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FIFTEENTH QUARTERLY PROGRESS REPORT
Covering the Period April 1 to June 30, 1979

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

August 15, 1979

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ABSTRACT

Progress has been made during this quarter on the assembly of the Process Development Unit (PDU) consisting of four of the critical components of the 50 MT/year Experimental Process System Development Unit (EPSDU), to be operated full scale but in an 8-hour batch mode. The target operation date of October 1, 1979, still appears attainable.

An experimental wetted-wall condenser, about 1/10 the size of the PDU/EPSDU design was operated to demonstrate that recirculated liquid zinc chloride can indeed be used to wash down the condensed by-product of the fluidized-bed reactor containing finely divided solid zinc and some silicon dust. The temperature distribution proved to be more critical than anticipated but the condenser now appears to be operable. Some improvement in condensation efficiency is desirable, however.

Procedures were established for safe handling of $SiCl_4$ leaks and spills from the EPSDU and PDU.

Preparations are being made to conduct zinc vaporization experiments in that portion of the PDU before operation of the entire PDU is initiated.

INTRODUCTION

This Fifteenth Quarterly Report is the fourth 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 has as its ultimate objective 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.

Work during this report period was concentrated on the construction of the Process Development Unit (PDU) consisting of four critical units of the EPSDU, the fluidized-bed reactor, the reactor by-product condenser, the zinc vaporizer, and the electrolytic cell. The critical units of the PDU are to be of the full-scale EPSDU design so that their operability in a batch mode (8-hour) can be evaluated and appropriate changes made, if necessary, prior to committing them to operation in the EPSDU. It is believed that in this way, considerable time can be saved in the initial operation of the EPSDU that might normally be taken in design modification activities.

In addition to the PDU construction, experimental support activity was continued with the mock-up of the wetted wall condenser described in the Fourteenth Quarterly Report. In addition, techniques of coping with $SiCl_4$ leaks and spills were studied.

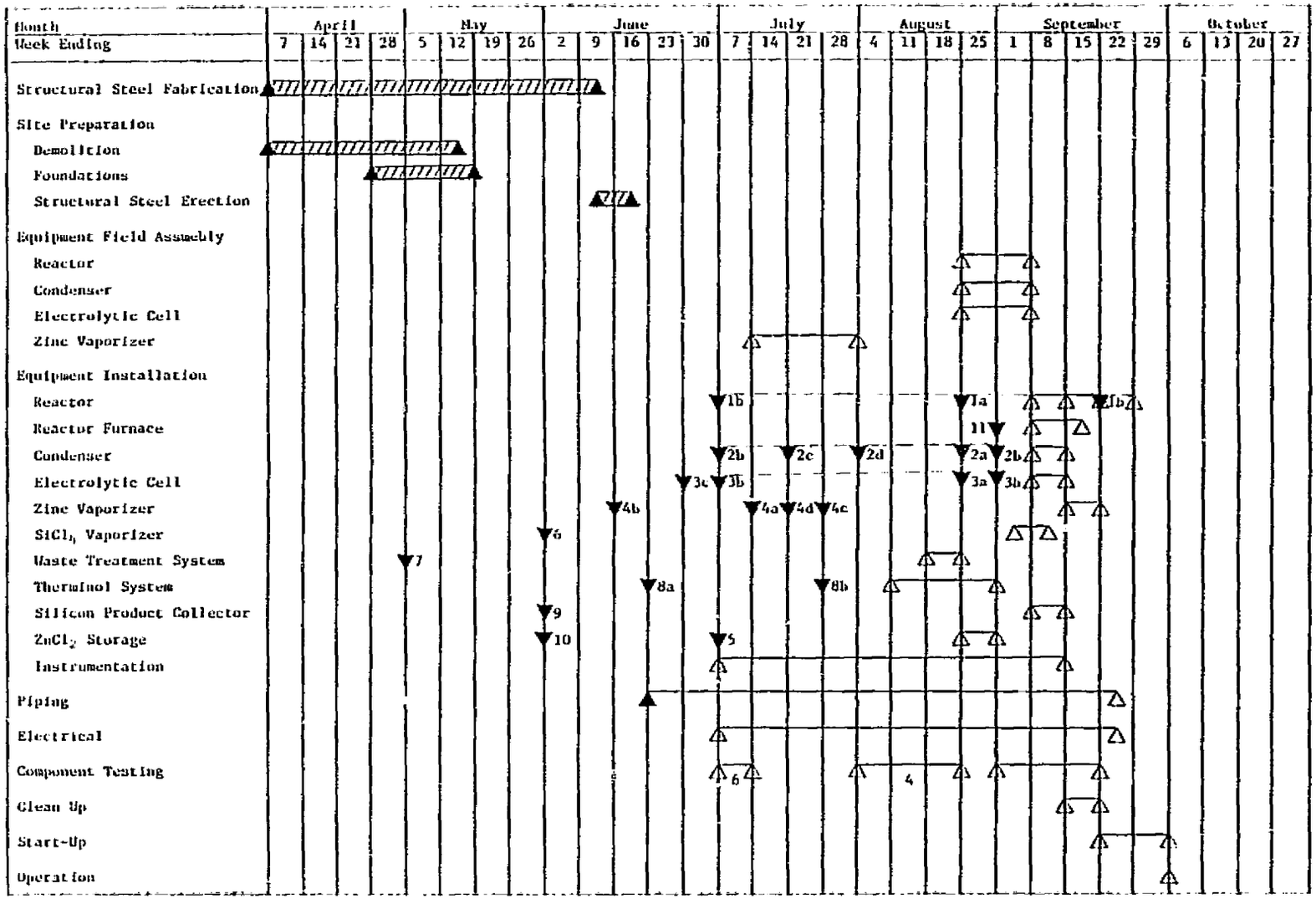
These topics will be discussed in turn.

