REPORT

June, 1987 - May, 1988

CHEMICAL REACTION ENGINEERING LABORATORY

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INTRODUCTION

Focus in our Chemical Reaction Engineering Laboratory (CREL) remains on education and training of graduate students with innovation and research advances arising as a useful, integral byproduct of our activities. Our broad long term goal is the development of general methodology for handling transport-kinetic interactions in processing and preparation of materials and chemicals. Currently we are working on gaining an improved understanding as to how such transport-kinetic interactions affect preparation of fine particles, film growth, composites manufacture, catalyst performance and three phase reactor operation.

The breadth and depth of our research activities could not have been sustained without the continued support of our industrial sponsors. We are greatly indebted to all participating companies and industrial advisors. In return, we try to make our research efforts relevant to their long term needs.

It is gratifying to report that our emphasis on students' education, which is our primary mission, has been nationally recognized through the Chemical Manufacturers Association Catalyst Award presented to Dr. M. P. Duduković. We feel that this award in great part is the recognition of the educational and research atmosphere that CREL provides which our ex-students remember and cherish.

For our research contributions to Czochralski crystal growth NASA awarded two certificates of recognition to the reserch team of Duduković-Ramachandran-Srivastava. We would like to thank our ex-research associate, Dr. R. K. Srivastava, currently with Combustion Engineers, for excelling in this work.

SUMMARY OF MAIN ACTIVITIES

During the period from June 1, 1987 through May 31, 1988 research activities in CREL encompassed two main areas of: i) new materials preparation and ii) multiphase reactors. The underlying theme is the improved understanding of transport-kinetic interactions. The generic tools used are modeling, experimentation, expert systems and control.

In the area related to preparation of new materials several projects are under way. Kinetic-transport interactions affecting the size and morphology of geothite (precursor of magnetic particles) are under study (D. O'Connor). Phenomena governing the formation and growth of silicon particles in an aerosol reactor have been quantified (Y. B. Yang). Mass transport and oxygen incorporation into a growing silicon crystal in the CZ process are being modeled (D. Dorsey). Improved understanding of molecular transport in the novel Temporal Analysis of Products (TAP) microreactor is generated (B. S. Zou). A comprehensive model for plasma reactors is being developed (S. Pirooz). Finally, in a joint effort with our Materials Research Laboratory (MRL), headed by Dr. J. L. Kardos, we are replacing the art with a sound scientific basis in autoclave processing of high performance, thermoplastic, composite materials (S. J. Choi, I. S. Yoon). Intelligent, expert system, pultrusion processing of high performance composites is currently studied (H. T. Wu).

We were also furtunate that Mr. Jay Turner, whom Professor Duduković met and "recruited" during his sabbatical at UCLA, decided to join CREL after obtaining his M.S. degree at UCLA under Professor S. K. Friedlander's direction. Jay had a productive period of research in Germany at the University of Duisburg where he was a research associate. Jay's work on nozzles as aerosol reactors is added to this report to illustrate the power of reaction engineering concepts in new technologies. The area of aerosol reactors began to flourish at UCLA in 1983/84 when it was "catalyzed" by Professor Duduković in the fertile field of unsurpassed aerosol know-how of Dr. Friedlander's group.

In the area of multiphase reactors two main goals are pursued: i) introduction of novel, state-of-the-art, experimental techniques for measurement of flow characteristics and ii) investigation of novel contactors. Flow distribution and its prediction in trickle-bed reactors are studied (R. Holub). Assessment of the flow pattern of the fluid external to the particles, via tracer studies, is investigated in trickle beds (P. Hanratty). Evaluation of liquid recirculation profiles and liquid turbulence via a computer aided radioactive particle tracking facility (CARPT) is pursued in bubble columns (N. Devanathan). Gas-liquid contacting in rotating packed beds, which show potential as novel experimental three phase reactors, is systematically studied (A. Basic).

It should be recognized, that despite the variety of topics being covered, all of these are in-depth studies that result in publications in top quality journals. Through weekly CREL meetings our graduate students, who develop the expertise in their own research project, get exposed to a variety of problems and broaden their background considerably.

Regarding graduate students, the main news is that three of them completed their D.Sc. theses in 1987. Steven Lai completed his D.Sc. work on "Modeling of Fluidized Bed Reactors for Manufacture of Silicon from Silane" in August 1987 and returned to Taiwan. Brent Thomas successfully defended his D.Sc. thesis on "Modeling of Laminar Radial Flow Electrochemical Cells" also in August 1987 and returned to an industrial position with Hycal in Calgary, Canada. Ed Beaudry completed his D.Sc. thesis on "Modeling of Trickle-Bed Reactors at Low Liquid Flow Rates" in December 1987 and has been teaching at Oregon State University since September 1987. N. Devanathan, R. Holub and I. S. Yoon successfully defended their D.Sc. thesis proposals in Spring 1988. Among most pleasant news is that D. O'Connor is now a proud father of a baby girl - Elizabeth. Mr. Guangda Gao, Associate Professor at the Tiang Su Institute of Chemical Technology joined CREL in May 1987 for a year as a visiting scholar. He is conducting work on trickle-bed reactors.

Among other newsworthy items one should mention the donation of a Xytel automated reactor system from Monsanto (Dr. P. L. Mills) to CREL for which we are grateful. Together with the TAP system owned by CREL this gives us a solid basis for future work in catalysts and materials preparation and characterization.

Among major events in the department that impact CREL is the addition of the Gasche Laboratory funded by Autoclave Engineers. This laboratory will concentrate its efforts on the chemistry aspects of catalyst and materials development and on invention of novel tools for characterization of surfaces and microstructures. We look forward to further interaction with the Gasche Laboratory. Our interaction with Materials Research Laboratory has also increased during the past year.

During the past 12 month period CREL was active as always in publishing the results of our research. Our group is a leader in the Engineering School in publications in refereed journals. CREL's productivity is illustrated in Table 1. It should be noted that the School of Engineering total production of D.Sc. degrees per year varies between 15 and 20. CREL accounts for a substantial fraction of these. CREL's funding remains stable as indicated in Table 2.

Three professors, M. P. Duduković, B. Joseph and P. A. Ramachandran, continue to channel most of their research activities through CREL.

TABLE 1

CREL PRODUCTIVITY:

DOCTORAL DEGREES GRANTED FOR WORK IN CREL:

1985/86:	4:	R. Dave	- Composites (jointly with MRL)
		S. S. Jang	- On-Line Control
		S. Munjal	- Rotating Packed Bed
		K. Myers	- Bubble Column
1986/87:	3:	E. Beaudry	- Trickle-Beds
		S. Lai	- Fluidized-Bed-Silicon
		B. Thomas	- Electrochemical Reactors

NUMBER OF CREL GRADUATE STUDENTS (RESEARCH ASSOCIATES)

Year	84/85	85/86	86/87	87/88
Number	9(1)	12(2)	10(3)	10(2)

CREL CONTRIBUTIONS TO THE LITERATURE

	84/85	85/86	86/87
Publications	15	14	18
Presentations	19	25	14

TABLE 2

CREL FUNDING

	84/85	85/86	86/87	87/88
INDUSTRIAL FEES	120,000	130,000	122,500	120,000
INDUSTRIAL FELLOWSHIPS	35,000	35,000	35,000	(—)
JPL	144,000	55,000	—	—
EPRI		70,000	70,000	70,000
NSF	43,000	—	—	123,880
	342,000	290,000	227,500	313,880

INDUSTRIAL PARTICIPATION FEES ARE VITAL TO THE CONTINUITY OF THE CREL CONCEPT WHICH IS UNIQUE IN CRE

LISTING OF ACTIVE PROJECTS

Projects active in May 1988 are classified into two categories of multiphase reactors and development of new materials. The projects working title and graduate students involved are listed below:

Area I. MULTIPHASE REACTORS

Name		Title: key words
N. Devanathan	1.	Investigation of Liquid Hydrodynamics in Bubble Columns via a Computer Automated Radioactive Particle Tracking Facility: New experimental technique for monitoring of liquid recirculation, turbulence and gas holdup radial profiles.
R. Holub	2.	Hydrodynamics in Trickle-Bed Reactors: New diagnostic model for assessment of liquid maldistribution with experimental verification. New postulates for liquid distribution.
P. Hanratty	3.	Dynamic Modeling of Trickle-Bed Reactors: Novel way of tracer data interpretation.
A. Bašić	4.	Hydrodynamics and Mass Transfer in Centrifugal Gas-Liquid Contactors: Novel three phase reactor. Experimental study of liquid holdup. Theory for transport.

Area II. DEVELOPMENT OF NEW MATERIALS

Name		Title: key words
Y. B. Yang	1.	Modeling of the Aerosol Reactor for Production of Polycrystalline Silicon: Population balances, method of moments and fractals combine in arriving at a model that simulates well experimental evidence.
D. Dorsey	2.	Oxygen Transport During Silicon Single Crystal Growth by the Czochralski Method: Simulation of heat transfer, forced and free convection and magnetic field effects on oxygen mass transfer and crystal incorporation rates.
D. O'Connor	3.	Preparation of Magnetic Particles: Factors Influencing Crystal Growth and Particle Morphology of Iron Oxide (goethite) in Aqueous Solutions at High pH: Effect of mixing on initial precipitate and of oxygenation rate on product morphology.

B. S. Zou	4.	Quantification of the Mass Spectrometer Measured Responses of a Pulse, Catalytic, Microreactor (The TAP Experiments): Monte Carlo simulation of mass spectometer responses for various reactor configurations and pulse magnitudes.
S. Pirooz	5.	Modeling of DC Plasma Reactors: Calculation of electron in ion densities in various plasma regions.
S. J. Choi	6.	Modeling Devolatilization of Thermoplastic (Polyimide) Composites: Setting a framework for quantification of autoclave cure cycles based on first principles. (Joint project with MRL).
I. S. Yoon	7.	Modeling the Process Cycle of Thermoplastic Composites with Experimental Verification: Experiments to verify devolatilization and resin flow models. (Joint project with MRL).
H. T. Wu	8.	Intelligent Processing of Composites: Control of the Pultrusion Process: Examination of the ability of expert systems in manufacture of composites. (Joint project with MRL).
J. Turner	9.	Monodisperse Particle Production by Vapor Condensation in Nozzles: Theoretical assessment of the operability range of subsonic nozzles for production of monodisperse particles via condensation. Based on M.S. thesis under the direction of S. K. Friedlander.

REVIEW OF ACTIVE RESEARCH PROJECTS

INVESTIGATION OF LIQUID HYDRODYNAMICS IN BUBBLE COLUMNS VIA A COMPUTER AUTOMATED RADIOACTIVE PARTICLE TRACKING (CARPT) FACILITY

A. Problem Definition

Liquid circulation or gulf streaming is a phenomenon commonly encountered in bubble columns caused by nonuniform holdup profiles. It is primarily responsible for liquid phase mixing. The assumption of complete backmixing can lead to overdesign if high conversion is desired or to reduced selectivity in the case of complex kinetics.

How this gulf streaming is affected by column size (diameter and height), column and distributor design, physical properties of the gas-liquid mixture and operating conditions (superficial velocities) is presently not well understood. Neither a theory based on first principles nor abundant data are available. The inviscid models (1-3) make use of the single phase vorticity transport equations which are not applicable for two phase flow. The "principle" of minimization of maximum vorticity used to close the problem has no physical basis. Joshi and Sharma (3) proposed multiple circulation cells in tall columns without experimentally confirming their existence. In addition, they assigned the same clockwise rotation to cells above each other, which is physically impossible (4). Information on the existence of such cells is vital for model development for liquid mixing. Liquid circulation has also been described by 1-D momentum balances for gas and liquid phase (5). The model requires as inputs the eddy viscosity and the gas holdup profile. The predictions of the 1-D model can be significantly improved by a) developing a suitable relationship for eddy viscosity and its dependence on column geometry and operating conditions and b) introducing a gas phase continuity equation. To determine the eddy viscosity values it is necessary to measure the Reynolds' stresses for the liquid phase.

Liquid mixing in bubble columns is caused by a) convection b) turbulent dispersion c) bubble wakes and by d) molecular diffusion (which is negligible). These mechanisms are usually lumped into a single effective axial dispersion coedficient in the widely used dispersion model. It has been argued (6) that at least in the churn-turbulent regime, the dispersion model is without theoretical basis. Myers (6) developed a phenomenological slug and cell model for churn-turbulent flow. In this investigation, we seek to improve our data base which should be helpful in selection of proper models.

The motivation for this long term research project is provided by the realization that in the late 1970s, considerable effort and funds were spent on attempting to quantify liquid behavior in large scale bubble columns needed for coal liquefaction and other synfuels. Now when the demand for immediate results (which by the way were not forthcoming in the 1970s) is not as pressing, is the time to systematically develop the needed theoretical and experimental data base in this area.

B. Research Objectives

The overall objectives of this research are to test a novel experimental technique for determining liquid velocities in bubble columns, to examine its capability in providing liquid turbulence parameters and utilize the data obtained in improving the models for liquid circulation and backmixing. The research consists of a two prong approach as outlined below:

1. Experimental:
    - Development of noninvasive CARPT facility for measurement of local liquid velocities and turbulence parameters.
    - Assesment of the effect of distributor design, liquid properties and operating conditions.
    - Development of constitutive equations for a priori prediction of eddy viscosity and turbulent dispersion coefficients.
2. Theoretical:
    - Development of 1-D model for liquid circulation and comparison of model predictions with experimental data.
    - Solution of a convection-diffusion model for spread of a non-volatile tracer. Experimental verification using CARPT facility by the introduction of liquid radioactive tracer.

C. Research Accomplishments

Originally developed by Lin et al. (7), the CARPT facility has undergone systematic improvements as shown in Table 1. A single radioactive particle (1-2 mm in diameter) emitting gamma radiation of constant energy, which is dynamically similar to the recirculating liquid, is introduced into the column. As it moves along with the liquid, the particle is tracked using an array of strategically located scintillation detectors. The frequency of gamma rays arriving at each detector decreases with increasing distance between the tracer and the detector. The photon countrate obtained at each detector (the intensity) is related to the distance between the source and the detector using pre-established calibration. The instantaneous position of the tracer is then accurately calculated from the distances using an optimized linear regression scheme. Prudent use of the purposely introduced redundancy in distance measurements helps overcome the problem of intrinsic noise associated with the quantized nature of gamma emission. Time differentiation of the displacement yields local velocities. Ensemble averaged velocity profiles and other turbulence quantities can be computed after acquiring data for a sufficient length of time. The radioactive particle contains Sc-46 isotope ($t_{1/2}$ = 84 days, source strength = 1 mCi) coated with a polymer of sufficient thickness so as to make it neutrally buoyant in water. To fit the

Table .1: Development of CARPT Facility

Investigator/ Years	Place	Remarks
Lin/ 1981-84	Urbana, IL	12 detectors, low acquisition rates, first results on solids velocity.
Moslemian/ 1984-86	Urbana, IL	16 detectors, binary counters, first results on Reynolds' stresses.
This work/ 1987-89	FAU, FL	16 detectors, GPIB - CAMAC modular interfaces, application to fluidized beds and bubble columns.

intensity(I_i) vs distance (r_i) data, the source is placed at several points in the column and the time averaged intensities are recorded at each detector i. The following polynomial is used:

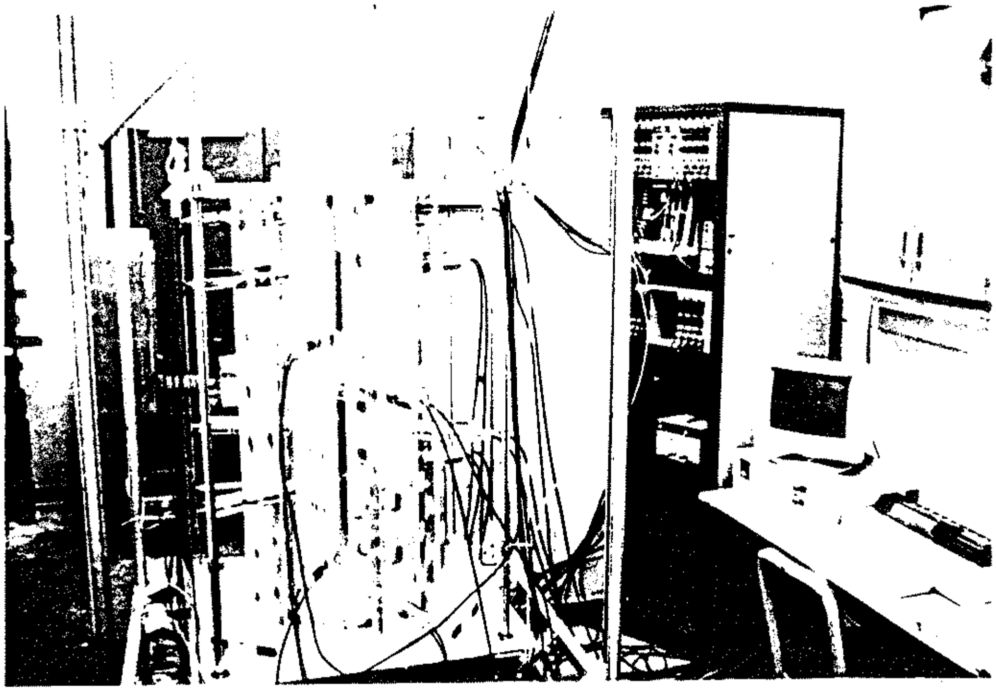
$$r_i = f\left(\frac{1}{I_i}\right) = a_{0i} + a_{1i}\left(\frac{1}{I_i}\right) + a_{2i}\left(\frac{1}{I_i}\right)^2 + \dots \tag{.1}$$

in which, a_i are the polynomial coefficients. In the dynamic experiment, the movement of the tracer is monitored by the array of scintillation detecors, typically for 3-5 hours. Using the calibration curves, the intensities recorded by the detector are converted to the distances between the tracer and each detector. The distance between the tracer and ith detector is given by:

$$(\xi - x_i)^2 + (\eta - y_i)^2 + (\zeta - z_i)^2 = r_i^2 \tag{.2}$$

Here x_i, y_i and z_i are the coordinates of the centers of the detectors. The redundancy in data from multiple detectors is used to obtain the optimized coordinates of the tracer, ξ, η and ζ using a weighted linear regression scheme (7). From the successive tracer locations, the instantaneous velocities of the tracer can be obtained.

