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SILICON HALIDE—ALKALI METAL FLAMES AS A SOURCE OF SOLAR GRADE SILICON

Fifth Quarterly Report

MASTER

By
D. B. Olson
W. J. Miller

October 1978

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AeroChem Research Laboratories, Inc.
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Approved by
Hartwell F. Calcote
Director of Research

AeroChem Research Laboratories, Inc.
Princeton, New Jersey

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FOREWORD AND ACKNOWLEDGMENTS

This is the fifth quarterly progress report on a program which began 17 May 1977; it covers the period 1 June 1978 through 30 September 1978.

Major contributions to the experimental effort on the program during this report period were made by G. Rolland and L. Koenig.

ABSTRACT

This program is designed to demonstrate the feasibility of using alkali metal-silicon halide diffusion flames to produce solar-cell-grade silicon in large quantities at low cost. Prior work has demonstrated that high purity silicon (metallic impurities < 5 ppm) can be produced using Na + $SiCl_4$ and Na + SiF_4 flames. Much lower flame temperatures were observed in the latter case as well as low silicon yields due to Na_2SiF_6 formation.

Work performed during the current reporting period has shown that reactor wall temperatures of approximately 1000 K are sufficient to prevent formation of Na_2SiF_6. Silicon produced from SiF_4 appears identical in form and purity to that from $SiCl_4$ although product collection and separation are less thermochemically favored in the fluoride system. To separate the silicon from the byproduct salt in an efficient and continuous manner, higher temperatures are necessary. Resistively heated thin-walled graphite tubular reactors have been used to achieve these temperatures (> 1700 K), and successful product separation has been experimentally demonstrated using a Na + $SiCl_4$ flame. Keys to this success appear to be sustaining high reaction temperatures and not using a diluent gas in the reactant flows.

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I. INTRODUCTION

The object of this program is to determine the feasibility of using continuous high-temperature diffusion flames of alkali metals and silicon halides to produce silicon in large quantities and of suitable purity for use in the production of photovoltaic solar cells. Reactions of gaseous Na or K with silicon halides (e.g., $SiCl_4$, $SiHCl_3$, or SiF_4) are highly exothermic, luminescent[1-3] and, in fact, have many characteristics in common with conventional oxidation flames. High adiabatic flame temperatures have been calculated[1] for these systems from reliable thermochemical data and, at these temperatures, the product alkali salt exists as a gas while the silicon is present as a condensed phase. A process is proposed in which the difference in physical state of desired and undesired products is utilized to separate the silicon from the byproduct salt in a continuous and efficient manner.

The envisaged process has several distinct advantages: First, since in any practical process the alkali metal reagent must be purified, the distillation stage is moved to the inlet of the reactor and the Na or K is injected as a gas possessing the enthalpy of vaporization that would be largely lost in a separate distillation process. Using the alkali metal as a vapor contributes significantly to maintaining the high temperatures in the post-flame gases for product separation. Further, little or no inert gas diluent is required (or desired) in these diffusion flames--an obvious economic advantage. Added diluent also increases the gas/particle flow velocity which very well may necessitate a larger reactor to achieve appropriate residence times.

An experimental program is planned, in addition, to examine these reaction systems using liquid phase injection of the reagents. Fewer materials interaction and reaction handling problems are expected using liquids since much lower temperatures are required. The primary question to be answered is whether high purity silicon can be produced in this manner.

This effort is now at the end of the first quarter of its second year. During the first year (phase I) thermochemical calculations[1] were used to identify Na + $SiCl_4$ as the prime system of interest. The K or Na + SiF_4 reaction is less favored thermochemically, but has not been eliminated from consideration due to several other factors (such as the cost and availability of reactant raw materials[4]). Initial experiments performed in a simple low pressure opposed-jet configuration have demonstrated[1-3] (i) the feasibility of using either K or Na metal vapors as reagents; (ii) that the reactions with any of the silicon halides are hypergolic, and produce stable chemiluminescent high-temperature flames; (iii) that $SiCl_4$ and $SiHCl_3$ flames are similar in apparent reaction rate while SiF_4 flames are slower, much less exothermic, and less chemiluminescent (the latter difference being directly attributable to the lower adiabatic flame temperature); (iv) that for $SiCl_4$ and $SiHCl_3$ atomic silicon emission is observed from the flame zone, indicating that the kinetic processes leading to Si are very rapid and that the flames are probably mixing rate limited; and (v) that the products, if allowed to deposit on cold reactor walls, form a mixture of very small (submicron) separate silicon and alkali metal salt particles.

