N76 12477

LOW-COST PROCESSES FOR SOLAR-GRADE SILICON

under

RESEARCH AND DEVELOPMENT OF LOW-COST PROCESSES
FOR INTEGRATED SOLAR ARRAYS

GRANT NSF/RANN/SE/GI-29729

for

15 April 1974 - 14 July 1975

at

$144,892

by

LEE P. HUNT
DOW CORNING CORPORATION

LEON D. CROSSMAN, ASSOC. PRINCIPLE INVESTIGATOR

under subcontract to

UNIVERSITY OF PENNSYLVANIA
MARTIN WOLF, PRINCIPLE INVESTIGATOR

Presented at

NATIONAL SOLAR PHOTOVOLTAIC PROGRAM REVIEW MEETING
LOS ANGELES, CALIFORNIA

July 22-25, 1975

ABSTRACT

Dow Corning's objective is to determine the best process for the high-volume production of solar-grade silicon (SoG-Si) at less than $10/kg within the ERDA milestone of having a pilot plant available by mid-1980.

The overall process screening approach (Visual Aid 2) which began with over 200 possible reactions leading to silicon has reduced this number to ten (V.A.3.) which still fall within the constraints mentioned above. Two of these reactions involve the direct reduction of silica to silicon via aluminum or carbon*. Seven other reactions involve the use of various reductants to convert silica to silicon via intermediate silicon monoxide. The tenth reaction uses recyclable SiF_4 to transport *in situ* produced silicon via intermediate SiF_2; this is currently under study by the University of Pennsylvania.

The reactions described above, in addition to processes involving silicates and/or electrolytic techniques, have been divided into two broad categories (V.A.4.): (1) metallurgicalgrade silicon (MG-Si) process upgrading, and (2) other processes. This was done since the commercial process for producing MG-Si already meets the high-volume, low-cost guidelines for SoG-Si** and, therefore, has a good probability of meeting the mid-1980 pilot plant milestone. The "other processes: are still in the conceptualization or research stage.

Upgrading the MG-Si process is being pursued in four associated areas in order to improve the purity of the normally 98% material (V.A.5.). The first two work areas involve purification of raw materials entering the process in addition to upgrading the arc furnace itself. These areas will be pursued, assuming contract extension. Success appears very favorable based upon suggestions from raw materials suppliers, arc furnace manufacturers, and MG-Si producers (B.A.9.).

The second two areas of process upgrading comprise improving the purity of the silicon after it leaves the arc furnace by reactive gas blowing and unidirectional freezing. Since both methods have been shown to reduce aluminum and heavy metal impurities by one to two orders-of-magnitude (V.A.7.), it is planned to study these methods in conjunction in a specially designed gradient furnace. Neither of the two methods, however, significantly reduce the levels of boron or phosphorus thereby stressing the need for initiating efforts in the raw material and arc furnace areas. The delivery time for an experimental arc furnace results in this item being on the critical path for meeting the mid-1980 pilot plant milestone (V.A.14).

---

*This is today's commercial, submerged-electrode, arc furnace process for metallurgical-grade silicon.

**One furnace can generate greater than 10,000 tons per year of MG-Si selling at $1/kg.

The best cell produced to date was fabricated from MG-Si that had been blown with an O_2-Cl_2 mixture, unidirectionally solidified, and 6-float-zone passed (to determine a base boron level of 0.04 ohm-cm). The cell showed a 10.7% AMO efficiency with I_{sc} = 33 ma/cm^2 and V_{oc} = 0.62 v (V.A.8.).

In the "other processes" category, the use of silicates as a silicon source and of electrolysis as a process were studied. Silicates were deemed unfavorable since their inherent chemical composition involves the presence of another metallic element (V.A.11.). The best electrolytic process uses a 1000°C fused salt of silica in cryolite. Preliminary analysis of this process was viewed pessimistically for the reasons cited in V.A.10.

A summary of key results appears in Visual Aid 12.

Summarized future plans appear in Visual Aid 15.

