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VAPOR-ELECTROCHEMICAL METHCD FOR SILICON
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# NOVEL DUPLEX VAPOR-ELECTROCHEMICAL METHOD FOR SILICON SOLAR CELLS

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## SUMMARY

Optimization and scale-up studies of the $SiF_4$-Na reaction have continued. The dependence of the reaction initiation time and of the efficiency of the reaction on Na particle size and reactor temperature have been studied. Close to 100% utilization of Na has been obtained, and formation of by-product fluosilicate has been decreased to below 10 per cent. A $SiF_4$-Na reactor has been built to scale up the reaction by a factor of about 4 and is now being tested. A scaled-up melting system has been built and successfully used to separate Si from kilogram quantities of Si-NaF mixtures. Support studies of the volatilization of NaF performed in a smaller melting system indicated minimal loss of NaF as vapor at $1410^{\circ}$C. The wetting of graphite was also investigated to determine the constituents of the NaF phase which promote good wetting.

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## PREFACE

The JPL Low-Cost Silicon Solar Array Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program aimed at the development of low-cost solar arrays. The work reported here was performed for the Jet Propulsion Laboratory, California Institute of Technology, by agreement between NASA and DOE.

## ACKNOWLEDGMENTS

## TASK I
## $SiF_4$-Na REACTION: SOLID Na FEED

### Solid Na Feed

Studies of the reaction between gaseous $SiF_4$ and solid Na are being continued
- to increase the reaction rate
- to decrease the yield of unwanted by-product $Na_2SiF_6$
- to increase the amount of Na reacted
- to scale up the reactor, using the best operating parameters.

The required information is being obtained by determining the effects of various operating conditions, such as size and shape of the Na metal feed, rate of Na addition and reactor temperature. The criteria established to follow the reaction rate are the $SiF_4$ pressure change that occurs in the reactor when Na is added, and the $SiF_4$ flow rate, which indicates the rate of the reaction between $SiF_4$ and Na.

The $SiF_4$ pressure in the reactor, which is initially 760 torr, exhibits several time-dependent characteristics, as shown in Figure 1.

- An induction period $t_1$ is required for the added Na to heat up to reaction temperature. This is usually 0.1 to 3 min, depending on the mass of the Na added and on the reactor temperature.

- The primary reaction of most of the added Na occurs with a maximum rate (minimum $SiF_4$ pressure or maximum $SiF_4$ flow rate) at $t_2$, a value which also depends on Na mass and is typically 1 min.

