AeroChem TN -201

DOE/JPL 954777-79/6
Distribution Category: UC-63

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

(NASA-CR-158091) SILICON HALIDE-ALKALI METAL FLAMES AS A SOURCE OF SOLAR GRADE SILICON Quarterly Report (AeroChem Research Labs., Inc.) 15 p HC A02/MF A01 CSCL 10A

N79-16358
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SIXTH QUARTERLY REPORT

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JANUARY 1979

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 to initiate a major effort toward 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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FOREWORD AND ACKNOWLEDGMENTS

This is the sixth quarterly progress report on a program which began 17 May 1977; it covers the period 1 October 1978 through 31 December 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-grade silicon in large quantities and at low cost. Prior work has shown that these flames are stable and that relatively high purity silicon can be produced using Na + $SiCl_4$ flames. Silicon of similar purity is obtained from Na + SiF_4 flames although yields are lower and product separation and collection are less thermochemically favored. Continuous separation of silicon from the byproduct alkali salt has been demonstrated in a heated graphite reactor.

During the current reporting period the process has been scaled up to reduce heat losses and to produce larger samples of silicon. Reagent delivery systems, scaled by a factor of 25, have been built and operated at a production rate of 0.5 kg Si h^{-1}. Very rapid reactor heating rates are observed with wall temperatures reaching > 2000 K. Heat release parameters were measured using a cooled stainless steel reactor tube. External heat input is not required. A new reactor has been designed based on these measurements and construction is underway.

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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 envisioned 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 experimental program is designed to demonstrate the viability of the production/separation processes and to obtain physical and chemical variables useful for this and other high-temperature silicon production processes. Prior work[1-4] showed that relatively pure silicon could be produced in low temperature reactors where the silicon and salt particles codeposited onto the walls. More recent experiments[5] using a heated graphite reaction tube have demonstrated continuous high temperature separation of the silicon from the byproduct alkali metal salt. Results obtained during the present reporting period, discussed in detail in Section II, center on the scale-up of the experiment to alleviate problems due to heat losses and to produce larger amounts of silicon. Larger reagent delivery systems have been built and operated at a production rate of 0.5 kg Si h^{-1}. Heat-release parameter measurements and their use in designing an optimized reactor are also discussed in Section II.

II. TECHNICAL DISCUSSION

A. REAGENT DELIVERY SYSTEMS

During this reporting period we have scaled up the experiment to alleviate problems due to heat losses and to produce larger amounts of silicon. As an initial guideline we chose a scale factor such that the reaction exothermicity (without salt condensation) would be about equal to the electrical power previously used to heat the graphite flow reactors, about 1.2 kW, i.e., a scale-up by about a factor of 25 to a production rate of silicon of ≈ 0.5 kg h^{-1}. To produce silicon at this rate, 3.1 kg h^{-1} of $SiCl_4$ is consumed requiring $\approx$ 150 W for its vaporization. This energy flux could not be maintained across the glass vaporizer walls so a platinum wire immersion heater was built. A $SiCl_4$ recharging system was also added since the 150 cm^3 capacity of our vaporizer was inadequate at the much higher flow rate. With this system the reaction is not limited by $SiCl_4$ flow rate or capacity. Flow meters were installed in the halide delivery line to allow close adjustment of the $Na/SiCl_4$ equivalence ratio.

The required 1.7 kg h^{-1} of Na corresponds to a flow rate of 220 ℓ min^{-1} of vapor at 1200 K and 0.5 atm. It was decided that an experimental confirmation of the Na flow rate would be required. The heat input needed to vaporize this quantity of Na is 2.0 kW and was found to be easily within our present vaporizer capability. Experiments were performed in which the gaseous Na delivered during a ten minute period was condensed and weighed to determine the flow rate. An orifice with 3.0 mm diam was found to produce the desired flow rate with one atmosphere Na vapor pressure in the vaporizer. (Higher pressures are not used for reasons of safety.) The 0.8 ℓ capacity of the liquid reservoir in this vaporizer allows runs of about 30 min duration without recharging. This is adequate for our present experiments and no significant problems are foreseen in constructing a liquid sodium recharging system in the future when even larger scale runs are undertaken.