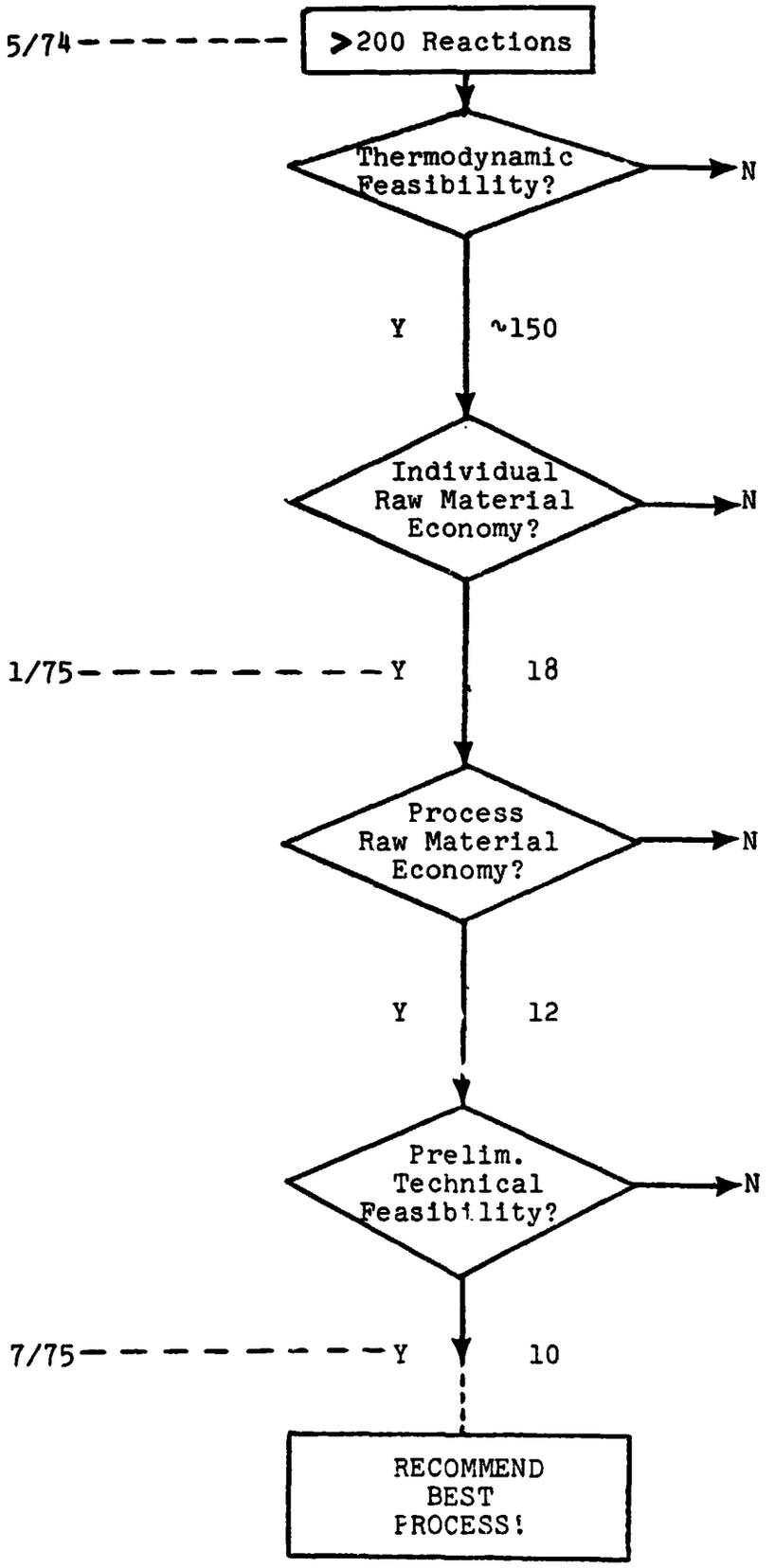
DOW CORNING OBJECTIVE

To Determine The Best Process For

Producing Silicon For Solar Arrays

- At <$10/kg
- At High Volume Rates
- Within ERDA Milestones

PROCESS SCREENING PROCEDURE



REMAINING PROCESSES

No. Reactions	1975 Raw Mat'l. Cost For Reaction ($/kg Si)	Reaction Type
2	0.12 for C 0.97 for Al	$SiO_2 \xrightarrow{C^* \text{ or } Al} Si$
1	0.12 (SiF_4 recycled)	$SiO_2 \xrightarrow{2C} Si \xrightarrow{SiF_4} 2SiF_2 \xrightarrow[-SiF_4]{} Si$
7	0.12 min. to 2.06 max.	$SiO_2 \xrightarrow{Al,\ C,\ \text{or } Mg} SiO \xrightarrow{Al,\ C,\ H_2 \text{ or } Mg} Si$