- A secondary reaction is sometimes observed occurring with a maximum rate at $t_3$, at about 5 min, shown by the dashed line plotted in Figure 1. The cause of this secondary reaction is not yet understood, but may be associated with the release of Na previously coated with reaction products.
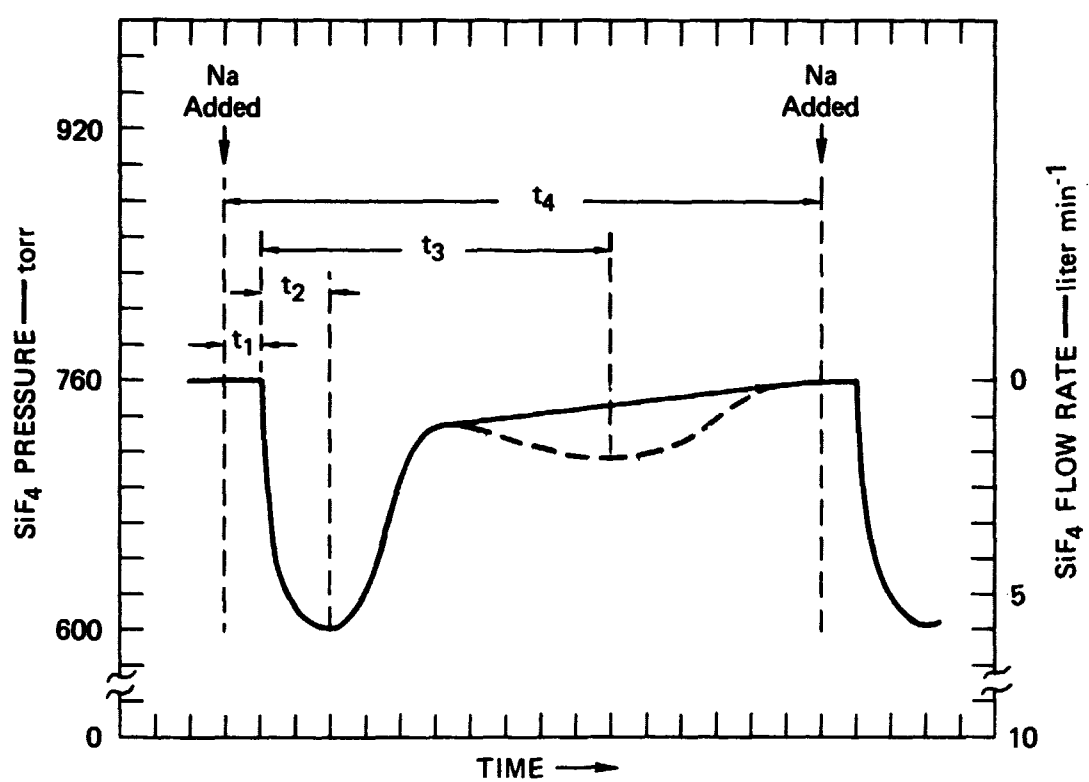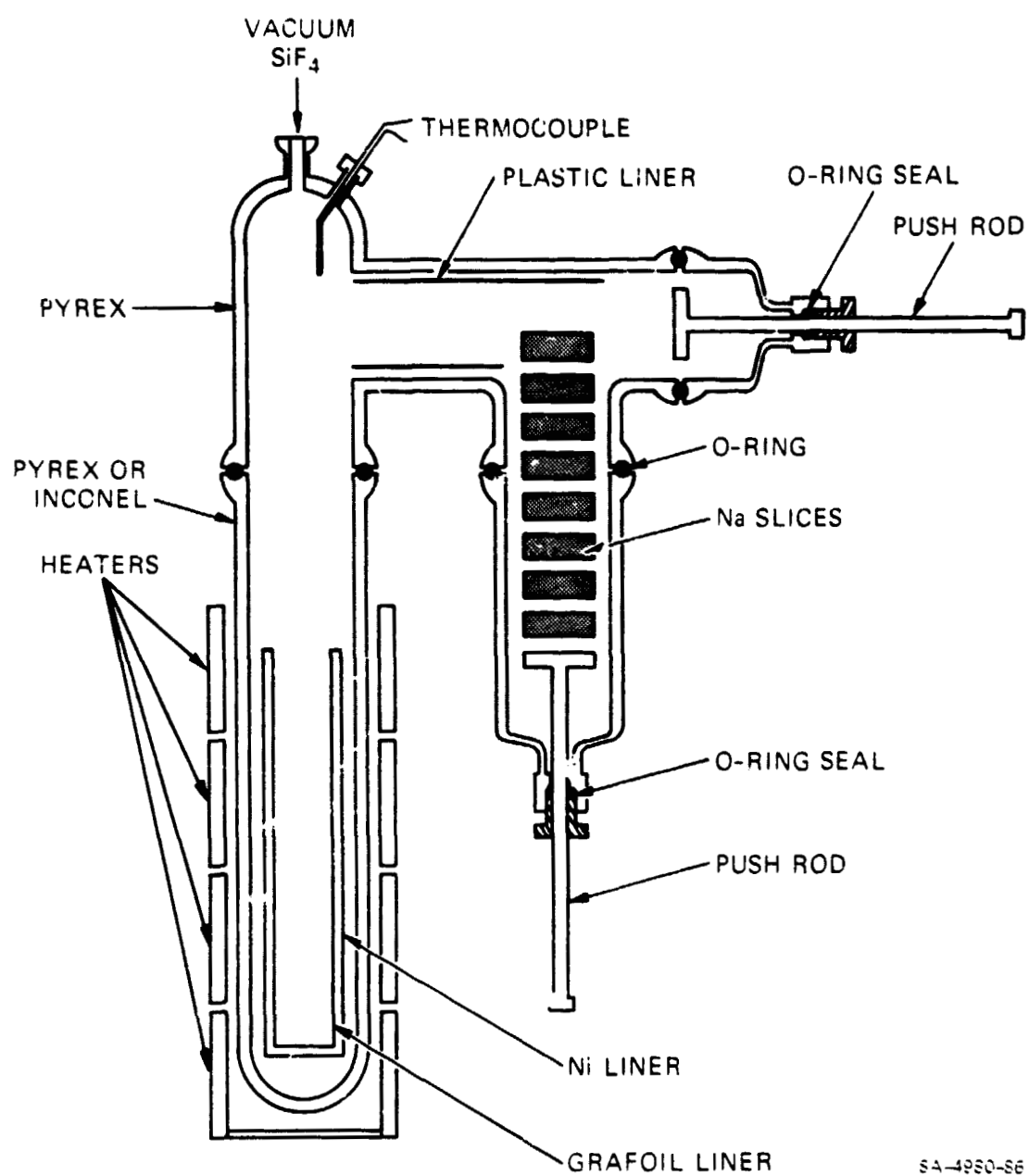
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FIGURE 1 SCHEMATIC REPRESENTATION OF FOUR REACTION PERIODS ASSOCIATED WITH SiF$_4$ – Na REACTION

- Another aliquot of Na is added at $t_4$, typically at about 6 min, when the $SiF_4$ flow rate becomes sufficiently low to indicate that reaction of the previously added Na is negligible, usually less than $10^{-3}$ moles Na/min or 0.2 g Na/min.