PDU ACTIVITIES

The Process Development Unit (PDU), consisting of four critical units of the EPSDU plus auxiliary equipment, was described in the Fourteenth Quarterly Report, where a process flow sheet was given (Figure 1) together with a list of the questions the operation of the PDU is expected to answer.

Progress on the procurement, fabrication, and installation of the various components of the PDU is summarized in the schedule given in Figure 1.

Suppliers were contacted at the end of June and it was confirmed that they would be able to meet delivery dates consistent with initiation of the operation of the PDU by October 1, 1979, as planned. In addition, the equipment items for which BCL has the responsibility to construct have been assembled and are awaiting installation.



▼ = Equipment delivery milestone; △ = Current activity; ▲ = concluded activity; --- = change in schedule.

1. Reactor components: (a) shell, (b) graphite liner
2. Condenser components: (a) shell, (b) graphite liner, (c) sump tank, (d) pump
3. Electrolytic cell components: (a) shell, (b) graphite liner, (c) power supply
4. Zinc vaporizer system: (a) quartz shell, (b) control valve, (c) melt/storage tank, (d) graphite crucible
5. Instrumentation
6. $SiCl_4$ vaporizer
7. Waste treatment system
8. Therminol system: (a) components, (b) pump
9. Silicon product collector
10. $ZnCl_2$ storage
11. Reactor furnace

FIGURE 1. PDU CONSTRUCTION AND INSTALLATION SCHEDULE

EXPERIMENTAL SUPPORT

The scope and magnitude of the support effort have been tailored to accommodate the PDU schedule when necessary. During this report period, all of the support effort has been concentrated on (1) study of $SiCl_4$ emissions control, (2) study of a single-tube wet-wall condenser (PDU type) used in conjunction with the "miniplant", and (3) assembly of equipment for full PDU scale zinc vaporization experiments.

$SiCl_4$ Emission Control

In the operation of the PDU, every effort will be made to avoid the leakage of chemicals, of course. However, when modifications of equipment are made, or unforeseen leakage occurs, the release of $SiCl_4$ to the atmosphere can lead to an unpleasant and corrosive condition, although seldom highly dangerous. Three categories of $SiCl_4$ emission were considered:

(1) Mostly vapor, or up to ~1 gallon of liquid
(2) Up to several gallons of liquid, sudden release
(3) Spillage of a major portion of the inventory.

Techniques of blanketing the spills with foam, reacting the spills with appropriate chemicals, soaking up the $SiCl_4$ with blanket and powder absorbents, and combinations of these techniques were explored.

Noxious fumes from Catetory-(1) emissions are best handled by appropriate ventilation (flexible suction ducts). The $SiCl_4$ is allowed to evaporate and hydrolyze in the ambient. Depending on the location and extent of release, a coarse water spray could be used to contain the noxious fumes and wash the released material down the drain. Category (2) spills are best handled by a coarse spray of water and washed down the drain at high dilution. This practice is common at commercial plants handling $SiCl_4$. Loss of $SiCl_4$ inventory [Category (3)] is to be localized by the provision of a concrete dam in the area of the $SiCl_4$ supply and vaporizer. Spills of this category can best be handled by providing a quickly installed cover

over the dam area. After this containment, the $SiCl_4$ can be pumped to emergency storage, released slowly to the disposal system, or flushed down the drain with a large excess of water.