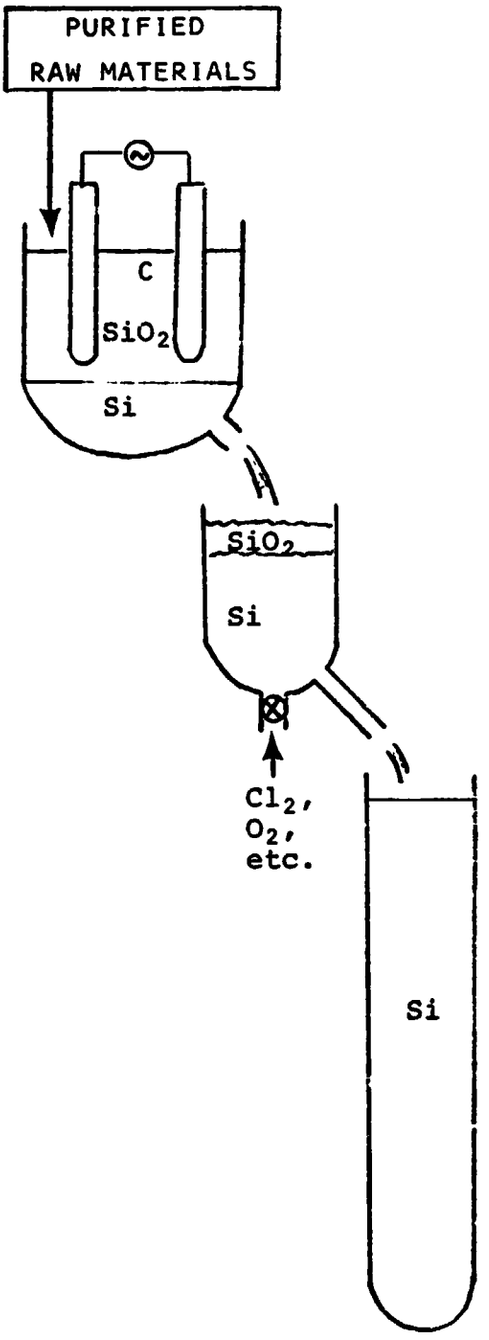
* Commercial Arc Furnace Process

PROCESS CATAGORIZATION

- UPGRADING THE METALLURGICAL-GRADE SI PROCESS
  - A PROVEN COMMERCIAL PROCESS
  - CAPABLE OF MEETING MILESTONES SOONER THAN R&D STAGE PROCESSES
  - ALL SI COMPOUNDS FROM REDUCTION OF QUARTZITE
  - CURRENT MG-S TS $1/KG
  - PRESENT RATES >10,000 T/Y PER FURNACE

- OTHER PROCESSES
  - SiO GENERATED IN ARC FURNACE
  - SiF_2 TO TRANSPORT SI
  - ELECTROLYTIC
  - SILICATES

UPGRADING MG-SI PROCESS



AREAS OF WORK		IMPURITY STATUS
I.	RAW MATERIALS	B REMOVED? P + OTHERS TO BE TESTED.
II.	ARC FURNACE	B,P, + OTHERS TO BE TESTED.
III.	REACTIVE GAS BLOWING AND/OR SLAGGING	AL & HEAVY METALS REMOVED.
IV.	UNIDIRECTIONAL SOLIDIFICATION	AL & HEAVY METALS REMOVED.

