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NOVEL DUPLEX VAPOR-ELECTROCHEMICAL METHOD FOR SILICON
SOLAR CELLS

Quarterly Progress Report No. 10, May 1-July 31, 1978

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Work Performed Under Contract No. NAS-7-100-954471

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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. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, by agreement between NASA and DOE.

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SUMMARY

The reactor to produce silicon by the reaction between gaseous SiF_4 and liquid sodium was scaled up to produce 100 g of silicon per batch. To recover the silicon from the large volume of products of this reaction, the aqueous leaching process was scaled up to treat up to 2-kg batches of reaction product.

Rapid leaching was determined to be effective in minimizing loss of silicon due to oxidation. About 95% of the weight of silicon believed to be present in the reaction products was recovered.

An alternative approach to recover the silicon from the reaction products is to heat the products above the melting temperature of silicon. Results from preliminary melting experiments are very promising, in that two separate phases of Si and NaF were obtained. Examination of the frozen melt shows that the silicon agglomerated as large globules of greater density than NaF. The NaF prevents the silicon from wetting and reacting with the graphite and permits the granular Si particles to agglomerate when molten.

INTRODUCTION

During this quarter our efforts were focused on producing 1-kg batches of silicon by the SiF_4 -Na reaction and on improving the methods of silicon recovery from the reaction products.

The reactor used for the SiF_4 -Na reaction was modified and enlarged to produce batches as large as 1 kg of reaction products containing about 100 g of silicon. The sodium delivery system was also modified by enlarging its capacity to 1 kg of sodium and installing filters to additionally clean the liquid sodium delivered to the reactor. The leaching apparatus used for separating silicon from the reaction products (Si , NaF , Na_2SiF_6) was scaled-up to process batches of about 2 kg of reaction products. During this scaled-up leaching, various problems were encountered that were not observed in the leaching studies performed previously¹ with smaller amounts of the reaction products. Attention was given to solving these new problems, including silicon loss due to oxidation promoted by fluoride ions in the leachant. This loss of silicon was decreased significantly by decreasing the time required for leaching.

Recovery of silicon by high temperature fusion of the otherwise untreated granular products of the SiF_4 -Na reaction was investigated. Heating the mixture above the melting point of silicon in an inert atmosphere of argon and subsequent cooling produced two clearly immiscible phases of NaF and silicon. The NaF also prevented the silicon from wetting and reacting with the graphite walls.

¹Quarterly Progress Report No. 6.

EXPERIMENTAL PROGRAM

Scale-up of the SiF_4 -Na Reactor

The apparatus for the SiF_4 -Na reaction has been scaled-up to permit production of (1-kg) batches of reaction products (Figure 1). The diameter of the glass reactor was maintained at 3 inches while the length was extended from 1 to 4 feet. A sheet nickel liner protected the glass from the sodium, and consisted of three one-foot long sections and a bottom cup all interconnected by nickel cylindrical springs. This arrangement of sheet nickel liners facilitates the removal of the reaction products. A layer of NaF powder added to the bottom of the cup prevents the reaction product from sticking. The reaction is started by heating the bottom of the reactor with an external electrical heating mantle, as in the previous apparatus.*

The sodium liquefier has also been enlarged to contain 1 kg of liquid sodium. The stainless steel walls of the new liquefier are thin (1/16 inch) to allow for fast heating and cooling. The external heat is provided by heating tape, and the temperature of the sodium is monitored by a thermocouple (TC3, Figure 1) and is maintained at about 150°C . The liquid sodium is forced by argon pressure into the reactor through 3/8-inch o.d. stainless steel tubing. The scale that forms on liquid sodium is removed by two in-line filters (F1, F2). A stainless steel bellows valve (V3) controls the sodium flow. The liquid sodium is fed into the reaction zone through a nozzle. The nozzle coupling is detachable, permitting the testing of different nozzle configurations. Recent designs include nozzles with multiple orifices varying from 0.016 to 0.030 inch in diameter. These nozzles provide a continuous supply of sodium, with drop size and drop frequency depending primarily on orifice size, temperature, and argon pressure. The temperature in the liquid sodium near the nozzle is measured by a thermocouple (TC 2 Figure 1) and is maintained at around 130°C . Control of temperature at this point is critical since at higher temperatures, the

* Quarterly Progress Report No. 5.

