280
9/11/78

12.459
DOE/JPL/954862-2

DEVELOPMENT OF A MODEL AND COMPUTER CODE TO DESCRIBE
SOLAR GRADE SILICON PRODUCTION PROCESSES

Second Quarterly Report, January 1—March 31, 1978

By
R. K. Gould
R. D. Thorpe

May 1978

Work Performed Under Contract No. NAS-7-100-954862

AeroChem Research Laboratories, Inc.
Princeton, New Jersey

MASTER

U.S. Department of Energy

Solar Energy

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Paper Copy \$4.00
Microfiche \$3.00

DEVELOPMENT OF A MODEL AND COMPUTER CODE TO DESCRIBE SOLAR GRADE SILICON PRODUCTION PROCESSES

MASTER

SECOND QUARTERLY REPORT
R. K. GOULD and R. D. THORPE
MAY 1978

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

JPL Contract No. 954862
DRL Item No. 4, DRD No. QR
LSSA Silicon Material Task

Approved by

Hartwell F. Calcote
Director of Research

AeroChem Research Laboratories, Inc.
Princeton, New Jersey

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

FOREWORD AND ACKNOWLEDGMENTS

This report covers the period 1 January 1978 to 31 March 1978. During this period P.J. Howard contributed to the program and Prof. D.E. Rosner (Yale University) consulted on the program.

ABSTRACT

This program aims at developing a mathematical model, and a computer code based on this model, which will allow prediction of the product distribution in chemical reactors in which gaseous silicon compounds are converted to condensed-phase silicon. The reactors to be modeled are flow reactors in which silane or one of the halogenated silanes is thermally decomposed or reacted with an alkali metal, H_2 or H atoms. Because the product of interest is particulate silicon, processes which must be modeled, in addition to mixing and reaction of gas-phase reactants, include the nucleation and growth of condensed Si via coagulation, condensation, and heterogeneous reaction.

During this report period the free shear layer turbulent mixing code with (i) gas-phase chemical kinetics routines and (ii) particle routines that compute particle/gas momentum and energy exchange (particle slip and thermal lag) have been debugged and tested. The routine that treats Si nucleation and thus provides source terms for the particle growth (coagulation and condensation) has been coded and is being debugged. Particle coagulation routines are also being inserted into the main code. The condensation model to be included in the code is nearly complete and coding of this routine will be started shortly.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	iii
I. INTRODUCTION	1
II. TECHNICAL DISCUSSION	1
A. The Model	1
B. Sample Calculations	3
III. CONCLUSIONS	5
IV. PLANS	5
V. REFERENCES	5

LIST OF TABLES

Table

I	TEST CASE INPUT INFORMATION	7
II	REACTION SCHEME	8

LIST OF ILLUSTRATIONS

Figure

1	SAMPLE RADIAL PROFILES OF SiCl_4 , Na, AND NaCl	9
2	SAMPLE RADIAL PROFILES OF Si, Si_3 , SiCl, SiCl_2 , AND SiCl_3	9
3	SAMPLE RADIAL PROFILES OF GAS AND PARTICLE VELOCITIES	10
4	SAMPLE RADIAL PROFILES OF GAS AND PARTICLE TEMPERATURES	10

I. INTRODUCTION

This program aims at developing a mathematical model, and a computer code based on this model, which will allow prediction of the product distribution, as a function of time, in chemical reactors in which gaseous silicon compounds are converted to condensed-phase silicon. The reactors to be modeled are flow reactors in which silane or one of the halogenated silanes is thermally decomposed or reacted with an alkali metal, H_2 or H atoms. Because the product of major interest is condensed-phase silicon, the model must allow calculation of its rate of formation (via chemical reaction followed by nucleation), and the growth rate of the particulate Si via coagulation, condensation, and heterogeneous reaction. Since the efficiency of the particulate Si collection process will depend on the particle size distribution of the Si this must also be computed.