The above reaction periods have been ascertained by continuous recording of the $SiF_4$ pressure and by visually observing the $SiF_4$ flow rate, using a rotameter. Data acquisition equipment has been extended (1) to record the $SiF_4$ flow rate, using an electronic flow meter, and (2) to measure the total amount of reacted $SiF_4$ by electronically integrating the $SiF_4$ flow rate. These improved techniques for measuring $SiF_4$ flow should provide a better basis for understanding the kinetic parameters of the $SiF_4$-Na reaction.

After completing a $SiF_4$-Na run, the reaction product, which is in the shape of a cylinder, is divided along its length into segments corresponding to the different rates of Na addition. These segments are pulverized with a plastic hammer, and Grafoil is removed as completely as possible. The reaction products are analyzed to determine the amount of unreacted Na by an acid titration, the amount of Si, NaF and $Na_2SiF_6$ by x-ray diffraction, and impurities by emission spectroscopy. The x-ray technique is carried out by adding to the product sample a known amount of KCl as a reference substance. Using standard mixtures, the weight fraction of the $Na_2SiF_6$ is determined from the ratio of the peak intensities of $Na_2SiF_6$ and KCl. The method is rapid and accurate to about ±5%.

The apparatus for carrying out the $SiF_4$-Na reaction has recently been modified, as shown in Figure 2. The vertical Na feeder provides greater control of the amount of Na that can be added to the reactor than was possible with the horizontal feeder used previously (Quarterly Report No. 12). To study the effect of high temperatures, an Inconel reactor was constructed to replace the pyrex reactor used in previous work. The

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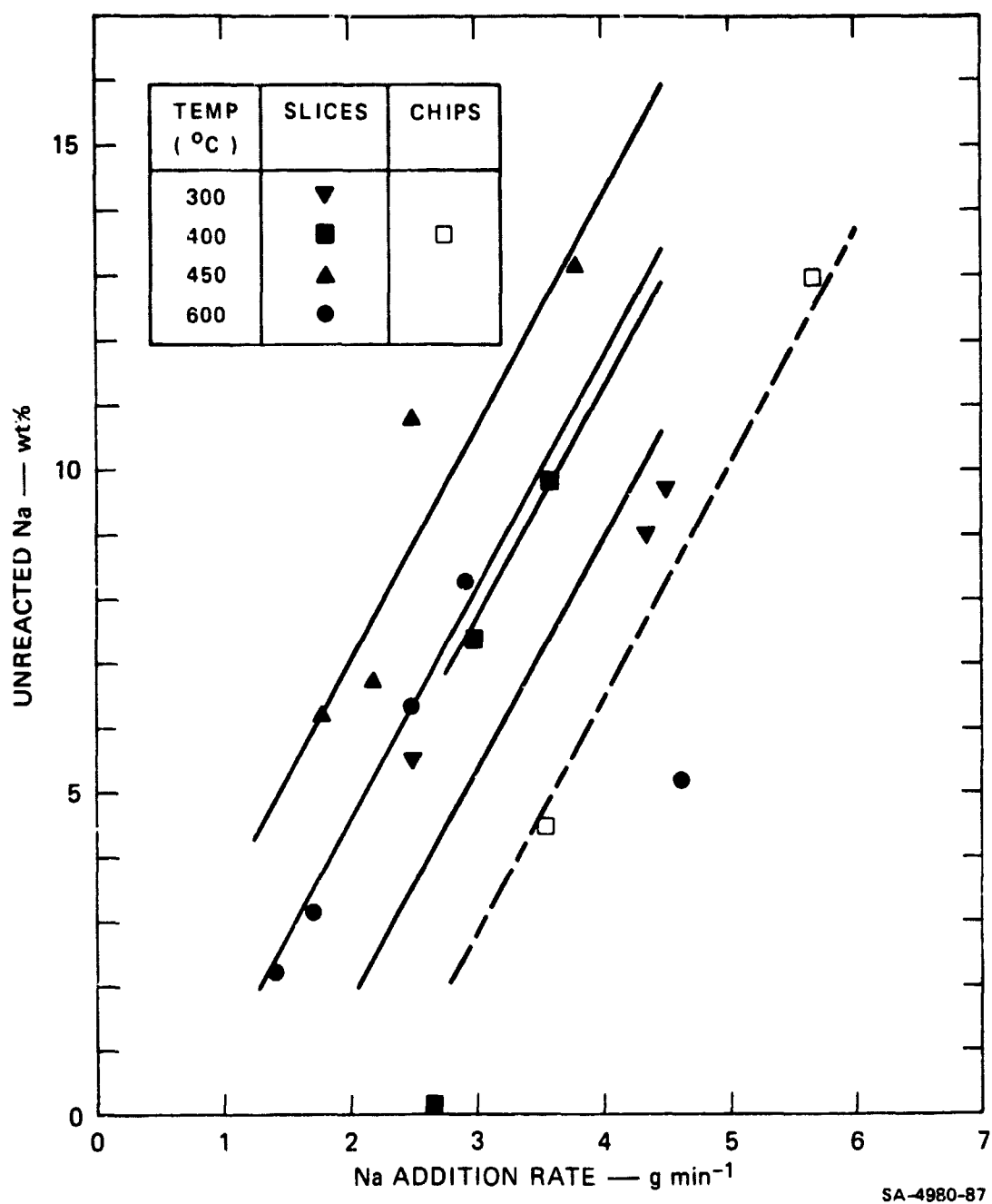FIGURE 2 REACTOR FOR THE SiF$_4$-Na REACTION: SOLID Na FEEDING TECHNIQUE