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FIGURE 1 SCALED-UP APPARATUS FOR SiF_4 - Na REACTION

reaction will take place within the nozzle and will plug the flow of sodium by the accumulated reaction products.

SiF_4 gas is admitted through valve VI and is introduced concentric to the sodium line. With this configuration, the incoming SiF_4 produces some cooling of the sodium, preventing the sodium from reacting prematurely. The nickel "convection breaker" ring also helps to diminish the convective heat transfer from the bottom of the reactor to the nozzle region, thus diminishing the tendency for reaction at the nozzle.

Scale-Up of the Leaching Process

Aqueous leaching apparatus for recovering silicon from 2 kg of reaction product is shown schematically in Figure 2. Dilute H_2SO_4 was added to a 10-gal polypropylene container and agitated with a large Teflon stirrer as the powdered reaction product was slowly added. During addition of the reaction product to the leachant, an atmosphere of nitrogen gas was maintained to minimize the hazards from hydrogen gas produced by reaction of residual unused sodium with water. After the slurry was mixed for about 20 min, the leachant was allowed to settle for about 30 min and was then filtered by suction through a polypropylene fritted disk filter (5 inches diameter) with a filter paper (Whatman No. 3) held on the disk by suction. The leachant was collected in a 5-gal glass filter bottle that was evacuated with a mechanical vacuum pump. The total leaching time in the first two runs was relatively large (7 to 10 days) because of insufficient vacuum capacity. In later runs, the leaching time was decreased substantially by improving the vacuum and using two parallel filter systems operating simultaneously.

For leaching smaller batches of reaction product (100 g), a 4-liter polypropylene container was used with stirring. The leachant was removed either by centrifugation using four 0.6-liter centrifuge cups or by filtration.

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FIGURE 2 LEACHING APPARATUS

Fluoride and sodium ion concentrations in the leachant were measured using specific ion electrodes (Orion). A 1-ml aliquot of a filtered solution was diluted with 9 ml of H_2O , and then 0.2 ml of Ionic Strength Adjuster (ISA)--a solution of NH_4Cl in NH_4OH --was added. The pH was adjusted to about 9 by the addition of concentrated NH_4OH . The pH value of 9 was selected as a compromise to minimize the interference of OH^- and H^+ ions when measuring the two ion concentrations, $[F^-]$ and $[Na^+]$, in one solution. The errors in measurement become significant only at ion concentrations less than 10^{-5} M fluoride and 10^{-4} M sodium. Thus, the measurement of the sodium ion concentration is subject to greater error than that of the fluoride ions.

The oxidation of silicon by the leachant was studied by measuring hydrogen evolution in the apparatus shown in Figure 3. A 1-g sample of powdered silicon (material recovered by leaching) was added to 100 ml of a given aqueous solution in a 125-ml polypropylene bottle. The hydrogen gas was collected by water displacement in an inverted graduated cylinder.

The metallic sodium content of the reaction product was determined by adding the reaction product to a known quantity of excess acid and titrating the remaining acid with a standardized alkaline solution. The difference in titre of the acid solution before and after the addition of the reaction product was used to calculate the amount of sodium.

Results of Leaching Runs

The results of seven leaching runs (Runs 2-8) are summarized in Table 1. The table includes entries for (1) the run number, (2) the recovery procedure, (3) the leaching conditions (type of leachant, number of leaching steps, leachant volume required per kilogram of reaction product, and total time that the silicon was in contact with the leachant), (4) mass of reaction product used, (5) the weight percent of sodium in the reaction product, and (6) the weight percent of recovered silicon and the corrected weight percent of recovered silicon referred to the mass of the reaction product minus the mass of sodium.