Figure 1 shows an overview of the CARPT facility constructed as a part of this research at Florida Atlantic University. At this location the funds were available for assembling the equipment. It consists of the column (12" in diameter with a porous plate distributor), a versatile detector support structure (for locating the detector assembly around the column at any required axial location), the signal processing and data acquisition system (see figure 2 for the hardware implementation) and the air supply system (including the air compressor capable of delivering 400 scfm at 125 psig).



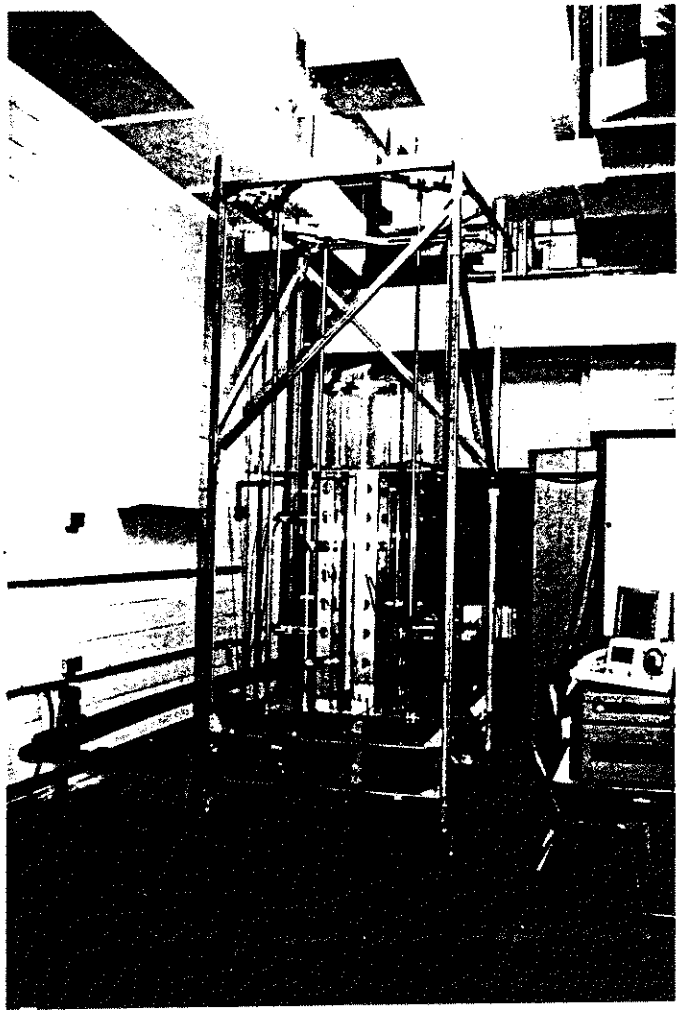


Figure 1: Overview of CARPT Facility showing column and detector support structure.

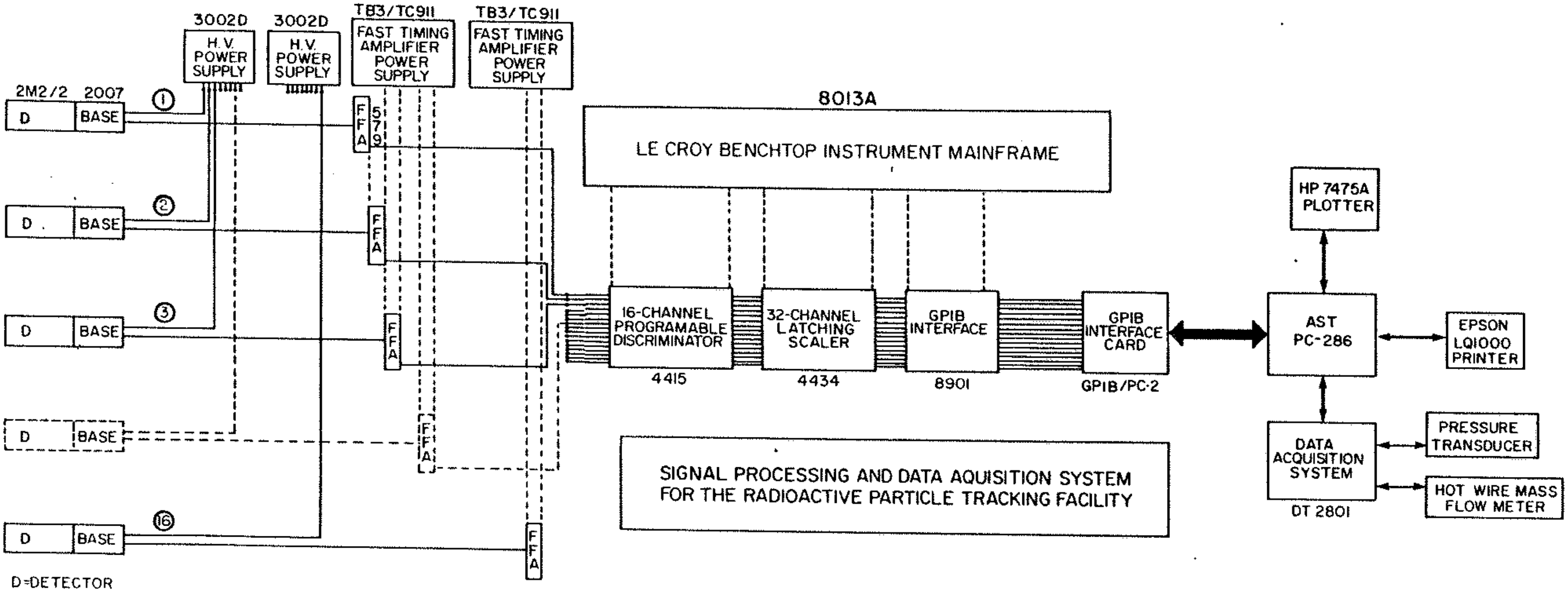


Figure 2: Signal processing and data acquisition system.

In order to demonstrate unambiguosly that the particle tracking technique is applicable to gas-liquid two phase flows, some preliminary experiments were conducted in a mini bubble column 14.7 cm in diameter and 30 cm high. First it is necessary to show that the intensity vs distance relationship is monotonic and the void fluctuations can be accounted for by in-situ calibration. The bounds of pure gas ($\epsilon_G = 1$) and pure liquid ($\epsilon_G = 0$) for source positioned along the axis of the detector (this precludes the solid angle effect) is shown in figure 4. The graph shows a monotonic decrease of intensity and a minor dependence on the phase composition. The experimental results compare well with theoretical predictions also shown in figure 4. The attenuation and buildup of photons, the solid angle effect and the detector efficiency calculations were considered in the theoretical predictions. Figure 5 shows the effect of solid angle when the source is placed at the same distance from the detector and the half angle is varied. The solid angle has a significant effect on the intensity and necessitates the use of many detectors for accurate location of the particle position. To assess the capability of the CARPT facility to locate the position of the tracer, eight detectors were arranged around the column and calibration experiments were carried out to determine I_i vs r_i relation for each detector. A fifth order polynomial fits the data reasonably well. The source was then placed at several known locations and the positions were "tracked" experimentally. Table 2 shows the actual tracer locations and the corresponding experimentally determined locations. The mean error in locating the particle in any one direction is less than 2 mm. By adding more detectors and optimizing their locations, this error could be minimized further.

D. Future Work

The research work to be accomplished is briefly outlined below:

1. The CARPT facility will be used to determine liquid velocity profiles atleast at three superficial gas velocities using both porous and perforated plate distributors. The effect of liquid viscosity will be examined using glycerol-water mixtures. In each case the turbulence quantities (eddy viscosity and dispersion coefficients) will also be computed.

2. A 1-D model for liquid circulation was developed and shown to match limited experimental data of Hills (8).(see 1987 annual report for details). The model will be tested using the experimentally measured eddy viscosity (radially varying) values.

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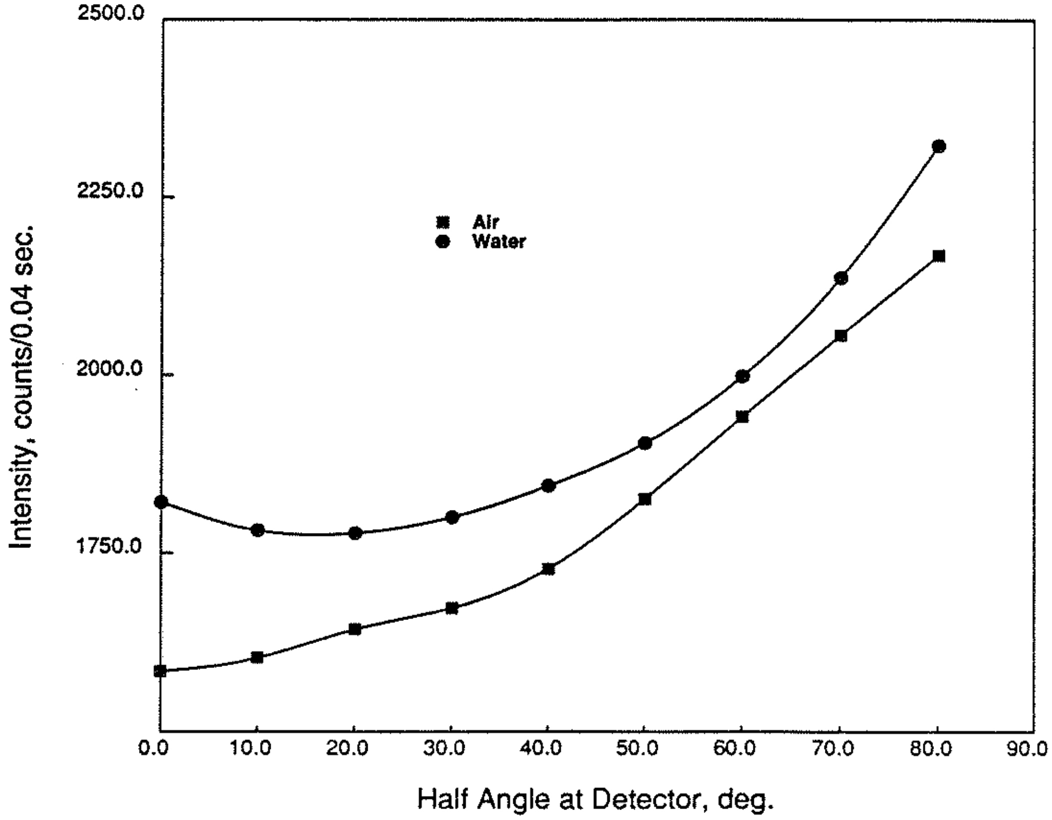

Figure 4: Effect of solid angle on intensity.

S.No.	ACTUAL LOCATION,cm			DETERMINED LOCATION,cm			ERROR, |Δx| ,cm		
	x	y	z	x	y	z	x	y	z
1.	0	-3.	3.	-0.13	-2.60	2.97	0.13	0.40	0.03
2.	0	5.	5.	-0.22	5.25	5.35	0.22	0.25	0.35
3.	0	3.	2.	-0.12	3.08	2.10	0.12	0.08	0.10
4.	-5.	0	8.	-5.30	-0.06	8.23	0.30	0.06	0.23
5.	5.	0	5.	5.14	0.20	5.25	0.14	0.20	0.25
6.	3.	0	3.	2.98	0.08	3.11	0.02	0.08	0.11
7.	3.	0	11.	3.15	0.05	10.98	0.15	0.05	0.02

Table .2: Typical errors in locating particle position

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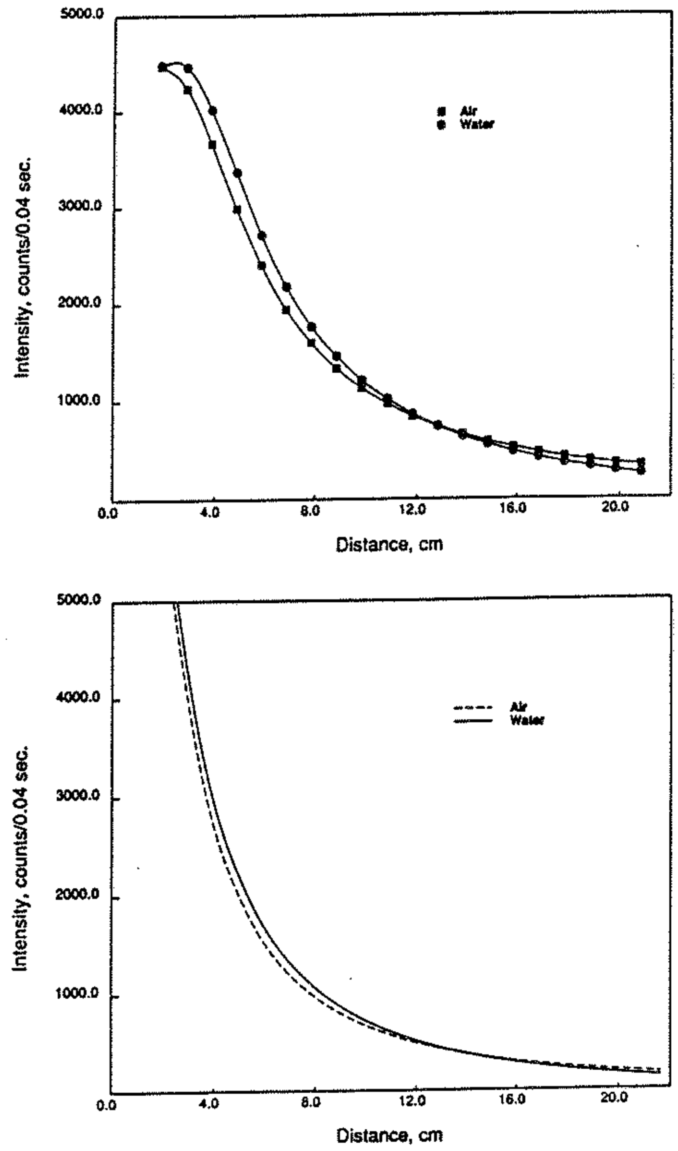

Figure 3: Intensity vs distance relationship, experimental (top) and predicted (bottom).

HYDRODYNAMICS IN TRICKLE BED REACTORS

A. Problem Definition

The hydrodynamics of cocurrent, gas-liquid downflow in packed beds is an important, yet poorly understood phenomenon. Flow regime transition, pressure drop, liquid holdup, and gas-liquid-solid contacting efficiency are several important factors in trickle bed design and scale-up.

Prediction of flow regime is accomplished using empirically developed maps or expressions which were derived from relatively small diameter beds. Christensen, *et al.* [1], observed the onset of pulsing in large beds as occurring locally (i.e the pulses did not span the entire bed) and conjectured that the transition point to pulsing across the entire bed is a function of the bed diameter. A dependence on bed diameter is not included in any of the flow regime maps or empirical models used to predict the onset of pulsing. Fundamental models of the transition to pulsing based on the governing equations of two-phase flow in porous media are only beginning to appear, [2,3,4]. The predominant approach is to attribute the onset of pulsing to a balance of surface tension and inertial forces. While preliminary results of this approach seem promising, the model is based on an accurate knowledge of the surface tension force. Surface tension forces have not been measured in trickle beds due to the small magnitudes, and the functional forms used in the models have not been verified. Also, Levec, [5], discovered that the transition to pulsing is a function of bed history. Bed histories which include pulsing show a transition to pulsing at much lower gas and liquid flow rates than bed histories which do not include pulsing. This effect is not described in either the flow regime maps or the empirical models.