To scale up the experiments and allow better process control a larger flow tube apparatus was built. Experiments were performed in this unit using Ar or H_2/Ar diluent under a variety of velocity and pressure conditions.

The experiments using H_2/Ar diluent were designed to simulate and explore the effects of varying experimental conditions in the arc-jet process proposed by the Westinghouse Corp.[5] These simulations achieve the same reaction-zone enthalpy by moderately preheating the reactant $SiCl_4$ and H_2/Ar and by using vapor phase instead of liquid phase Na. The silicon produced from a series of comparative experiments[6] using relatively cool ($\approx$ 1200 K) walls was found to be a fine powder of high crystalline particles, containing only small amounts ($<$ 5 ppm) of metal impurities. No differences were observed between the Ar or H_2/Ar containing systems.

In our last report[6] we discussed preliminary results on the Na + SiF_4 system. The product from a Na + SiF_4 flame run in a quartz reaction tube with cool walls was found to contain only about 30% of the expected free silicon, the remainder being tied up due to the reaction $SiF_4 + 2NaF = Na_2SiF_6$. During this first quarter of phase II of this project we have continued to pursue Na + SiF_4 studies with an investigation of diffusion flames in a heated quartz flow tube. The Na + $SiCl_4$ (+ Ar) flow tube experiments have also been continued with experiments at higher pressures and temperatures in a resistively heated graphite flow tube at $T > 1700$ K. In these latter experiments continuous high temperature separation of silicon from the byproduct NaCl was demonstrated. Finally, we have studied product separation characteristics in a batch mode by heating product samples to temperatures above the melting point of silicon.

II. TECHNICAL DISCUSSION

A. Na + SiF_4 EXPERIMENTS

In our last report[6] we discussed the possible interference to the production of Si in the Na + SiF_4 system due to the formation of Na_2SiF_6. Further experiments were performed during this quarter using a heated quartz flow tube. No Na_2SiF_6 was found in the product deposited in the hot zone of the reactor where the wall temperature was approximately 1000 K. The solid deposited downstream of the heated tube did, however, contain some Na_2SiF_6; heating a washed sample of this cold-zone product to 1250 K, hot enough that any Na_2SiF_6 decomposes[4] to SiF_4(gas) and NaF(solid), produced measurable weight loss (due to SiF_4 evolution) and a corresponding amount of water soluble NaF(s). We conclude from these experiments that Na_2SiF_6 formation would not be a problem in an actual process reactor where the wall temperature could be maintained at or above 1000 K. There appears to be little difference with respect to color, particle size, or purity between silicon produced at high temperatures using either SiF_4 or $SiCl_4$. The Na + SiF_4 adiabatic flame temperatures[1] are, however, significantly lower than those of Na + $SiCl_4$ and, in addition, the boiling point of NaF is almost 300 K higher than the boiling point of NaCl; both of these factors make the separation of products in the Na + SiF_4 case more difficult. The boiling point of KF, however, is almost equal to that of NaCl and so product separation would be more favored in the K + SiF_4 system than in the Na + SiF_4 case.

B. DILUTE Na + $SiCl_4$ EXPERIMENTS (INCLUDING ARC-JET SIMULATIONS)

An improved version of the sodium vaporizer has been constructed for use in the arc-jet simulation tests; it gives better control and a quantitative measure of the flow of sodium vapor. Basically it is an insulated stainless steel oven in which the temperature is adjusted to obtain the desired Na vapor pressure, and Ar carrier gas is used to entrain and deliver the Ar/Na mixture at a measured flow rate. Low Na mass delivery rates are obtained not by low flow rates of Na vapor (which sometimes give problems due to condensation of the vapor in the delivery tube) but by lowering the temperature of the oven (i.e., the Na vapor pressure) and controlling the Ar flow rate. Conversely, high Na delivery rates are achieved by raising both the oven temperature and the Ar flow rate. The quantitative delivery rate of Na is computed by assuming gas-liquid equilibrium in the oven.