Wet-Wall Condenser Studies

The by-product from the fluidized-bed reactor of the PDU/EPSDU is a unique mixture consisting nominally of the following (per one 25 MT Si/year fluidized-bed reactor):

Si dust	0.16 lb/hour
$SiCl_4$(g)	29.61 lb/hour
Zn(g)	22.77 lb/hour
$ZnCl_2$(g)	80.87 lb/hour
Ar	1.15 lb/hour.

This mixture leaves the reactor at ∿925 C. If it were gradually cooled, and no reaction occurred, the bulk of the zinc (86.4 percent) should condense out by the time the temperature reaches 766 C, near which temperature the $ZnCl_2$ should start to condense out with 99.3 percent of the $ZnCl_2$ and 99.8 percent of the zinc having condensed by the time the temperature reaches 527 C,(1) still well above the melting point of zinc (420 C) and $ZnCl_2$ (283 C). However, if this by-product mixture were allowed to cool gradually, the unreacted $SiCl_4$(g) would react with the unreacted Zn(g) to form additional silicon* in the condenser, which, added to the 0.16 lb/hour of dust already in the by-product, would probably exceed the capacity of the electrolytic cell to chlorinate it. Hence, the by-product mixture must be quenched to prevent further reaction.

The wetted-wall condenser, in which liquid $ZnCl_2$ is recirculated to wet the condensing surface, was designed to accomplish the condensation in such a way as to have the following advantages:

(1) Operation of the condenser surface at 350 C would effectively quench the by-product mixture and prevent further silicon formation

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* The equilibrium efficiency of the reaction $SiCl_4 + 2Zn(g) = Si(s) + 2ZnCl_2(g)$ increases with decreasing temperature.

(2) Operation below the melting point of zinc permits keeping the condensed finely divided solid zinc in suspension in the $ZnCl_2$ until the $Zn/ZnCl_2$ mixture is heated to above the melting point of zinc in the electrolytic cell, where the zinc coalesces.

(3) Operation at 350 C permits use of stainless steel in contact with the zinc (finely divided solid) without the swelling of the metal caused by formation of the Θ phase encountered above the melting point of zinc.

It is essential that the flow of recirculated $ZnCl_2$ be sufficient to prevent drying of the wetted wall, otherwise accumulation of silicon dust or zinc powder would constrict the condenser.

As discussed briefly in the Thirteenth Quarterly Report, a mock-up of the wetted-wall condenser was made to study the effectiveness of the principle in this application.

Figure 2 is a schematic diagram showing the major features of the wetted-wall condenser. The by-product mixture used to evaluate the condenser was generated by a "miniplant" reactor similar to that pictured in Figure 13 of the Phase I-II Final Report[1], except that the zinc vapor was routed to the axial inlet with the $SiCl_4$ introduced from the four surrounding inlets, as had been the practice from Run No. 56 on in the miniplant to avoid silicon deposition on the orifice plate.

As discussed in the Fourteenth Quarterly Report, the condenser pictured in Figure 1 is a partial mock-up of the EPSDU/PDU equivalent where condensation occurs in three parallel 1.5-inch-diameter channels, each 240 inches long, in which the gas flow direction is reversed 180 degrees at the halfway point. The mock-up condenser was purposely designed on the basis of throughput per unit condensing surface area to be 30 percent undersized so that its limitations might be more easily discerned.

Duplication, in the experimental condenser, of the Reynolds number (4100) at which the gases enter the condenser of the PDU would have required

