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

**Silicon Material Task Low-Cost Silicon Solar Array Project
Fourth Quarterly Progress Report, July 1, 1976—September 30, 1976**

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October 21, 1976

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**Battelle Columbus Laboratories
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MASTER

**ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
Division of Solar Energy**

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FOURTH QUARTERLY PROGRESS REPORT
Covering the Period July 1, 1976, to September 30, 1976

on

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FOR PRODUCTION OF LOW-COST SILICON

JPL Contract 954339

Silicon Material Task
Low-Cost Silicon Solar Array Project

to

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY

by

J. M. Blocher, Jr., M. F. Browning, W. J. Wilson,
and D. C. Carmichael

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ABSTRACT

The effort this quarter has been devoted to the operation of a "miniplant" for the preparation of silicon by the zinc reduction of silicon tetrachloride. This is in accordance with a previous decision to concentrate all development work on this process because it was concluded to have an economic advantage over other candidate processes explored earlier.

The general purpose of operating the "miniplant" was to accumulate operational data of value for (1) designing a larger system and further refining the economic analysis and (2) identifying and correcting unanticipated operational problems which might be encountered when operating at the planned higher production rates and with newly designed equipment.

Of the 22 runs made in the newly designed equipment this quarter, 12 were carried out under conditions which yielded meaningful data. The

remainder were terminated at startup, or shortly after, by equipment failure such as leakage, breakage, heater failure, or line plugging. The operation time of five runs was limited only by the amount of zinc available, since this is a batch system in the present plant design. The remainder of the runs from which meaningful data were obtained were terminated primarily by constriction of (1) the exit portion of the system with reaction-product condensate and silicon dust or (2) the inlet orifices of the reactor by premature deposition of silicon. These two problem areas which have been identified this quarter are somewhat unique to the zinc reduction system but can undoubtedly be overcome with proper equipment design and operation.

The results of many of the runs made during this quarter substantiated data obtained previously in that useful quantities of the available silicon can be deposited on the seed bed. In the newly designed system, production rates as high as 188 g/hr, a run time of 2-1/2 hours, and bed yields (percent of theoretical) typically above 65 percent have been achieved thus far. As these were not all associated with the same run, the optimum conditions for economical and trouble-free operation remain to be determined.

INTRODUCTION

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

The objective of the current program is to determine whether the application of advances in technology within the last 15 years would sufficiently improve the efficiency and rate of production of the zinc reduction of silicon tetrachloride or the thermal decomposition (or hydrogen reduction) of silicon tetraiodide to enable the production of solar grade-silicon by these processes at a cost of <\$10/kg and at a reasonable energy consumption. In the early days of the semiconductor industry, both processes, although not fully developed, had been

demonstrated to be capable of producing high-quality semiconductor-grade silicon.

The First Quarterly Report presented the results of initial thermodynamic and experimental evaluations of the process options to be considered. The Second Quarterly Report presented additional experimental data in support of the process options, but its major content involved the estimation of plant construction and operating costs for the various forms of the processes being evaluated. The cost of the zinc reduction of silicon tetrachloride in a fluidized bed was estimated to be \$9.12/kg Si, i.e., below the \$10/kg target. However, none of the modifications of the iodide processes appear to permit production below \$20/kg Si. Although some operational problems were encountered during the initial shakedown experiments using the equipment, promising results were obtained which further supported the overall feasibility of the process.

In accordance with recommendations made in the Second Quarterly Report, Battelle-Columbus was authorized to pursue the development of the fluidized-bed zinc reduction of silicon tetrachloride which had been shown to have the potential of meeting the LSSA Project goals.

Included in the Third Quarterly report were the results of an additional economic analysis which showed no economic advantage in operating on either side of the $2/1 \text{ Zn/SiCl}_4$ stoichiometric ratio adopted for the economic analysis presented in the Second Quarterly Report. It was further shown that any technological advantages that might accrue from off-stoichiometry operation could be purchased at a moderate cost, within limits. For example, operation with 43 percent excess of either reactant was concluded to raise the product cost by less than 10 cents per kilogram.

The Third Quarterly Report covered the design, construction, and shakedown operation of a miniplant designed to prepare silicon at a rate of over 200 g/hr in runs of 4- to 6-hour duration.

