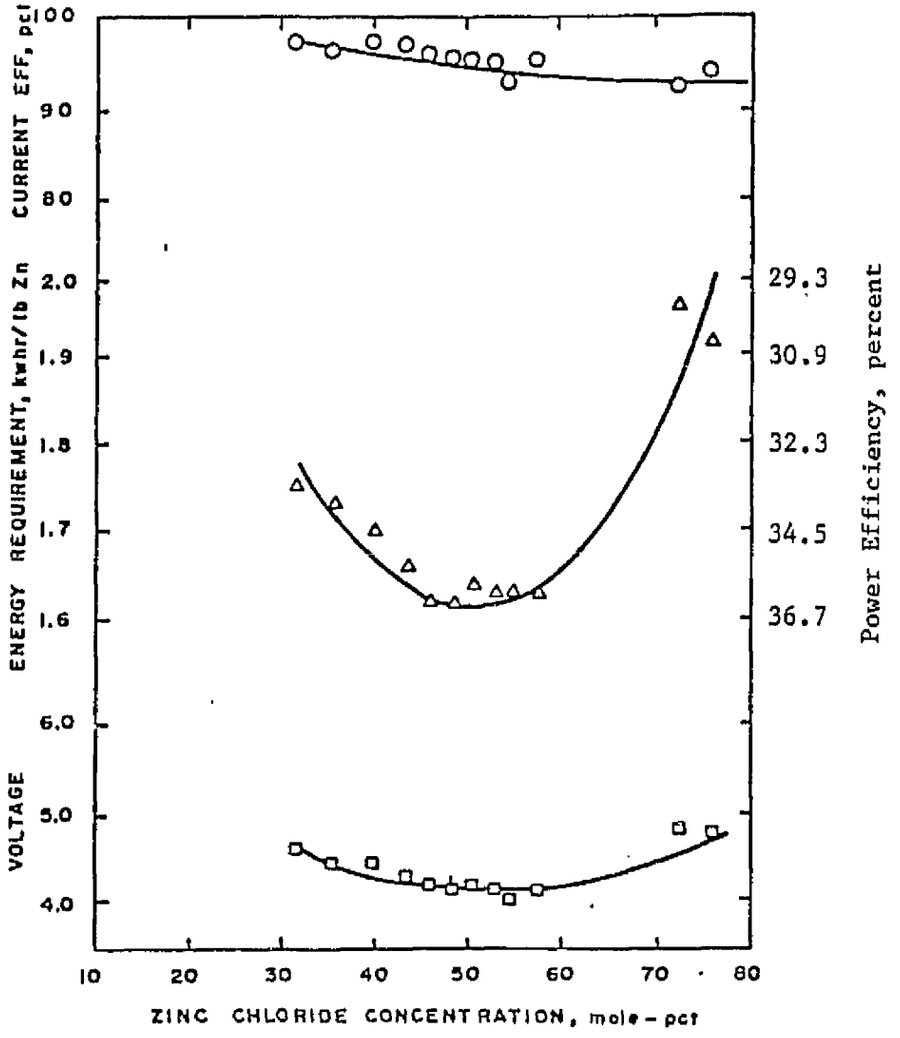

FIGURE 5. EFFECT OF $ZnCl_2$ CONCENTRATION ON THE VOLTAGE, CURRENT EFFICIENCY, AND ENERGY REQUIREMENT IN THE $ZnCl_2$-KCl SYSTEM AT 500 C(1)

TABLE 1. SUMMARY OF $ZnCl_2$ PRODUCT ELECTROLYSIS EXPERIMENTS AT 500 C[a]

Run Number[b]	Electrode Configuration	Electrode Spacing, cm	Current Density, amp/cm^2	Power Efficiency, percent	Current Efficiency, percent	Average Temperature, C
2	Planar electrodes inclined 4 degrees	1.27	0.59	31.9	86.1	477
3	4 degree inclined electrodes, 8 degree slotted anode[c]	1.27	0.72	28.0	93.7	501
4	4 degree inclined electrodes, 8 degree slotted and perforated anode	1.27	0.76	30.9	95.3	492
5	4 degree inclined electrodes, 8 degree slotted and perforated[d] anode, forced gas purge[e]	1.27	0.76	30.7	95.1	502
6	12 degree inclined planar electrodes	1.27	0.80	31.8	95.1	503
7	12 degree inclined planar electrodes	1.90	0.75	31.5	96.1	504

(a) $ZnCl_2$ by-product of the miniplant, containing approximately percent $ZnCl_2$, percent zinc, and percent Si; admixed 55 m/o with 45 m/o KCl.
(b) In Run 1, the cell temperature range was excessively broad, so the data are not included.
(c) Four 0.32-cm rectangular grooves in the direction of incline, spaced 1.6 cm, the "bottom" of the grooves inclined at 8 degrees to horizontal.
(d) 0.32-cm-diameter holes through anode at 1.27-cm intervals along the grooves.
(e) Argon purge of underside of anode ~3X rate of Cl_2 evolution.

have been consistently above 90 percent. In this case, a problem was experienced with recovery of the zinc product which may account for the low current efficiency. It is probably advisable to discount the results of Run 2.

