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

Third Quarterly Report

By
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March 1978

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AeroChem Research Laboratories, Inc.
Princeton, New Jersey

U.S. Department of Energy

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

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D.B. OLSON AND W.J. MILLER

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FOREWORD AND ACKNOWLEDGMENTS

This is the third quarterly progress report on a program which began 17 May 1977; it covers the period 1 December 1977 through 28 February 1978.

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

ABSTRACT

The object of this program is to determine the feasibility of using continuous flames of alkali metals and silicon halides in a large scale process to produce solar-grade silicon at low cost. Primary emphasis is being given to the reaction of Na with SiCl_4 .

During this quarter we have completed the measurements of K or Na + SiCl_4 , Na + SiHCl_3 , and K or Na + SiF_4 flame spectra. The dominant feature of these emission spectra is alkali metal atomic emission. Flames of SiCl_4 or SiHCl_3 also show several chemiluminescent bands of unknown origin in the visible. Molecular emission from SiH was observed in the SiHCl_3 spectra while both flames showed ultraviolet emission from SiCl and Si, the latter indicating that, despite the fact that different species must be involved (SiCl and SiH, respectively), the rate of formation of Si atoms must be very fast in both cases, although, not unexpectedly, somewhat more rapid with SiCl_4 . The silicon emission was found to be nonthermal in origin preventing a spectroscopic determination of the flame temperature from those measurements.

Construction of the scaled-up tubular flow reactor has been completed and experiments begun. Stable flames of Na + SiCl_4 diluted with H_2/Ar were achieved and samples of solid product were taken from the reactor walls. Microscopic examination of the product showed it to be comprised of very small ($< 1 \mu\text{m}$ diam) particles of white and brown material. Washing of this solid removed the NaCl which was present in a stoichiometric (4:1) ratio to the silicon. Analysis of the washed product confirmed it to be silicon with 0.5-2% NaCl and traces of Fe, Cr, and Ni.

Thermochemical calculations of the input conditions necessary to simulate the Westinghouse silicon process showed that we can achieve the same total enthalpy (and reaction zone temperature) by using vaporized reactants with H_2/Ar heated to 1300 K. Construction of the necessary H_2/Ar oven has been completed and experiments have begun.

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I. INTRODUCTION

The object of this program is to determine the feasibility of using continuous high temperature flames of alkali metals and silicon halides to produce high purity "solar grade" silicon in large quantities. These flames have been observed previously¹⁻³ and were found to be characterized by fast kinetics and a variety of chemiluminescent emissions. Equilibrium thermochemical calculations⁴ indicate that high adiabatic flame temperatures are attained and that solid or liquid silicon is the only condensed phase present in the equilibrium product distributions at these temperatures. The possible separation of the condensed silicon from the gas-phase reaction products thus offers the potential for a large scale industrial process for the preparation of high grade silicon.

Prior to this reporting period⁵ we established low-pressure opposed-jet diffusion flames of $K + SiCl_4$ and $Na + SiCl_4$ which were found to be stable, highly exothermic, and chemiluminescent. Solid product samples were collected from the reactor walls and were found to be a mixture of brown and white powders, presumably amorphous silicon and alkali halide. Microscopic examination of this solid product showed what seemed to be agglomerates of particles with $< 1 \mu m$ diam. Washing with slightly acidic water removed the alkali salt leaving a dark brown solid. Visible emission spectra from these flames were found to consist primarily of alkali metal atomic emission lines and several chemiluminescent bands in the blue and green.

Construction of a larger-scale tubular flow reactor was begun. This reactor is designed to provide better product retention and separation and greater control over reaction conditions than is possible in the opposed-jet burner housing. The new apparatus will also be modified to study, at the laboratory-scale, the Westinghouse proposed silicon production process,⁶ which uses the reduction of $SiCl_4$ diluted with an arc-jet heated H_2/Ar mixture.

During this quarter we have extended the spectroscopic examination of the $Na + SiCl_4$ flame to include the ultraviolet wavelengths, established opposed-jet flames of $Na + SiHCl_3$, $Na + SiF_4$, and $K + SiF_4$, and obtained emission spectra and solid product samples from each. We have continued to refine our reagent handling systems in order to overcome problems with erosion of the flow control orifice by the alkali metal vapor, and completed construction of the tubular flow reactor.