Prediction of pressure drop and liquid holdup in trickle beds has been accomplished by empirically modified forms of the momentum balance equations for an assumed pore scale geometry. The accuracy of such correlations is quite good when care is taken to operate the bed in a manner which closely matches the assumptions on pore scale geometry and bed uniformity. Uniform liquid distribution was modeled by Saez, Carbonell, and Levec, [5,6], using the Ergun equation for single phase flow and modifying the equation with relative permeabilities to account for the two-phase flow situation. The approach parallels the modification of Darcy's law (see Scheideggar, [7]) for two-phase flow in sand beds, rocks, and similar porous media. Nonuniform liquid distribution was modeled by Greenfield, *et al.* [8,9], using two separate approaches which fit the data well over a limited set of operating conditions. The nonuniform liquid distribution which was modeled is that related to the hysteresis in pressure drop associated with bed history. This hysteresis was first measured by Kan and Greenfield [10], Levec [5], and Christensen, *et al.*, [1]. The bed histories which lead to the hysteresis in pressure drop can be described by the following thought experiment. Operating a trickle bed at a constant gas flow rate, the liquid flow rate can be increased from zero to give a set of pressure drop and bed holdup data. The increasing liquid flow rate mode is represented on Figures 1 and 2 by the lower of the two curves. Once the liquid flow rate is high enough to achieve pulsing, it can be decreased back to zero, but a different set of pressure drop and bed holdup data will be obtained. The decreasing liquid flow rate mode is represented on Figures 1 and 2 by the upper of the two curves. While the relationship between the pressure drop and holdup on each of the legs of the hysteresis loop have been modeled in a phenomenological manner based on assumed pore scale flow distributions, no model has been developed for the interior region of the hysteresis loop (which also represents possible operating states).

The gas-liquid-solid contacting efficiency is a important factor in trickle bed design, scale-up, and operation. The contacting efficiency is determined by the complex relationship between the flow regime, pressure drop, holdup, and bed history. In reference to the observed hysteresis in pressure drop, the current view is that the lower leg of the loop (i.e. the lower pressure drop) represents some degree of separation of the gas and liquid flow and a poor gas-liquid-solid contacting efficiency. The upper leg of the hysteresis loop (i.e. the higher pressure drop) is viewed as the case of uniform gas-liquid distribution and a high contacting efficiency. Quantitatively describing the gas-liquid solid contacting efficiency in each of these cases or over the wide range of intermediate operating conditions has not been done on a hydrodynamic basis due to the lack of understanding of the interaction between the microscopic and macroscopic phenomena which determine the phase distribution.

B. Reseach Objectives

The objectives of this project are:

1.) Develop and test a diagnostic model of phase distribution in trickle beds which quantitatively predicts the fraction of a bed in ideal and non-ideal flow patterns.

2.) Propose and test the governing laws of phase distribution in trickle beds. These governing physical principles should allow the prediction of pressure drop, liquid holdup, and gas-liquid-solid contacting efficiency.

C. Research Accomplishments

Progress has been made on both objectives.

1.) A diagnostic model based on observed pressure drops in trickle beds has been developed which predicts the occurrence of liquid maldistribution, and semi-quantitatively calculates the important characteristics of the maldistributed flow. The model is called the THREE ZONE MODEL since the bed is divided into three noninteracting regions called the Film, Dry, and Rivulet zones. The accessibility of each phase to each zone is shown in Figure 3. The model was tested using the experimentally observed pressure drop hysteresis, [1,5,10, and Figures 1 and 2], where the lower pressure drop on the increasing liquid flow rate leg has been attributed to liquid maldistribution and gas bypassing. The curve with the higher pressure drop, found by decreasing the liquid flow from pulsing, has been attributed to entirely film flow. The results of the model, as tested on two such hysteresis loops found in the literature, are shown in Figure 4 in terms of the fraction of the bed occupied by each zone. As can be seen, the model does predict a large deviation from film flow for the increasing liquid flow rate curve, and predicts that most of the bed is in film flow for the decreasing liquid flow rate curve. The same trends predicted by the model for the increasing liquid flow rate case were measured by Charpentier, [11], with electrical conductivity probes, but his results are not quantitative due to the calibration of the probes and the intrusive nature of the measurement. The experimental work needed to modify the THREE ZONE MODEL and increase the accuracy of the predictions is underway.

2.) A model for gas-liquid distribution in a system of slits (i.e. a simple pore model of a trickle-bed) has been proposed and numerically tested. The results predict the occurrence of multiple steady state phase distributions. The basis of the model is the postulate that hydrodynamic steady states correspond to states of minimum rate of viscous energy dissipation subject to the mass balance constraints imposed on the system. Results of the simulation for two different liquids (air is the only gas) flowing cocurrently downward in two identical slits are shown in Figures 5 through 8. The solid line indicates the pressure gradient and liquid saturation for an uneven distribution and the dashed line indicates the even distribution of gas and liquid between the two slits. The model has been used to simulate phase distribution in the case of three identical slits. The results are similar except that two steady states involving uneven distribution are predicted as shown on Figures 9 through 11 by the solid and dot-dash lines. The model does include a memory effect since a barrier in potential (a resistance defined by the viscous energy dissipation) lies between the different steady state distributions. In other words, if an uneven, steady state distribution was to become an even, steady state distribution, the intermediate, transient states have a much larger viscous energy dissipation than either two steady states. The results of these initial tests indicate that the model provides a foundation for future models of the hydrodynamics and phase distribution in trickle-beds.

D. Further Research Plans

The research is proceeding on the two goals.

1) The THREE ZONE MODEL is being modified and tested with experimental data to strengthen the ability to quantify the degree of phase maldistribution.

2) Use of minimum rate of viscous energy dissipation to predict phase distribution in complex geometries is planned. The first such geometry will be a network of pores which has previously been used to model trickle bed hydrodynamics except that simple mixing rules, [12], or random accessibility, [13], have been used to determine the gas-liquid distribution. In the current approach, the steady state liquid distribution will be determined by minima in the rate of viscous energy dissipation.

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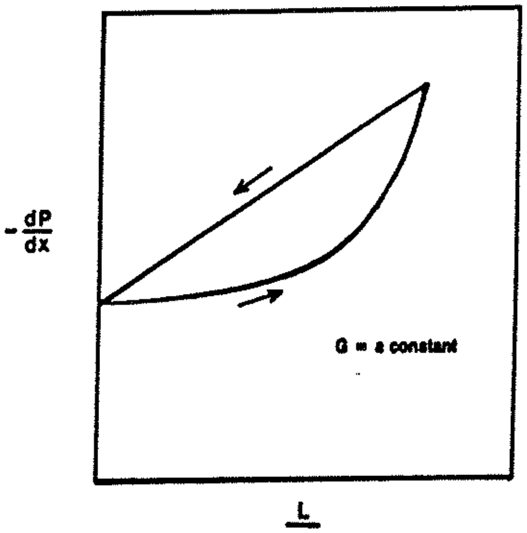

FIGURE 1 SCHEMATIC OF A PRESSURE DROP HYSTERESIS LOOP FROM A TRICKLE BED REACTOR. ARROW ON LOWER CURVE INDICATES INCREASING LIQUID FLOWRATE FROM ZERO, AND ARROW ON UPPER CURVE INDICATES DECREASING LIQUID FLOWRATE FROM PULSING.

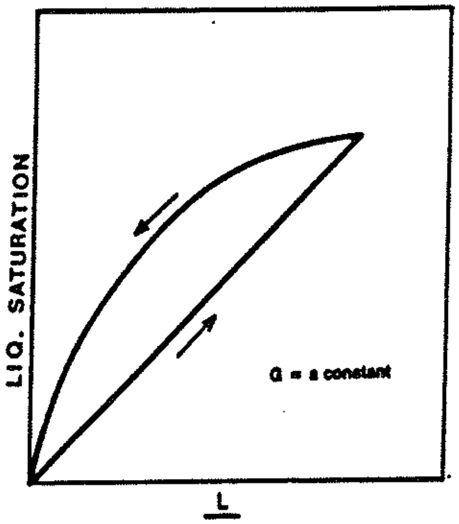

FIGURE 2 SCHEMATIC OF THE LIQUID SATURATION HYSTERESIS ASSOCIATED WITH FIGURE 1

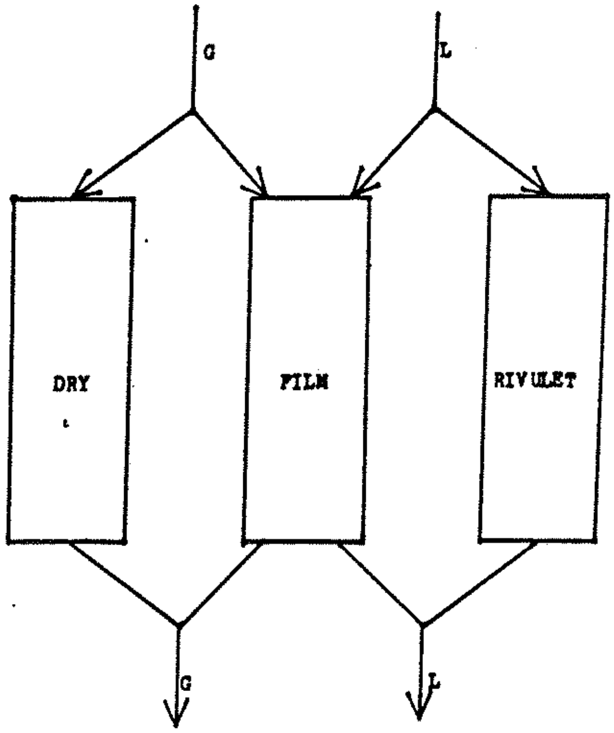

FIGURE 3 SCHEMATIC OF THE THREE ZONE MODEL. THE ACCESSIBILITY OF EACH PHASE TO EACH ZONE IS SHOWN.

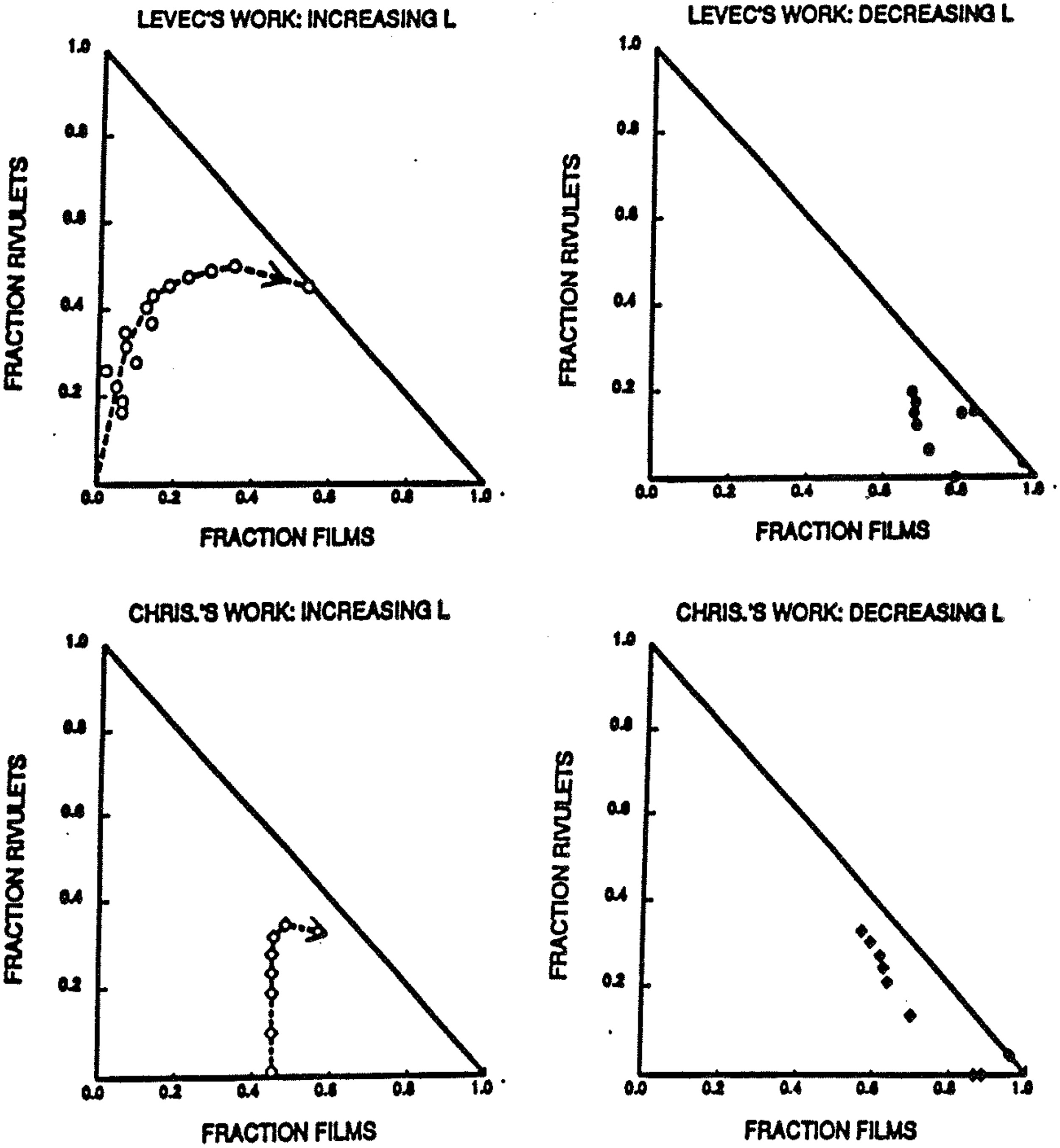

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FIGURE 4 TEST RESULTS OF THE THREE ZONE MODEL. POINTS ARE MODEL PREDICTIONS FOR THE INPUT DATA OF THE INDICATED AUTHORS. ARROWS ON THE DOTTED LINES INDICATE THE TREND WHEN INCREASING THE LIQUID FLOW RATE FROM ZERO (SEE FIGURE 1).
NO DEFINITE TREND FOUND FOR DECREASING THE LIQUID FLOW RATE FROM PULSING

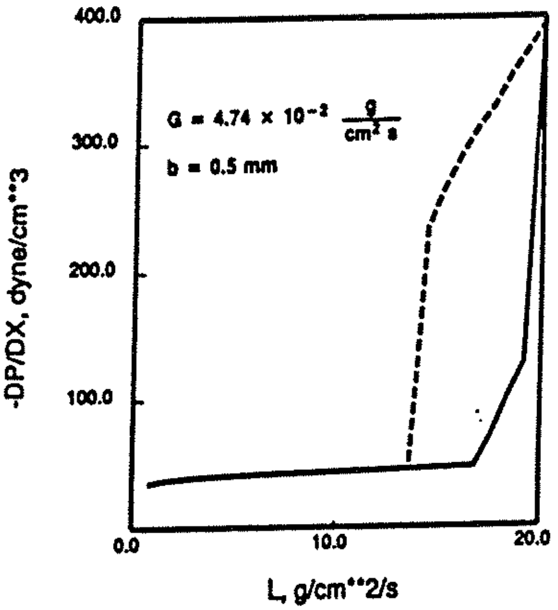

FIGURE 5 PRESSURE DROP HYSTERESIS LOOP FOR THE TWO SLIT SYSTEM. AIR AND WATER AS THE FLOWING PHASES.

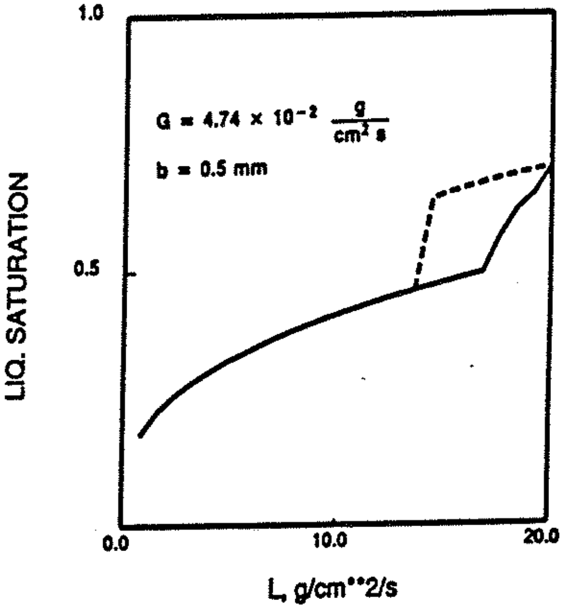

FIGURE 6 LIQUID SATURATION HYSTERESIS LOOP ASSOCIATED WITH FIGURE 5. AIR AND WATER ARE THE FLOWING PHASES.

