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NOVEL DUPLEX VAPOR-ELECTROCHEMICAL METHOD FOR SILICON SOLAR CELLS

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Optimization and scale-up studies of the SiF₄-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 SiF₄-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°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.

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TASK I

SiF₄–Na REACTION: SOLID Na FEED

Solid Na Feed

Studies of the reaction between gaseous SiF₄ and solid Na are being continued

- to increase the reaction rate
- to decrease the yield of unwanted by-product Na₂SiF₆
- 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 SiF₄ pressure change that occurs in the reactor when Na is added, and the SiF₄ flow rate, which indicates the rate of the reaction between SiF₄ and Na.

The SiF₄ pressure in the reactor, which is initially 760 torr, exhibits several time-dependent characteristics, as shown in Figure 1.

- An induction period t₁ 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 SiF₄ pressure or maximum SiF₄ flow rate) at t₂, 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 t₃, 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.
FIGURE 1 SCHEMATIC REPRESENTATION OF FOUR REACTION PERIODS ASSOCIATED WITH SiF₄ – 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$_2$SiF$_6$ 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$_2$SiF$_6$ is determined from the ratio of the peak intensities of Na$_2$SiF$_6$ 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
Figure 2: Reactor for the SiF₄-Na Reaction: Solid Na Feeding Technique
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°C. The reactor is lined with nickel sheet (7 cm 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 SiF₄-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°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°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°C and is least at 300°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).
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°C in which the reaction product continued to be exposed to SiF₄ overnight, during the cooling of the reactor. In all other cases, the SiF₄ 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°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 SiF₄ 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°C, and even higher temperatures may be attained locally.

- Higher temperatures (> 600°C) favor decomposition of Na₂SiF₆, which is an undesirable by-product because it consumes SiF₄. The yields of Si should be greater at higher reactor temperatures because less SiF₄ is thus consumed.

- At the highest reactor temperature studied (600°C), some Na vapor condensed on the cooler walls of the reactor. It condensed as droplets which apparently did not react completely with SiF₄, because they were at a low temperature (>200°C), and probably because a protective crust formed.
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 $\text{SiF}_4$-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 $\text{Na}_2\text{SiF}_6$ 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 $\text{Na}_2\text{SiF}_6$ was less than 10 wt. pct. Without external heat, the wall temperature ranged between $200^\circ$C and $250^\circ$C and $\text{Na}_2\text{SiF}_6$ 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 $\text{Na}_2\text{SiF}_6$ content of the products ranged from 20 to 30 wt. pct. It was also determined that the amount of $\text{Na}_2\text{SiF}_6$ 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) $\text{Na}_2\text{SiF}_6$. Shorter intervals (2-3 min) produced less than 10 wt. pct. The effects of higher temperature on $\text{Na}_2\text{SiF}_6$ formation will be studied with the new 7 cm i.d. Inconel reactor.

A reactor has been constructed to scale up the $\text{SiF}_4$-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.
MELT SEPARATION

As mentioned in previous reports, we have demonstrated that the Si and NaF produced by the SiF₄-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 kilograms of reaction products.

A small induction furnace was used to check new designs and improvements 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°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 is fed, causing plugging. Tests with the small induction 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°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°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 removed from the crucible. The contact angle of NaF on graphite at 1400°C was determined by observing a sessile drop of molten NaF on a graphite platform. The contact angle was approximately 60°, 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° (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
FIGURE 4  NaF DEPOSIT ON GRAPHITE AFTER CONTACT WITH MOLTEN NaF AT 1400° C

FIGURE 5  VAPOR CONDENSED NaF ON GRAFOIL AFTER COOLING
FIGURE 6  SCALED UP MELTING SYSTEM, GENERAL VIEW

A. Heating Chamber, B. Cover, C. Feeder, D. Power Supply
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
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 SiF₄ 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 SiF₄ atmosphere to consume unreacted Na that may be present. The heater chamber is kept under an Ar flow. Gas pressures for SiF₄ 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°C to melt the salt. The melt temperature was then raised to and maintained at 1400°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
contained a starting bed of 0.5 kg of NaF at 1100°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°C for 30 min. The temperature was then increased to 1470°C (+20°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