VACUUM
SiF$_4$

THERMOCOUPLE

PLASTIC LINER

O-RING SEAL

PUSH ROD

PYREX

PYREX OR
INCONEL

O-RING

Na SLICES

HEATERS

O-RING SEAL

PUSH ROD

Ni LINER

GRAFOIL LINER

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Inconel reactor is heated along its length with four separate heating tapes, each with a thermocouple and a temperature controller. The heating tapes are rated for temperatures up to $800^{o}C$. The reactor is lined with nickel sheet (7cm i.d.), which in turn is lined with Grafoil. The greatest Na load that this reactor can accommodate is about 400 g Na, corresponding to the production of about 120 g Si.

Many reaction studies were made, with Na slices of various thickness and shapes, to determine the effects of the amount of surface area of the Na feed. For one study, Na chips were prepared by grating metallic Na with a stainless steel kitchen grater. The results generally indicate that the $SiF_4$-Na reaction is more complete (less unreacted Na) when the feed particle size is small and the addition rate is low. This trend is shown in Figure 3, which relates the amount of unreacted Na to the Na addition rate. The four solid lines show results using Na slices (0.4 cm thick and 6 cm diameter) at four reactor temperatures. The results shown by the dashed line were obtained using Na chips (typically 0.05 x 0.5 x 2 cm). The indicated reactor temperature is the lowest temperature of the reactor walls, but the wall temperature was often $100^{o}C$ higher in the vicinity of the reaction zone. In each run the Na was fed at different rates. Typically, the disks were added first one at a time, then two at a time, and finally three at a time. About equal amounts of Na were added for each addition rate. The results in Figure 3 are in general agreement with the earlier work on disks (6 mm thick), based on experiments in which the reactor bottom was heated, but not the walls. (Quarterly Report No. 12, Figure 2).

Figure 3 indicates that the amount of unreacted Na decreases with the lower Na addition rate. At a given addition rate, less unreacted Na resulted from a feed of chips than from a feed of slices (reactor temperature of $400^{o}C$). The figure also indicates the effect of reactor temperature: the amount of unreacted Na for a given addition rate passes through a maximum at about $450^{o}C$ and is least at $300^{o}C$.

FIGURE 3    EFFECTS OF Na ADDITION RATE AND REACTOR TEMPERATURE ON AMOUNT
OF UNREACTED Na

Na added as slices (6 cm diameter and 0.4 cm thick) or as chips (0.05 cm X 0.5 cm
X 2 cm).

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Two data points in Figure 3 should be noted. The reaction product containing zero unreacted Na (2.7 g Na/min as slices) was produced in a separate run at $400^{\circ}$C in which the reaction product continued to be exposed to $SiF_4$ overnight, during the cooling of the reactor. In all other cases, the $SiF_4$ was removed by evacuation at the end of the run, while the reactor was still hot. The other data point of interest represents the run at $600^{\circ}$C for the highest Na addition rate (4.5 g Na/min). We believe that the unexpectedly small amount of unreacted Na in this part of the reaction product (3 slices per addition) results from the distillation of some Na from the reaction zone and condensation in the upper part of the reactor. In fact, Na droplets were observed on the upper reactor wall when the reactor was opened.