B. SCALED-UP Na + $SiCl_4$ EXPERIMENTS

In the first test of these scaled-up systems the reactor was a 1.5 cm i.d., 0.3 cm wall thickness graphite tube loosely held inside a stainless steel tube. This combination was heated to 1200 K by a "clam shell" resistance heater prior to beginning the experiment. The Na + $SiCl_4$ flame was run for six minutes before solid product deposits clogged the reaction tube. Approximately 4.7 moles Na and 1.4 mole $SiCl_4$ were delivered, corresponding very closely to the desired rate of silicon production. The graphite tube was found to be fractured into pieces and saturated with silicon. Both reagent systems performed without problems.

Subsequent experiments were carried out in larger (4.3 cm i.d.) alumina reaction tubes. With the tube preheated to 1400 K, introduction of the reagents quickly raised the wall temperature to 1900 K where it stabilized for the remainder of the experiment. From this initial wall heating rate, the reaction heat release was estimated to be 1.2 kW, corresponding closely to that computed assuming no NaCl condensation. Samples of deposits from the middle of the reaction zone were found to be ≈ 90% silicon and ≈ 10% NaCl. Near the cool reagent inlet flange and at the downstream end of the flow tube the product was ≈ 75% silicon. Thus good separation of the silicon from the alkali salt is occurring in the high temperature region of the reactor.

An experiment was also run without preheating the reactor tube. Figure 1 shows the measured wall temperature profile. Initially a rapid wall heating rate (800 K min^{-1}) was observed during the period in which both salt and silicon condensation would occur ("I" in Fig. 1). The reaction exothermicity under these conditions and flow rates is about 5.7 kW. The temperature then stabilized briefly at the boiling point of NaCl (II), and from there rose above 2000 K where the Pt/Pt-10% Rh thermocouple failed. Thus the ultimate reactor temperature could not be measured. The experiment was terminated due to excess heating of the outer glass vacuum system wall. Although the reaction tube deposits contain a high portion (≈ 75%)of NaCl, the amount of silicon recovered as elemental Si in this experiment was about 90% of the total which could have been produced. Figure 2 shows that the solid products (NaCl and Si) were predominantly collected in the section of the reactor near the inlet, while Fig. 3 indicates where the silicon deposited.

Thus input of additional energy to preheat the reactor does not appear to be necessary. However, longer run times are needed to reach steady-state in the reactor to achieve good separation of the silicon from the byproduct salt. Nucleation and condensation rates appear to be large enough for efficient silicon collection under experimental conditions of about 160 ms residence time and 0.5 atm in the flow tube.

C. PROCESS VARIABLE MEASUREMENTS

Heat release parameters necessary to optimize the reactor size or further scale up to produce larger amounts of silicon have also been measured. To do this a 6 cm i.d. stainless steel tube with four separate cooling coils was installed into the reactor, cf. Fig. 4, and wall cooling air temperature profiles for each section were measured during reactor operation, from a cold start. These profiles are shown in Fig. 5. The total heat production was computed from the temperature profiles and the heat capacity of the cooling air and reactor, and is shown in Fig. 6 for each reactor section and the total (Σ). Most of the heat is seen to be produced in zones A and B which are 10 and 16 cm long, respectively. From the reactant flow rates we calculate an exothermicity of 4.2 kW, in good agreement with the experimental results.

Measured heat flux through the reactor walls is presented in Fig. 7. In the first 25 cm of the reactor an average value of 5 W cm^{-2} was obtained. Volumetric heat release data is given in Fig. 8. An average value of 3 W cm^{-3} was measured for the portion of the reactor near the inlet. These data clearly show that the reaction takes place in sections A and B of this reactor, confirming that the kinetics of the reaction are rapid, probably mixing limited. Thus smaller reactor volumes can be used, simplifying reactor design and construction.