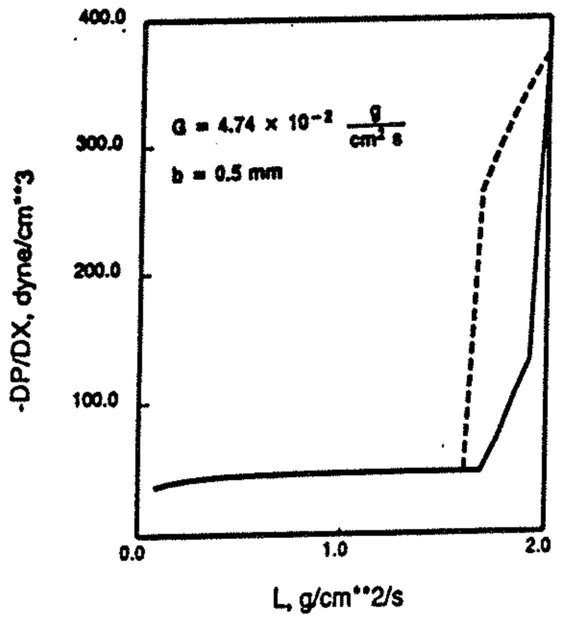

FIGURE 7 PRESSURE DROP HYSTERESIS LOOP FOR THE TWO SLIT SYSTEM. AIR AND A WATER/GLYCEROL MIXTURE (VISCOSITY = 10 cp) AS THE FLOWING PHASES.

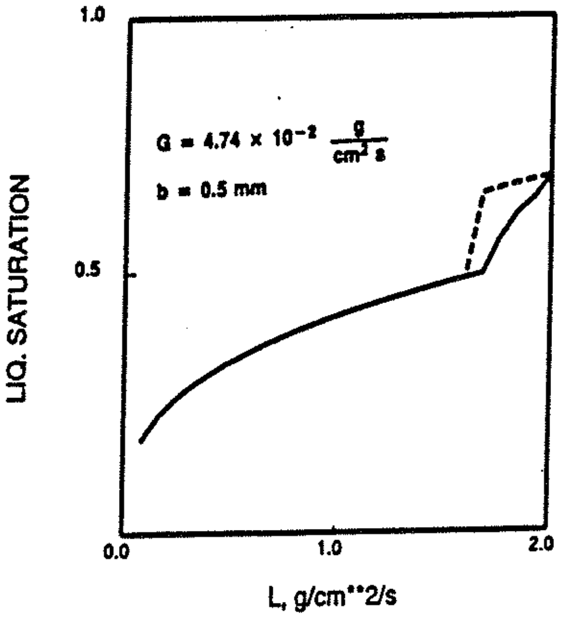

FIGURE 8 LIQUID SATURATION HYSTERESIS LOOP ASSOCIATED WITH FIGURE 7. AIR AND THE WATER/GLYCEROL MIXTURE AS THE FLOWING PHASES.

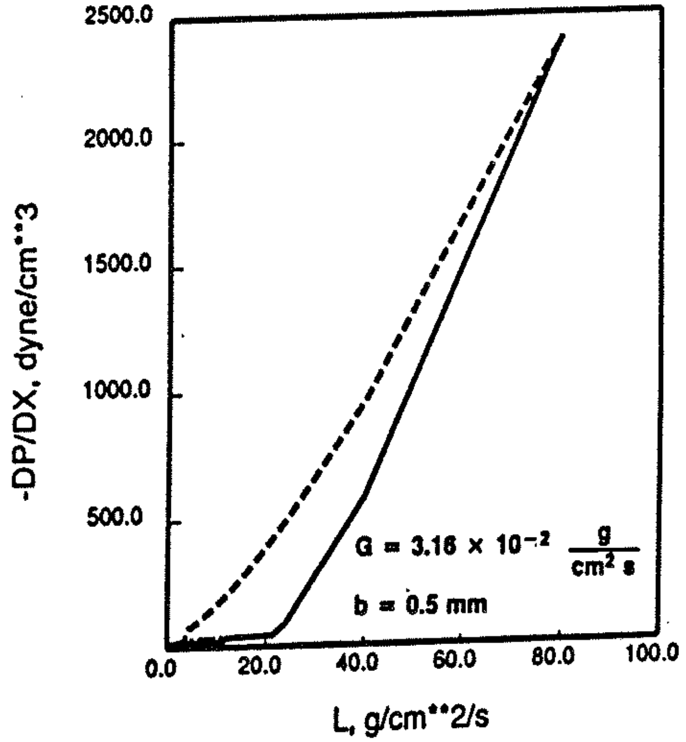

FIGURE 9 PRESSURE DROP HYSTERESIS LOOP FOR THE THREE SLIT SYSTEM. AIR AND WATER AS THE FLOWING PHASES.

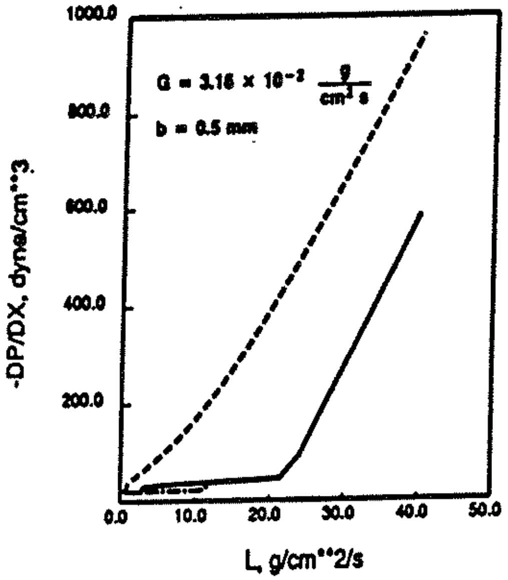

FIGURE 10 PRESSURE DROP HYSTERESIS LOOP FOR THE THREE SLIT SYSTEM. MAGNIFICATION OF THE LOWER LIQUID FLOW RATES OF FIGURE 9. AIR AND WATER AS THE FLOWING PHASES.

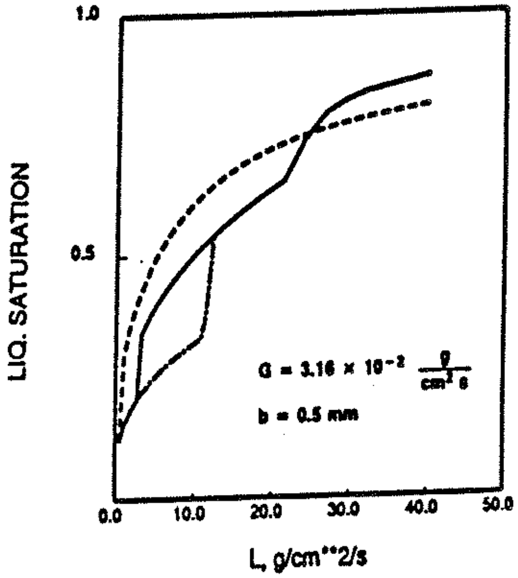

FIGURE 11 LIQUID SATURATION HYSTERESIS LOOP FOR THE THREE SLIT SYSTEM CORRESPONDING TO FIGURE 10. AIR AND WATER AS THE FLOWING PHASES.

DYNAMIC MODELLING OF TRICKLE-BED REACTORS

A. Problem Definition

The scale-up of trickle-bed reactors from pilot-plant or labratory data is difficult. Problems with scale-up can be attributed to flow maldistributions, incomplete liquid-solid contacting, catalyst deactivation, etc.. It is important to assess when flow maldistribution is present. Impulse tracer studies provide one method to examine, through the response curve, flow maldistribution. However, the impulse response curve, E-curve, represents the combined effects of the flowing fluid and the fluid which enters the catalyst pore structure. A method for decoupling the contribution to the E-curve of the tracer which enters the catalyst particles has been developed in CREL. The new method gives a procedure to determine the E-curve for the external fluid, i.e. the fluid which doesn't enter the catalyst pore structure. Flow maldistribution should then be easily identified from the external E(t) curve, $E_{ext}(t)$. The goal of this project is to show the improvements that this method offers over the method of moments (3) , and to experimentally verify the new method.

B. Research Objectives

1. Use computer simulation to determine the merits of the new method for identification of the E-curve for the external flow compared to the method of moments.
2. Experimentally verify the new method for both liquid-full and trickle flow operation.

C. Research Accomplishments

The method to decouple the particle effects from the overall E(t) curve to give the E-curve for the external fluid, $E_{ext}(t)$, was reported by Beaudry (1) and is based on the work of Villermaux (2) in liquid chromatography. Figure 1 demonstrates the procedure used to calculate $E_{ext}(t)$. First, a pulse tracer study is conducted to determine the overall E(t) curve for the reactor, Figure 1a. Second, the E(t) curve is transformed to the Laplace Domain to get E(s), Figure 1b. Third, the coordinate system is transformed (s-axis to p-axis) by the equation $p = s + k_{ex}H(s)/\epsilon_L$, Figure 1c, where k_{ex} is the exchange coefficient between the flowing liquid and the particle phase, ϵ_L is the liquid holdup, and $H(s)$ is the particle transfer function. Finally, the E(p) curve is inverted back to the time domain to give the $E_{ext}(t)$ curve, Figure 1d.

This new method was tested and compared against the method of moments (2) using computer generated overall E(t) curves with known $E_{ext}(t)$ curves. To simulate different tracers the adsoption equilibrium constant was varied between 0.0 and $1 \bullet 10^{-3}$ (m^3 liquid/ kg particle). To the overall E(t) curves random and/or periodic error of maximum magnitude δ_c, 0-5% of the maximum E(t) value, was added to simulate experimental data. Since experimental error was added to data, the E-curves were exponentially extrapolated when the values for E(t) dropped below $2\delta_c$.

Two simple flow models were chosen for the E*ext*(t) curves. To test for the case of near ideal flow, 15 CSTR's in series was chosen to model $E_{ext}(t)$. To test for the case of a maldistributed reactor, 10 CSTR's in series parallel with 5 CSTR's in series was used to model the $E_{ext}(t)$ curve.

The method of moments gives a technique by which the dimensionless variance, σ_E^2, of the external flow can be determined. The magnitude of σ_E^2 ($\sigma_E^2 = (\mu_2 - \mu_1^2)/\mu_1^2$ where μ_1 and μ_2 are the first and second moments of the E-curve) gives an indication of the maldistribution or ideality of the system, $\sigma_E^2 = 0$ indicates plug flow and $\sigma_E^2 > 1$ indicates flow maldistribution. The dimensionless variance of the external flow can be determined by the method of moments by calculating the dimensionless variance for the E-curve at a few different flowrates and extrapolating the results to zero flow. The intersection should give the dimensionless variance for the external flow(4).

Initial comparison of the two methods shows that the new method gives more information about the flow within the reactor, it gives the entire $E_{ext}(t)$ curve for the reactor and possibly information about the particle scale model, while the method of moments gives only σ_E^2 for the external flow. However, the new method requires knowledge of the particle scale model and experimental determination of the system dependent parameters (effective diffusivity, liquid-solid mass transfer coefficient and the absorption equilibrium constant), while the method of moments requires no knowledge of either the tracer or catalyst properties. Computer simulation was used to determine the applicabillity of the two methods in the presence of experimental error.

The first case studied , near ideal flow, was with the $E_{ext}(t)$ modeled by 15 CSTR's in series. For no added error, the E-curve was exponentially extrapolated at $\sim 0.5\%$ of the maximum E(t) value. The new method was able to determine virtually the same $E_{ext}(t)$ curve regardless of the adsorption equilibrium constant, K_a. The method of moments, however was not able give the correct σ_E^2, see Figure 2, and in some cases actually predicted negative values (which is physically meaningless). At 4% of the maximum E(t) value for error, the new method was still able to give a very good approximation of the actual $E_{ext}(t)$ curve, see Figure 3. At small times, the deviation from the actual curve was the greatest , however, the deviation from the actual curve never exceeded the magnitude of the added error. With 4% relative error, values for σ_E^2 of the external E-curve were not obtainable because there was no discernible pattern for the σ_E^2 vs flowrate plot, see figure 4. Therefore, the new method has been shown to work in the presence of experimental error (provided that the correct particle scale model , exchange coefficient k_{ex}, effective diffusivity D_e adsorption constant K_a are known) while the method of moments fails.

Since at very low relative error, the results of the method of moments could be interpretted as showing that the system has no flow maldistribution, the two methods were investigated for a maldistributed system. The $E_{ext}(t)$ curve was modeled by 10

CSTR's in series parallel to 5 CSTR's in series. With no added error (however the E(t) curve was exponentially extrapollated at 0.5% of the maximum E(t) value), the method of moments was not able to show conclusively whether or not the system was maldistributed, see Figure 5. For $K_a = 0$ and $K_a = 4 \bullet 10^{-4}$ (m^3 liquid/ kg particle) the results suggested a non-maldistributed system, while for $K_a = 1 \bullet 10^{-3}$ the results indicated a maldistributed system. The results based on the method of moments seem to be very tracer dependent and therefore this is an unreliable method. For 3% relative error, the method of moments gives similar results to that of Figure 3 and therefore, the method fails. For 3% relative error, the new method gives a good approximation of the actual $E_{ext}(t)$, see Figure 6. From the $E_{ext}(t)$ curves, the flow maldistribution of the system can be easily seen.

Therefore, the results of the computer simulation show that the new method works in the presence of experimental error and the method of moments fails absolutely in the pressence of reasonable error (3-4% of the maximum value) and gives inconclusive and unreliable results for small error ($\leq$ 1% of the maximum E(t) value). The results of the computer simulation justify persuing experimental verification of the new method.

Presently experimental work is being done to verify the new method. Impulse tracer studies are being done for both liquid-full and gas-liquid flow.

D. Future Work

Experimental verification of the new method for both liquid-full and liquid- gas flow.

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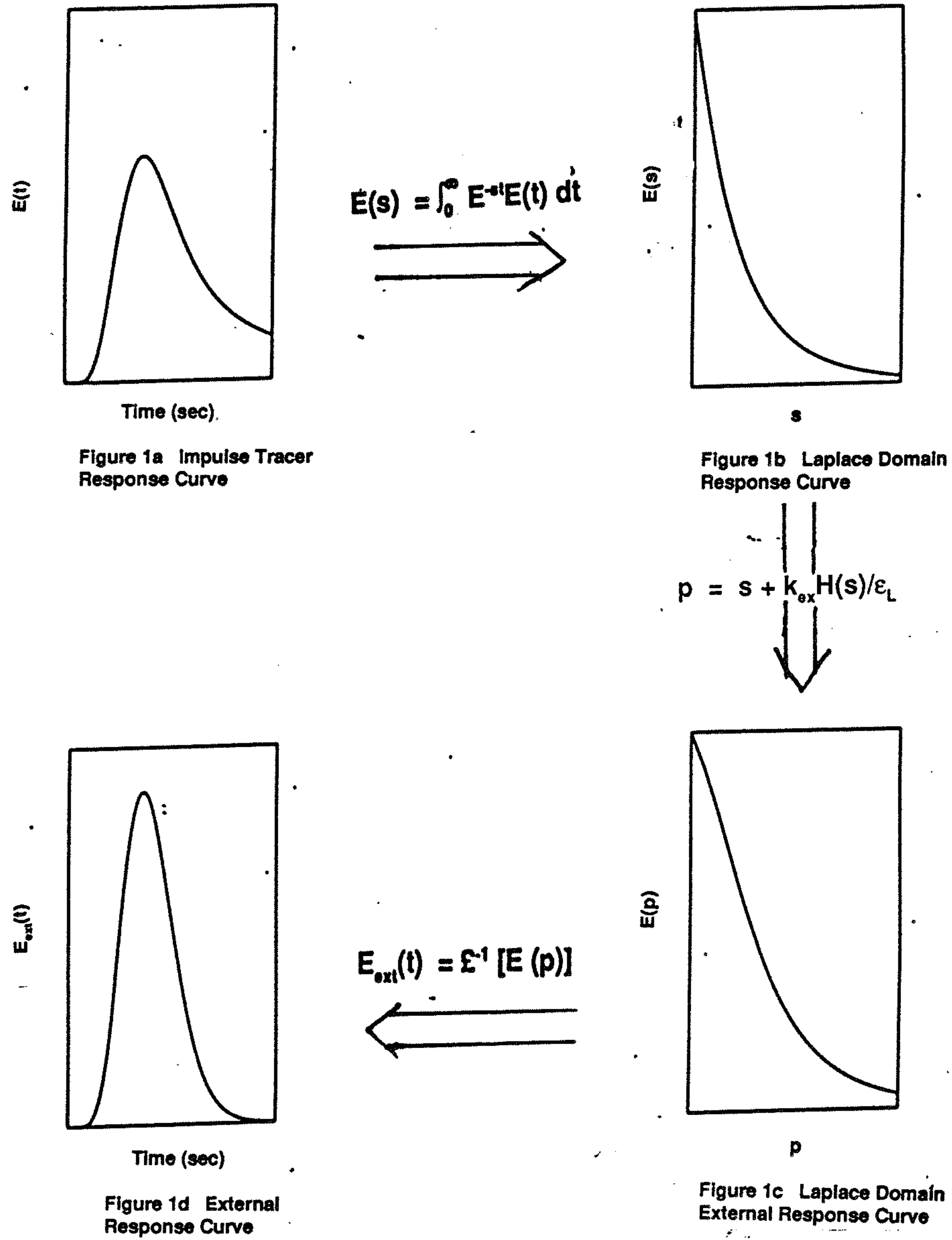