PROGRESS THIS QUARTER

Activities during this quarter have included (1) a study of the condensation of the by-products of the miniplant fluidized bed and (2) operation of the miniplant at increasing rates of silicon deposition to accumulate operational data. In conjunction with the above, it was intended that an experiment be made with a seed bed of semiconductor-grade silicon for the preparation of quality evaluation specimens. The by-product condensation study was prompted by problems with plugging of the line leading from the fluidized bed to the Zn/ZnCl₂ condenser.

The condensation study, and operation of the miniplant will be discussed in turn.

Condensation of Reactor By-Products

If condensation of the reaction by-products, zinc chloride, and unreacted zinc does not occur properly, the exit lines are not kept clear, and the resultant constriction forces operation under erratic conditions, and possibly premature termination of the run. As little difficulty was experienced in this regard with the initial experimental unit, problems with the miniplant were not anticipated.

It was recognized that the zinc by-product, being less volatile than the zinc chloride, would condense preferentially; however, it appeared from working with the initial experimental unit and a separate experiment (page A-8 of Second Quarterly Report) that the product condensate would flow freely even though it contained some silicon crystallites, either gas-phase nucleated or grown by continued reaction* at lower temperature

* As the reaction

is exothermic, it becomes more favorable thermodynamically as the temperature is decreased. Thus, on cooling the fluidized bed by-products, a tendency for further reaction exists to the extent that kinetic limitations permit.

downstream of the fluidized bed. Silicon powder and silicon needles have been observed under various conditions, the needles appearing to grow predominantly on liquid zinc. Although the forms and origin of this by-product silicon have not been characterized, it is believed that none of this material is amorphous; hence, it will be referred to by the general term "crystallites".

Despite favorable indications from the prior work, work with the miniplant and subsequent calculations have indicated that the condensation pattern may be very sensitive to the temperature of the line connecting the reactor to the condenser ("crossover line"), and to the dwell time of the gases in the line. Under certain conditions a mass of silicon crystallites and droplets of unconsolidated liquid zinc can build up to constrict this line. Two differences between the initial experimental equipment and the miniplant appear to contribute to the different behavior, (1) the lower gas flow through the relatively larger line of the miniplant, and (2) the fact that the miniplant employs a quartz crossover line with a lower thermal conductivity than that of the metal line employed in the experimental unit.

In order to better understand the condensation of Zn/ZnCl_2 mixtures, possibly containing entrained silicon crystallites, preliminary calculations of the dewpoints of the exhaust gases and the progress of condensation were made for representative cases. Equilibrium condensation was assumed, and the small solubility of zinc in liquid ZnCl_2 (0.78 mole percent at 500 C to 1.97 mole percent at 700 C*) was neglected.

Table 1 gives the dewpoints of various hypothetical by-product mixtures. Since zinc is the least volatile component, it tends to be the first to condense. Only at low Zn/ZnCl_2 ratios, corresponding to high conversions of Zn to ZnCl_2 (e.g., $\text{Zn}/\text{ZnCl}_2 < 0.109$ at 850 C and < 0.132 at 650 C), would ZnCl_2 be expected to condense first. This is evident in data of Table 1. Only at 70 and 75 percent conversion of the SiCl_4 from a feed of $\text{Zn}/\text{SiCl}_4 = 1.5/1$ (93.33 and 100 percent conversion of Zn) does the ZnCl_2 condense first.

* D. H. Kerridge and S. A. Tarig, J. Chem. Soc., A 1967 (7), 1122-5.

TABLE 1. DEWPOINTS (°C) OF BY-PRODUCT OF ZINC REDUCTION OF SiCl_4 CONTAINING INDICATED AMOUNTS OF DILUENT [First Condensate = Zn(1) Unless Otherwise Noted]

SiCl_4 Converted, percent	0 Percent Diluent			25 Percent Diluent			50 Percent Diluent		
	Zn/ SiCl_4 Ratio			Zn/ SiCl_4 Ratio			Zn/ SiCl_4 Ratio		
	1.5	2.0	2.5	1.5	2.0	2.5	1.5	2.0	2.5
0	860	869	876	834	846	850	800	809	815
25	833	851	862	807	824	835	773	789	800
50	786	824	843	759	797	815	726	761	780
70	715 (ZnCl_2)	789	823	691 (ZnCl_2)	761	874	662 (ZnCl_2)	727	758
75	721 (ZnCl_2)	777	816	670 (ZnCl_2)	749	788	667 (ZnCl_2)	715	752

Table 2 shows, for example, the progress of condensation for the by-products of an initial reaction mixture containing $\text{Zn/SiCl}_4 = 2/1$ with 25 mole percent diluent after 50 percent conversion of the SiCl_4 to silicon. It is evident for the case represented by the data of Table 2 that over 90 percent of the zinc has condensed before the ZnCl_2 dewpoint is reached. Thus, the ZnCl_2 cannot be relied upon here to "wash down" the zinc condensate and any silicon that might be present.