We will continue to study the effects of reactor temperature, including the following considerations:

- A crust of reaction products forms around some of the unreacted Na and produces a barrier for diffusion of $SiF_4$ and Na. Higher reaction temperatures would be expected to increase the diffusion rate through the crust and to increase the vapor pressure of Na. However, higher temperatures also produce a more dense, glassy appearing reaction product, which might decrease the overall diffusion rate across the crust. It is noted that pure NaF melts at $995^{\circ}$C, and even higher temperatures may be attained locally.

- Higher temperatures ($> 600^{\circ}$C) favor decomposition of $Na_2SiF_6$, which is an undesirable by-product because it consumes $SiF_4$. The yields of Si should be greater at higher reactor temperatures because less $SiF_4$ is thus consumed.

- At the highest reactor temperature studied ($600^{\circ}$C), some Na vapor condensed on the cooler walls of the reactor. It condensed as droplets which apparently did not react completely with $SiF_4$, because they were at a low temperature ($>200^{\circ}$C), and probably because a protective crust formed.

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- The reactor walls must be sufficiently hot (at least $150^{\circ}C$) to induce the reaction of the added Na. In early runs, we heated only the bottom of the reactor to initiate the $SiF_4$-Na reaction and depended on the heat of the reaction to sustain the temperature. In some cases, added Na would not react if the temperature of the reaction products cooled, e.g., because Na was added too slowly or too fast. Currently, the reactor is heated along its length, so that cooling below a selected temperature will not occur.

As part of the optimization studies, the amount of by-product $Na_2SiF_6$ is being studied by an x-ray method. The results show that the amount formed is influenced by the outside wall temperature of the reactor tube. With external heat provided to the 7 cm i.d. glass reactor, the temperature at the reaction zone level ranged from $400^{\circ}C$ to $600^{\circ}C$, and the $Na_2SiF_6$ was less than 10 wt pct. Without external heat, the wall temperature ranged between $200^{\circ}C$ and $250^{\circ}C$ and $Na_2SiF_6$ ranged from 10 to 20 wt. pct. When the reactor wall was air cooled, the wall temperature was less than $100^{\circ}C$, and the $Na_2SiF_6$ content of the products ranged from 20 to 30 wt pct. It was also determined that the amount of $Na_2SiF_6$ formed increased with the length of time between Na additions. Intervals greater than 6 minutes resulted in the formation of 15 wt pct (or greater) $Na_2SiF_6$. Shorter intervals (2-3 min) produced less than 10 wt pct. The effects of higher temperature on $Na_2SiF_6$ formation will be studied with the new 7 cm i.d. Inconel reactor.

A reactor has been constructed to scale up the $SiF_4$-Na reaction by a factor of about 4, to produce about 0.5 Kg Si per run. The outer reactor wall is a Pyrex tube (15 cm o.d.). On the inside wall is a sheet nickel liner (15 cm o.d. and 60 cm high), with a Grafoil sheet liner placed inside the Ni. This larger scale reactor will be used to study scale-up design and to increase the yield of reaction products needed for melt-recovery of Si. Also, the larger reactor may decrease the problem of lowered yields due to adherence of reaction products to Grafoil. In the 7 cm i.d. reactor, reaction products adhering to the Grafoil have typically amounted to 20 wt. pct. of the total.

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## TASK 2

## MELT SEPARATION

As mentioned in previous reports, we have demonstrated that the Si
and NaF produced by the $SiF_4$-Na reaction can be separated by heating the
mixture at temperatures above the melting point of silicon. During this
quarter, we scaled up our melting system so that it can handle several kilo-
grams of reaction products.

A small induction furnace was used to check new designs and improve-
ments before they were implemented in our large resistance furnace. The
furnace can accommodate a small graphite susceptor crucible (2.5 cm o.d.,
10 cm long) and can be heated to $1500^{\circ}C$ in an Ar atmosphere in 10 to 15
minutes. To understand the behavior of NaF during melting, a series of
experiments was performed in the small furnace. NaF volatilization was
studied because it is relevant to the melt separation of the Si-NaF mixture.
For example, in the large scale furnace, large amounts of NaF vapors might
deposit on the cooler walls of the graphite pipe through which the mixture
of reaction products if fed, causing plugging. Tests with the small induc-
tion furnace indicate that the rate of evaporation was 2.8 mg $cm^{-2}$ $hr^{-1}$ as
measured by weight loss for NaF heated to the melting temperature of silicon
($1410^{\circ}C$) for 1 hour. This rate is equivalent to a loss of less than 2 wt.
pct. of the initial weight of NaF. Thus, the evaporation of NaF should not
present a major problem at temperatures up to $1410^{\circ}C$.

