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DEVELOPMENT OF PROCESSES FOR THE PRODUCTION OF SOLAR
GRADE SILICON FROM HALIDES AND ALKALI METALS

Third Quarterly Report for April 1—June 30, 1980

By
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THIRD QUARTERLY REPORT

for the period 1 April to 30 June 1980

R.K. GOULD

SEPTEMBER 1980

**JPL Contract No. 955491
LSA Task 1, SILICON MATERIAL**

Approved by:

**Hartwell F. Calcote
Director of Research**

AeroChem **Research Laboratories, Inc.**
Princeton, New Jersey

FOREWORD AND ACKNOWLEDGMENTS

During this report period C.R. Dickson and A. Wilczynski contributed to this program.

ABSTRACT

This program is directed toward the development of processes involving high temperature reactions of silicon halides with alkali metals for the production of solar grade silicon in volume at low cost. Experiments are performed to evaluate product separation and collection processes, measure heat release parameters for scaling purposes, determine the effects of reactants and/or products on materials of reactor construction, and make preliminary engineering and economic analyses of a scaled-up process. During this report period work concentrated on preparing samples of silicon for purity analyses. The results of six such analyses are given. In general, they indicate that the process is capable of producing very pure silicon. A number of impurity elements appear in 0.1-10 ppma concentrations in one or another of the samples in unpredictable patterns. This would be expected for the one hour runs performed since atmospheric dust has easy access to collection surfaces during assembly and laboratory conditions do not allow clean assembly procedures to be followed. Particularly encouraging is the observation that sodium levels are below 10 ppma in most runs.

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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 previously¹⁻⁶ and were found to be characterized by fast kinetics and a variety of chemiluminescent emissions. Equilibrium thermochemical calculations⁴ indicate that high adiabatic flame temperatures (≈ 2400 K) are attained and that solid or liquid silicon is the only condensed phase present in the equilibrium product distributions at these temperatures. Thus, separation of the condensed silicon from the gas-phase reaction products offers the potential for a large scale industrial process for the preparation of high purity silicon.

The present process⁷ has several distinct advantages. Before mixing in the reactor, both reagents are vaporized, thereby contributing to a purer silicon product. The enthalpy of vaporization that would normally be lost in a separate distillation process for reagent purification can, in this configuration, contribute to maintaining the high temperatures in the post-flame gases necessary for product separation. Also the product separation may be a purification process since impurities may be carried away with the salt vapor instead of condensing with the silicon. Finally, little inert gas diluent is required (or desired) in these diffusion flames which results in an obvious economic advantage.

The aims of this program are to achieve product separation, to test various reactor-collector designs, and to run the silicon test apparatus for extended periods of time. The set of runs performed during this report period were each between 60 and 70 min in duration as limited by the reactant reservoir supplies. Silicon samples weighing between 50 and 200 g were obtained and sent for analysis. The results of these analyses are given below. Technical effort on the process phase work ended on 15 May 1980. At the beginning of the next report period work will commence on Phase II studies of silane decomposition kinetics.

II. TECHNICAL DISCUSSION

A number of one hour runs were made during this report period. The results of analyses of these runs are presented in Table I.

Table II shows analyses of the silicon tetrachloride and sodium used in these runs as well as typical analyses of 304 stainless steel which is a major construction material for the current apparatus. The reactor material is Stackpole 2020 graphite. Manufacturer's literature indicates this material to have about 1500 ppm "ash content".

The runs producing the analyzed samples were very similar. The major differences were in the choice of collector material. For the 4/10 and 4/25 runs Stackpole 2020 graphite crucible collectors with pedestal separators were used. For the 5/12 run a high purity Poco graphite collector was used. The collectors for the 4/18 and 4/22 runs were shallow, 100 cm³ Coors alumina dishes. Another difference in the runs was that a molybdenum tube was used in the first four runs to line the sodium inlet to the reactor. The downstream end of this tube was eaten away during this series and this is believed to account for the high, but decreasing, levels of Mo in the samples. This tube was subsequently replaced by graphite in the 5/12 run.