The basic model and computer code used as a starting point in developing this model is an axisymmetric, nonequilibrium, parallel stream mixing code which has been used for a number of years to treat systems in which parallel laminar or turbulent flows mix and undergo chemical reactions. This code, the Low Altitude Plume Program¹ (the LAPP code), treats only gas-phase chemistry; one of the major tasks is therefore the inclusion of "particle chemistry", i.e., nucleation and particle growth. The code, as implied by its name, treats the fluid dynamics of an open system. Thus modifications will also be required to account for the presence of reactor walls. The extent of these modifications depends, to a large degree, on the thoroughness with which phenomena occurring in boundary layers must be studied. Appropriate means of treating boundary layer phenomena are currently being examined.

II. TECHNICAL DISCUSSION

A. THE MODEL

The basic features of the LAPP code and the gas/particle momentum and energy interaction model now included in it are described in the previous quarterly report.² Current efforts are aimed at expanding the code capabilities to include models for (i) particle nucleation and (ii) growth via coagulation and condensation. The mathematical formulations of the

nucleation and coagulation models are also described in the last quarterly report.² Some modifications to the formulations of the coagulation rates have, however, been made in the interim. In particular, the turbulence enhanced coagulation rate coefficient K_{ij}^{turb} has been modified. The expression for K_{ij}^{turb} previously given includes only the effect of the unequal inertial response of particles of differing size to the motion of the turbulent eddies. This rate coefficient is zero for equal sized particles. As is pointed out in Ref. 3, there is another contribution to the coagulation rate from mutual particle "overtaking" due to the turbulent velocity gradients. This term is non-zero for equal sized particles. In addition, the efficiency of the coagulation process, assumed to be unity in Ref. 3, is considerably less than unity for unequal sized particles and must be considered. These efficiencies, which are now also included, are functions of the Stokes number (the ratio of the relaxation time of the particles to the time the particles take to flow around one another.)⁴

The condensation model now being included in the program is formulated as follows: For large particles (Knudsen number $\ll 1$) the rate of increase in mass of a particle is assumed diffusion-limited and is computed using the equation

$$\dot{m}_i = 2\pi r_i \left(Y_{Si} - (Y_{Si})_{eq,i} \right) \rho \cdot D_{Si} (Sh_i)_{Kn \gg 1}$$

where $\dot{m}_i$ is the rate of increase of mass of a particle in the i th mass class and r_i and $(Sh_i)_{Kn \gg 1}$ are the radius and Sherwood number for such a particle, respectively. Y_{Si} is the mass fraction of Si monomer (atoms) present in the gas phase far from the particles (taken to be the average gas-phase concentration in the stream tube). $(Y_{Si})_{eq,i}$ is the Si mass fraction at the i th mass class particle surface which is taken to be the Si equilibrium pressure at the particle temperature (which is mass class dependent and different, generally, from the gas temperature). The gas density is ρ and D_{Si} is the diffusion constant for Si. The Sherwood number is a function of the particle slip (relative to the mean flow), Reynolds (Re), and Schmidt (Sc) numbers and is taken to be

$$(Sh_i)_{Kn < 1} = 2(1 + 0.3 Re_i^{1/2} Sc_i^{1/3})$$

For very small particles (Knudsen number ≥ 1) diffusion will be very fast and the rate of mass increase will be limited by the actual incorporation

of material at the surface, i.e., for an accommodation coefficient of unity,

$$\dot{m}_i = \pi r_i^2 \left(Y_{Si} - (Y_{Si})_{eq,i} \right) \rho \left[\frac{8 RT_{p,i}}{\pi W_{Si}} \right]^{1/2}$$

where W_{Si} is the molecular weight of Si (28 g) and R is the universal gas constant. The Sherwood number in this case is

$$(Sh_i)_{Kn \geq 1} = \frac{1}{2} \left[\frac{8 RT_{p,i}}{\pi W_{Si}} \right]^{1/2} r_i / D_{Si}$$