Figure 1a Impulse Tracer Response Curve

Figure 1b Laplace Domain Response Curve

Figure 1c Laplace Domain External Response Curve

Figure 1d External Response Curve

Figure 1 Procedure for Extracting the E-curve for the External Flowing Liquid from Overall E-Curve

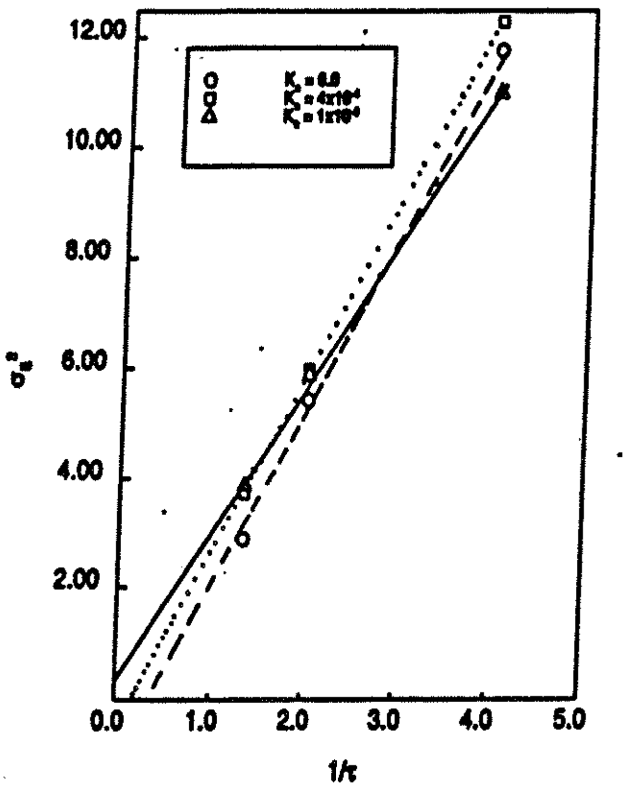

Figure 2 Method of Moments for Near Ideal Reactor with No Error

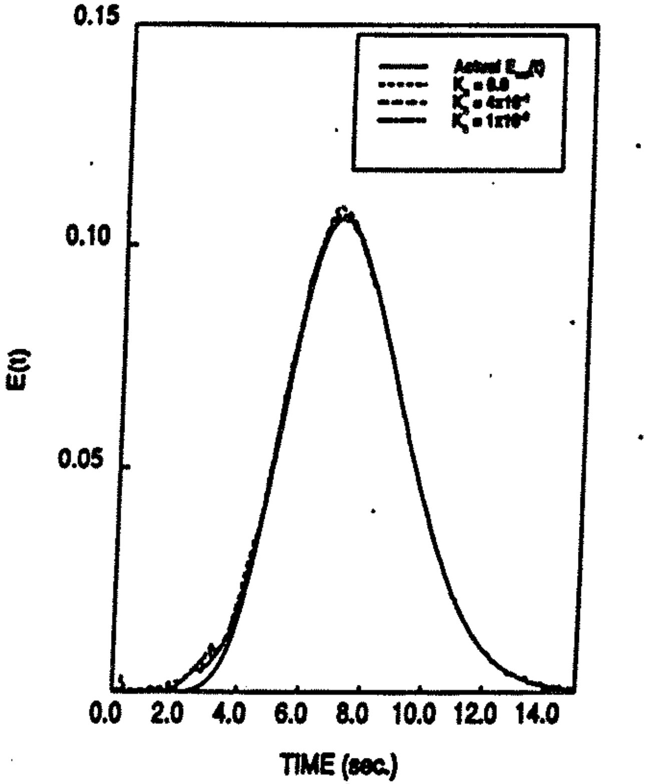

Figure 3 The New Method for Near Ideal Reactor with 4% Error

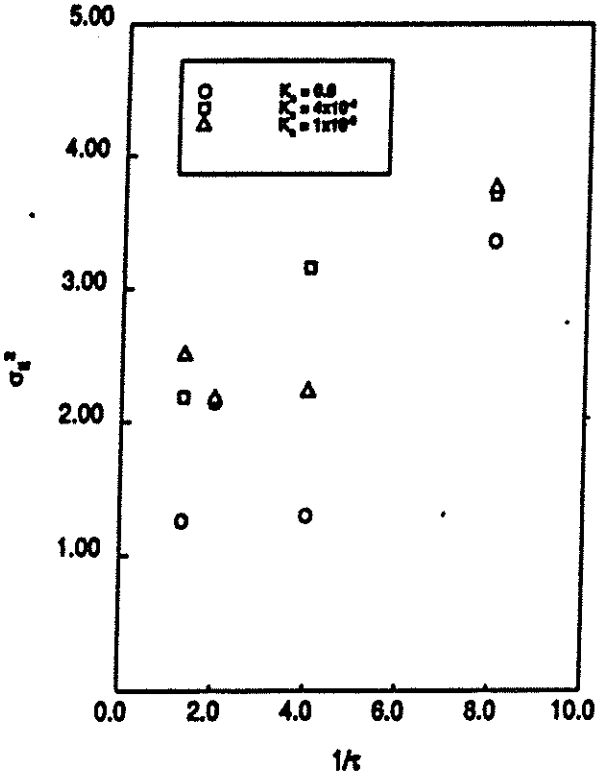

Figure 4 Method of Moments for Near Ideal Reactor with 4% Error

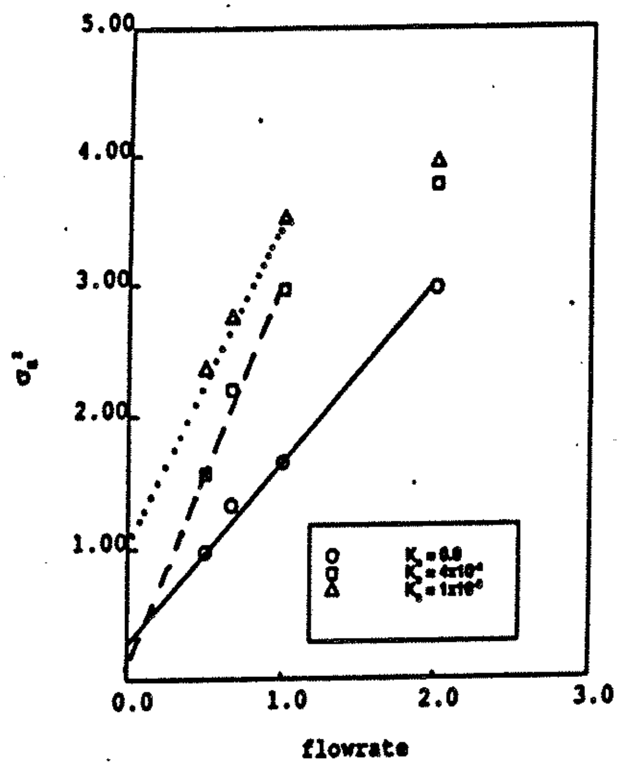

Figure 5 Method of Moments for Maldistributed Reactor with No Error

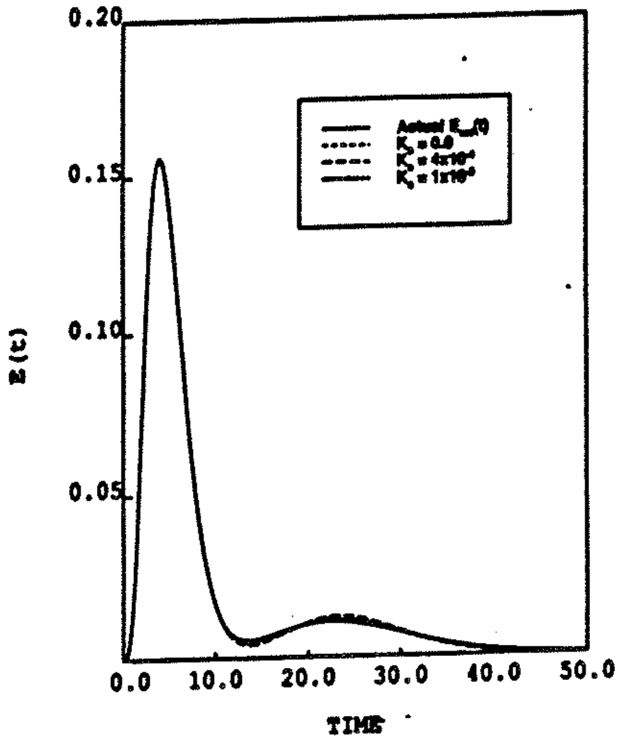

Figure 6 The New Method for Maldistributed Reactor with 3% Error

HYDRODYNAMICS AND MASS TRANSFER IN CENTRIFUGAL GAS-LIQUID CONTACTORS

A. Problem Definition

Centrifugal gas-liquid contactor (HIGEE) is a device in which centrifugal force is employed as an adjustable drive for flow of liquid through a porous medium countercurrently to pressure drop driven gas.

Interphase transport of momentum and mass, in the packed bed, in presence of a centrifugal body force are the phenomena that govern the performance of centrifugal contactors. An understanding of these processes is necessary for developing a theoretical basis for description of centrifugal gas-liquid contactors. Such a theory should explain the high performance of these devices in mass transfer operations. It should also indicate the feasibility of using centrifugal contactors in other processes (for example such as involve three phase systems with chemical reactions). Finally, such a theory should provide a sound basis for reliable design and scaleup of the rotating packed bed devices.

Development of such a theory is the motivation for this project which addresses the problem of transport phenomena in the porous packing of a centrifugal gas-liquid contactor from first principles.

B. Research Objectives

The theory being developed is based on the hypothesis that liquid phase present in the rotating packed bed is in the form of thin films which cover the surface of the packing. Liquid phase is assumed to be in the asymptotic regime of laminar film flow. In order to quantify this theory, an approach has been undertaken with the following objectives:

- Devise a statistical model which allows the random surfaces of the packing to be treated as a collection of well defined elementary surfaces of known orientation.
- Analyze the problem of mass transfer in film flow on elementary surfaces thus defined.
- Obtain experimental information, by measurement, of liquid holdup and the state of distribution of the liquid phase in the rotating packed bed. This information will either confirm the liquid film hypothesis, or indicate a need for a different approach.

C. Research Accomplishments

In the analysis aimed at representing the packing surface by regular elements, it was concluded that it was necessary to consider at least three kinds of elementary surfaces. These different elementary surfaces are distinguished according to their orientation with respect to the rotation axis and the radial direction. The three types of surfaces were termed rotating disk, rotating cup (or cone) and rotating blade. For each of these surafces the hydrodynamic problem can be defined in a similar way. For asymptotic film flow behavior analogous results are obtained. Hovewer, film thickness is different in each case. Schematic of a rotating blade, disk and and cup given in Figure 1a, 1b and 1c, respectively. Elementary surfaces arise by rotation of plane π which is defined by axes x and y. The rotation velocity vector is denoted by ω and radial direction by r. Film flow is studied in the coordinate system (x,y,z). Direction z is always perpendicular to the elemenatry surface and the thickness of the film flowing on the surface is measured in this direction.

The mass transfer problem can be formulated in analogous ways for all three elementary surfaces. Results in each case reflect different film thickness. The effect of film thickness and shape of the gas liquid interface on the rate of the overall mass transfer process in the liqiud film is important for this model. An extensive review of the literature on mass transfer in laminar liquid films showed that this effect had not been addressed before.

The mathematical problem of mass transfer in liquid films of variable thickness (as is always the case in films on rotating surfaces) cannot be solved by analytical methods used for films of constant thickness and numerical analysis is necesary. A modification of the method of orthogonal collocation was developed. The method proved to be efficient as was evidenced by high acuracy achieved with a relatively low number of interior collocation points (at most four).

As an example, consider the mathematical problem:

$$(2\eta - \eta^2)\frac{\partial C}{\partial \tau} = \frac{\partial^2 C}{\partial \eta^2} \tag{.1}$$

$$\tau = 0: \quad C = 0 \tag{.2}$$

$$\eta = 0: \quad C = 0.8 \tag{.3}$$

$$\eta = 1: \quad \frac{1}{Bi}\frac{\partial C}{\partial \eta} - h(\tau)\,(C - 0.2) = 0 \tag{.4}$$

This problem describes a mass transfer process in the liquid film flowing on the rotating disk. Asymptotic film thickness is assumed and denoted by h. τ and η denote the dimensionless streamwise and transverse coordinates, respectivelly.

Initially, $\tau = 0$, liquid contains no solute. At $\eta = 0$ dissolution of the solid surface takes place and solute concentration at the solid surface is constant and equal to the saturation value (C = 0.8). At the gas-liquid interface, $\eta = 1$, transport of the same solute is governed by the gas side resistance which is taken into account by the Biot number, Bi. It is assumed that the same solute is present in the gas phase with an equivalent concentration of 0.2. The direction of the mass transport across the gas-liquid interface can change along the liquid film, as it is determined by the sign of the gas-liquid local concentration difference.

Results of this problem, obatained by the new method, are given in Figure 2 in form of concentration profiles across the film (C vs η) at different distances, τ, from the initial point.

D. Future Work

The problem of describing random packing by elementary surfaces of known orientation is still to be completed. Namely, the analysis yet to be performed should answer the question of how much of the surface area of random packing can be identified with rotating disks, cones or blades.

In the problem of hydrodynamics of liquid films on elementary surfaces, it remains to analyze the length of the entry region in each case and establish its dependence on the operating parameters (liquid flow rate, rotating speed, bed size) and system properties. This is necessary in order to establish those condiditions for which the asymptotic film thickness and velocity profiles, that were assumed, indeed hold on the scale of elementary surfaces.

Finally, experimental determination of liquid holdup and liquid structure by measurement of electrical resistance and capacitance of the bed will be done. Results will be analyzed in terms of the liquid film model developed utilizing the concept of elementary surfaces.

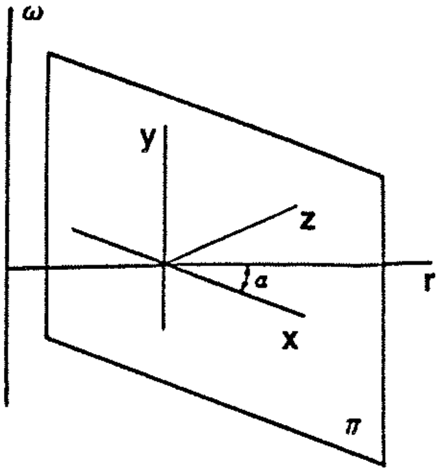

Figure 1a: Rotating blade

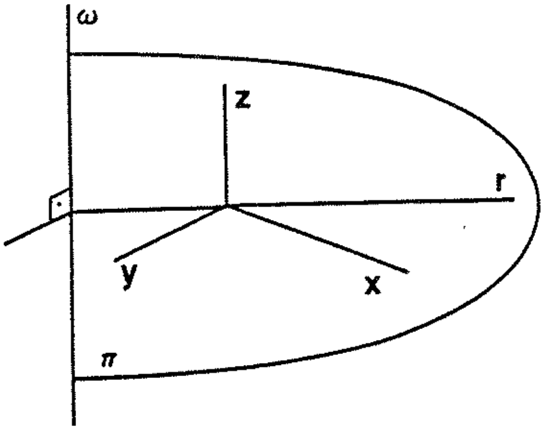

Figure 1b: Rotating disk

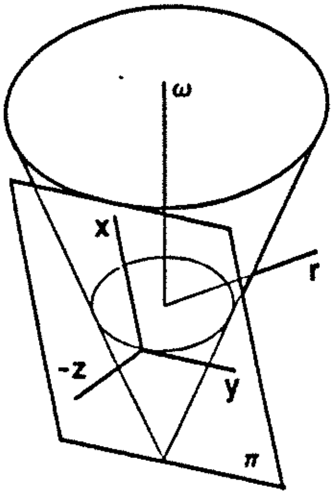

Figure 1c: Rotating cone

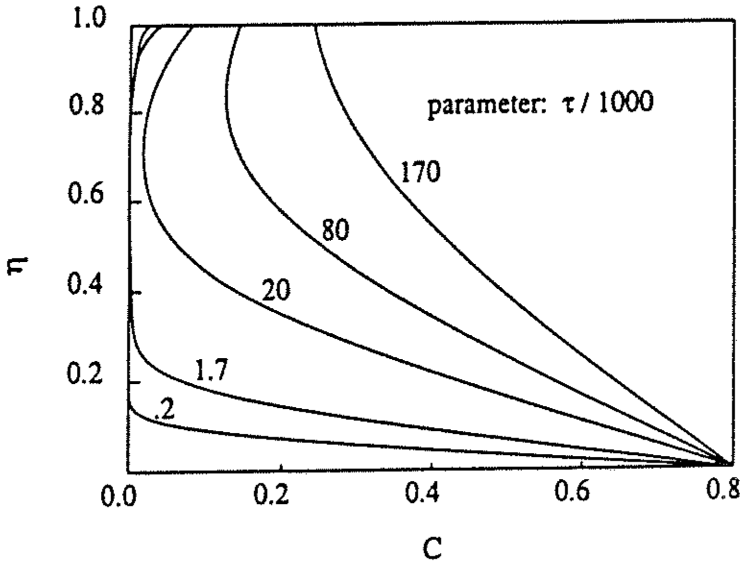

Figure 2

MODELING OF THE AEROSOL REACTOR FOR PRODUCTION OF POLYCRYSTALLINE SILICON

A. Problem Definition

One attractive approach in producing bulk powder silicon, with the possibility of conveying silicon particles to the Czochrolski's crystal growth apparatus, is by homogeneous gas phase pyrolysis of silane in an aerosol reactor. Particle sizes as large as $10\mu m$ in mass mean diameter were produced in a laboratory tubular reactor using seed particles of $0.16\mu m$ in diameter at CalTech. If the particles can be grown to bigger sizes, for example 50 to $100\mu m$, this aerosol reactor would provide a very desirable means for commercial production of polycrystalline silicon. In order to accomplish this goal, two steps are required: (1) Establish a basic theory of particle growth, set up a laboratory scale reactor, and experimentally demonstrate the feasibility of growing large size particles. (2) Apply the theory of particle growth together with the reaction kinetics and transport effects to construct a detailed reactor model. An appropriate model could provide the necessary information on how to improve the laboratory reactor in order to grow the aerosol to super-micron size, and would present guidelines for design of large scale reactors.