III. PLANS

An optimized reactor is now under construction to be used to demonstrate production of larger quantities of silicon. Our aim is to collect high purity liquid silicon at the reactor outlet with the NaCl (and hopefully most other impurities) being collected on cooled surfaces far from the Si collector. A small (8 cm diam, 25 cm long) cylindrical graphite reactor has been designed. The reactor will operate near 0.5 atm and reaction products ($NaCl(g)$ and $Si(\ell)$) will leave the reactor through a small converging nozzle exhausting into a large volume held at a low ($<$ 10 Torr) pressure. The jet from the reactor impinges on a graphite crucible where $Si(\ell)$ droplets will be collected. A large (65 cm diam, 80 cm long) all-metal vacuum housing is being acquired to contain the reactor and Si collector. Its water cooled walls will provide surfaces for NaCl collection for the time being. More detailed design calculations are being carried out. Our efforts in the next quarter will be directed toward construction of this system and making it operational. Important questions to be answered experimentally are whether the thick walled, high density graphite will withstand the environment and how efficiently the silicon particles are collected.

IV. NEW TECHNOLOGY

No reportable items of new technology have been identified.

V. REFERENCES

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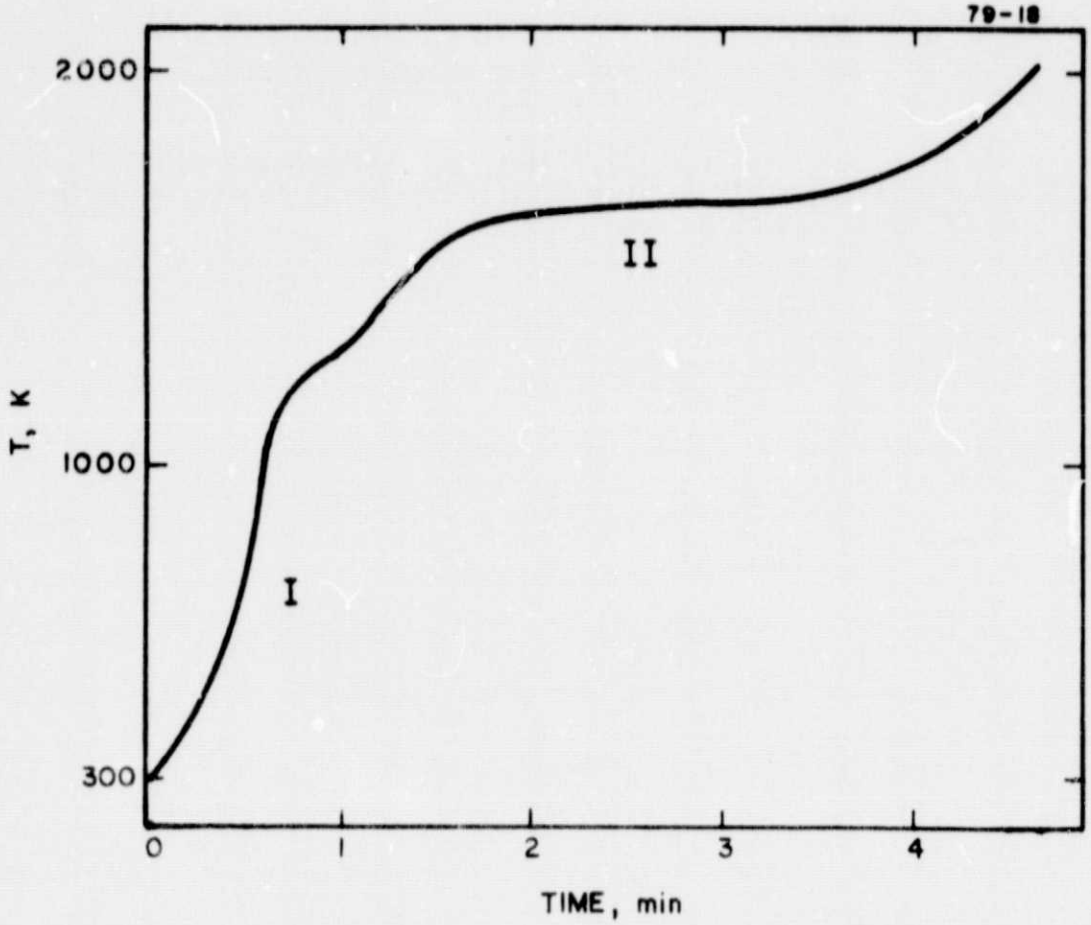