Table 1

SUMMARY OF RESULTS OF SILICON RECOVERY BY LEACHING

Run No.	Recovery Procedure	Leaching Conditions ^a				Reaction Product ^b		Na in Reaction Product (wt%)	Si Recovered (wt%)		Remarks
		Leachant	No. of Steps	Volume (liters/kg)	Total Time (days)	Weight (g)	Batch		Recovered	Corrected for Na	
2	Filter	H ₂ SO ₄	6	89	7	2333	A	14	5.2	6.0	Comparative effects of H ₂ SO ₄ and HCl.
3	Centrifuge	H ₂ SO ₄	8	160	3	100	B	16	7.8	9.3	
4	Centrifuge	HCl	8	160	3	100	B	16	7.9	9.4	
5	Centrifuge	H ₂ SO ₄	8	200	1.2	100	C	0.9	8.9	9.0	Low Na
6	Filter	H ₂ SO ₄	7	340	0.3	100	C	0.9	9.6	9.7	Low Na, rapid leaching
7	Filter	H ₂ SO ₄	8	138	1.1	2000	D	13	8.7	10.0	High Na, rapid leaching
8	Filter	H ₂ SO ₄	9	134	1.2	2000	E	20	6.0	7.5	High Na, rapid leaching

^a Initial leachant concentration 1.2 N H₂SO₄; subsequent leaching with 0.6 to 1.2 N H₂SO₄ until [F⁻] was < 10⁻³ M; Si product finally washed with deionized water, then dried at 110°C.

^b Determined by titration.

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FIGURE 3 SCHEMATIC OF APPARATUS USED FOR MEASURING RATE OF GAS EVOLUTION BY REACTION OF SILICON WITH AQUEOUS FLUORIDE SOLUTIONS

In all runs, the leaching was continued until the fluoride ion concentration was less than 10^{-3} M, usually 2×10^{-4} M. The product was then washed with several liters of water and dried in an air oven at 100°C . For most leaching runs, the sulfuric acid concentration was maintained in the range of 0.6 to 1.3 N in which sodium fluosilicate has the highest solubility, as shown in Table 2. Also included in Table 2 are the solubilities of Na_2SiF_6 in hydrochloric acid solutions.

A total of 9028 g of reaction product was leached to obtain 530 g of silicon. The percent silicon recovered depended primarily on the recovery procedure, as will be discussed below for each run. The sequence begins with Run 2 (Run 1 was a preliminary run with incomplete data):

Run 2--For this batch, the leaching process was carried out over a period of 7 days. The initial leaching step used 1.2 N H_2SO_4 . In subsequent steps, 0.6 N H_2SO_4 was used.

The concentrations of fluoride and sodium ions measured for each of the six leach steps are shown in Figure 4. Also shown in Figure 4 is the ratio of the fluoride and sodium ion concentrations, $[\text{F}^-][\text{Na}^+]$. This ratio is about 3.0 following the first leaching, indicating that NaF has been removed and Na_2SiF_6 remained the principal solid present. Although an ion ratio of 1.0 is expected for NaF, the low ratio (0.5) for the first leach indicates that the reaction product contained excess metallic sodium (or sodium oxide). For the last two leaching steps, the $[\text{Na}^+]$ concentrations were apparently low because of H^+ interference with the operation of the $[\text{Na}^+]$ selective electrode, and hence the ion ratio $[\text{F}^-][\text{Na}^+]$ is less than the expected value of 3.

Runs 3 and 4--The objective of these runs was to study the comparative effects of 1.2 N H_2SO_4 and 1.2 N HCl as leachants. Small 100-g batches of reaction products were leached for 3 days. The silicon yields are almost identical, 7.8 and 7.9 wt% or about 55% of theoretical maximum*, indicating

* A theoretical silicon yield of 100 percent implies that no Na_2SiF_6 is formed, as discussed in Appendix A.

Table 2

SOLUBILITY OF SODIUM FLUOSILICATE IN SULFURIC AND
HYDROCHLORIC ACID SOLUTIONS AT 20°C

Concentration of Acid (N)	Solubility of Na_2SiF_6 (M) in	
	H_2SO_4^a	HCl^b
0	0.042	0.034
0.312	0.057	0.058
0.625	0.062	0.068
1.25	0.072	0.072
2.50	0.072	0.055
5.00	0.058	0.026

^aThis study: 2.0 g Na_2SiF_6 added to 50 ml H_2SO_4 solution and equilibrated at 20°C for 5 days. Fluoride analysis at pH ~ 7 with F^- -ion specific electrode.