If the liquid zinc condensate (melting point = 693 K) were free flowing, this would not be a problem. However, the presence of silicon crystallites in the zinc condensate apparently leads to "balling up" of the zinc under certain conditions in the crossover, preventing its coalescence and movement to the condenser. Three solutions to the problem were considered:

- (1) Operation at Zn/SiCl_4 ratios low enough to assure high conversion of zinc, and condensation of ZnCl_2 first with resultant "wash-down" of zinc (+ silicon crystallites)
- (2) Operation of the "crossover line" (currently having a slope of only $\sim 25^\circ$) under conditions that would limit the formation of silicon crystallites and reaction-product condensate until the by-products reach the vertical walled condenser in which this type of condensate is more easily handled; condensation would be carried out above the melting point of zinc
- (3) Operation of a "quench" condenser so that the zinc (+ silicon crystallites) would be condensed as solid from the vapor phase or at least condensed on a liquid film of ZnCl_2 (normally in excess), to assure free flow.

The first option has the disadvantage of decreasing the percent conversion of SiCl_4 , i.e., tending to negate one of the primary advantages of the zinc-reduction process over the other contenders. The second option

TABLE 2. CONDENSATION OF Zn AND ZnCl₂ FROM BY-PRODUCT OF
50 PERCENT CONVERSION OF SiCl₄ IN A REACTION
MIXTURE CONTAINING 50 MOLES Zn + 25 MOLES SiCl₄
+ 25 MOLES INERT DILUENT

Condenser Temperature, C	Zn Condensed		ZnCl ₂ Condensed	
	Moles In Interval	Cumulative Percent	Moles In Interval	Cumulative Percent
802	0	0	0	0
777	7.062	28.25	0	0
752	6.033	52.38	0	0
727	3.943	68.15	0	0
702	2.601	78.56	0	0
677	1.653	85.17	0	0
652	1.760	92.21	10.335	41.34
627	0.877	95.72	6.653	67.95
602	0.431	97.44	3.490	81.91
577	0.276	98.55	1.976	89.82
552	0.129	99.06	1.096	94.20
527	0.120	99.54	0.643	96.77
502	0.039	99.70	0.389	98.33
477	0.038	99.85	0.192	99.10

is the most attractive, if the necessary conditions can be achieved by reducing the dwell time in the crossover line and/or adjustment of the temperature of the crossover line to prevent zinc condensation. Introduction, at the crossover, of additional diluent or recycled chlorine to prevent silicon crystal growth are other possibilities. It should be noted that dwell time of the unreacted Zn and SiCl_4 in the crossover line could be decreased by increasing diluent concentration in the reactant mixture. However, the addition of diluent is made at the expense of rate of production of silicon in the gas-throughput-limited fluidized bed. The third option requires the maintenance of steep temperature gradients in the by-product handling system, leading to complexity of design. Attention is being concentrated on the second and third options.

It is essential for the most economical operation of the zinc reduction process that the conditions for free flow of zinc from the reaction by-product condensate be found for two additional reasons.

- (1) The presence of any appreciable thickness of silicon crystallite/zinc droplet film on the condenser surface will decrease its heat-transfer coefficient, thus increasing condenser size and cost.
- (2) Lack of separation or difficult separation of zinc and zinc chloride into layers in the electrolytic cell will complicate the process and increase its cost.

As the rated capacity of the present condenser has not yet been reached, the first limitation has not been encountered. The second has not arisen, as it has not been possible to proceed with a study of the electrolytic cell beyond the initial experiments with synthetic by-product, reported earlier (pages A6-8 of Second Quarterly Report).

It is anticipated that an experimental support effort will be needed, apart from the miniplant operation, to define the proper condensation conditions for the free flow of zinc and the segregation of zinc and zinc chloride.