FIGURE 1 REACTOR WALL TEMPERATURE PROFILE DURING A Na + $SiCl_4$ RUN

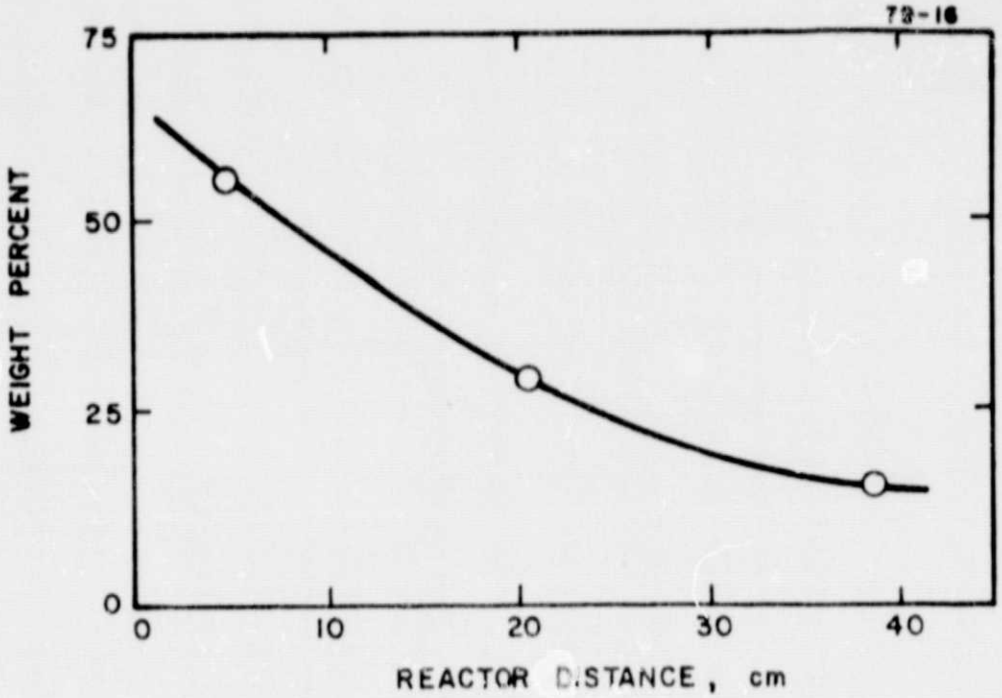

FIGURE 2 SOLID PRODUCT DISTRIBUTION