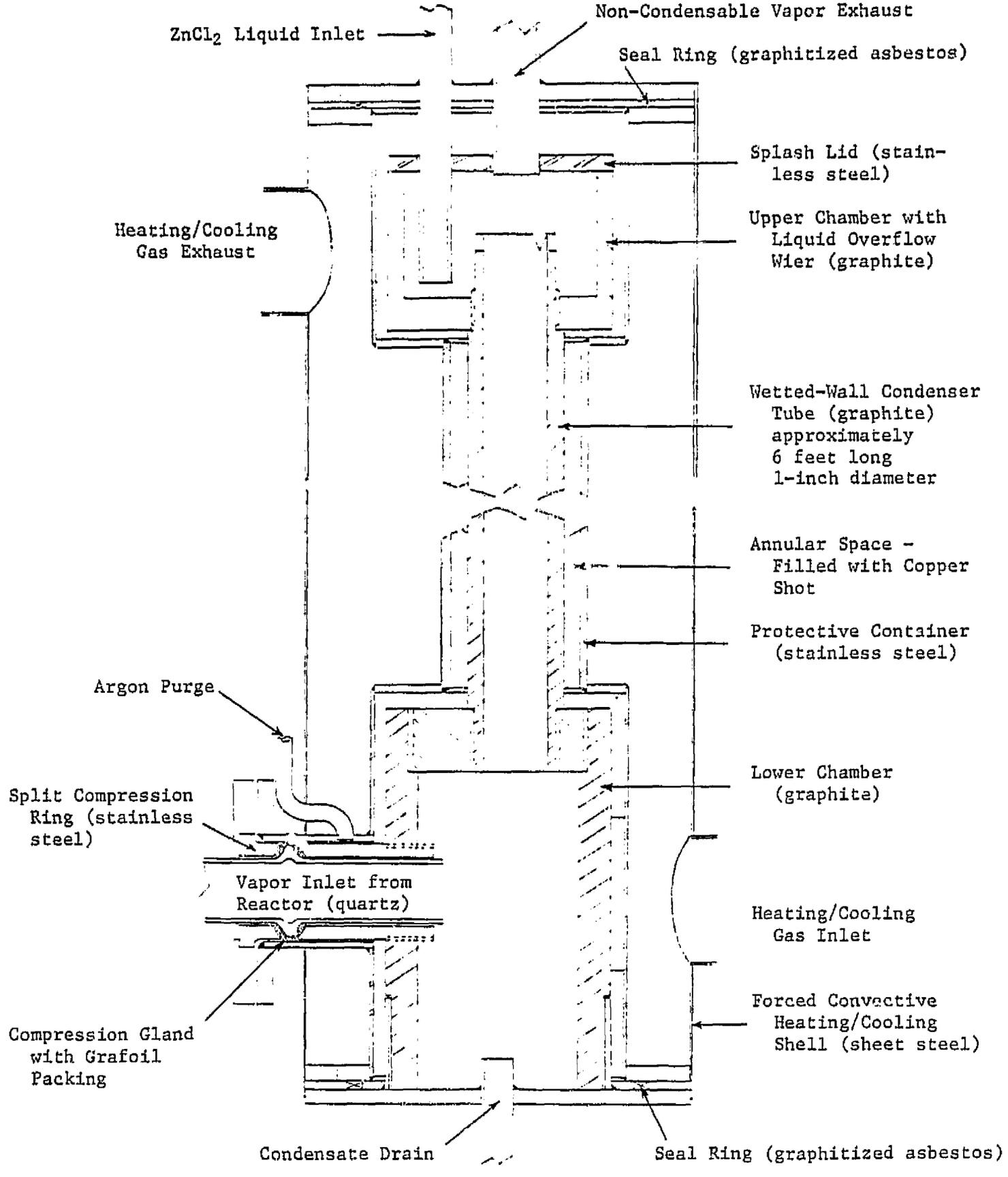

FIGURE 2. SCHEMATIC DIAGRAM OF LABORATORY-SCALE WET-WALL CONDENSER

SCALE: 1/2" = ∿1"

the use of a tube less than 0.4 inch in diameter and over 17 feet in length, depending upon the output of the miniplant. Since this was thought to be overly constricted and would require more head room than was available, a rationale was sought for using a larger diameter tube that would not only decrease the danger of flooding or constriction, but would permit the use of a shorter tube for the same surface area.

Since by the time about 50 percent of the zinc and zinc chloride have condensed, the Reynolds number for flow in the PDU condenser will have dropped out of the transitional range (N_{Re} = 4100) into the laminar flow range (N_{Re} < 2500). Under these conditions, the flow rate would not be expected to have a great effect on condenser efficiency at constant area per unit throughput. Hence, the adoption of the 1-inch-ID* by 6-foot-long condenser tube was believed to be justified.

The normal flow rate of the $ZnCl_2$ down the wetted-wall tube was chosen to be that of the PDU design, which corresponds to 0.2 gallon of $ZnCl_2$ for the same by-product throughput per tube.