Operation of the Miniplant

The design and construction of the major miniplant components were described in the Third Quarterly Report along with the shakedown operation, a series of runs designed to discern and correct deficiencies of design inherent in the operation of newly designed equipment. As the result of these experiments, a number of operational problems were overcome, and the data revealed a consistency with predictions based on thermodynamic calculations and experience with this and similar silicon deposition systems. At no point were any problems with the fundamental design apparent.

During the fourth quarter, the larger-capacity Zn/ZnCl_2 condenser shown in Figure 5 of the Third Quarterly Report was installed in the miniplant and a series of runs was made in which the stoichiometry of the reactant mixture was varied and the rate of reactant feed was increased incrementally* toward the goal of obtaining a silicon deposition rate of >200 g/hr in the miniplant.

All of the runs during the fourth quarter were made at a fluidized-bed temperature of 1200 K (927 C), as trouble had been experienced in Runs 29 through 31 made at 1123 K (850 C)** last quarter, which appeared to be related to condensation of zinc in the bed***. In one run

* Along with incremental increases in seed particle size to maintain proper action of the fluidized bed and to avoid elutriation of the smaller particles.

** These runs were made at the lower temperature in an effort to take advantage of the attendant increase in thermodynamic efficiency.

*** As the boiling point of zinc at atmospheric pressure is 1181 K, operation at 1123 K allows for only 0.55 atm of zinc in the vapor before condensation will occur. Although this is a useful zinc concentration level in the reactant mixture, careful control is necessary to avoid exceeding it momentarily and either (1) tending to agglomerate the bed or (2) generating the needle-like silicon that appears to be formed preferentially in contact with liquid zinc.

(No. 47, see Appendix A) made at near-stoichiometric composition ($\text{Zn}/\text{SiCl}_4 = 1.97/1$ versus stoichiometric $2/1$) and a small amount of inert diluent or bleed gas (3.4 percent), a silicon deposition rate of 188 g/hr, i.e., very near the goal, was obtained in a 1.5-hour run. Under those conditions, a silicon tetrachloride conversion efficiency of 71.2 percent would be expected. The 40.7 percent of the silicon fed recovered as deposited silicon represented 57.1 percent of the thermodynamically predicted value. Unfortunately a large fraction (29 percent) of the bed was blown over into the exit line at some time(s) during the run. Had this not occurred, the deposition efficiency and rate should have been even higher*. The run times would also have been extended had it not been for the loosening of a friction-fit closure on the liquid zinc feed system which forced termination.

The blown over bed in this case was judged to be the result of unusual bed action which tended to "shot gun" rather than progressively elutriate the silicon particles into the exit line. This condition is not typical of good fluidized-bed operation and can be minimized by proper reactor design and operation.

A run time of 2.5 hours was attained in Run No. 36 (before construction of the exhaust line forced termination).

As can be noted in the data of Table A-1 (Appendix), the amount of silicon deposited on the bed continues to average about 65 percent of that predicted thermodynamically. Additional amounts of silicon powder are routinely collected downstream of the bed, amounting to 10 to 20 percent of that deposited on the bed. Part of this can be formed by reaction downstream of the bed, so it is not possible to determine what part is gas-phase nucleated in the bed. It is anticipated that the overall conversion of SiCl_4 to silicon deposited as dense material on the bed can be increased by improved reactor design.

* Since the blown over material contained no uncoated particles and many fully coated particles (as compared with those in the fluidized-bed product), the material was not wholly blown over at either the beginning or end of the run. No statistical analysis of the coating thickness was made to chart the progress of elutriation during the run.

As can be seen from Table A-1 and associated footnotes, most of the mechanical problems leading to the abortion of runs in the mini-plant have related to the zinc feeder system. The fact that the zinc feeder system is constructed of quartz with ball joint connections results in a system inherently difficult to align and operate without breakage.

Such mechanical problems should be solved with the application of some additional ingenuity; however, the constriction of the by-product exit system and the constriction of the reactor inlet system will require more basic attention. It is believed that these problems relate to the exothermic nature of the deposition reaction as well as to the high-temperature dewpoints of the by-product mixtures. Such problems are not encountered with the normal endothermic vapor deposition reactions.

The steps that have been taken to alleviate the latter problems, and those being considered for implementation in the future, are discussed below.