Several dilute stoichiometric Na + $SiCl_4$ (+ Ar) flow-tube experiments have been performed this quarter with wall temperatures of approximately 1000 to 1300 K, where the vapor pressure of NaCl is $\leq$10 Torr (see Fig. 1). The experimental apparatus has previously been described.[3,6] Briefly, vaporized reagents are injected through coaxial nozzles into a heated flow tube. Conditions of these experiments are given in Table I. At low total pressures (50-150 Torr) and linear flow velocities of about 2 m s^{-1}, little solid product was found on the heated tube walls. Subsequent experiments (8A and 9A) performed at similar wall temperatures but with higher total pressures ($\approx$ 375 Torr) and lower gas velocities did show some solid product retention in the reaction tube. Higher reactor pressures also give higher adiabatic flame temperatures (i.e., greater heat release) which also favors salt vaporization and, in fact, the solid from one of these experiments was 27% insoluble in water, thus showing more than 100% enrichment over stoichiometric product yield of 12% silicon. The problems in these experiments appear to be twofold. First, the reactor tubes and Chromel heating elements used in prior work[3] are inadequate for the temperatures required for complete separation of the silicon from the salt. Even though quartz tubes are desirable for high purity work, they devitrify upon cooling from temperatures above 1300 K and must be replaced after each experiment. Alumina tubes, used in some recent experiments, withstand high temperatures without cracking but it has been demonstrated earlier[6] that the silicon produced using such reaction tubes is contaminated with Al. Second, in these highly dilute systems, with argon comprising 50-70 mole % of the mixtures, the small silicon particles are entrained in gas flow and are difficult to separate and collect.

C. PRODUCT SEPARATION EXPERIMENTS

Independent experiments have been performed during this reporting period treating the product separation problem without the added complexity of running the Na + $SiCl_4$ flame. A high temperature crucible/heater made of graphite and heated by passing high currents (up to 150 A) through the graphite was constructed. This 10 cm long, 2.0 cm diam crucible was made of ultra-high purity graphite, MacKay grade UF4S, with 0.13 cm wall thickness, and was used to heat samples of NaCl, Si, or Si/NaCl. Samples of NaCl in direct contact