UPGRADING MG-SI BY UNIDIRECTIONAL SOLIDIFICATION (WORK AREA IV)

	Impurity Levels (ppma)		
Impurity	MG-Si	CZO Seed	CZO 50% Point
B	39	39	44
P	37	23	21
Al	780	<10	60
Cu	40	< 4	< 4
Fe	910	< 5	140
Heavy Metals*	20-150	< 6	< 5-20

* Ti, V, Cr, Mn, Ni

UPGRADING MG-SI BY REACTIVE GAS BLOWING (WORK AREA III)

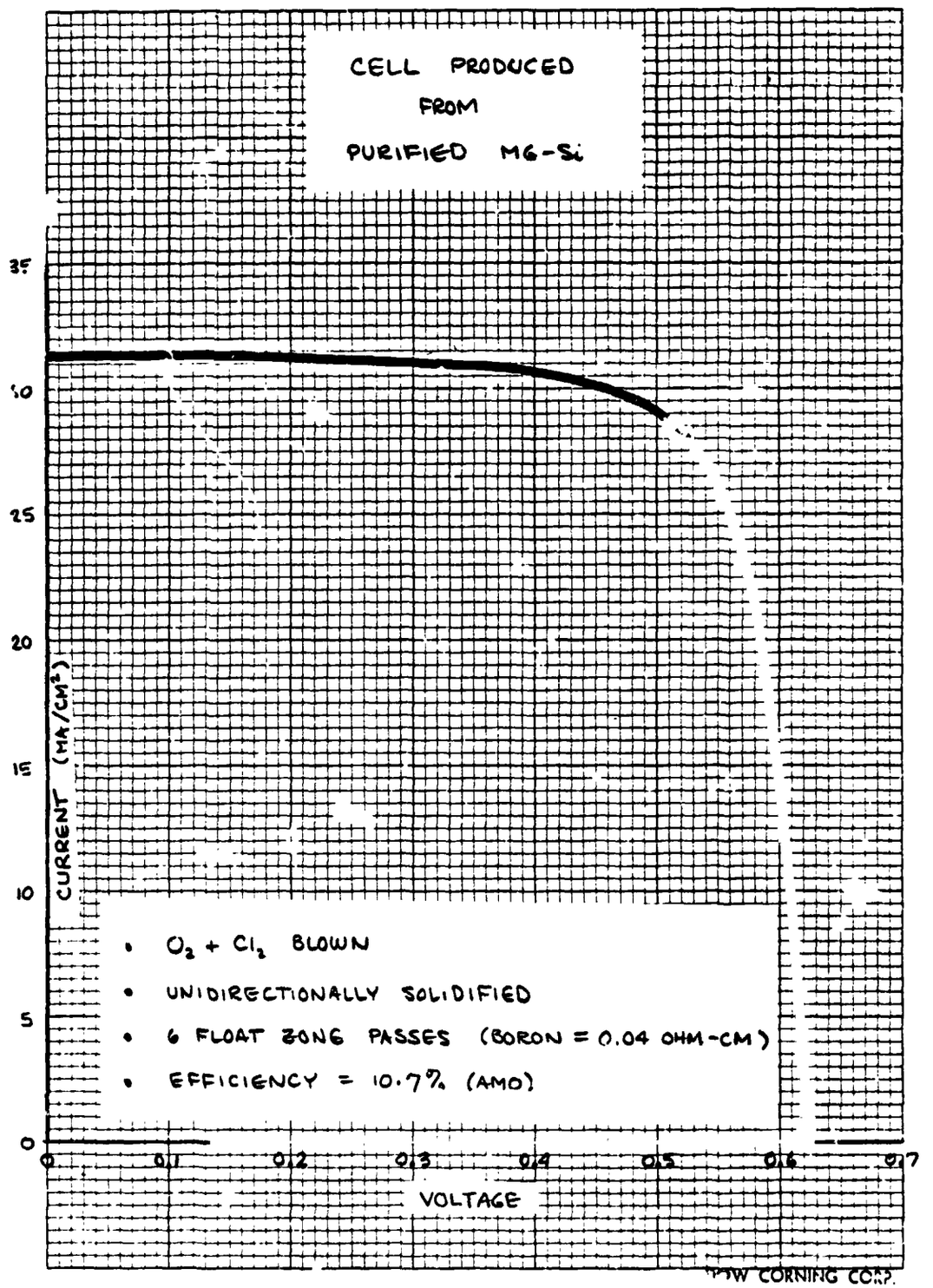
Best Data To Date Via Emission Spectroscopy

	Impurities in MG-Si (ppma)		
Impurity	Not Blown	Cl_2 Blown	O_2 Blown
B	39*	38*	36*
P	23	21	23
Al	1600	83	470
Cu	35	4	4
Fe	1600	40	40
Heavy Metals†	50-100	< 5	5-40

* ~0.04 ohm-cm by FZ evaluation

† Ti, V, Cr, Mn, Ni

V.A.8.