Small particles grow by the following major mechanisms: (1) agglomeration of fines on seed particles, (2) condensation of silicon vapor on particle surface, and (3) CVD reaction on particle surface. Successful growth of the aerosol requires that the seed aggregates scavenge effectively the fines formed by homogeneous nucleation at a maximum decomposition rate of silane. Previous work on modeling aerosol reactors neglected the agglomeration of the aerosol which is very important for the system of interest. Therefore a model accounting for agglomeration has to be developed.

B. Research Objectives

The purpose of this research is to study the transport-kinetic effects in production of powder silicon. Specificallv it is desired to model the aerosol reactor and to investigate the possibility of growing larger particles for commercial application. The research objectives are:

1. Critical Evaluation of Union Carbide's and CalTech's attempts to grow silicon particles by condensation, agglomeration and CVD growth to $50-100\mu m$ sizes.
2. Modeling the second stage of CalTech aerosol reactor with seed particles. This will include the mass balances for both silicon vapor and silane, and population balances for fines and seed particles.
3. Comparison of model predictions with the experimental results.
4. Determination of whether one could, in a series of reactors, accomplish particles growth to $50-100\mu m$ and estimation of the required temperature profile.

C. Research Accomplishment

A rather involved mathematical model, based on first principles, has been developed to simulate the agglomeration, coagulation, condensation as well as CVD reaction occurring in a seeded aerosol reactor for production of silicon particles. Mass balances on silane and silicon vapor as well as population balances are considered. Although the mathematical formulation of model equations follows well established conservation laws, not only is there no analytical solution for the resulting integral-differential equations, but a straightforward numerical approach quickly runs into severe, practically prohibitive requirements on computer time and memory. Therefore, as an approximation, the population balances for the particles are reduced to dual moment equations for fines and seed aggregates with application of fractal dimension and parametized distribution functions. Two techniques are discussed in developing the moment equations. The first consists of approximating the collision frequency functions with effective values, and the second uses collision frequency functions to generate the moment equations.

The dominant particle growth mechanism in this system seems to be scavenging of small fines, which initially have very small size and late are fused to a $0.1\mu m$ range. As illustrated in Figure 1, the agglomeration of small fines on seed aggregates accounts for 90 % of the seed growth on average, while condensation of silicon vapor contributes about 10 % and CVD reaction on seeds less than 2 %. This mechanism suggests that in order to grow the particles successfully the reactor should be designed so that the seed aggregates can always scavenge the fines effectively.

The model simulations are in remarkable agreement with the available experimental results on particle mass distributions. Figure 2 shows the model predictions compared with the experimental data for 1 % silane feed. Figure 3 shows the model predictions for 2 % silane feed. The simulations demonstrate that the detailed model with breakage considered can describe the mass distribution of product particles very well. Breakage of agglomerants becomes important only at SiH_4 higher than 1 % which lead to formation of loose aggregates (lower fractal dimension).

The process parameters, such as feed silane concentration, seed number concentration, temperature profile along the reactor, gas flow rate etc. are related to the silane yield into product aggregates, mean particle sizes, fines' loss as well as the size distribution of product aggregates and fines. Figure 4 illustrates the product yield and the mass mean diameter as a function of feed silane molar fraction. It is seen from this figure that as the feed silane molar fraction increases, the yield decreases because more fines are generated at larger silane concentration and growing fines also scavenge the smaller fines. However, the mass mean diameter of aggregates increases with increasing silane fraction. The temperature profile employed in the experiment is shown in Figure 5 as the wide solid curve with $n = 1$. If the temperature profile is changed by varying the power dependence n on reactor dimensionless length Z, the yield of seed aggregates is also changed as shown in Figure 6. The best yield about 74 % is achieved for 1 % silane feed with $n = 0.75$ because of the balance of two rates – coagulation rate among fines and scavenging rate of fines by seeds.

After investigating the flow rate and seed number concentration effects on the yield, the optimal operating conditions are identified. If the flow rate is reduced by 50 % and the seed number concentration is decreased by 20 % with $n = 0.75$, the yield can increase to 78.9 % and the mass mean diameter would be $7.0\mu m$ for 1 % silane feed in nitrogen system. It is also examined that using hydrogen as carrier gas would grow the particles up to $12\mu m$ in mass mean diameter with yield about 80 % for 1 % silane feed under optimal operating conditions, due to larger diffusivity of silicon vapor and larger collision frequency between fines and seeds in hydrogen system.

It is estimated that about 1000 reactors in a series, without diluting the seed number concentration from stage to stage, are required in order to grow dense particles to $50\mu m$ in diameter, if 1 % SiH_4 feed in hydrogen is chosen with the seed number concentration of $2.5 * 10^4 \#/cm^3$ and with temperature profile shown in Figure 5 with $n = 0.75$. However, if the seed number concentration is diluted by a factor of 1.2 from stage to stage, only 30 reactors in a series are needed for growing dense particles to $50\mu m$ in diameter.

D. Further Research Plan

1. Modify the detailed model to take into account the process of fusing seed aggregates to dense particles that will be used as seeds in the next stage reactor.
2. Experimentally verify the model prediction for the third stage of aerosol reactor.

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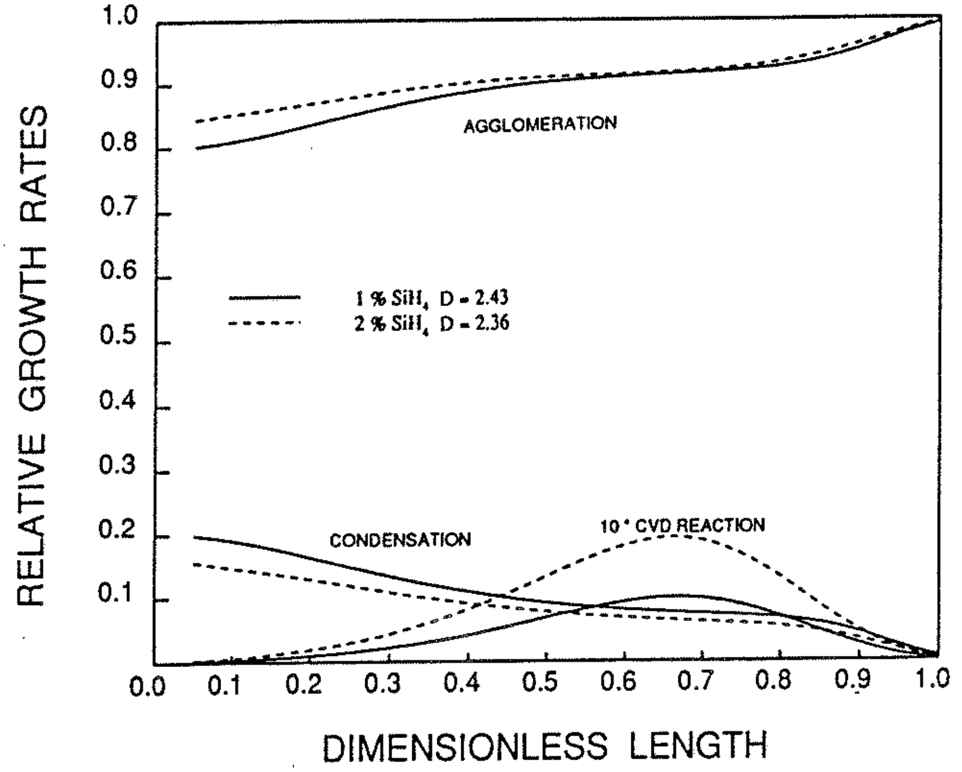

Figure 1 Seed Growth Mechanism

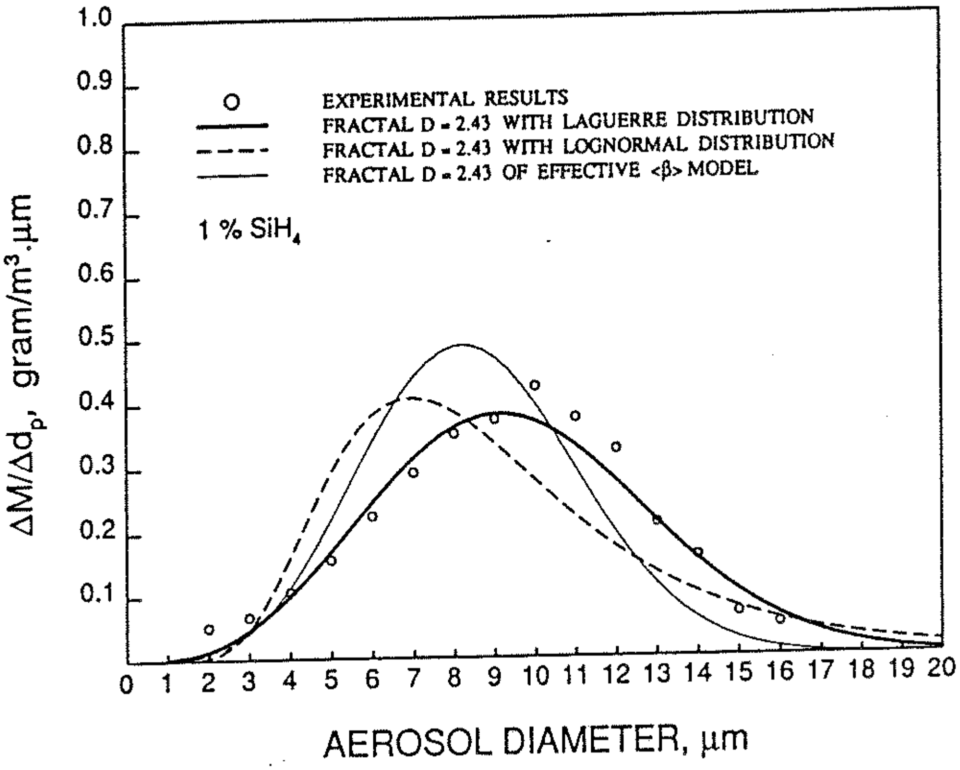

Figure 2 Mass Distribution of Product Aggregates

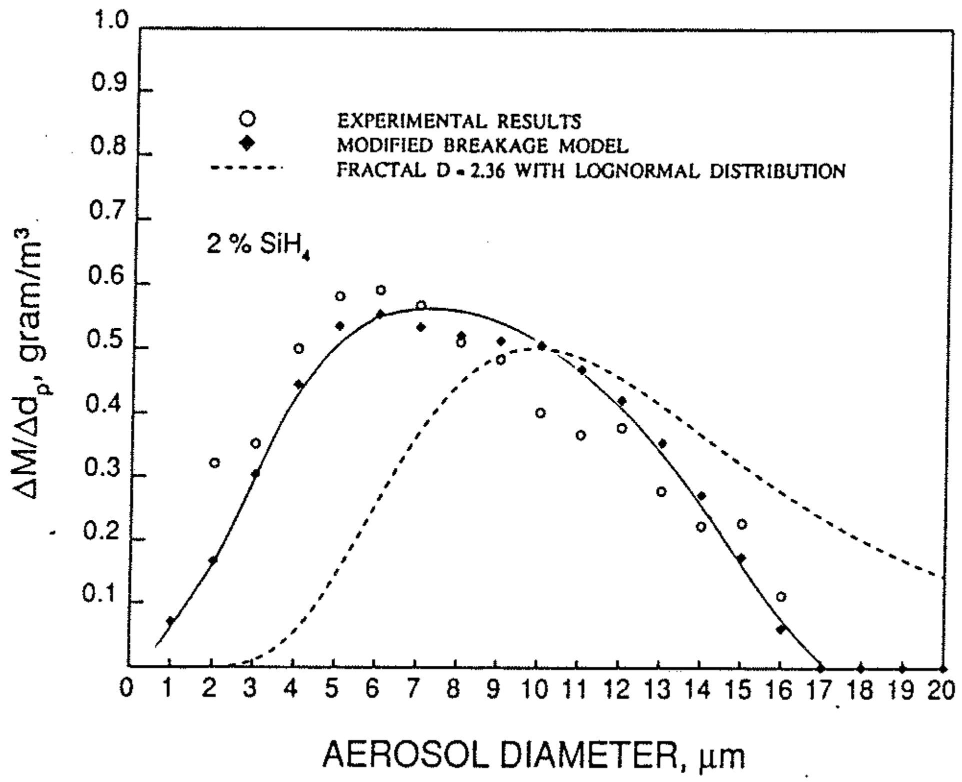

Figure 3 Mass Distribution of Product Aggregates

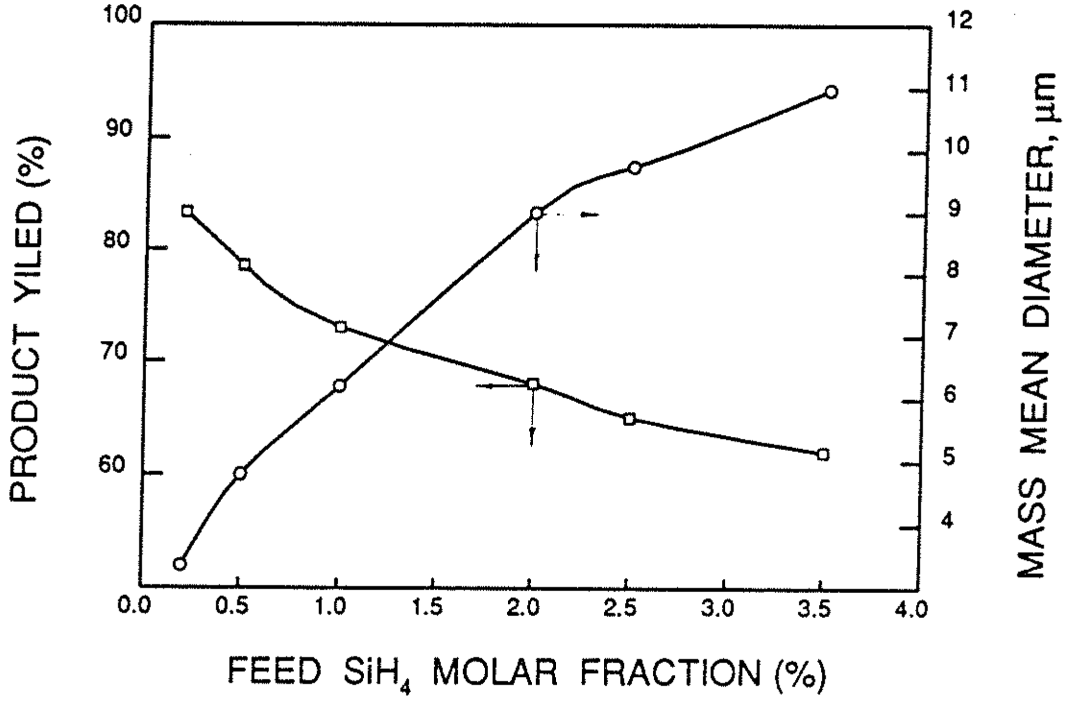

Figure 4 Product Yield and Mean Mass Diameter As a Function of Feed SiH_4 Molar Fraction