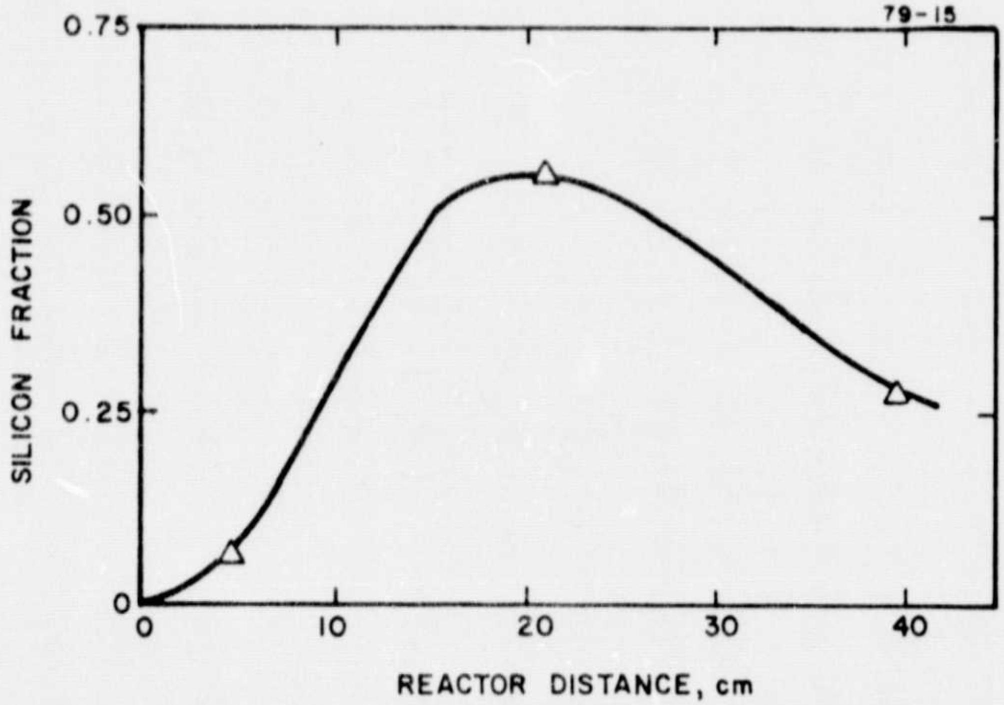

FIGURE 3 DISTRIBUTION OF SILICON DEPOSITION

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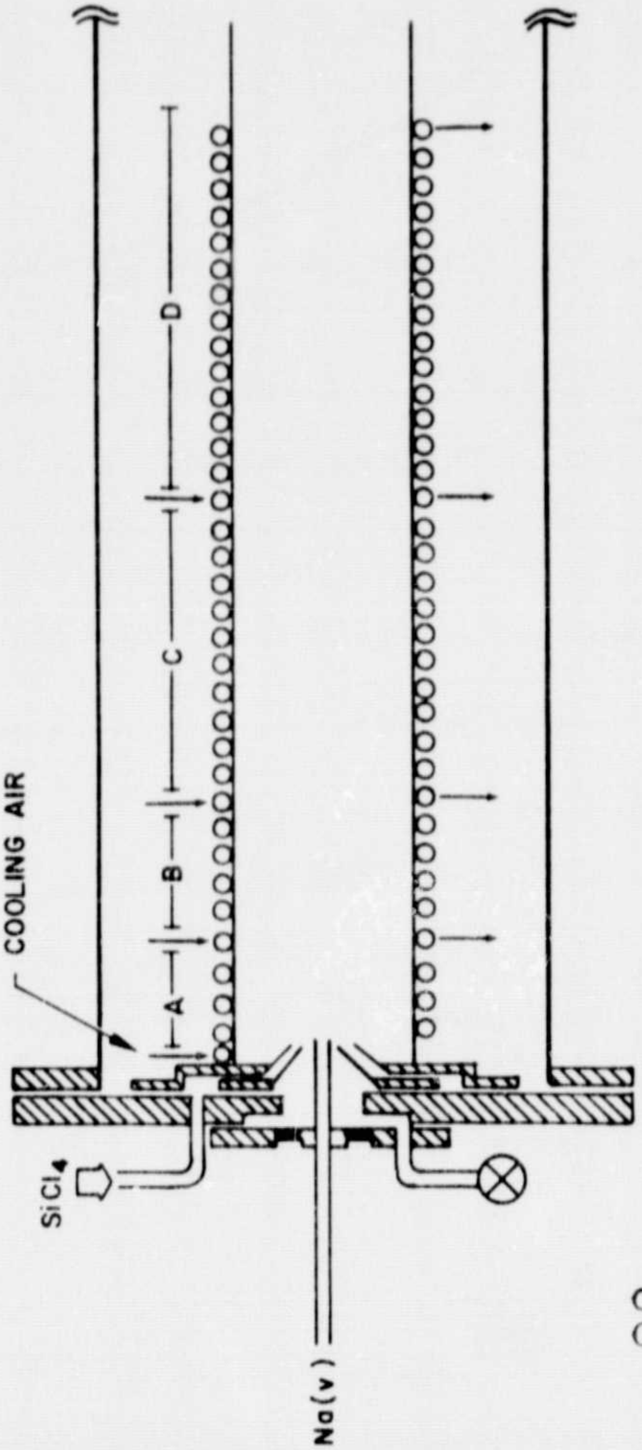