Prevention of Exit Line Constriction and Related Zn/ZnCl₂ Condensation Problems

As mentioned above, it was not until the larger capacity Zn/ZnCl₂ condenser was installed in the miniplant along with its larger quartz "crossover" line that plugging of the line due to non-coalescence of zinc droplets associated with by-product silicon was observed, although some acicular silicon had been observed in the condensates from prior runs. After a few attempts to adjust the temperature of the line to avoid silicon growth in the condensate*, it was decided to heat the line to the point of driving the condensation of zinc over into the condenser when it could be quenched, and/or washed down with liquid ZnCl₂. This adjustment appears to be effective for the present purpose. However, trouble-free extended operation of the miniplant will benefit from further study of the by-product condensation problem, as discussed in the section of this report devoted to that subject.

* Along with partially successful attempts to avoid silicon growth or deposition of entrained silicon by decreasing reactant dwell time in the line by means of adding inert gas.

Prevention of Plugging at the Reactant Inlet Orifices

As has been pointed out before, unless the zinc and SiCl_4 gaseous reactants are mixed in the bed, the reaction can result in the deposition of silicon on surfaces contiguous with the inlets, and either bridge the inlet orifices or form a tube of stagnant deposition-sintered bed material extending into the bed*. As a minimum, the reactant flow pattern is disrupted, leading to an uncontrolled situation. Although problems of this type have been encountered in the past and have been corrected by improved control and reactor inlet design, the problem has been aggravated in recent runs by the increased feed rates. It is probable that a fundamentally different reactor inlet design will be required as the rate of reactant feed is further increased.

The preferred reactor inlet design would introduce the reactants separately into the fluidized bed, thus minimizing direct contact between the reactant streams. Several possibilities are available, but the multi-orifice design used earlier in this program (Third Quarterly Report, Figure 2, insert) will be given further consideration because of its scale-up potential.

CONCLUSIONS

Owing to a greater incidence of problems that were anticipated with the miniplant, it has not been possible within the fourth quarter to reach the 12-month goal of preparing quality evaluation specimens at rates of >200 g/hr in runs lasting 4 to 6 hours. However, the >200 g/hr goal was nearly attained in one run yielding 188 g/hr in a 1.5-hour run, using metallurgical-grade silicon seed.

In contrast with the normal endothermic fluidized-bed vapor deposition reactions, undesired silicon deposition has been encountered

* The sintered material can grow at one or the other of the inlets depending upon which reactant is in excess.

in the reactor inlet and outlet systems which has led to constrictions at these locations and, in some cases, early termination or abortion of the runs. These problems, aggravated by the exothermic nature of the reaction, have been defined, and it is believed that they will yield to experimental support programs carried out in conjunction with the mini-plant operation.

PLANS FOR NEXT QUARTER

Plans for the next quarter will be directed at the initiation of a program leading to the design of a 25 MT/year experimental facility for the preparation of solar-grade silicon by zinc reduction of silicon tetrachloride in a fluidized bed of seed particles. Three concurrent phases will be involved:

- Phase 1. Research and development in support of
Phase 2
- Phase 2. Design of the 25 MT/year facility, including
modelling studies
- Phase 3. Iterative economic analysis to provide
(a) estimates of the construction and
operation costs of the 25 MT/year facility,
and (b) overview estimates for a 1000 MT/year
production plant.

Activities during the next quarter in Phase 1 will be directed at optimizing the conditions for condensation and free flow of the by-products of the reactor, and optimizing the reactor design. Experimental work both with the miniplant, and independent of the miniplant, is anticipated. Prior to extended work with the miniplant, the 500-g quality-evaluation sample which was scheduled for submission at the end of the current quarter will be prepared.

Activities in Phase 2 during the next quarter will involve the preparation of a detailed flow sheet, and identification of sources and

determination of costs of equipment and materials that can be directly purchased. An effort will be made to identify the sources of certain equipment designs that might be bought or furnished.

APPENDIX A

SUMMARY OF MINIPLANT OPERATION DATA

TABLE A-1. SUMMARY OF MINIPLANT OPERATION DATA

(All runs made at 1200 K (927 C) with 240 g bed of metallurgical-grade silicon of stated particle size; reactor inlet design as shown in Figure 2 of Third Quarterly Report (insert), with minor modifications of position and direction of zinc and SiCl_4 inlets plus increased orifice size with increased flow.)