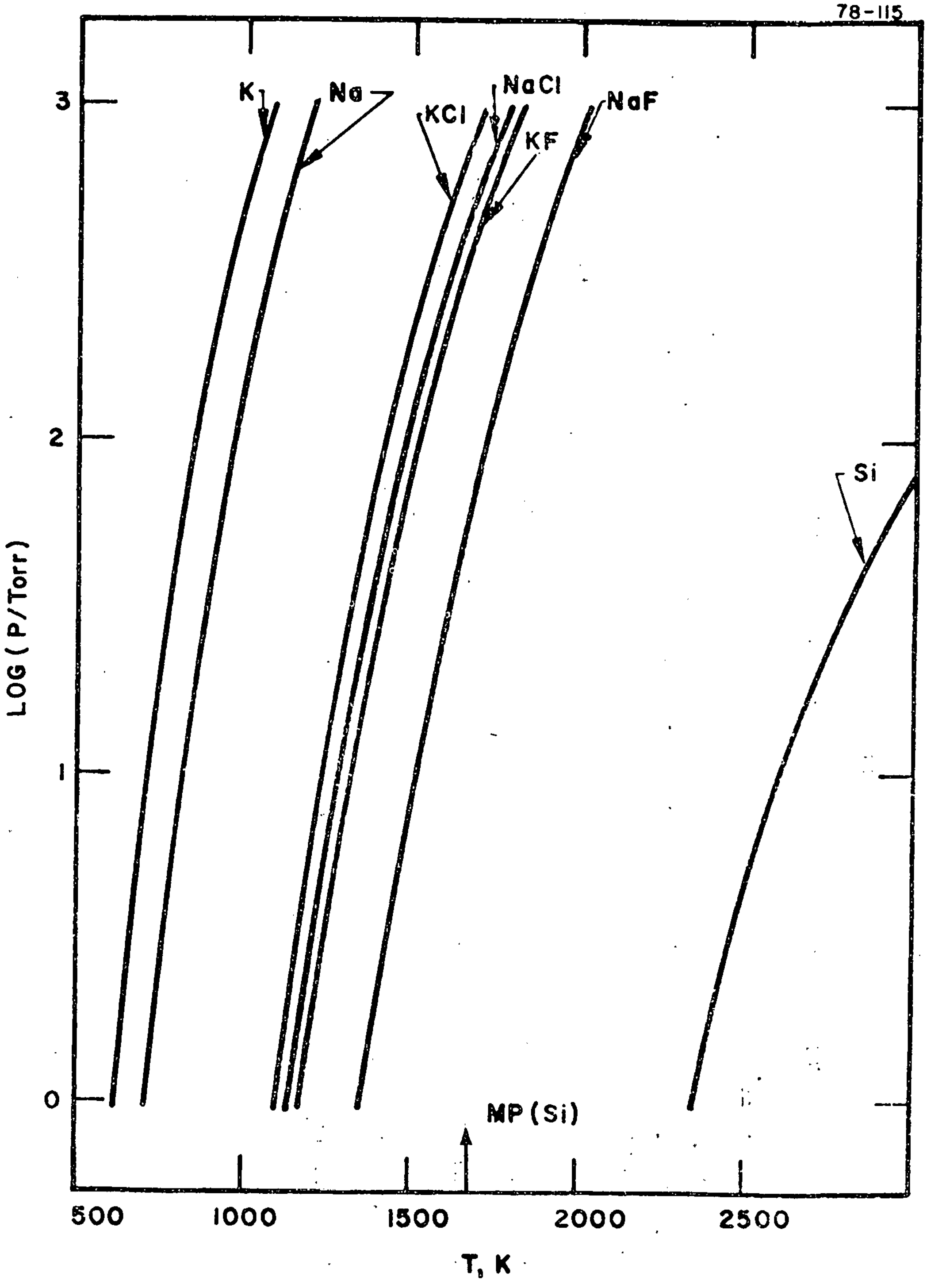

FIGURE 1 VAPOR PRESSURE DATA FOR SEVERAL SPECIES IMPORTANT IN ALKALI METAL-SILICON HALIDE FLAMES

TABLE I

CONDITIONS OF Na + $SiCl_4$ FLOW TUBE EXPERIMENTS

		Reactor			$SiCl_4$	Ar			
Run No.	Date (1978)	Tube Type (cm)	P (Torr)	T(K)	T(K)	Volume Flow Rate (STP)cm^3 s^{-1}	T(K)	Duration (min)	Comments
4A	7/6	6.4 quartz	75	1000	400	80	870	30	— — —
5A	7/11	2.5 s.s.	75	1000	400	60	875	35	Product 16% insoluble
6A	7/17	2.5 alumina	60	1050	530	65	910	38	Product 17% insoluble
7a	7/19	2.5 alumina	150	1150	400	60	880	40	Very little product in reaction tube
8A	7/23	2.5 alumina	375	1150	450	75	1100	30	— — —
9A	8/10	2.5 alumina	325	1350	450	50	950	85	Product 27% insoluble

with the graphite crucible could be melted and vaporized with the rate of the process easily controlled by varying the heater current. Granular samples of crystalline silicon were also melted, but the liquid Si appears to either wet the graphite and simply flow through the thin walls, or react with the walls forming silicon carbide. In either case a portion of the liquid silicon escapes to the outside of the crucible. In another experiment a high purity quartz liner was used to hold a sample of silicon inside the graphite crucible/heater while the Si was melted. This experiment was not successful because, although the silicon melted, the quartz was softened enough to flow. There is only a small temperature range above the melting point of silicon within which quartz retains its integrity, and apparently in our experiments the temperature control or homogeneity was inadequate to stay within this range. A few preliminary experiments were also performed in which Si/NaCl powder samples obtained from a Na + $SiCl_4$ flame experiment were heated in a quartz crucible to a temperature above the boiling point of NaCl but considerably below the melting point of silicon. It may be possible to separate the product species by boiling the salt away in this manner, but experimental problems (e.g., leaks, etc.) have so far prevented this test from being successful.

D. HIGH TEMPERATURE FLOW TUBE EXPERIMENTS

Wall temperatures in our previous flow tube experiments[6] have been limited to less than about 1300 K. Under these conditions the post-flame gases cool sufficiently rapidly that the alkali metal salt and the silicon appear to condense simultaneously and deposit on the reactor walls in an approximately stoichiometric (4NaCl + Si) ratio. In order to separate these products on a continuous basis, higher temperatures are needed. To this end, a modified apparatus was constructed using resistively heated thin-walled graphite reaction tubes similar in design to the graphite crucible described in the previous section. Two types of experiments have been performed in this apparatus. In the first, the effluent gas/particle stream from a 15 cm long 2.5 cm diam unheated quartz flow reactor was directed into a 10 cm long, 2.2 cm diam graphite crucible heated to a temperature above the melting point of silicon. Optical pyrometry was used to measure the crucible temperature which could easily be maintained above 1700 K.