FIGURE 4 REACTOR CONFIGURATION FOR MEASURING HEAT RELEASE RATES

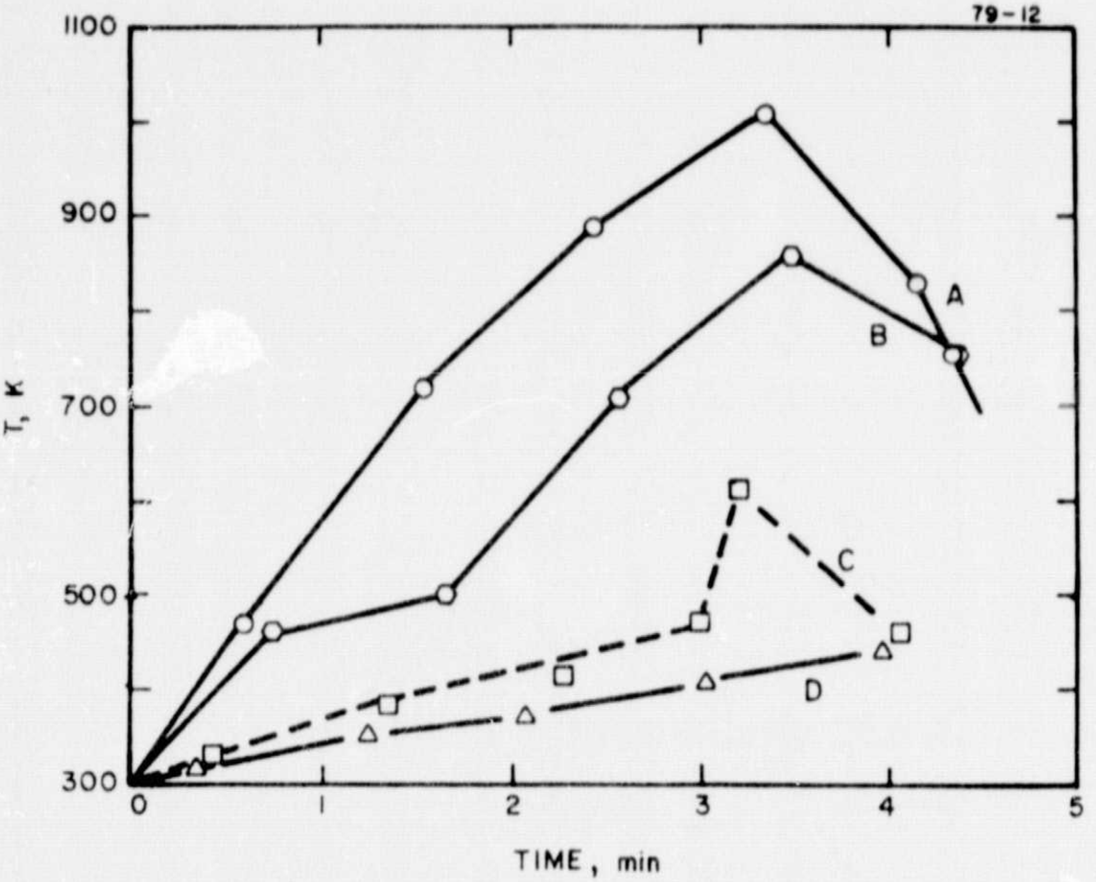

FIGURE 5 TEMPERATURE PROFILES OF THE WALL COOLING AIR FOR THE REACTOR AS SHOWN IN FIG. 4