^bInterpolated from: "Solubilities, Inorganic and Metal-Organic Compounds," W. F. Linke, American Chemical Society, Washington, D.C., 1965, 4th Edition,

FIGURE 4 ION CONCENTRATIONS IN THE LEACHANT DURING SLOW LEACHING — RUN 2
(TOTAL LEACHING TIME 7 DAYS)

that these two acids behave similarly. The improved yield of silicon compared with the previous runs is attributed to the shorter time in which the silicon was exposed to oxidizing conditions in the leachant.

Run 5--This run was made to determine the silicon yield from a reaction product containing a known low content of metallic sodium. It is well known that silicon is oxidized in alkaline solution, and local alkaline regions could occur in the leachant as metallic sodium reacts with water of the leachant. Localized heating due to this reaction should tend to promote oxidation of the silicon.

To test this hypothesis, we selected a reaction product that was low in metallic sodium content (0.9 wt%). The leachant was 0.6 N H_2SO_4 , and the leaching time was 1.2 days, but otherwise, the procedure was similar to Runs 3 and 4.

The silicon yield was 8.9 wt% Si (62% of theoretical), an increase over than for Runs 3 and 4 (7.8 to 7.9 wt% or 55% of theoretical). However, when the silicon yields of Runs 3, 4, and 5 are calculated with respect to the mass of the reaction products minus the mass of metallic sodium, the corrected yields are in agreement, that is 9.3, 9.4, and 9.0 wt% for Runs 3, 4, and 5, respectively, or about 70% of theoretical. These results suggest that a minor role is played by oxidation of the silicon by a high local alkaline concentration due to sodium in the reaction product.

Run 6--In this run, the time of leaching was further decreased to minimize the oxidation of the silicon by the leachant. The same low-sodium content reaction product was used as in Run 5.

The reaction product (100 g) was initially added to 4 liters of 1.2 N H_2SO_4 , and the resulting slurry was transferred to a plastic Büchner funnel with a filter paper (No. 3). Subsequently, the solids were leached with six aliquots of 1.2 N H_2SO_4 and a final wash with water.

The silicon yield was 9.6 wt% (67% of theoretical), which is an improvement over the results obtained in Run 5. The greater yield is most probably due to the shorter contact time of the silicon in the leachant, 0.3 days for Run 6 compared with 1.2 days for Run 5.

Run 7--In this run, we recovered the silicon from a large batch of reaction product (2000 g) containing a high sodium content (13 wt%) by leaching in as short a time as possible (1.1 days) so as to minimize oxidation by the leachant. The leachant was 1.3 N H_2SO_4 at all times. Ion concentrations are shown in Figure 5. The initial fluoride ion concentration was higher in Run 7 than in Run 6 because the initial leachant volume was smaller in Run 7 (20 liters) than in Run 6 (40 liters). The smaller leachant volume permitted NaF to reach its solubility limit (about 1M at 25°C).

The silicon yield was 8.7 wt% of reaction products, which, when corrected for the metallic sodium content, is 10.0 wt% or 70% of the maximum possible. The corrected value is in satisfactory agreement with that of Run 6 for which a low-sodium reaction product and short leaching period were used. To account for this agreement, we must consider that oxidation of silicon was not significantly different between Runs 6 and 7, although the leaching time in Run 7 was longer and the sodium content was greater. Regarding the leaching time, the essential point (which will be discussed below) is that oxidation appears to be promoted by fluoride ions derived from the solution of NaF. The time for leaching most of the sodium fluoride was less than 2 hr for both Runs 6 and 7.

Run 8--This run was performed essentially in the same way as Run 7, except that the reaction product contained more sodium (20 wt%). The yield of silicon was 6.0 wt% (42% of the theoretical maximum). This reaction product had been exposed for a long time to air, and the moist white appearance of the surface indicated that some metallic sodium had been converted to a hydrated Na_2O or NaOH. When the above yield is

FIGURE 5. ION CONCENTRATIONS IN THE LEACHANT DURING RAPID LEACHING — RUN 7
(TOTAL LEACHING TIME 1.2 DAYS)

corrected for the sodium in the metallic form in the form of NaOH, the corrected silicon yield could be within the range 7.5 to 9.2 wt% Si, or 52% to 64% of theoretical. Thus the corrected silicon yield from this reaction product approaches the values of earlier runs, although some silicon may have been oxidized by contact with moist alkaline salts.