At the conclusion of a 65 min run, using a stoichiometric low pressure ($\approx$ 50 Torr) Na + $SiCl_4$ flame with 25(STP)cm^3 s^{-1} Ar flow in the nominal 1 g min^{-1}

Na vapor stream, no solid product of any form was found in the heated graphite crucible itself. However, in the 1 to 3 cm region of the quartz exit tube just downstream from the crucible, a very hard silver-colored silicon deposit was found. A considerable amount of solid product with the brown appearance of a Si/NaCl mixture was also deposited upstream of the crucible inside the cooler quartz delivery tube. Downstream of the heated crucible a powder ranging in color from light brown to almost pure white deposited on the walls. We conclude from these observations that, although the solid product delivery from the flame zone to the graphite crucible was not highly efficient, a considerable quantity of NaCl/Si did reach the high temperature region of the crucible. Under these conditions of pressure, temperature, and residence time, proper conditions for depositing Si on the walls while maintaining the NaCl as a vapor were apparently achieved just downstream of the crucible. No Si was retained in the crucible because the Ar flow rate was probably too large, resulting in too short a residence time in the hot region.

Subsequent experiments were performed without Ar in the reactant flow and with hot walls surrounding the flame zone. This experimental arrangement is shown in Fig. 2. Slightly thicker walls (0.20 cm instead of the earlier value of 0.13 cm) in the graphite reaction tube were also used. The wall temperature prior to beginning the experiment was somewhat lower than the melting point of Si, the wall temperature estimated optically to be between 1500 and 1600 K. However, the heat release from the flame would be expected to significantly raise this temperature. A Na + $SiCl_4$ flame without diluent was sustained for 50 min consuming about 135 g of $SiCl_4$ and 75 g of Na. The initial (static) reactor pressure was constant at 175 Torr throughout the experiment since the reaction products are all condensables. Since no argon was added during the experiment, no pumping was needed.

Upon disassembly of the reactor, the graphite tube was found to have a hard coating of silicon, some as crystals and some as sintered powder. NaCl was observed only around the exit opening. The solubility of samples taken from various areas of the apparatus was determined in order to estimate the amount of NaCl remaining. The silicon from the upstream area of the reaction tube, where the majority of the product deposited, was found to be essentially all insoluble ($>$ 95%). A sample from the downstream area of the reaction tube near the exit was $\approx$ 70% insoluble, whereas just past the tube exit on the outer walls, where the temperature was significantly lower, the sample was completely