CELL PRODUCED
FROM
PURIFIED MG-Si
CURRENT (MA/CM²)
35
30
25
20
15
10
5
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
VOLTAGE
• O₂ + Cl₂ BLOWN
• UNIDIRECTIONALLY SOLIDIFIED
• 6 FLOAT ZONE PASSES (BORON = 0.04 OHM-CM)
• EFFICIENCY = 10.7% (AMO)
HW CORNING CORP.

UPGRADING POLY-SI PROCESS
(WORK AREAS I & II)

I. RAW MATERIALS

- IMPURITIES FLOW THROUGH FURNACE
  - QUARTZ'TE CAN BE UPGRADED (B < 1 PPMA)
  - CARBON SOURCES CAN BE UPGRADED
  - EFFECT OF B FROM RAW MAT'L → POLY-SI DOCUMENTED

II. ARC FURNACE

- UPGRADE LINER, TAP HOLE PLUG, LADLE, ETC.
- NEEDED TO
  - TEST RAW MATERIALS
  - GENERATE SiO
- HAVE VISITED MANUFACTURERS OF ARC FURNACE AND POLY-SI

OTHER PROCESSES

- ELECTROLYTIC (BEST)

	SiO_2 IN Na_3SiF_6 ELECTROLYSIS	ARC FURNACE
TECHNOLOGY EXTENT	EXPERIMENTAL	COMMERCIAL
PRODUCTION RATE (KG SI/HR)	0.1	1000-2000
SI PURITY (WT. %)	99	98
PROCESS ENERGY (KWH/KG SI)	34	13

PESSIMISTIC DUE TO

- 4 ORDERS-OF-MAGNITUDE LOWER RATE
- SAME PURITY LEVEL
- HIGHER PROCESS ENERGY

OTHER PROCESSES

- SILICATES (E.G., $Al_2Si_2O_7 \equiv Al_2O_3 \cdot 2SiO_2$)
  - RULED OUT DUE TO INHERENT IMPURITY CONTENT

SUMMARY OF KEY RESULTS

TEN PROCESSES REMAIN IN RUNNING

- MG-SI UPGRADING FURTHEST ADVANCED COMMERCIALLY
- SiF_2 BY UNIVERSITY OF PENNSYLVANIA
- AL REDUCTION OF SiO_2 REMAINS
- REST INVOLVE SiO