The effect of perforating the anode (Run 4) to aid in the chlorine release was in the direction expected, i.e., an increase in both current and power efficiency.

In Run 5, the effect of bringing in a purge gas (argon) under the low side of the anode to increase salt circulation* was investigated. No net effect was observed. Thus, if any advantage was gained from increased salt circulation, it may have been offset by increased shielding of the anode by the additional gas.

Increasing the inclination of the electrodes to 12 degrees to horizontal (the maximum that can be accommodated in the EPSDU electrolytic cell design) appears to have been beneficial despite the absence of grooving and perforation. Increasing the electrode spacing from 1.27 to 1.9 cm decreased the power efficiency by only 1 relative percent [a 5 relative percent decrease was recorded at the Bureau of Mines[1] in 13 m/o $ZnCl_2$-36 m/o KCl-51 m/o LiCl under otherwise comparable conditions].

Work with the experimental cell will be continued to determine whether the power efficiency can be brought up to the 36 percent level obtained in the Bureau of Mines work. However, it should be noted that the 2 kwh per pound of zinc adopted as the electrolytic power requirement in the process cost calculations (Phase I/II Final Report) corresponds to a power efficiency of only 29.3 percnet. The net cost reduction of reaching 36 percent power efficiency would amount to $0.12 per kg of silicon.

Materials Compatibility/Permeability

Tests were made during the report period on (1) the compatibility of stainless steel and nickel-base alloys with zinc and $ZnCl_2$ and (2) silicon carbide permeability.

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* Directed at decreasing possible local $ZnCl_2$ depletion. Argon was introduced at about 3X the volumetric chlorine generation rate.

Although it was expected that, because of the nickel-zinc eutectic at 876 C, nickel-base superalloys would be attacked by zinc vapor, exposure of these and the austenetic stainless steel alloys was undertaken to show the difference. Chromium was also included in this study.

The nickel-base alloys Inconel 625 and 617 were indeed badly attacked by zinc vapor at 900 C with 304, 310, and 316 stainless steels showing lesser attack. Chromium showed the least attack of any of the materials evaluated. Although it would appear from this test that chromium should be selected for use in those areas having a potential for exposure to zinc vapor, 310 stainless steel was selected for the following reasons:

(1) Chromium is a poor structural material and would normally be used only as a coating applied by plasma spray or electroplating processes which typically results in defect chromium coatings

(2) Stainless steel (especially 310) has good structural integrity at the temperature at which the reactor shell is expected to operate and exhibited moderately good resistance to zinc vapor (0.04 ipy formation of θ phase).

The reactor is to be lined with silicon carbide-coated graphite and appropriately purged to discourage access of the zinc vapor to the stainless steel. A further precaution could be employed, if a need is indicated, i.e., spraying the shell internally with tungsten, which is known to be resistant to zinc vapor, or possibly with chromium. Thus, only the inherent porosity (e.g., <10 percent) of the tungsten coating and such flaws as are present in the chromium coating will be factors in permitting exposure to zinc vapor.

To explore the possibility that a lining might be avoided in equipment in contact with $ZnCl_2$ at 350 C where zinc might remain suspended as a solid, coupons of nickel-base alloys and stainless steels were exposed to $ZnCl_2$ containing residual suspended zinc for periods up to 552 hours.

E-brite 29-4 and E-brite 26-1 sheet specimens and a Type 316 stainless steel weldment experienced weight losses of 1.5 to 2 x 10^{-4} gm/cm^2

after 552 hours [equivalent to ~0.004 inch/year (linear)]. The Type 316 stainless steel weldment initially (after 144 hours) had experienced a weight gain of 1.75×10^{-4} gm/cm^2 (0.014 inch/year). A Haynes Alloy-20 flat sheet specimen, on the other hand, experienced a net weight gain of only 1×10^{-5} gm/cm^2 after 552 hours of exposure (0.0002 inch/year) but initially (after 144 hours) had gained 2.4×10^{-4} gm/cm^2 (0.018 inch/year). A Type 310 stainless steel weldment reacted in a manner similar to the Haynes 20, gaining a maximum of 2.6×10^{-4} gm/cm^2 (0.02 inch/year) after 144 hours with a net weight gain after 552 hours of 1.5×10^{-4} gm/cm^2 (0.003 inch/year).

Dimensional measurements were taken at intervals during the exposure testing to compare the changes in the weld metal with those of the adjacent material. The Type 310 and 316 stainless steel weld beads experienced thickness losses of 2.1 and 4.3×10^{-3} cm, respectively, after the first 300 hours of exposure with little or no measurable change thereafter. The material adjacent to these two welds experienced alternating increases and decreases in thickness of the order of 2 to 6×10^{-4} cm/side over the course of the exposure period. The other alloys tested showed greater variations in both weight and thickness over the duration of the test.