When NaF was melted in the small graphite crucible and subsequently
cooled, it shrank 5% with respect to the melt diameter and was easily re-
moved from the crucible. The contact angle of NaF on graphite at $1400^{\circ}C$
was determined by observing a sessile drop of molten NaF on a graphite
platform. The contact angle was approximately $60^{\circ}$, indicating that the
NaF does not readily wet the graphite surface.

Scanning electron microscopy was used to examine the surface of graphite that had been in contact with liquid NaF. Crystals and also frozen spherical droplets of NaF were observed (Figure 4a) and these tended to concentrate along rough areas produced during machining of the graphite crucible (Figure 4b).

Also, NaF which had condensed and solidified from vapor onto a smooth, cool Grafoil surface formed droplets whose contact angle with the graphite was always less than $90^{\circ}$ (Figure 5), again indicating very poor wetting of the Grafoil by NaF.

On the basis of these preliminary studies, it was concluded that NaF, by itself, will not significantly attack graphite containers at temperatures near the melting point of Si.
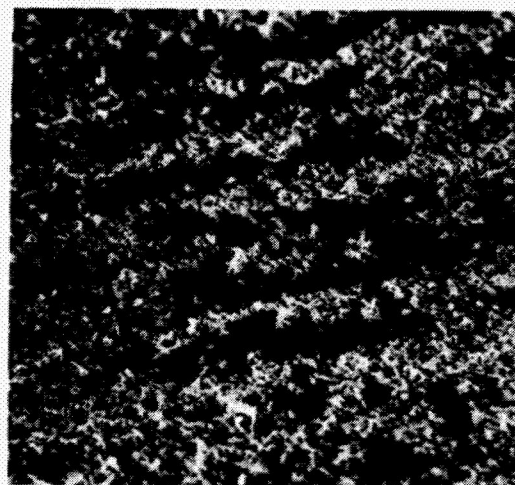
As part of our scale-up work, a 2 in. diameter Fairchild silicon-crystal growing furnace has been modified to melt the $SiF_4$-Na reduction products (Figure 6). The furnace consists basically of a water-cooled cylindrical heating chamber (A), a water-cooled cover (B), and a gas solid feeder (C) connected to the heating chamber through a port on the upper section of the cover. A 40 kw power supply (D), a gas supply system and a vacuum system constitute the rest of the apparatus.

The cylindrical heating chamber of the furnace, shown in Figure 7, contains a graphite resistance heater (A) (8 in. i.d., 8 in. length), five concentric Mo heat shields (B) enclosed in a gas-tight, water-cooled, stainless steel chamber (C), and a graphite crucible (D) placed inside the heater and joined by a graphite lid to the graphite pipe (E). The ensemble is enclosed by the cover (F), which slides down and makes the chamber gas tight by means of an O-ring (G).

Figure 8 shows the cover of the heating chamber and the feeder. The upper part of the cover has two circular ports (4 in. diam). One of the ports (A) is connected to a vertical tube down which the reaction products are fed, and the other has a glass window to observe the inside of the

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(a) MORPHOLOGY OF THE NaF DEPOSIT MAGNIFICATION 500X