Silicon Oxidation by the Leachant

The first evidence that silicon may be oxidized during leaching was that gas bubbles continued to rise to the surface of the leachant many days after the sodium metal in the reaction product had reacted with the water. To determine the parameters that controlled this oxidation, we measured gas evolution rates under various conditions of fluoride and acid concentrations. Mass spectrographic analysis indicates that the evolved gas was hydrogen.

The rate of hydrogen evolution was measured using the apparatus shown in Figure 3. In the first series of three experiments, the sodium fluoride concentration was held constant at 0.60 M while the acidity was adjusted with H_2SO_4 and NH_4OH to initial pH values of -0.08, 6, and 9.7. The results in Figure 6 show that the rate of hydrogen evolution was essentially independent of pH, and that the rate was constant up to about 300 min, thereafter decreasing. The weight percent of silicon that was oxidized was calculated from the volume of hydrogen evolved and is shown on the right-hand ordinate of Figure 3.

Figure 7 shows that at lower fluoride ion concentrations in 1.2 N H_2SO_4 , the hydrogen evolution rate decreased for 0.060 M and 0.0060 M NaF and for a saturated solution (0.07 M) of Na_2SiF_6 . For these solutions, the rate of gas evolution also decreased with time. The result of the gas evolution rate for 0.60 M NaF in 1.2 N H_2SO_4 is also shown in Figure 7 for comparison.

A comparison of the hydrogen evolution rates due to oxidation of silicon in solutions of NaF and Na_2SiF_6 is shown in Table 3. The dependence

Table 3

RATES OF HYDROGEN EVOLUTION FROM SLURRIES OF
SILICON CONTAINING FLUORIDE SALTS AT 24°C

Salt		pH ^a	Calculated F ⁻ Ion Concentration (M)	Initial H ₂ Evolution Rate ^b (cc/min)
Type	Concentration (M)			
NaF	0.60	-0.08	3.2×10^{-4}	0.5
	0.60	6.0		0.5
	0.60	9.5		0.5
	0.060	-0.08	3.2×10^{-5}	0.014
	0.0060	-0.08	3.2×10^{-6}	0.0060
Na ₂ SiF ₆	0.07 ^c	-0.08	1.8×10^{-5}	0.015 ^d

^a Adjusted with H₂SO₄ and NH₄OH.

^b From data in Figures 6 and 7.

^c Saturated solution.

^d Measured at 1 hr, after rate stabilized.

FIGURE 6 HYDROGEN EVOLUTION FROM REACTION BETWEEN SILICON POWDER AND SOLUTIONS CONTAINING 0.60 M NaF AT 20°C (100 g Si in 100 ml solution)

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FIGURE 7 HYDROGEN EVOLUTION FROM SILICON SAMPLES IN CONTACT WITH 1.2 N H_2SO_4 SOLUTIONS CONTAINING DIFFERENT CONCENTRATIONS OF FLUORIDE ION

of hydrogen evolution rate and fluoride ion concentration is shown in Figure 8. The actual fluoride ion concentrations for these solutions were calculated from the equilibrium reactions.

and from the concentrations of the NaF or Na_2SiF_6 dissolved in solutions. The results in Figure 8 show that the rate of hydrogen evolution and hence the rate of silicon oxidation is proportional to the equilibrium fluoride ion concentration.

We postulate that fluoride promotes the oxidation of silicon by removing a protective silica layer on the silicon surface, thereby enabling the oxidation by water to proceed as:

Although this is a tentative explanation, it may be considered that lower concentrations of fluoride are less effective in removing the silica protective layer so that the oxidation rate decreases. To account for the independence of the oxidation rate on pH (i.e., for 0.60 M NaF solutions), we suggest that two requirements must be met. First, the removal of the silica layer should be very rapid and independent of pH for the high fluoride (or HF) concentrations. Second, the rate limiting step at the high fluoride ion concentration is the above oxidation reaction, which apparently is independent of pH.