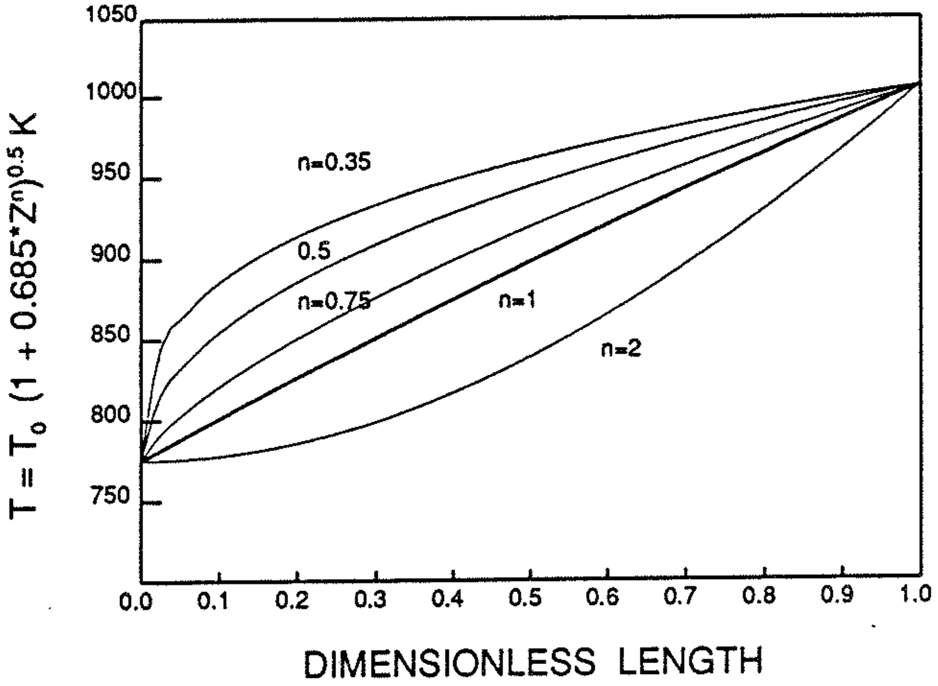

Figure 5 Temperature Profile Along the Reactor

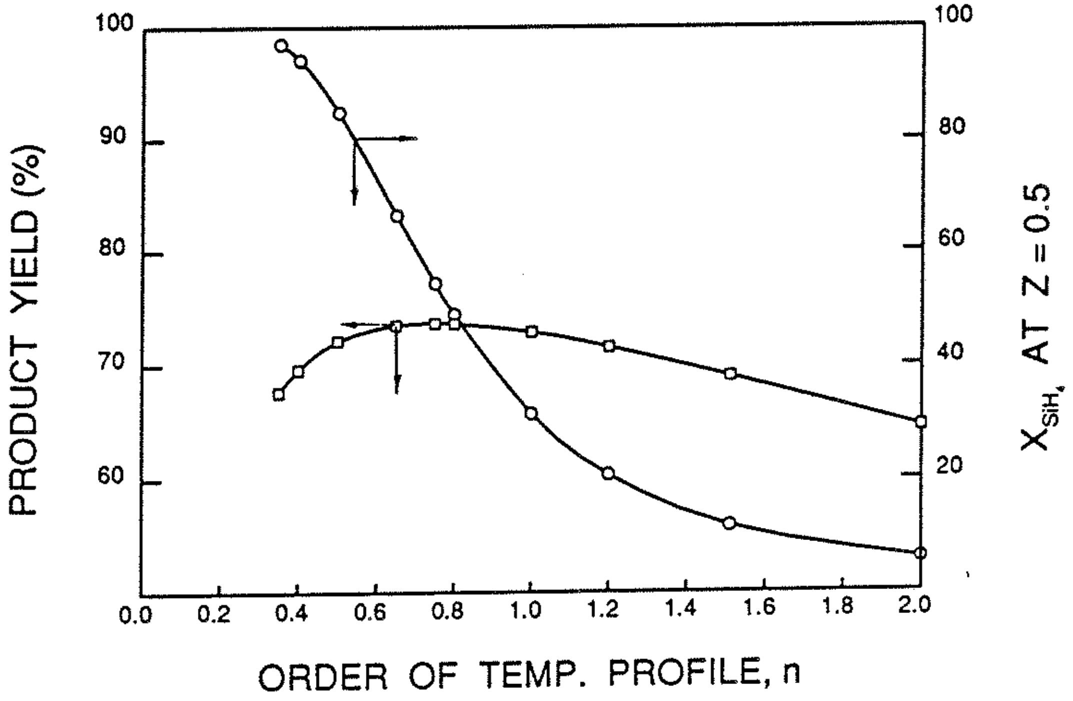

Figure 6 Product Yield and SiH_4 Conversion at Halfway Reactor As a Function of Temperature Profile

OXYGEN TRANSPORT DURING SILICON SINGLE CRYSTAL GROWTH BY THE CZOCHRALSKI METHOD

A. Problem Definition

Single crystal silicon with uniform electrical properties is required for many semiconductor applications. To obtain uniformity, dopants and oxygen must be evenly distributed within the grown crystal. For power devices (e. g. power switches), high resistivity and low oxygen content is also required.

The Czochralski(CZ) process is a method for growing single crystals from melts. Over 80 % of the bulk single crystal silicon produced is grown by the CZ-technique. A schematic of the CZ-apparatus is shown in Figure 1. Pure polycrystalline silicon and dopants (e. g. boron and phosphorous) are placed in a quartz crucible and heated to form a melt. A seed crystal of the desired crystallographic orientation is contacted with the melt surface. A short "neck" region is grown at a high pull rate in order to propagate out of the crystal any dislocations which were generated by the thermal shock of the initial crystal-melt contact. The crystal pull rate is then considerably reduced to allow the crystal diameter to increase to the desired value ("shoulder" growth stage). The crystal is then grown at a constant diameter until the melt is nearly exhausted. Oxygen enters the melt due to the slow dissolution of the quartz crucible. It leaves the melt either by evaporating from the free surface or by being incorporated into the growing crystal.

During the crystal growth process, the crystal pull rate and heater power input are adjusted in order to control the diameter of the growing crystal. Furthermore the crystal and crucible are both rotated in order to favorably effect the heat and mass transfer within the melt. In recent years, there have been a number of experimental works where the effect of an externally applied magnetic field, oriented either parallel or perpendicular to the crystal growth axis, has been studied. It was found that the effect of the field is to damp out the turbulent and oscillatory flows in the melt, which are the cause of periodic crystal growth rates, and which in turn are a major cause for the generation of structural defects in the crystal. It was also found that in some of these studies, lower oxygen contents were obtained than those normally observed in the standard CZ-process.

B. Research Objectives

The purpose of this work is to study the oxygen transport for both the standard and magnetic Czochralski (MCZ) processes. Models will be developed for determining the global oxygen transport in both the CZ and MCZ processes. Based on this study, the viability of the MCZ-process for producing low oxygen content single crystal silicon will be determined.

C. Research Accomplishments

C.1 Global Oxygen Transport Model

A global model for oxygen transport has been adapted from a model proposed by Carlberg, King and Witt [1]. In this model, perfect mixing in the bulk of the melt is assumed, and all the resistance to mass transfer is considered to exist in thin boundary layers adjacent to the crystal, crucible and free surface. Due to the slow crystal growth rate (~ 1 in/hr), it is further assumed that the system is in a pseudo-steady state, and that a dynamic oxygen equilibrium exists in the melt throughout the growth cycle. A mass balance on oxygen therefore yields:

$$\text{Dissolution Rate} = \text{Evaporation Rate} + \text{Incorporation Rate} \qquad (1)$$

Many models exist that relate the operating parameters to the incorporation rate. These are particularly well established for the case of the standard CZ-process (in the absence of a field). Models for dissolution and evaporation are not available in the open literature. The approach here will be to describe dissolution and evaporation in terms of mass-transfer coefficients. These mass-transfer coefficients will then be related to the operating parameters through a boundary layer analysis.

C.2 Crucible Bottom Dissolution

The dissolution mass-transfer rate from the crucible bottom was determined by assuming that the crucible bottom can be well approximated by a disk rotating adjacent to a semi-infinite body of fluid. The boundary layer thickness is small enough for this to be a valid assumption. It was determined that

$$Sh_B = \frac{k_{CB}\sqrt{\nu\omega_C}}{D} = 0.754 \qquad (2)$$

where Sh_B is the Sherwood number for the crucible bottom, k_{CB} is the dissolution mass-transfer coefficient for the crucible bottom, ν is the kinematic viscosity of the melt, ω_C is the crucible rotation rate and D is the diffusivity of oxygen in molten silicon.

C.3 Evaporation from the Free Surface

Work has begun on determining an expression for the mass-transfer coefficient for evaporation. The flow in this boundary layer is dominated by the thermocapillary effect. This is flow which is caused by a surface tension gradient where the surface tension gradient is due to a temperature difference across the free surface. This boundary layer is approximated by a semi-infinite fluid (in a rectangular geometry) which has a constant shear stress on the free surface (corresponding to a linear temperature profile) for $x > 0$, where x is the downstream distance from the point where the shear stress is first applied (the shear stress is zero for $x < 0$). A similarity solution for the flow in the boundary layer was found for this case, and it is compared with an exact numerical solution as determined by the finite elements package *FIDAP* in Figure 2. The assumptions inherent in the similarity solution are not valid for small x, but it was found that the two solutions agree in the asymptote if the similarity solution is shifted a short distance.

Given the velocity profile from the similarity solution, an expression for the evaporation mass-transfer coefficient for the high Schmidt number (Sc) limit was obtained. The Schmidt number is given by

$$Sc = \frac{\nu}{D} \tag{3}$$

For a very large value of Sc, the mass-transfer boundary layer is confined to a region directly adjacent to the free surface. In this case the velocity field in the convection-diffusion equation can be represented by the surface velocity, which has a simple analytical form. The result for the mass-transfer coefficient (k_s) is:

$$k_S = 0.524 D Sc^{\frac{1}{2}} \left(\frac{\gamma}{\nu x}\right)^{\frac{1}{3}} \tag{4}$$

where γ is the shear stress along the free surface. For oxygen in molten silicon, the value of Sc is uncertain, and has been taken to be 3.75 and 30 by different workers. These values are in the range where neither the high or low Sc asymptotic solutions are valid. For this reason the universal correlation method of Churchill and Usagi [2] will be used to obtain an expression which is valid for all values of Sc.

D. Future Research Plan

1. Continue the development of expressions for the mass-transfer coefficients for the case of no applied magnetic field. This will complete the global oxygen transport model for the perfect mixing case where the boundary layers are in laminar flow.
2. It is expected that there is actually interfacial turbulence at the free surface. This will enhance the evaporation mass-transfer rate. To account for this the roll cell approach of Ruckenstein [3-4] will be used to estimate the mass-transfer coefficient for evaporation.
3. The model will be extended to account for the effect of an externally applied magnetic field. New expressions for the transport coefficients will be developed for this case. Since the magnetic field will reduce the mixing in the bulk melt, models which account for incomplete mixing in the bulk will also be developed.
4. Parametric studies will be conducted with the completed models in order to determine favorable operating regimes and to assess the viability of the MCZ-process for producing low oxygen content single crystal silicon.

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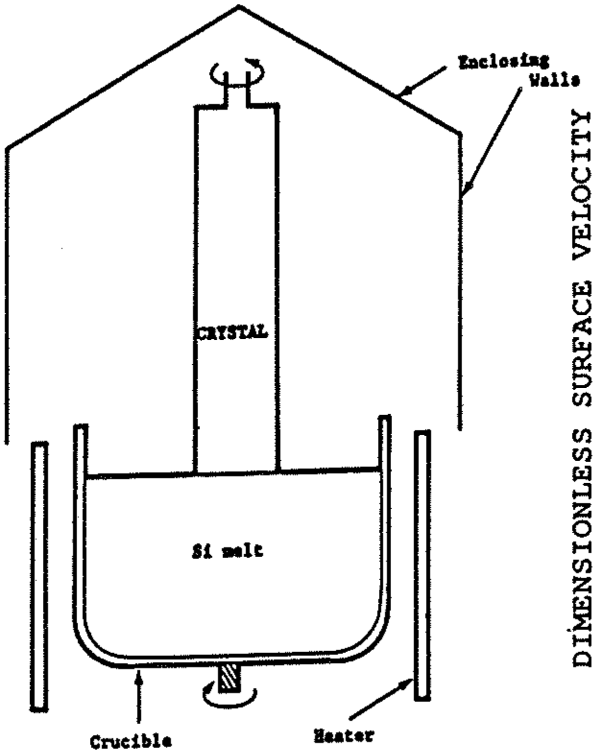

Figure 1: Schematic of a Czochralski single crystal puller

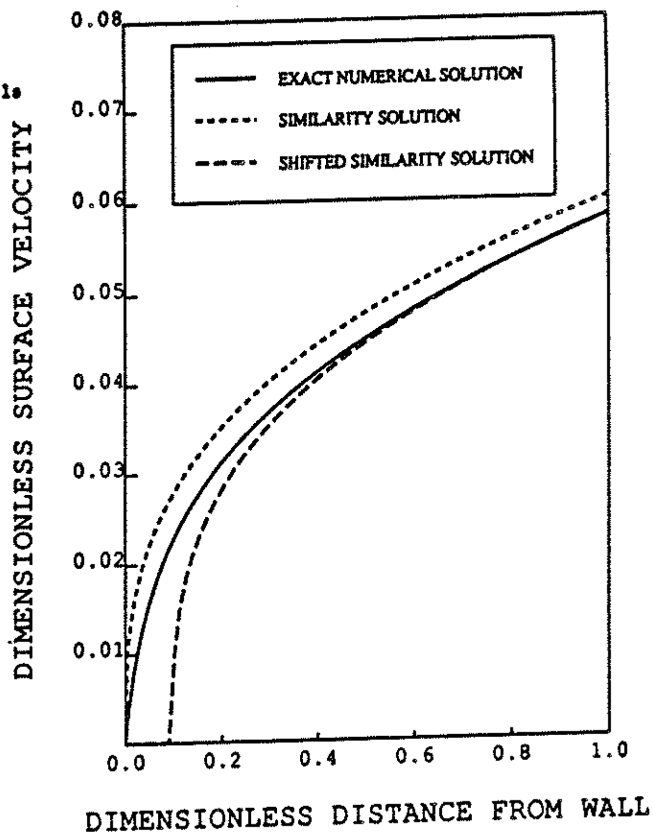

Figure 2: Comparison of the surface velocity as determined by the similarity solution and the finite element solution.

Preparation of Magnetic Particles: Factors Influencing the Crystal Growth and Particle Morphology of Iron Oxide (Goethite) in Aqueous Solutions at High pH.

A. Problem Definition

Iron oxide particles find two primary uses: 1. Because of their bright colors, iron particles are used as pigments in a wide variety of applications; and 2. Iron oxide particles continue to be important in the manufacture of magnetic tapes, disks, and other magnetic media.

Iron oxide particles are generally produced in an aqueous solution in which the pH, temperature, pressure, ionic strength, and types of ions as well as transport effects control the properties of the final product. The chemistry behind the processes is complex and not well understood. As a result the formation of particles with the proper characteristics is often difficult and a quantitative approach to modelling the particle growth is not currently available.

The focus of this work will be on the growth of iron oxide particles for use in magnetic media. Here, a common process used in the manufacture of $\gamma - Fe_2O_3$ particles is the production of goethite ($\alpha - FeOOH$) particles from an aqueous slurry of ferrous hydroxide at a high pH. Because the goethite particles are not magnetic, they must be reduced and carefully reoxidized through gas-solid reactions to form $\gamma - Fe_2O_3$ magnetic particles. Although the goethite is only an intermediate, its morphology remains fixed during its transformation to $\gamma - Fe_2O_3$.

The particle morphology is an important factor in determining the magnetic field associated with a $\gamma - Fe_2O_3$ particle. Magnetic anisotropy has a strong effect on the magnetic properties of a particle. For this system, shape anisotropy and crystal anisotropy are of primary importance. Considering crystal anisotropy to be a property of the material, the magnetic properties of a particle (and thus the tape) can be manipulated by changing the particle shape.

After a particle is magnetized and removed from a field, demagnetizing forces in the particle act in opposition to the magnetic field of the particle. It can be shown (3) that for a prolate spheroid of large aspect ratio (a rod), the demagnetizing field along the minor axes is constant (in proportion to the magnetization) and that the field along the major axis varies as

$$\frac{4}{a^2}(\ln 2a - 1)$$

where a is the aspect ratio. By the equation above, increasing the particle aspect ratio will result in a decrease in the demagnetizing field along the length of the rod. Thus, by changing the particle length and aspect ratio, the magnetic properties of the particle can be manipulated.