(b) DISTRIBUTION OF NaF ALONG MACHINING LINES ON THE GRAPHITE SURFACE MAGNIFICATION 100X
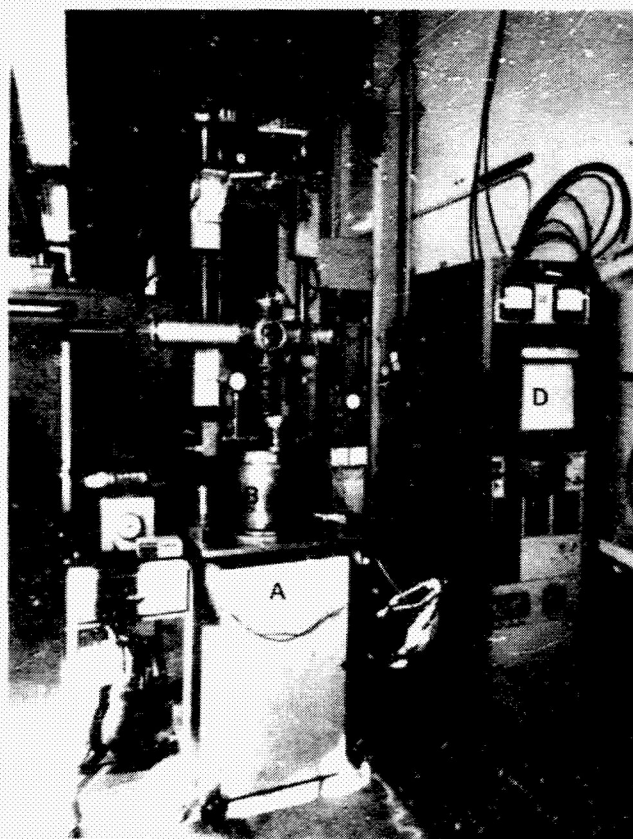
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FIGURE 4    NaF DEPOSIT ON GRAPHITE AFTER CONTACT WITH MOLTEN NaF AT 1400° C
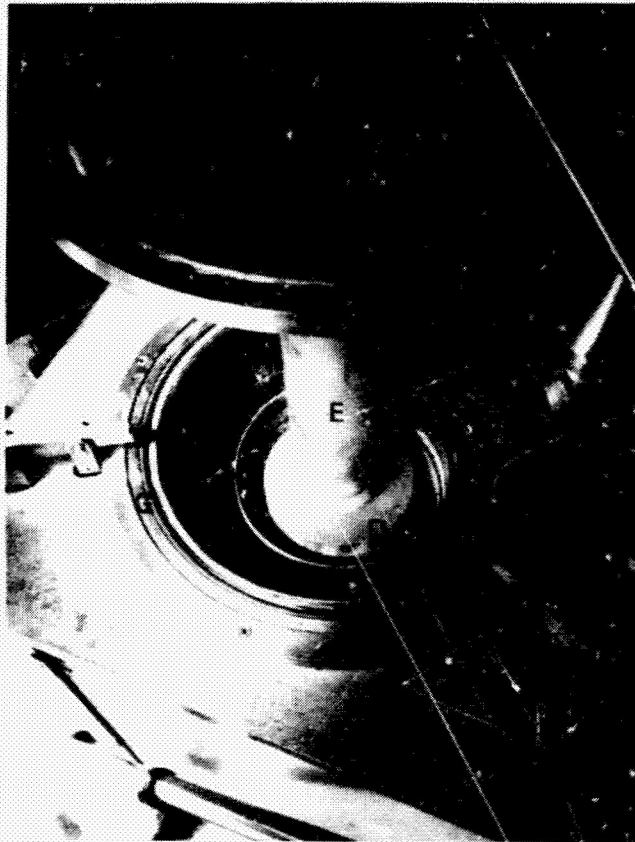


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FIGURE 5    VAPOR CONDENSED NaF ON GRAFOIL AFTER COOLING

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FIGURE 6      SCALED UP MELTING SYSTEM, GENERAL VIEW
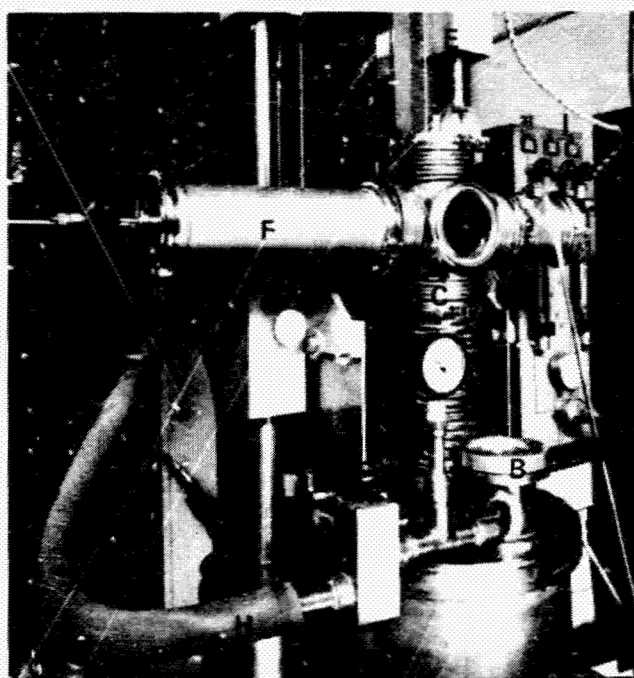A. Heating Chamber, B. Cover, C. Feeder, D. Power Supply

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**FIGURE 7**    SCALED UP MELTING SYSTEM

Detail of the heating chamber – A. Graphite Heater, B. Molybdenum
Heat Shields, C. Water Cooled Inner Wall of the Heating Chamber,
D. Graphite Crucible and Lid, E. Graphite Pipe, F. Cover, G. O-Ring

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FIGURE 8    SCALED UP MELTING SYSTEM