These data are consistent with those in the NACE "Corrosion Data Survey", Fifth Edition (1974), which reports corrosion rates of 0.020-0.050 inch/year in molten $ZnCl_2$ for Inconel 600 at 370 C, and >0.002 but <0.020 inch/year for Hastelloy B at 350 C. No data were reported for the alloys tested at BCL.

In light of the above results and availability of standard mill shapes, Type 316 stainless steel has been selected for use in those portions of the EPSDU exposed to $ZnCl_2$ at 350 C, with the exception of the pump used to circulate $ZnCl_2$ in the reactor by-product condenser which will be made of E-brite alloy if available.

Refrax -20*, a silicon nitride-bonded silicon carbide, was tested in various forms for permeability as a potential material for lining the

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* Carborundum Corporation, Niagara Falls, New York.

fluidized-bed reactor of the EPSDU. Refrax -20 is normally available (1) as a cast material, containing 5 percent clay as a binder and (2) as a pressed and sintered material. The cast material permits the greater design flexibility; however, the presence of the normal 5 percent clay binder is undesirable in terms of maintenance of high purity in the product of the EPSDU. Thus it became of interest to determine the effect of eliminating the binder in the cast material on permeability (and ultimately on strength, although that latter was not done, as will be explained). After the binderless cast material was re-fired* in oxygen (air) to develop a surface glaze, its permeability was measured to be 4×10^{-5} Darcy** as compared to no detectable permeability ($<1 \times 10^{-5}$ Darcy) for the cast material (re-fired) with a binder. Both are improved over that (4.5×10^{-3} Darcy) of a non-re-fired cast material with binder. After being informed of these results, the manufacturer agreed to investigate the possibility of coating the surface of the compacted material with a silicon slip prior to firing, to improve the glaze and reduce permeability. The permeability of the slip-coated and fired disk was found be to 4.0×10^{-4} Darcy, not much less than that of the uncoated disk, 5.8×10^{-4} Darcy. Both of these measurements showed an order-of-magnitude lower permeability than the 3.3×10^{-3} Darcy measured on material cored from a re-fired pressed and sintered Refrax -20 block.

The reason for failure of the silicon slip to more effectively decrease the permeability is not clear. However, the question has become academic in that a commercial source has been located for applying coatings of impermeable CVD silicon carbide to the required graphite parts of the fluidized-bed reactor essentially as designed. The CVD silicon carbide coating eliminates contact of the silicon EPSDU product with the graphite along with permeation of zinc vapor to the stainless steel shell. Such a design is preferred over that using Refrax -20 in any form.

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* Details proprietary with Carborundum.

** Permeation in ml/cm^2 per second of liquid of 1 centipoise viscosity through material under a pressure gradient of 1 atm per cm of thickness.

Vaporization of Zinc

One of the major advantages of the zinc-reduction process is that, except for a few volatile impurities such as cadmium (which, like zinc, will not be retained by molten silicon during initial cell processing), harmful impurities such as titanium have negligibly low vapor pressures at the boiling point of zinc, and except for possible entrainment in zinc mist, are left behind in the boiler. Misting must be minimized in any event, as it has been shown that surfaces of condensed zinc in contact with $SiCl_4(g)$ favor the nucleation of silicon needles which, if nucleated on a zinc mist, would be entrained, and carried out of the fluidized bed, thus not becoming part of the dense product heterogeneously deposited on the silicon seed granules.

Two experiments were run, in each of which about 50 percent of a sample of zinc was volatilized and condensed, and the initial material, condensate, and residue were analyzed for iron, lead, and cadmium. The results were inconsistent with regard to materials balance, probably due to the fact that in some cases the impurity content exceeded the solubility in solid zinc, and the samples taken from the solidified ingots may not have been representative because of segregation. The experiments are to be repeated with provisions made for sampling of the zinc while molten and presumably homogeneous. These data will be used to confirm the prospect of separating impurities in the one-plate distillation and to detect evidence of possible misting. Fortunately, activity-coefficient data are available for zinc solutions of the three elements chosen for study. The expected volatility ratios, α^*, at the 10 to 100 ppm level in the "alloy" at the boiling point are Fe/Zn = 10^{-9}, Pb/Zn = 0.016, and Cd/Zn = 16.

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* Content of impurity in vapor = αx content in liquid.

PLANS FOR FUTURE WORK

Work planned for the next report period includes:

(1) Completion of the acquisition of bids for the EPSDU components and redetermination of the EPSDU cost estimates based on the new information

(2) Consideration of the alternatives in steps leading to construction and operation of the entire EPSDU, which might be taken on an interim basis without loss of program efficiency

(3) Continuation of experiments with the electrolytic cell directed toward increasing power efficiency; review of the latest experience with $ZnCl_2$ electrolysis at the Bureau of Mines, Reno Station

(4) Continuation of experiments on the vaporization of zinc to determine the fate of impurities on single-plate distillation (simple boiling)

(5) Continuation of modelling of the fluidized-bed to study the possible segregation of large particles

(6) Continuation of the safety analysis of the EPSDU with emphasis on handling $SiCl_4$ spills.

REFERENCE

(1) Haver, F. P., et al., Bureau of Mines Report of Investigation No. 8133 (1976).