Run No. (a,d)	Particle Size, μ	Mole Ratio, Zn/SiCl_4	Argon, %	Run Time, hr	Silicon in Feed, g/hr	Equilibrium Silicon yield, (b)		Silicon Deposition on Bed,		Remarks (c)
						%	g/hr	g/hr	% of Equilibrium	
33	125 x 177	1.79	39.4	1.00	135.0	62.1	83.8	42.9	51.2	T,E
35A	155 x 216	1.12	35.3	1.00	210.8	42.8	90.2	60.4	67.0	T,E
36	163 x 224	1.11	24.4	2.50	210.0	43.4	91.1	58.6	64.3	T,E
37	149 x 210	1.31	12.0	1.88	303.6	51.1	155.1	101.2	65.2	T,Z
38	210 x 250	1.33	4.1	2.20	281.2	52.3	147.1	122.9	73.0	P,E
39	149 x 210	1.79	4.8	1.95	201.6	66.4	133.8	98.7	73.8	P,(E)
42	149 x 210	1.64	27.2	0.85	212.2	59.8	127.0	86.5	68.2	T,O,(I)
43	164 x 225	1.70	25.7	2.20	223.8	61.7	138.1	93.0	67.4	P
44	149 x 250	1.64	25.3	1.95	234.0	60.1	140.6	95.0	67.5	P
45	149 x 250	1.86	5.6	0.83	286.0	68.1	194.8	120.5	61.9	P
47	177 x 250	1.97	3.4	1.47	462.6	71.2	329.4	188.2	57.1	T,Z
50	250 x 297	1.79	3.5	0.82	484.1	66.6	322.6	159.3	49.4	T,I

(a) All runs in which reactant feed was initiated were assigned run numbers; only those yielding meaningful data are included in this Table. See foot note (d) for comments on those not included.

(b) Based on thermodynamic calculation from data used earlier in this program.

(c) Code: P = planned termination, zinc supply exhausted, T = terminated prematurely due to one of following: Z = problem(s) with zinc feed system, S = problem(s) with SiCl_4 feed system, E = constriction in exit line, I = constriction at reactor inlet(s), O = constriction in condenser outlet.

(d) Runs 32, 34A, 35, 46, and 48 were aborted due to problems with the zinc feed system. Run 34 was aborted due to a problem with the SiCl_4 feed system. Runs 40, 41, 48A and 49 were aborted because of plugging at the reactor inlet.

APPENDIX B

ERRATA - FIRST, SECOND, AND THIRD QUARTERLY REPORTS

Listed below are several errors which have been noted in the preceding quarterly reports that could mislead the reader if not corrected.

First Quarterly Report

- (1) On page 36, paragraph 6, line 2, the words "carbon containing" should be inserted before "solid phase".

Second Quarterly Report

- (1) In Table 19, page 45, the \$0.458 cost of the "Electrical" item, "Other Than Refrigeration" was omitted.
- (2) Appendix, page A-2, line 4, "experiment" should read "experiments".
- (3) Table A-1
 - (a) The Run No. in the right-hand column should read 88-23 (88 being the record book page number for internal ready reference, and 23 being the sequence number)
 - (b) The TDE value for Run 88-23 should read 77, and the TD percent of TDE should read 76.6 (further refinements led to somewhat different values; see Table B-1 of the Third Quarterly Report).
- (4) Appendix, page A-4
 - (a) Paragraph 2, line 6, "conical" should read "hemispherical"

- (b) Paragraph 3, "90-23" in line 3 should read "88-23"; "99" in line 4 should read "77"; and "65" in line 5 should read "77", in accordance with the changes in Item (3) above.
- (5) Appendix, Figure A-2, page A-5, the purge inlet and chlorine outlet in the electrolytic cell cover are not shown. "Ground graphite" should read "grooved graphite".
- (6) Appendix, page B-3, paragraph 3, line 3, "above" should read "alone".

Third Quarterly Report

- (1) Page 2, Introduction, Paragraph 2, lines 4 and 5, "titanium" should read "silicon" (two places).
- (2) Page 23, penultimate line, insert "\$" before "0.04".
- (3) Page 25, line 5, "combination" should read "continuation". Conclusions, (1), last line "\$" should precede "0.10".