MG-SI UPGRADED

- USING GAS BLOWING
- USING UNIDIRECTIONAL SOLIDIFICATION
- 10.7% EFFICIENT CELL PRODUCED

CRITICALITY OF EXPERIMENTAL ARC FURNACE IDENTIFIED

ELECTROLYSIS PROCESSES VIEWED PESSIMISTICALLY

SILICATES RULED OUT

MAJOR PROBLEMS

TECHNICAL

- REMOVAL OF B AND P

COST

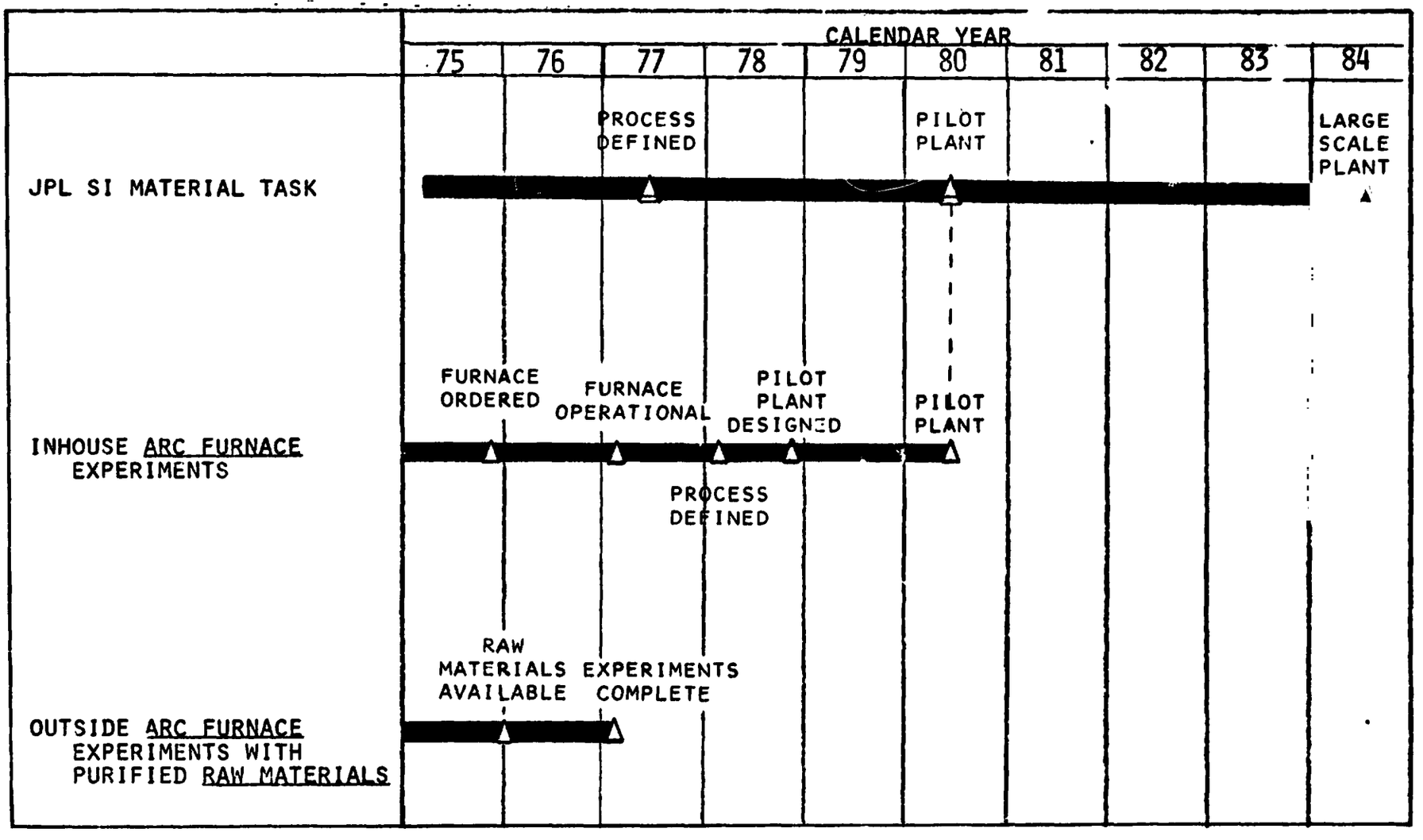
- CAPITAL FOR EXPERIMENTAL ARC FURNACE
- MANPOWER TO IMPLEMENT ALL PROGRAM PHASES

SCHEDULE

- MEETING ERDA MILESTONES

ACTION REQUIRED TO MEET PILOT PLANT MILESTONE FOR WORK AREAS I AND II

V.A.14.



SIX MONTH GOALS UNDER REQUESTED CONTINUATION OF FUNDING

PERIOD: 15 JULY 1975 -- 14 JANUARY 1976

COST: $56,600 ORIGINAL ESTIMATE
$129,529 CURRENT REQUEST

MAJOR GOALS (ASSUMES INTERFACING WITH JPL PROGRAM):

- MG-SI UPGRADING

  10/75 SLAGGING FEASIBILITY DETERMINED
  10/75 PURCHASE OF EXPERIMENTAL ARC FURNACE INITIATED
  11/75 FEASIBILITY DETERMINED OF COMBINED BLOWING/FREEZING IN GRADIENT FURNACE
  12/75 RAW MATERIALS AVAILABLE FOR UPGRADING
  12/75 PLANS COMPLETE FOR EXTERNAL ARC FURNACE EXPERIMENTS

- SILICON MONOXIDE

  10/75 PROCESS POTENTIAL EVALUATED
  12/75 EXPERIMENTS INITIATED

- ALUMINUM REDUCTION OF QUARTZITE

  7/75 ENERGY ANALYSIS PERFORMED
  9/75 PROCESS POTENTIAL EVALUATED
  12/75 EXPERIMENTS INITIATED

- ENERGY ANALYSIS

  9/75 COMPLETE FROM QUARTZITE TO CELL