Detail of the cover and feeder — A. Connection Port, B. Furnace
Viewport, C Feeder Tube, D. Feeder Cross, E. Window for
Temperature Measurement, F. Reaction Products/Reactants Feeder,
G. Feeder Viewport, H. Vacuum Line, I. Flow Meter Panel

chamber (B). The vertical feed tube (C) consists of a 4 in. water-cooled stainless steel pipe attached on top to a 5-way, 4 in. cross (D). The top of this cross has a glass window (E) that allows direct optical temperature reading. One lateral port of the cross is connected to the horizontal reaction product feeder (F) (this is similar to the one described in Quarterly Report No. 11), and another is attached to the $SiF_4$ gas inlet. The front port (G) has a window to observe the reaction products as they are fed through the lateral ports. Two O-rings placed on the upper exterior face of the graphite pipe provide a gas seal against the inner walls of the vertical feed tube. During operation, reaction products (RP) are fed from (F) through (C) into the graphite crucible. The RP are kept under an $SiF_4$ atmosphere to consume unreacted Na that may be present. The heater chamber is kept under an Ar flow. Gas pressures for $SiF_4$ and Ar are kept at nearly 1 atm, and Ar is leaked continuously through the vacuum pump (H). Gas flows are measured and controlled by a valve flow meter arrangement (I).

The melting system has a capacity to melt up to about 5 kg of reaction product per batch, to produce about 0.5 kg of silicon.

The first experimental run in this large furnace was a scaled up version of the NaF volatilization and NaF-graphite contact angle experiments previously run in the small RF induction furnace. In the large scale experiment, 0.5 kg of NaF was loaded in the graphite cup and heated to $1200^{o}C$ to melt the salt. The melt temperature was then raised to and maintained at $1400^{o}C$ for 30 min. Although NaF vapors (condensed fume) were visible and interfered with pyrometric temperature measurements, they did not produce any appreciable build-up or crust on the walls of the feeding pipe. The solid cylinder of NaF obtained after cooling had 5% smaller diameter than the crucible i.d., and could be easily slipped out of the crucible, confirming the nonsticking characteristics of NaF on graphite.
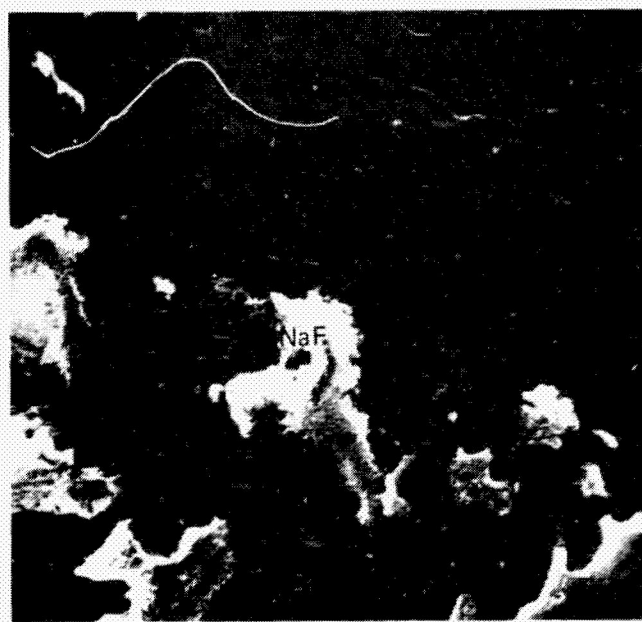
A batch (0.85 kg) of Si-NaF mixture (1:4 mol ratio) was prepared from components (not reaction product) and was also melted in the large furnace. The mixture was fed from the reactor feeder into the crucible, which

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contained a starting bed of 0.5 kg of NaF at $1100^\circ$C. The Si–NaF mixture
was fed continuously in small amounts (approximately 50 gram) over a period
of 10 min. The melt was maintained at $1100^\circ$C for 30 min. The temperature
was then increased to $1470^\circ$C ($\pm20^\circ$C) and held for 5 min. After cooling,
the solid was easily slipped out of the graphite crucible, which had been
lined with an inner Grafoil sheath. A clean phase separation was observed,
with all the Si agglomerated at the bottom of the crucible and the NaF in
an upper layer (Figure 9a).

Scanning electron microscopy with XES Scan (20X, Figure 9b) shows the
Si–NaF interphase with some Si which has not yet coalesced into the big
pool. This information is consistent with the mechanism previously reported,
by which individual grains start to fuse with each other through bridge
formation (Quarterly Report 12). The amount of isolated Si was estimated
to be less than 1% of the total amount of Si, even for brief melting times
(15 min).

(a) GENERAL VIEW, INCH SCALE



(b) DETAIL OF THE Si, NaF INTERPHASE,
MAGNIFICATION 20X

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FIGURE 9    CROSS-SECTION OF THE Si, NaF MIXTURE AFTER MELTING
IN THE FURNACE

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