II. TECHNICAL DISCUSSION

A. APPARATUS MODIFICATIONS

The overall configuration of the opposed-jet reactor has been described previously⁵; modifications have been necessary to the alkali metal vaporizer. After the failure due to corrosion of a number of fixed size orifices for flow control of the K or Na vapor (at $T \approx 1100$ K), they were replaced with a needle valve. The tapered needle and seat are located in the vaporizer at the upstream end of the delivery tube (see Fig. 1) while the valve body (threads and Teflon sealing material) is located at the end of a stainless steel extension rod some 20 cm away from the extremely hot region. This arrangement gives good control of the metal vapor delivery rate and cool operation of the valve body. The needle and seat were first constructed of 304 stainless steel and later nickel, but both materials were significantly eroded in less than two hours of operation. A needle and seat of Inconel were then made and they were found to be much more corrosion resistant. However, at this time we also modified our procedures to reduce small amounts of oxygen and/or oxides which might be present in the alkali metal vaporizer and which existing information indicates is a prime source of corrosion problems. A scavenger material which would react with any available oxygen to form a stable oxide was placed in the vaporizer along with the alkali metal. In order to prevent contamination of the sodium reactant, silicon is used as the scavenger. With these modifications the vaporizer performance is now quite satisfactory.

B. OPPOSED-JET DIFFUSION FLAME EXPERIMENTS

To better characterize reaction zone temperatures and to gain information about the transient species present and the energy-transfer processes occurring in alkali metal-silicon halide flames, we have recorded the emission spectra of these flames and, in the same experiments, collected solid product samples. The low pressure diffusion flames of $K + SiCl_4$ and $Na + SiCl_4$ exhibit similar spectra⁵ characterized by strong K or Na atomic emission lines along with several chemiluminescent bands in the blue and green. We have now examined the ultraviolet spectra of $Na + SiCl_4$ flames from 200 to 350 nm using the same equipment as in our earlier experiments but viewing through a quartz window. An ultraviolet bandpass filter (Corning 7-54, $240 < \lambda/nm < 400$) was also used in some experiments. Figure 2 shows a typical spectrum obtained

FIGURE 1 ALKALI METAL VAPORIZER

FIGURE 2 Na + SiCl₄ FLAME SPECTRUM FIGURE 3 Na + SiHCl₃ FLAME SPECTRUM

without the bandpass filter. Strong emissions attributable to Na were observed at 330, 309, 285, and 268 nm and to Si at 288 and 252 nm. Several weaker emission bands from 225 to 249 nm and at 295 nm were attributed⁷ to SiCl although Si also emits at 244 nm. The band at 259 nm remains unidentified. A calculation of the effective temperature of the Si, assuming equilibrium excitation, was made from the relative intensities of the emission observed at 288 and 252 nm and the corresponding published transition probabilities.⁸ Emission at the latter wavelength was assumed to be due to a combination of the Si lines at 251.4, 251.6, 251.9, 252.4, and 252.8 nm. This procedure yields a temperature of 4900 K--some 2500 K above the adiabatic maximum. Non-equilibrium excitation of this nature indicates either that the emitting silicon atoms are produced in highly exothermic chemical reactions leading directly to excited states, or possibly that Si atoms are long-lived enough to undergo energy-pooling collisions from high-energy electronic/vibration states of diatomic molecules. These Si atoms, then, are not in thermal equilibrium with the remainder of the gas and, if an accurate flame temperature is to be obtained spectroscopically, a different emitter will have to be monitored.

We have also obtained emission spectra from flames of Na + SiHCl₃, Na + SiF₄, and K + SiF₄. The spectrum from a Na + SiHCl₃ flame is shown in Fig. 3. The spectrum is dominated by Na lines with an overlapping broad continuum peaking at a wavelength of about 500 nm. The emission due to SiH⁷ observed at 414 nm in this flame had not been observed in the Na + SiCl₄ flames. The ultraviolet portion of this spectrum consists of Na lines at 330 and 309 nm plus a number of weaker bands at wavelengths less than 300 nm. The SiCl bands from approximately 215 to 245 nm and the Si atomic emission at 251 and 288 nm were again observed as in the Na + SiCl₄ flame but at much lower intensities.

Flames of SiF₄ with either Na or K were not found to exhibit the strong emissions that characterize the SiCl₄ and SiHCl₃ flames. Both SiF₄ flames were just barely visible, the spectrum showing only Na lines at 589 and 569 nm. No ultraviolet emission was observed. From the difference in the adiabatic flame temperature between SiF₄ and SiCl₄ systems (cf. Fig. 3, Ref. 4) the sodium emission intensity would be expected to be smaller by more than two orders of magnitude, roughly in accord with our observations.

For both of the SiF_4 flames the solid product collected from the reactor walls was found, after washing with water, to be a tan powder unlike the dark brown product of the SiCl_4 and SiHCl_3 flames. This difference in color is possibly the result of the silicon being present as much smaller particles. Since the abstraction reactions of Na with SiF_x , $x = 1-4$, are endothermic and, by analogy with similar reactions, are expected to occur slowly, the production of silicon and nucleation of the solid would be expected to be slower than for the reactions of other silicon halides.