While the source of Mo contamination is clear, the sources of other impurities are not obvious from the analyses. Volatile impurities such as As, Cd, P, Pb, Sr, and Zn appear to be a function of collector material and may tend to leach or evaporate from the graphite into the silicon. Use of high quality graphite would minimize this. All the elements listed except Na have moderately or highly volatile chlorides which could accompany the SiCl₄. The SiCl₄ is relatively pure as delivered, but is allowed to sit in a stainless steel reservoir for several hours before the run starts. This may result in leaching of many impurities (particularly As, B, P, and the transition metals) from the reservoir. Since some misting of the boiling SiCl₄ during the run is inevitable and the reflux column is not packed to prevent this, non-volatile chlorides could be delivered to the reactor. Misting of the sodium also undoubtedly occurs and in fact during the initial stages of the runs, reactor pressure pulses are observed which are attributed to the delivery of sodium droplets. Delivery of liquid sodium could result in the transfer of stainless steel components as well as boron and other non-volatile impurities in the sodium.

TABLE I
PLASMA EMISSION SPECTROSCOPY ANALYSIS
OF SILICON SAMPLES

Element ^a	<u>Concentration, ppma</u>					<u>Best</u>
	<u>4/10 Run^b</u>	<u>4/18 Run^b</u>	<u>4/22 Run^b</u>	<u>4/25 Run^b</u>	<u>5/12 Run</u>	
Al	8.7	2.8	7.1	1.7	0.8	0.8
As	0.7	< 0.1	0.05	0.4	< 0.2	< 0.2
B ^c	2.1	6.5	4.8	12.	< 0.1	< 0.1
Ca	0.2	< 0.4	1.3	0.5	3.4	< 0.4
Cd	0.1	< 0.03	0.005	0.1	< 0.001	< 0.001
Co	0.3	< 0.06	0.02	0.2	0.02	0.02
Cu	0.5	0.3	0.9	0.03	12.	0.03
Fe	13.8	10.2	7.1	0.5	2.7	0.5
Li	0.1	< 0.04	< 0.04	< 0.04	< 0.03	< 0.03
Mn	1.9	0.8	1.0	0.06	0.4	0.06
Mg	0.6	< 0.7	1.0	< 0.5	< 0.5	< 0.5
Mo	> 400.	12.	16.	0.5	4.6	0.5
Na	5.8	66.	7.5	12.	260.	5.8
Ni	11.	0.3	0.4	0.2	0.8	0.2
P	7.2	< 2.	< 1.	< 5.	< 1.5	< 1.
Pb	0.6	0.13	0.03	0.8	0.3	0.03
Se	1.0	< 0.3	< 0.2	0.4	< 0.2	< 0.2
Sr	< 0.02	< 0.02	< 0.02	< 0.02	0.1	< 0.02
Ti	0.7	0.02	0.1	0.03	0.1	0.02
V	0.8	0.04	0.1	0.02	0.03	0.02
Zn	0.03	0.007	0.1	0.02	3.5	0.007

^a K not detected.

^b Average of 3 analyses.

^c Boron concentration is a lower limit. The analytical method results in some leaching of boron from the sample.

TABLE II
COMPOSITION OF REACTANT AND CONSTRUCTION MATERIALS

Silicon Tetrachloride, CP Grade^a

B	0.09
Fe	0.31
P	0.08
Ti	0.35
V	0.27

Sodium, Commercial Grade^b

B	2.1
Ca	170.
K	210.

304 Stainless Steel^c

Cr, Fe, Ni	Principal
C	450.
Co	700.
Mn	1740.
P	230.
S	70.

^a Concentrations in (atoms of impurity)/(10⁶ atoms of silicon)

^b Concentrations in (atoms of impurity)/(10⁶ atoms of sodium)

^c Concentrations in ppm (wt)

In summary, when one considers the multitude of potential impurity sources, the rather crude state of operation of the reactant vaporizers, and the limitation of run times to less than 90 min, the impurity levels are surprisingly low. Several of the samples produced are quite definitely of "solar" quality (assuming processes involving single crystal formation in subsequent process steps). It is quite reasonable to expect, in fact, that refinements in the process would reduce impurities by factors of 10^3 or more resulting in semiconductor grade product.

III. PLANS

Work on this phase of this program was completed on 15 May 1980. Work on Phase II of the program involving a study of the kinetics of SiH_4 decomposition is expected to commence 1 July 1980.

IV. NEW TECHNOLOGY

No reportable items of new technology were identified in this quarter.

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