The decrease in rate of hydrogen evolution that occurs with time is probably due to a combination of factors including (1) decrease in surface area of silicon as the smallest particles become completely oxidized, (2) decrease in available fluoride ion concentration as $\text{SiF}_6^{= }$ is formed in acid solutions, and (3) formation of a protective silicic acid polymer ($\text{SiO}_2 \cdot x\text{H}_2\text{O}$) on the silicon surface.

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FIGURE 8 RELATIONSHIP BETWEEN HYDROGEN EVOLUTION RATE DUE TO SILICON OXIDATION IN 1.2 N H_2SO_4 AND EQUILIBRIUM FLUORIDE ION CONCENTRATION (DATA FROM TABLE 3).

The practical consequence of these results is that the yield of silicon can be increased by rapid leaching to remove the fluoride ions originating from sodium fluoride. The remaining sodium fluosilicate provides a very low fluoride ion concentration, especially in acid solutions, because $\text{SiF}_6^{=}$ ions do not dissociate readily; hence the oxidation rate of silicon is slow.

Significant oxidation occurs during the time that the fluoride ion concentration due to NaF is high. For example, in Run 7, most of the NaF was leached out in the first two leach steps, requiring 2 hr. From the slope of the line in Figure 6, we estimate that 3.0% of the original mass of silicon was oxidized in 2 hr. If we assume that this oxidation of silicon is the only loss leading to the recovery of 10.0 wt% silicon for Run 7, the original silicon content in the reaction product was about 10.3 wt%. Accordingly, in Run 7 the leaching process recovered about 97% of the available silicon.

Impurities in Silicon Recovered by Leaching

Emission spectrographic analyses were performed on the silicon recovered from the seven leaching runs of Table 1. Impurity concentrations are shown in Table 4. Elements not detected in the emission spectrograph are listed at the bottom of Table 4.

The probable sources of most of the impurities are indicated in the second column of Table 4. Nickel is transferred from the nickel liner of the reactor. To prevent this contamination, we are testing other types of liner materials. Iron and chromium appeared in only a few samples and were probably introduced accidentally during handling of the reaction products. Copper and the alkaline earth metals (Mg, Ca, and Ba) were probably present in the sodium metal and, when required, can readily be removed by distillation of the sodium. Aluminum was probably introduced into the early reaction products by the aluminum foil used to handle the sodium. Supporting this conclusion is the fact that the aluminum impurity

Table 4

EMISSION SPECTROGRAPHIC ANALYSES OF
IMPURITIES IN SILICON RECOVERED BY LEACHING

Impurity		Impurity Concentration (ppm by wt) ^a						
Element	Probable Source	Run Number ^b						
		2	3	4	5	6	7	8
Ni	Nickel liner	80	8	< 8	60	1500	1200	8
Fe	Accidental	<20	35	<20	<20	20	<20	<20
Cr	Accidental	7	< 7	< 7	< 7	< 7	< 7	< 7
Cu	Na metal	6	8	4	12	8	4	4
Mg	Na metal	6	12	6	6	6	4	5
Ca	Na metal	< 7	20	10	15	7	7	7
Ba	Na metal	<10	10	<10	<10	<10	<10	<10
Al	Al foil ^c	20	150	15	100	20	< 5	< 5
Na	Incomplete leaching	7500	3500	2500	1500	2500	2500	3500

^a The symbol, <, indicates that the element was below the detectability limit given by the number.

Elements below detectability limits (in parenthesis) are:
V(20), Zr(35), Mn(8), B(30), P(4500), Ag(5), Mo(35), and Ti(12).

^b Refers to run numbers of Table 1.

^c Used to handle Na in Runs 2 through 6.

became undetectable in the last two runs when polyethylene sheet was used to handle the sodium. Finally, the high levels of sodium indicate that the leaching process was incomplete. The sodium concentration can be decreased drastically (~ 1 ppm) by melting the silicon leach product.*

The impurities listed in Table 4 were shown to be in the silicon bulk and not at the surface. For example, silicon samples were treated for 6 days with concentrated HF or concentrated HCl. Emission spectroscopy of the treat samples shows that the treatment produced virtually no change in the concentration of the impurities.