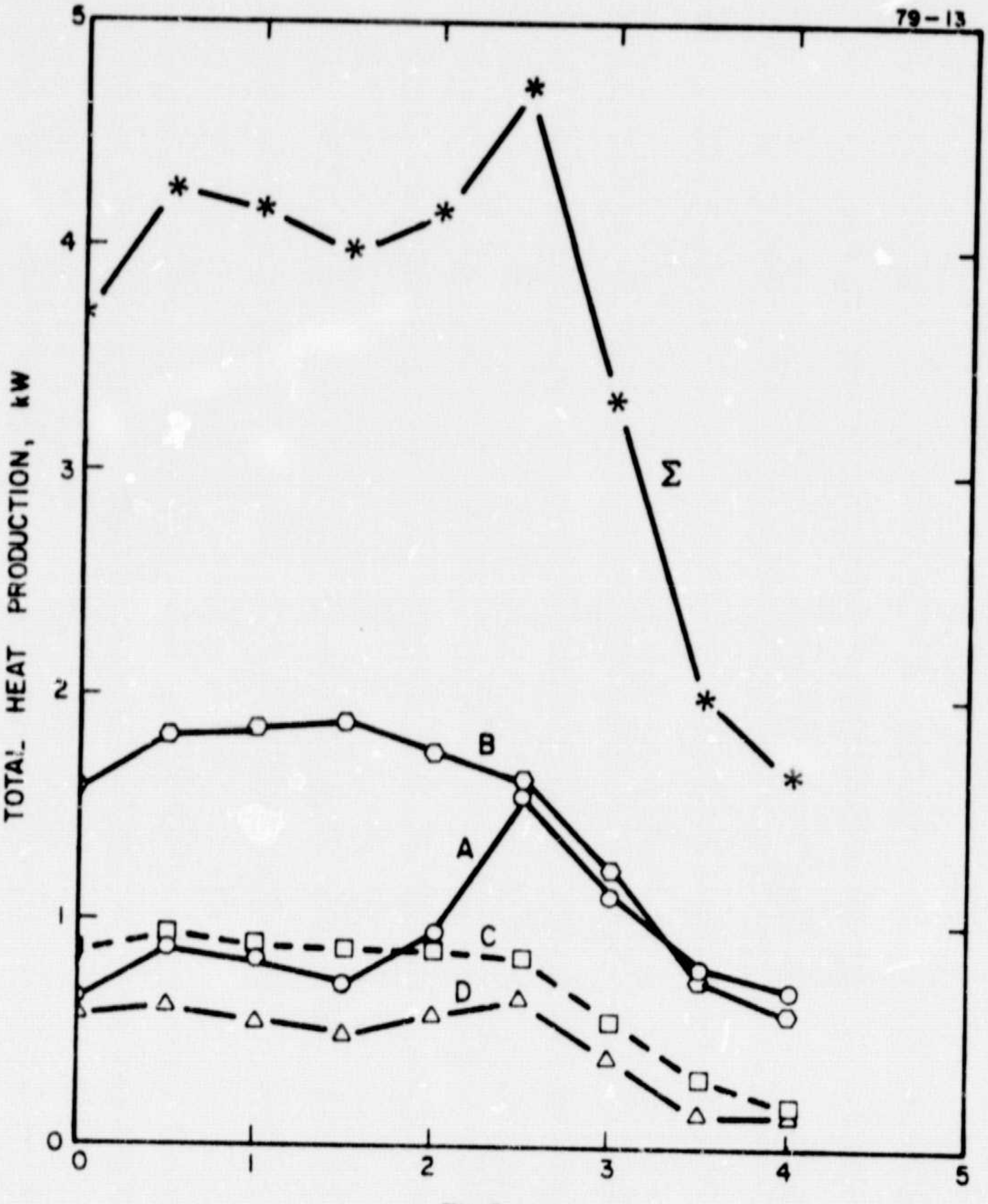

FIGURE 6 HEAT PRODUCTION PROFILES

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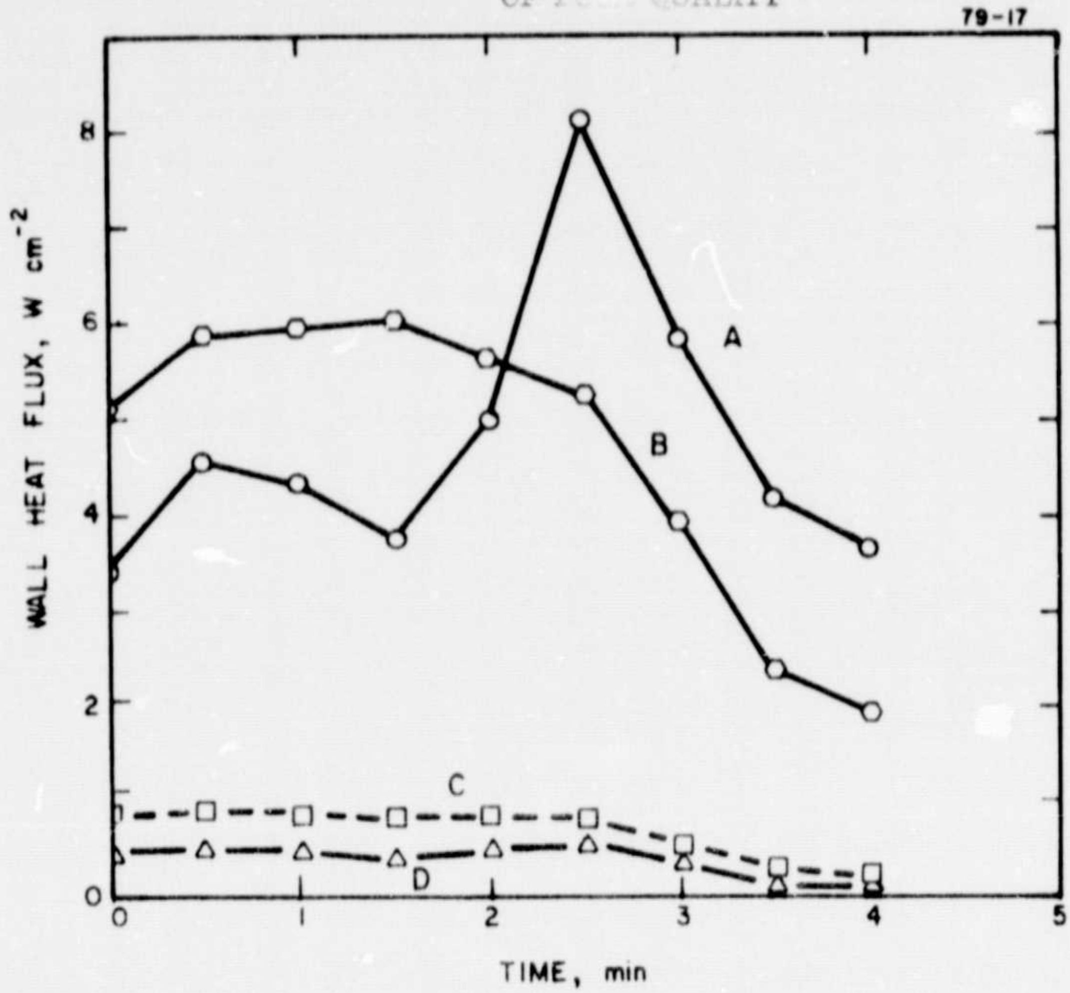