C. FLOW REACTOR DESIGN

In the opposed-jet reactor experiments the reaction products have little net flow velocity and a majority of the product either settles to the bottom of the chamber or condenses on its walls. The tubular flow reactor is designed to allow the addition of a permanent (inert) gas to the reactants and therefore impose a flow to the reaction products. Experiments concerning the rates of product condensation and deposition will be possible in this apparatus in addition to the production of larger quantities of product with better control of the reactor pressure, reactant delivery rates, and other conditions. Construction of this apparatus is now essentially complete.

The tubular flow reactor consists basically of a 2 m long, 15 cm diam Pyrex pipe with reagent and inert gas delivery at one end and connection to a vacuum system at the other end. Figure 4 shows the overall configuration of the apparatus. An inner tube of smaller diameter is used to increase the linear flow velocity of the gas and to allow insulation and heating of the reactor walls in future experiments. Currently this inner tube is a 1.2 m long, 64 mm diam Pyrex tube. Fused quartz of similar size will be used when heating of the walls is incorporated. A glass wool particle filter is used to prevent fine particles that do not deposit on the reactor walls from reaching the Stokes 300 cfm vacuum pump.

The inlet flange is shown in Fig. 5 and the alkali metal and silicon halide vaporizer are shown in Figs. 1 and 6, respectively. In the current configuration, the SiCl_4 is added using a 4 cm diam ring injector of 3 mm diam stainless steel tubing. This will be changed shortly to addition through a concentric annulus as described previously in Fig. 4 of Ref. 4. Details of the modifications to the alkali metal vaporizer are shown in Fig. 1.

FIGURE 4 TUBULAR FLOW REACTOR

FIGURE 5 FLOW REACTOR INLET FLANGE

FIGURE 6 SILICON HALIDE VAPORIZER

One of the objectives of experiments with this apparatus is to simulate the reaction conditions of the Westinghouse process^{6,9} for silicon production. To achieve this we will heat a mixture of H_2 and Ar to approximately 1300 K. (See the following section of this report for a discussion of the required input conditions.) A diagram of the oven to heat this gas is shown in Fig. 7. The oven consists of a standard 1.2 kW resistance heater in a well insulated container. Tests show that this apparatus can achieve temperatures greater than the required 1300 K.

D. FLOW REACTOR EXPERIMENTS

The experiments designed to simulate the Westinghouse arc-jet reactor^{6,9} were started during this quarter. It was recognized at the outset that it would be impossible and indeed unnecessary to construct an exact small scale analog of this apparatus. Instead reactions were to be run under thermodynamically identical conditions with the input enthalpy distributed among all the reactants rather than being concentrated mainly in the H_2 /Ar arc-jet stream as in the Westinghouse apparatus. Table I summarizes the input conditions of

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FIGURE 7 H_2 /Ar OVEN

TABLE I
COMPARATIVE THERMOCHEMICAL PARAMETERS FOR ARC-JET SIMULATION

Reactant	Mole Fraction	AeroChem Simulation Reactor			Westinghouse Arc-Jet Reactor		
		State	T (K)	H (kcal)	State	T (K)	H (kcal)
4H ₂ /Ar	0.333	gas	1300	2.24	gas	~ 3600 ^a	19.18
Na	0.533	gas	1200	16.12	liquid	500	1.12
SiCl ₄	0.134	gas	600	-20.28	liquid	298	-22.18
		Total		-1.92			-1.88

^aEstimated from Fig. 5.2 Ref. 9 for heating value of 6 kcal g⁻¹.

each of the two reactors. The enthalpy of the H₂/Ar (mol ratio 4:1) stream issuing from the arc jet was taken as 57.6 kcal mol⁻¹ (6 kcal g⁻¹), a value lying in the center of the 90 to 136 kg h⁻¹ operating envelope for silicon production. The enthalpies for liquid Na at 500 K and SiCl₄ in its standard state at 298 K for the arc-jet input were taken from the JANAF Thermochemical Tables.¹⁰ After multiplying by the appropriate mole fractions specified in Ref. 9 and summing, a value of -1.88 kcal mol⁻¹ is obtained.

To match this enthalpy in the apparatus of Fig. 4 in which the Na and SiCl₄ are both introduced as vapor at the temperatures indicated in Table I, the H₂/Ar fraction must have a heat content of 2.28 kcal or 6.72 kcal mol⁻¹. This enthalpy is achieved in a H₂/Ar = 4:1 mixture at a temperature slightly in excess of 1300 K. These conditions are easily attainable with conventional resistively heated laboratory furnaces such as the one indicated in Fig. 7.

The adiabatic flame temperatures in both reactors are, of course, identical since the total input enthalpies and compositions have been matched. The temperature is 2370 K. The product composition at this temperature, calculated as in our prior work⁴ with the Air Force ISP thermochemical equilibrium code, is given in Table II. Silane, the chlorosilanes, Si₂, and Si₃ were calculated to be present in quantities less than 10⁻⁴ mole fraction and are not listed in the table. The only significant gas-phase silicon-containing species is seen to be SiCl₂, accounting for 7% of the total silicon present. Hydrogen is only slightly reactive, producing small amounts of HCl in the product distribution.