In order to compute the rate of mass increase throughout the broad particle size range desired, we will interpolate between the two regimes, using

$$Sh_i = (Sh_i)_{Kn \geq 1} (Sh_i)_{Kn < 1} / \left[(Sh_i)_{Kn \geq 1} + (Sh_i)_{Kn < 1} \right]$$

and

$$\dot{m}_i = 2\pi r_i \left(Y_{Si} - (Y_{Si})_{eq,i} \right) \rho D_{Si} Sh_i$$

B. SAMPLE CALCULATIONS

At this time the code is being exercised as each subroutine is added. Currently the gas-phase chemistry and "inert" (non-coagulating, no nucleation, no condensation) particle routines appear fully operational. Sample output from the code at this stage of its development is shown in Figs. 1-4. These figures show plots of output for a test case in which a jet of Na(g) in Ar/H₂ passes through a coflowing stream of SiCl₄, also in Ar/H₂. The jet is loaded with particles of radii 1, 2, 5, 10, 20, and 50 μm . The particle material is given a density of 2 g ml⁻¹ and the particle to gas weight ratio is 0.30, evenly divided amongst the size groups. Table I gives the test case values for the input variables and Table II gives the gas kinetic scheme used in this case. It should be emphasized here that the scheme of Table II is not complete but is sufficient to be useful in checking the code performance. In particular Si n-mer growth is not included nor are Si₃ and several reactions between SiCl_x radicals. The rate coefficients used for the chlorosilanes are estimates based on analogy with rate data on halogenated hydrocarbons. Back reaction rate coefficients are obtained using JANAF⁵ tables of the thermochemical properties of the species involved. Activation energies for endothermic reactions are assumed to be approximately the same as their endothermicities.

In Fig. 1 the concentrations of the two reactants SiCl_4 and Na and the major product NaCl are plotted for downstream distances of $x/r = 2.5$ and 20.0. (The x-axis represents the centerline of the axisymmetric jet. The radial distance is y and r is the initial jet radius.). The figure shows clearly the mixing-limited nature of the fast overall reaction of Na with SiCl_4 .^{*} The volume of that portion of the mixing layer in which Na and SiCl_4 co-exist in appreciable amounts, and in which rapid reaction between these reactants thus occurs, remains small over the distance shown. However, the stable product, NaCl, mixes rapidly into the jet and the surrounding gas. In Fig. 2, Si, Si_3 , SiCl , SiCl_2 , and SiCl_3 concentrations are plotted. As one would anticipate, the concentration of the relatively stable species SiCl_2 builds up rapidly. SiCl_3 becomes a prominent species since, in the reaction scheme of Table II, this species is stable in the absence of Na or H and it is produced both by reaction of SiCl_4 with Na or H and by the reaction of SiCl with SiCl_4 . The other prominent species of Fig. 2 is Si_3 which is an artifact of the reaction scheme of Table II. A complete scheme will allow this species to react further to eventually form a liquid or solid Si phase.

In Fig. 3 the velocities of the gas and the 5 and 50 μm particles are plotted. Downstream, at the jet center, the particle and gas velocities have equilibrated. Off axis, though, the particle velocities show a second maximum. The source of this maximum is, in part, the somewhat artificial nature of this sample problem in which particles were placed in the flow field uniformly across the jet. While the gas velocity decreases rapidly downstream at $y/r \approx 1$, the particle inertia causes their velocity to exceed that of the gas. The effect is compounded by the occurrence of large energy input from the highly exothermic reactions in this region of the flow. The resultant gas density decrease reduces the drag on these particles, causing them to maintain their high initial velocity downstream. The temperature profiles of the gas and particles shown in Fig. 4 clearly show the presence of this narrow reaction zone at $x/r = 2.5$. These very strong temperature gradients are smoothed somewhat by turbulent mixing at $x/r = 20$. The large

* In this case mixing occurs as the two streams shear against one another and a turbulent shear layer forms. In many practical cases mixing will be forced by having the streams directed at angles to one another and will thus be even faster.

lag between the particle and gas temperatures is due to the rapidly increasing gas temperature and the thermal lag of the particles. In addition, convective heat transfer to the particles is proportional to the radius, while radiation proceeds as the square of the radius, thus increasing the thermal lag for large particles when $T_{\text{gas}} > T_{\text{particles}}$.

III. CONCLUSIONS

The code currently handles two-phase flow with gas-phase "inert" particles adequately. Sample calculations for particle-laden flows in which Na is reacted with SiCl_4 give physically reasonable results, within the confines of a somewhat artificial test case.