FIGURE 7 WALL HEAT FLUX PROFILES

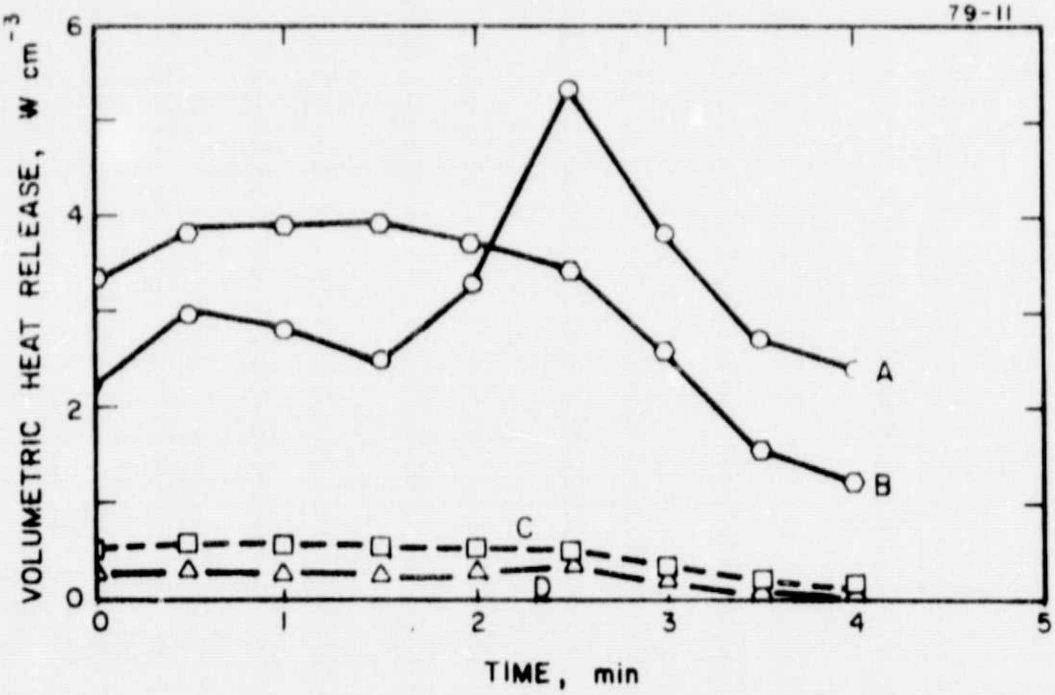

FIGURE 8 VOLUMETRIC HEAT RELEASE PROFILES