Conclusions

The studies of the leaching process and of the oxidation of silicon that occurs during leaching lead to the following conclusions:

- o The leaching process using vacuum-assisted filtration has been successfully scaled-up to treat 2-kg quantities of the reaction product from the SiF_4 -Na reaction. Further scale-up by a factor of about 4 should be possible without major investments in capital equipment. At present, about one working day (8 hr) and about 270 liters of leachant, ($1.2 \text{ NH}_2\text{SO}_4$) are required to leach 2 kg of reaction product as a laboratory procedure.
- o The recovery of silicon is increased by rapid leaching. It is now believed that rapid leaching decreases fluoride ion concentration which, in turn, promotes silicon oxidation. Detailed studies are needed to verify the proposed mechanism. The maximum silicon yield obtained was 10.0 wt% after correcting for the unreacted sodium in the reaction products. This is equivalent to a recovery of 70% of the maximum theoretical value, assuming that no Na_2SiF_6 was formed. For the leaching procedure, a recovery of 97% is calculated,

* Quarterly Progress Report No. 7, Table 1.

assuming that the only loss of silicon is by oxidation in the first 2 hr of leaching, when the fluoride ion concentration is high.

- o Loss of silicon during leaching due to possible oxidation by localized regions of alkaline solution, produced by excess unreacted sodium in the reaction product, is not significant. However, silicon may be oxidized when a reaction product high in excess sodium is stored and exposed for long periods of time to atmospheric moisture.
- o Type of acid (HCl or H_2SO_4) is not a primary factor in determining the recovery yield of silicon by leaching. An acid concentration of about 1.2 N is recommended in order to increase the solubility and leaching rate of Na_2SiF_6 . Otherwise, acid concentration in the range of 0.6 to 1.2 N does not affect silicon recovery.
- o The impurities in the silicon recovered from leaching were those present in the reaction product before leaching and are ascribed to impurities in the sodium metal and to contamination from the nickel liner of the SiF_4 -Na reactor. The high sodium content may be due to the presence of NaF in the reaction product since NaF is inaccessible to the leach solution. We plan to investigate why this sodium is leached slowly and how to increase the rate of its removal.

Silicon Recovery by Melting the Products of the SiF_4 -Na Reaction

Recovery of silicon by melting the as-produced products of the SiF_4 -Na reaction was investigated as an alternative to recovery by leaching. The purpose of melting is to convert the silicon in the reaction products (Si , NaF , and Na_2SiF_6) from a powder to ingot form.

In the melting process Na_2SiF_6 will decompose to NaF and SiF_4 (gas), and it has been shown that silicon particles agglomerate and form a phase separate from NaF.

A 25-g sample of reaction products was placed in a graphite crucible and was melted at about 1500°C for 5 min using inducting heating. Temperature was measured using an optical pyrometer. After cooling, the crucible was cut in half as shown in Figure 9. In this sample, three globules of silicon appeared below a matrix of NaF. It is apparent that, while molten, the NaF wetted the graphite and formed a thin layer between the silicon and the graphite, thus preventing the silicon from wetting and reacting with the graphite. It is possible that the molten fluoride salt acts as a flux to dissolve surface oxide from the silicon granules, permitting them to agglomerate into large globules.

The liquid silicon sinks downward in the molten NaF because the density of silicon is greater. The densities of silicon and NaF as a function of temperature are shown in Table 5. The silicon and NaF liquids form immiscible phases, as expected, because of the predominate covalent nature of silicon and the predominate ionic structure of NaF.

Experiments were also performed to examine the melted reaction products under various conditions of heating. Under resistive heating in argon atmosphere for about 30 min, a single globule of silicon was produced. When excess sodium was present in the reaction product in one run, the graphite crucible cracked around 700°C , presumably because the sodium intercalated with the graphite. To avoid the problem of excess sodium, we crushed the reaction product and allowed the sodium to be oxidized in air. In the future, some melting experiments will be performed in high-density graphite which is expected to be less susceptible to intercalation by sodium.