IV. PLANS

Work in the coming quarter will center on completing the particle chemistry (nucleation, coagulation, condensation) routines. During the latter part of this period we will also be engaged in the necessary modifications to allow the code to compute interior (pipe) flows. To do this a simple "law of the wall" approach (a specification of zero velocity at the wall together with a realistic axial pressure profile) will be used. In cases where the modeling of phenomena occurring within the boundary layer is crucial such an approach will not be adequate and the use of a boundary layer code is called for. While coupling such a code to the one presently being developed is beyond the present scope of this program, some attention will be given to how this might be done and to exactly what is to be gained by doing so.

V. REFERENCES

1. Mikatarian, R.R., Kau, C.J., and Pergament, H.S., "A Fast Computer Program for Nonequilibrium Rocket Plume Predictions," Final Report, AeroChem TP-282, AFRPL-TR-72-94, NTIS AD 751 984, August 1972.
2. Gould, R.K., "Development of a Model and Computer Code to Describe Solar Grade Silicon Production Processes," First Quarterly Report, AeroChem TN-184, February 1978.
3. Saffman, P.G. and Turner, J.S., "On the Collision of Drops in Turbulent Clouds," J. Fluid Mech. 1, 16-30 (1956).

4. Fuchs, N.A., The Mechanics of Aerosols (Macmillan, New York, 1964)
Chap. IV.
5. JANAF Thermochemical Tables, Dow Chemical Co., Midland, MI (continuously updated).

TABLE I.

TEST CASE INPUT INFORMATION

Jet

Initial mole fractions Ar/H ₂ /Na/SiCl ₄	0.10/0.41/0.49/0.00
Initial gas velocity	40 m sec ⁻¹
Initial gas temperature	1100 K
Initial particle velocity	30 m sec ⁻¹
Initial particle temperature	1200 K

External Flow

Initial mole fractions Ar/H ₂ /Na/SiCl ₄	0.10/0.41/0.00/0.50
Flow velocity	6 m sec ⁻¹
Flow temperature	1000 K

TABLE II
REACTION SCHEME

Reaction			Rate coefficient, molecular units ^a
1.	Na + SiCl ₄	→ NaCl + SiCl ₃	7(-13)
2.	Na + SiCl ₃	→ NaCl + SiCl ₂	7(-13)
3.	Na + SiCl ₂	→ NaCl + SiCl	7(-13) exp(- 19000/RT)
4.	Na + SiCl	→ NaCl + Si	7(-13)
5.	2Si + M	→ Si ₂ + M	1(-32)
6.	Si + Si ₂ + M	→ Si ₃ + M	1(-32)
7.	H + SiCl ₄	→ HCl + SiCl ₃	8(-12)
8.	H + SiCl ₃	→ HCl + SiCl ₂	8(-12)
9.	H + SiCl ₂	→ HCl + SiCl	8(-12) exp (- 14000/RT)
10.	H + SiCl	→ HCl + Si	8(-12)
11.	H + H + M	→ H ₂ + M	3(-33)
12.	Na + HCl	→ NaCl + H	4(-13) exp(- 6000/RT)
13.	H + HCl	→ H ₂ + Cl	7(-11) exp(- 4500/RT)
14.	Cl + Cl + M	→ Cl ₂ + M	4(-32)
15.	H + Cl ₂	→ HCl + Cl	3(-10) exp(- 4800/RT)
16.	Na + Cl ₂	→ NaCl + Cl	3(-11)
17.	H + Cl + M	→ HCl + M	5(-33)
18.	SiCl + SiCl ₄	→ SiCl ₂ + SiCl ₃	2(-11)

^a A(-B) is $A \times 10^{-B}$

FIGURE 1 SAMPLE RADIAL PROFILES OF SiCl_4 , Na, AND NaCl
 — SiCl_4 ; ... Na; --- NaCl

FIGURE 2 SAMPLE RADIAL PROFILES OF Si, Si_3 , SiCl, SiCl_2 , AND SiCl_3
 .-.- Si; --- Si_3 ; ... SiCl; --- SiCl_2 ; — SiCl_3

FIGURE 3 SAMPLE RADIAL PROFILES OF GAS AND PARTICLE VELOCITIES

— U_g ; --- U_{p5} ; ... U_{p50}

FIGURE 4 SAMPLE RADIAL PROFILES OF GAS AND PARTICLE TEMPERATURES

— T_g ; --- T_{p5} ; ... T_{p50}