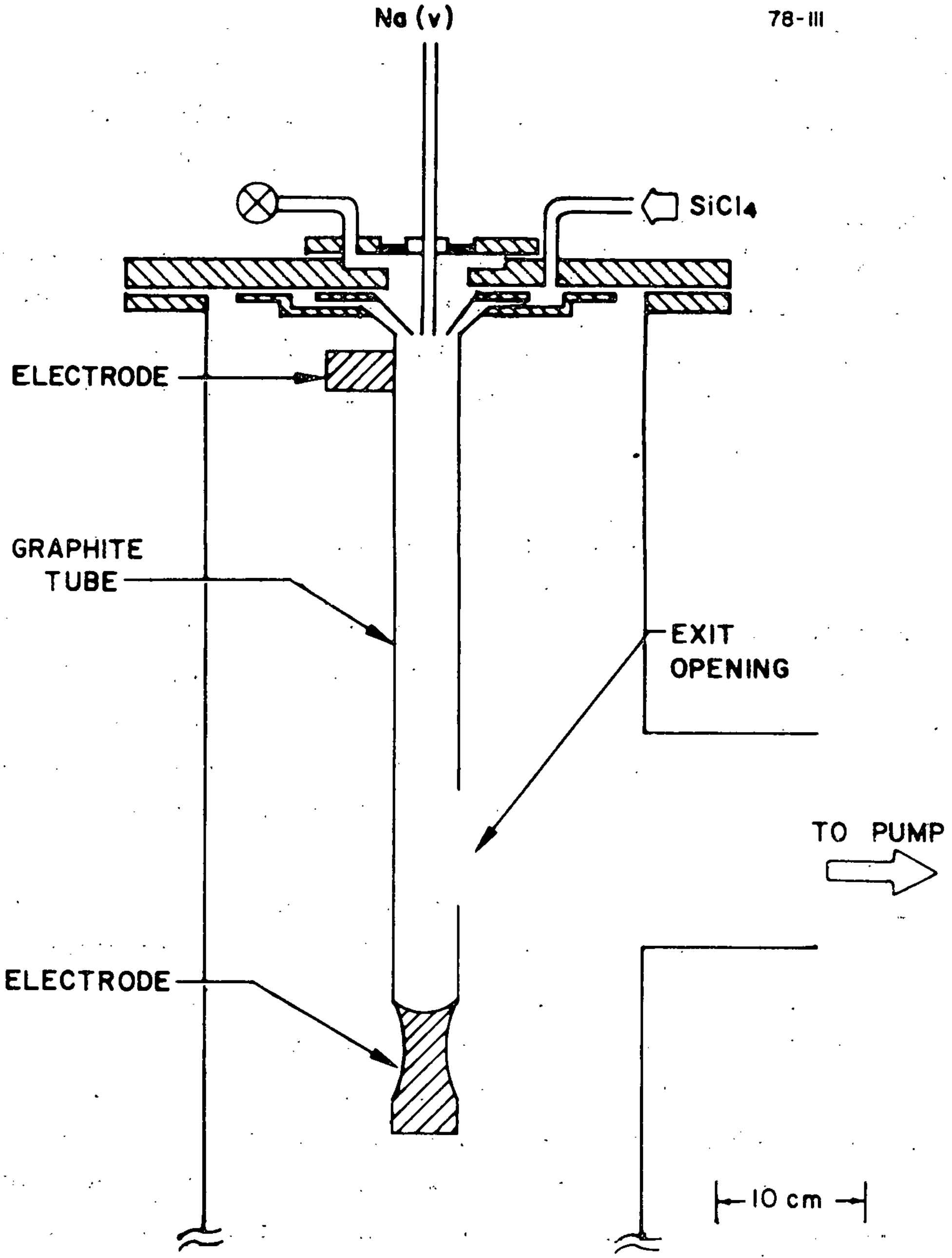

FIGURE 2 HIGH-TEMPERATURE GRAPHITE FLOW-TUBE APPARATUS

soluble. Further away from the graphite tube in the room temperature area where a small amount of very fine particles settled, the solubility of a sample was found to correspond to stoichiometric product (13.2% insoluble).

From these observations we conclude that a fully successful high temperature separation of the Si from the NaCl was demonstrated in this experiment. The key factors in this success appear to be the ability to sustain wall temperature almost equal to the melting point of silicon and not using argon in either reagent stream. The diluent, if present in the reagent flows, raises the reactor pressure and reduces the product residence time during which silicon collection on the walls must take place. The silicon/salt mixture found downstream from the reactor represents only a small fraction of the total amount of silicon produced, but demonstrates that the separation-collection process is not 100% efficient.

III. CONCLUSIONS

Flow tube experiments with wall temperatures of $\approx$ 1000 K have confirmed that Na_2SiF_6 is not formed in the high temperature Na + SiF_4 system. Silicon produced by this reaction appears to be identical to that produced by Na + $SiCl_4$, although the product separation and collection process are less favored in the fluoride system since the boiling point of NaF is higher and the reaction exothermicity smaller.

Experiments have been performed on continuous reaction product separation techniques important to both this work and to the Westinghouse effort. Resistively-heated graphite tubes have been used to sustain reaction temperatures in excess of 1700 K. Under these conditions thin graphite walls are found to be porous to liquid silicon. Thicker walls alleviate most of this problem, and a successful continuous separation of silicon from the byproduct NaCl has been demonstrated. Keys to this success appear to be sustaining high reaction temperatures and not using a diluent gas in the reactant flows.

IV. PLANS

During the next quarter we plan (i) high temperature Na + $SiCl_4$ experiments with higher mass flows to continue the study of product separation and collection processes, (ii) to further examine both thermochemically and experimentally the potential of the K + SiF_4 system relative to the Na + $SiCl_4$ system, and (iii) to begin the design and construction of a reactor to use liquid phase injection of reactants. When this apparatus is operational a series of experiments will be performed comparing liquid phase to vapor phase injection techniques. It will be of prime interest to determine whether impurities can be excluded from silicon produced in the liquid reagent experiments.

V. NEW TECHNOLOGY

No reportable items of new technology have been identified.

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