Part of a silicon globule was prepared for emission spectrographic analysis. Adhering NaF was removed, the silicon was fractured, and the

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FIGURE 9 SEPARATION OF SILICON AND NaF PHASES AFTER INDUCTION HEATING OF REACTION PRODUCTS IN GRAPHITE AT 1500°C FOR 5 MIN IN ARGON

Table 5

DENSITIES OF SILICON AND NaF AS
A FUNCTION OF TEMPERATURE

Temperature (°C)	Density (g/cm ³)	
	Si ^a	NaF ^b
20	2.32	2.79
988	-	1.96 (m.p.)
1410	2.53 (m.p.)	1.70
1500	2.49	1.65

^a Handbook of Chem. and Phys., 51st edition, R. C. Weast, ed. (Chemical Rubber Co., 1970).

^b Metals Reference Book, 4th edition, Vol. 1, Smithell, ed. (Plenum Press; 1967), p. 272. Values above 1100°C (were extrapolated using the following equation: $d = 2.577 - 6.2 \times 10^{-4} T$).

surface of a piece from the bulk was etched with 1.2 N HCl solution to obtain clean silicon. The only elements detected in the etched silicon are nickel (450 ppm), which originated from the nickel liner of the SiF_4 -Na reactor, and copper (8 ppm), which is an impurity in sodium metal.

The melting process for recovering silicon from the products of the SiF_4 -Na reaction appears very promising. Further work is in progress to explore opportunities for continuous production of pure silicon using the direct melting of reaction products.

FUTURE WORK

Attempts are now being made to obtain a large batch (1 kg) of high purity silicon by the SiF_4 -Na reaction. Studies will be continued to improve the efficiency of the aqueous leaching process in recovering silicon from the products of the reaction. Studies to recover the silicon by melting the reaction product will also be pursued, with emphasis on determining the purity of the silicon. Equipment is being assembled to evaluate the direct "thermite" reaction between sodium and Na_2SiF_6 to produce silicon on the scale of 1 kg per charge.

Appendix A

DEPENDENCE OF THE THEORETICAL SILICON YIELD ON THE AMOUNT OF SODIUM FLUOSILICATE FORMED IN THE REACTION PRODUCT

The reaction between sodium and silicon tetrafluoride can occur as follows:

The theoretical yield of silicon in the reaction product as well as the efficiency of use of SiF_4 is decreased by formation of Na_2SiF_6 in reaction (2). Ideally, the experimental conditions should favor reaction (1).

Information on the theoretical yield of silicon is useful for comparison with the experimental yields to determine how much silicon is lost in processing--for example, during leaching. Accordingly, it is of interest to calculate the dependence of the theoretical yield on the amount of Na_2SiF_6 formed.

Combining reactions (1) and (2), we obtain the net reaction

The theoretical weight fractions of silicon and Na_2SiF_6 are

$$w_{\text{Si}} = \frac{x\text{Si}}{Z} \quad (4)$$

$$w_{\text{Na}_2\text{SiF}_6} = \frac{y\text{Na}_2\text{SiF}_6}{Z} \quad (5)$$

where

$$Z = (4x - 2y)\text{NaF} + x\text{Si} + y\text{Na}_2\text{SiF}_6 \quad (6)$$

and the chemical symbols represent gram-formula weights. By substitution of the formula weights into Equations (4) and (5), we obtain

$$W_{Si} = \frac{28x}{196x + 104y} \quad (7)$$

$$W_{Na_2SiF_6} = \frac{188y}{196x + 104y} \quad (8)$$

For given values of $W_{Na_2SiF_6}$ in Equation (8), we can first solve for y ; when y is substituted in Equation (7), it provides the theoretical value of W_{Si} . The results of these calculations are shown in Figure A-1 as a plot of the theoretical silicon yield versus the amount of Na_2SiF_6 in the reaction product. The maximum theoretical yield of silicon varies linearly from a high value of 14.3 wt% to 6.93 wt% corresponding to 0 and 93.07 wt% of Na_2SiF_6 , respectively. Note that the maximum theoretical yield of Na_2SiF_6 is 93.07 wt%, assuming that all NaF reacts by reaction 2.

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FIGURE A-1 THEORETICAL SILICON YIELD CALCULATED FROM THE AMOUNT OF Na_2SiF_6 FORMED IN REACTION PRODUCT