A number of Na + SiCl₄ experiments have been performed in the tubular flow reactor using addition of cold Ar in the first experiments, then hot Ar,

TABLE II
CALCULATED EQUILIBRIUM PRODUCT COMPOSITION
OF Na + SiCl₄ REACTION DILUTED WITH H₂/Ar^a

Species	Mole %	Weight %
Ar	6.57	7.01
Cl	0.07	0.07
H	0.62	0.02
HCl	3.65	3.55
H ₂	23.92	1.27
Na	5.41	3.15
NaH	0.03	0.02
NaCl	46.40	72.37
Na ₂ Cl ₂	0.21	0.66
Si(g)	0.14	0.10
Si(l)	11.91	8.90
SiCl	0.11	0.18
SiCl ₂	0.94	2.48
SiCl ₃	0.01	0.03
SiCl ₄	(7.6 × 10 ⁻⁷)	(0.001)
SiH	0.03	0.02

^aConditions as in Table I for an adiabatic reaction temperature of 2370 K.

and finally hot H₂/Ar. Stable flames were achieved and have been sustained for periods up to 3/4 hr. Nominal reagent delivery rates were 0.03 and 0.12 mol min⁻¹ for SiCl₄ and Na. Experiments have been performed both at low pressures (~10 Torr) and medium pressures (100-200 Torr). Large quantities of solid product were observed to deposit more or less uniformly over the 1.2 m length of the inner (64 mm diam) tube, yet the gas at the end of the reactor was observed to still contain many very small particles. Samples of the solid product removed from the inner tube at various distances from the inlet flange were similar in color and texture. Comparison of the weights of these samples before and after washing with slightly acidic water showed no difference in the insoluble fraction, 9% to 11%, corresponding well with the weight fraction of Si in a mixture of Si + 4NaCl. We therefore have no indication of differential deposition of the Si and the NaCl. The early experiments,

however, were performed with very rapid cooling rates of the reaction products, as indicated by the thick deposits found very close to the inlet nozzle. Therefore, both the Si and the NaCl probably condense rapidly and co-deposit in a near stoichiometric ratio on the walls of the tube.

Analysis of samples of washed and unwashed product by X-ray fluorescence has not yet been entirely satisfactory, mostly because of difficulties with analytical standards for the trace impurities. This analytical work has shown, however, that the washed product is essentially ($\geq 98\%$) silicon with some (0.5-2%) NaCl present after one or two washes. No attempt was made to be thorough in removing the salt. Trace quantities of Fe, Cr, and Ni were found in all product samples but at levels lower than found in the sodium reactant when analyzed using the same method. More careful handling procedures with less contact of the product with stainless steel are presently being incorporated into our experiments.

III. CONCLUSIONS

Opposed-jet flame experiments have shown that reactions of Na or K with SiCl_4 or SiHCl_3 are rapid and highly exothermic. Based upon a few preliminary experiments the reaction of Na or K with SiF_4 seems much less likely as a candidate for production of silicon on a large scale. Further investigation is needed to support this conclusion.

The solid product of the $\text{Na} + \text{SiCl}_4$ reaction, collected from the walls of either the opposed-jet or tubular flow reactor, appears to be an agglomerate of very fine salt and silicon particles. The salt is easily removed by washing with water and the resulting dark brown powder is shown upon analysis to be predominantly silicon. Trace impurities of stainless steel are present and more careful handling of the product is indicated. No differential deposition of the salt and silicon has been observed to date on the cold flow reactor walls. Probably the reaction products are quenched very rapidly after the flame zone and nucleation of the solids occurs simultaneously. Experiments with slower rates of cooling of reaction products are needed.

Thermochemical calculations show that it should be possible to achieve a laboratory analog of the Westinghouse arc-jet process for sodium reduction of SiCl_4 by injecting the reactants as vapors and heating the H_2/Ar mixture to 1300 K.

IV. PLANS

During the next quarter we plan to concentrate our efforts on the reaction of $\text{Na} + \text{SiCl}_4$ in the tubular flow reactor under a variety of conditions, including high-temperature flames diluted with 1300 K H_2/Ar and incorporating slower cooling rates of the reaction products. The annular nozzle for SiCl_4 injection will be installed and is expected to provide better and more rapid mixing of the reactants. The inner Pyrex tube will be replaced with a heated and insulated quartz tube. Experiments will be performed to study the relative deposition rates of the silicon and salt in order to determine suitable operating conditions for the separation and collection of the product silicon. Larger quantities of the silicon will be collected and further analysis for trace impurities made.

V. NEW TECHNOLOGY

No reportable items of new technology have been identified.

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