Flow of $ZnCl_2$ to the condensing surface of the mock-up is provided by use of interchangeable $ZnCl_2$ reservoirs which, depending upon the $ZnCl_2$ flow chosen, provides for runs of about 1-hour duration** The initial run is made with pure $ZnCl_2$ drained from the upper reservoir to the lower. Subsequent runs are made with $ZnCl_2$ containing increasing amounts of suspended zinc and silicon dust as the positions of the reservoirs are interchanged. The reservoirs are of about 16-gallon capacity so that, starting with one containing ∿8 gallons of $ZnCl_2$, about 20 1-hour runs would be required to add $ZnCl_2$ (+ Zn + Si) to the point of reaching the capacity of the reservoir, at which time the concentration of zinc and silicon*** will have reached

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* N_{Re} = 1000.

** The capacity of the zinc reservoir limits the run time.

*** Finely divided zinc is the major component, the volume of the finely divided silicon is about 2 percent that of the zinc on a fully dense basis.

about 45 percent of that in the 950 C equilibrium by-product mixture. As this amounts to only 4.5 percent zinc in the $ZnCl_2$, the fluidity should not be prohibitively changed; however, data on the apparent viscosity of the mixture as a function of zinc concentration and particle size have not been obtained.

The first two 30-minute runs in the condenser mock-up assembly proceeded smoothly with good indication by boroscope examination that the wetted-wall principle was effective in clearing the condenser surface of silicon and zinc solids. It was observed, however, that, due to inadequate condenser cooling masked by a deficiency in the gas-temperature monitoring arrangements, excessive amounts of $ZnCl_2$ were escaping the condenser. With improved positioning and shielding of the gas temperature thermocouple, several runs were made to establish the proper condenser cooling conditions. However, overcooling at the bottom (inlet) end of the condenser led to constriction and floodi · of the fluidized-bed reactor with $ZnCl_2$.

At the end of June a run was made (No. 34868-52-8A) which was satisfactory from the operational standpoint, although it demonstrated that temperature control in the condenser and control of the temperature distribution at the inlet end of the condenser was fairly critical, thus explaining the problems experienced with earlier runs. Fortunately, temperature control should be less critical with the full-scale PDU/EPSDU condenser.

Although it can undoubtedly be improved further, the collection efficiency of the $ZnCl_2$ and zinc was much improved over that obtained in the earlier runs, as judged from the materials collected in a room-temperature glass-wool-packed back-up trap for the condenser. Assuming 63 percent conversion, the wet-wall condenser collected approximately 92 percent of the $ZnCl_2$ formed and 97 percent of the residual zinc vapor. It is anticipated that the carry-over of entrained materials will be decreased in the PDU wet-wall condenser design since the gas stream is made to change direction and the efficiency can probably be further improved by the addition of baffles or a $ZnCl_2$ spray. However, the amount and condition of the zinc and silicon particles that escaped the condenser point to the need for continued study of the condensation system despite the demonstration that

the wetted-wall principle is effective in maintaining a clean condensation surface with this inherently "dirty" condensate.

Zinc Vaporization Studies

As discussed in earlier reports, it was decided to defer further zinc vaporization studies until the PDU zinc supply system and vaporizer were available. Exploratory experiments had shown that zinc could be vaporized at ∿1 lb/minute (PDU requirement) from a vaporizer in which the required power is supplied by inductively coupling directly to the zinc. This work was limited by the capacity of the liquid zinc feed system. Consequently, it was considered expedient and economical to wait until the PDU equipment was available. Every effort has been made to assemble this equipment as soon as practical so that the zinc vaporization studies could be continued prior to the need of this equipment by the PDU for the October 1, 19"9, start-up. It was also intended that this item be given priority over all other support study items when it was expeditious to do so.

During this report period, most of the components of the zinc supply system and vaporizer have been received. The remainder are expected in early July and it is anticipated that the studies can be initiated late in July or early August.

PLANS FOR NEXT PERIOD

(1) Continue the PDU activity with the objective of having the unit ready for operation by October 1, 1979.

(2) Initiate zinc vaporizer experiments as soon as the PDU zinc feed and vaporizer equipment have been assembled.

(3) Continue the experimental support effort involving condenser design, zinc vaporization [Item (2) above], and other items as their need becomes apparent.

(4) As time permits, assemble an updated cost estimate for the construction of the EPSDU.

REFERENCE

(1) Final Report, Phases I and II, DOE/JPL 954339-78/11, Table 13 (July 9, 1978).