The relationship between the actual magnetic field generated by a group of particles aligned on a magnetic tape and that of a single particle is quite complex. However, a model of particle growth in the goethite process would certainly be of use in tailor making particles for specific applications.

The primary objective of this research is to relate the conditions of particle growth to the morphology of the final product. This will be achieved through experimental identification of the key operating variables and subsequent modelling of their effects. Therefore, the main goal is to develop a model of the growth of iron oxide particles which will predict both the mean size and size distribution of the particles formed. Finally, based on both the experimental and modelling work, an appropriate reactor design will be proposed.

B. Research Objectives

There are three main objectives of this research:

1. Measure the reaction kinetics in a three-phase slurry batch reactor and develop a model of the mass transfer with reaction of oxygen into the slurry.
2. Qualitatively understand the mechanisms of crystal growth and subsequently develop a model which will attempt predict the size distribution of the crystals.
3. Based on the understanding of the process gained in parts 1 and 2, recommend a reactor design which will provide the best control of the goethite product particle size.

C. Research Accomplishments

Based on an extensive study of the literature and preliminary experiments in our laboratory we have formulated the following framework for the study of this problem. The basic process consists of first precipitating $Fe(OH)_2$ in the absence of oxygen and then oxidizing the aqueous slurry to form goethite. The important chemical reactions are written as follows:

1. $FeSO_4 + NaOH_{(excess)} \Longleftrightarrow Fe(OH)_{2(solid)} + Na_2SO_4$
2. $O_{2(g)} \Longleftrightarrow O_{2(aq)}$
3. $Fe(OH)_2 + \frac{1}{4}O_2 \Longrightarrow \alpha - FeOOH + \frac{1}{2}H_2O$

The reactions as written above look deceivingly simple. The precipitation step is instantaneous and the oxidation step can be varied over a wide range and is thought to be limited by the rate of mass transfer of O_2 to the slurry (1).

In step 1, $Fe(OH)_2$ immediately precipitates from solution to form colloidal particles less than $0.1\mu m$ in size. If oxygen is present during this step, a non-stoichiometric Fe2+/Fe3+ solid will form and make it impossible to obtain pure goethite. After the initial precipitation, the $Fe(OH)_2$ particles will recrystallize (apparently through ostwald ripening) to hexagonal platelets of approximately $0.5\mu m$ in size. This ripening occurs concurrently with the oxidation step 2. The relationship between the initial $Fe(OH)_2$ morphology and final $\alpha - FeOOH$ particle is not clear, but preliminary experiments on our laboratory indicate that the $Fe(OH)_2$ ripening process does influence the $alpha - FeOOH$ particle growth.

In step 2, air or oxygen is bubbled through the $Fe(OH)_2$ slurry and the ferrous iron is oxidized to the ferric form. The desired product is goethite, characterized by a needle-like, acicular structure. The desired length ranges from approximately 0.1 to $1.0\mu m$ with an aspect ratio of between 5 and 15. With a large excess of NaOH present goethite is generally the only oxidation product formed. However, if the oxidation rate is too rapid, $\alpha - FeOOH$ will form. The $\alpha - FeOOH$ solid apparently has the same morphology as the initial $Fe(OH)_2$ solid (2), and is an undesirable product.

D. Future Work

There are a great many parameters which might be considered in this system. However, at this point it is necessary to try and hold the chemistry effects such as ionic strength, ion type and concentration, and thus pH constant. The focus of this research will initially be on the effects of the oxidation rate, $Fe(OH)_2$ precipitate morphology, and $Fe(OH)_2$ slurry density on the goethite crystal growth.

Effort is currently focused on designing and conducting three phase slurry batch experiments that will show how the oxidation reaction should be modelled. It has been suggested in the literature that the oxidation rate is limited by the rate of mass transfer of oxygen, however, whether the reaction rate can be considered instantaneous, very fast, or fast is not clear. Proper application of either the film or penetration theory to this system will allow the diffusion/reaction of oxygen into the slurry to be modelled and subsequently applied to any reactor configuration.

Because the oxygen solubility in the slurry is quite low, there will be no gas film mass transfer resistance. Also, because the $Fe(OH)_2$ particle size is much smaller than the liquid film thickness, the mass transfer rate of oxygen will be enhanced by reaction. By independently varying the ratio of slurry volume to gas-liquid interfacial area and measuring the oxygen consumption, it will be determined whether any oxidation reaction occurs in the bulk liquid. Further measurements of oxygen consumption at varying partial pressures and temperatures will allow the measurement of an enhancement factor and a determination of whether the reaction kinetics are of importance in this system.

Modelling of the goethite crystal nucleation and growth process including the effects of slurry density and $Fe(OH)_2$ precipitate morphology may be a bit more difficult. However, with careful experimental design and with the visual support of the Transmission Electron Microscope, it should be possible to unravel some of the major mechanisms involved in the crystal growth process.

One of the keys to understanding the crystal growth is to develop an understanding of where the nucleation of $\alpha - FeOOH$ takes place. It has already been shown in this laboratory that the structure of the $Fe(OH)_2$ solid phase can have an effect on whether an $\alpha - FeOOH$ phase nucleates. Further experimentation in this area will lead to a more qualitative understanding of the process that will eventually allow at least a simple quantitative model of the process to be formulated.

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QUANTIFICATION OF THE MASS SPECTROMETER MEASURED RESPONSES OF A PULSE, CATALYTIC, MICROREACTOR (THE TAP EXPERIMENTS)

A. Problem Definition:

If we knew what happens on the catalyst surfaces during reactions and which were the active/selective phases, we could develop better strategies to improve catalyst performance, i.e., selectivity, activity or rate. A new pulse micro-reactor system, called TAP, Temporal Analysis of Products, lets us approach this goal a little better[1].

Developed by Monsanto's John T. Gleaves and Jerry R. Ebner, the TAP reactor system is a useful tool for studying complex multiphase commercial catalyst systems. The TAP reactor system consists of a microreactor, a high speed pulse gas injection manifold(both contained in an ultra-high vacuum system), and a computer-controlled real time mass detector, see Figure 1. The gas pulses which are introduced by the high speed valve move through the catalyst bed and emerge with an encoded history of the reactions taking place between the reactant molecules and the catalyst surface. This history is analysed by the mass spectrometer and it gives a unique view of the catalytic reaction sequences, adsorption/desorption phenomena, and fleeting reaction intermediates.

Interpretation of the many types of TAP experiments is still in the development stage. Although TAP experiments that have been done before gave results which are unobtainable by other types of experiments, the results can only be explained by qualitative arguments. The quantitative treatment of these results is desirable so that the TAP technique will meet its full potential.

B. Research Objectives:

1. Develop quantitative models of the four main components of the TAP device. These are:

- the fast pulse gas delivery system,

- the catalyst micro-reactor,
- the high vacuum system, and
- the real time detector system.

2. Develop user-friendly algorithms for the handling of the TAP data of of different forms, to evaluate optimal uses of TAP and propose studies of test systems.

C. Research Accomplishments:

1. Based on the two assumptions that in the catalyst microreactor, the number of gas-solid collisions are much greater than the number of gas-gas collisions and most surfaces will reflect the incident molecules diffusely [2], we arrive at the conclusion that the gas molecules will be emitted from the catalyst bed with a Maxwellian velocity distribution and isotropic angular distribution. A Monte Carlo simulation has been performed to simulate the gas molecule motions from the outlet of the catalyst bed to the mass spectrometer detector. The results of the simulation are quite satisfactory in that they can verify our explanations of the experimental data, e.g.,why the response curves at high temperature have smaller areas than the low temperature curves, (see Figure 2). Our explanation for this is that the mass spectrometer is a concentration sensitive device. When the pulsing gas temperature increases , the mean velocity of the gas molecules also increases. Then the mean residence time of the gas molecules in the vacuum system decreases but their concentration in the M.S. detector zone does not change very much. Hence the position of the peak of the response curve is shifted to lower times at higher temperature ,the peak height is not changed much, and the area under the curve is decreased.

2. A simple Knudsen diffusion model is proposed to describe the flow phenomena in the microreactor catalyst bed. We are going to verify this model both theoretically and experimentally.

3. The tests we have performed before were done at Monsanto. The installation of our own TAP system is in progress. We expect that it will be operationable in early July.

D. Further Reseach Plan:

1. Use various methods to verify our assumptions and models. For example, pack well defined solid material in the microreactor and observe the response curves. The variables that should be changed are solid material pore structure, packing conditions, pulsing gas temperatures, pulsing gas molecular weight, etc.

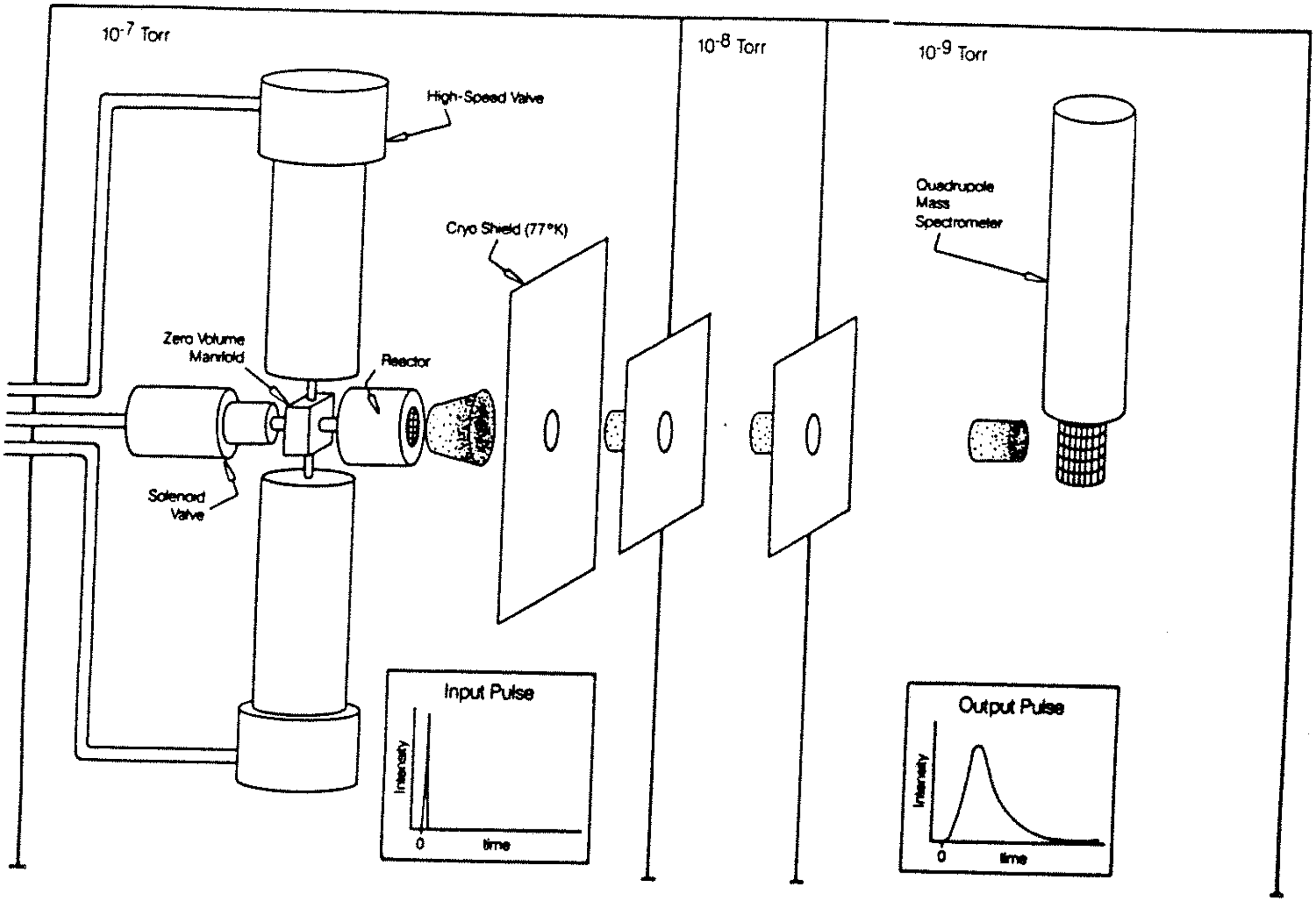

Figure 1: TAP System

2. Put pressure transducers in the glass beads section of the microreactor, and if possible, at the outlet of the microreactor. By doing so we can learn more precisely how the gas molecules flow in the various components of the TAP system.

3. Get the TAP system of our Laboratory operationable as soon as possible.

4. Develop a firm theoretical basis for the quantification of the TAP experiments. Develop the models of the flow for gas molecules in various solid pore structures. After that, we must incorporate adsorption/desorptions and chemical reactions into the flow models.

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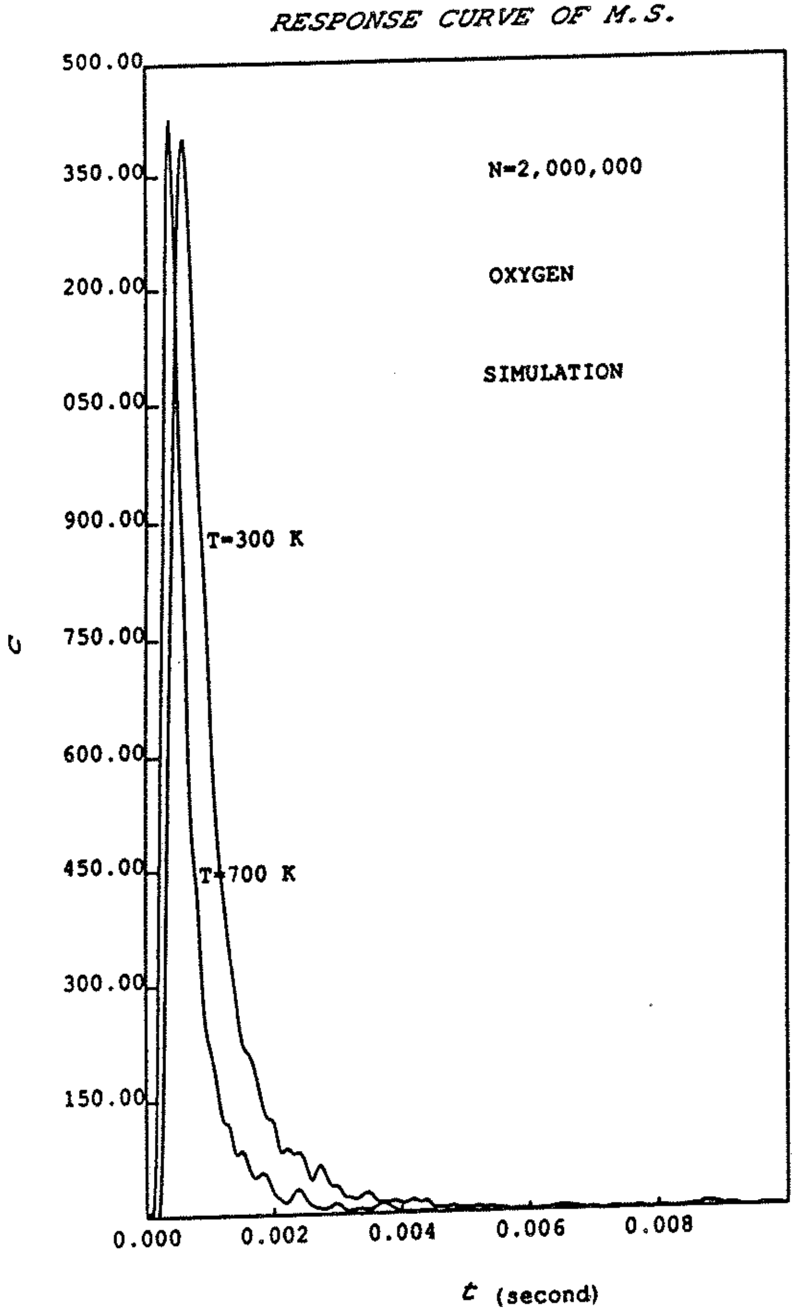

Figure 2: Comparison Between The High Temperature Curve And Low Temperature Curve

MODELLING OF DC PLASMA REACTORS

A. Problem Definition

Plasma processes, despite their increasing role in deposition and etching of thin films, are still an art and few modeling studies have appeared. The considerable interest in plasma deposition is driven by the ability to grow films at relatively low process temperatures, combined with special material properties, that can not be realized in conventional thermally driven processes. The applications of plasma processing can be divided into two categories: deposition of material, and removal of material.

Considerable experimental studies have been done on plasma reactors and the results were interpreted, for the lack of detailed models, on the basis of qualitative reasoning. Thus plasma processing techniques have been developed empirically for the most part and the dependence of processes on certain measurable parameters may be known only very approximately. In addition such knowledge is not fundamentally based. What is needed are quantitative models that predict the process parameters such as deposition or etching rate, film composition, etc. as a function of operating and design variables. The modeling required in this field can be subdivided into two major categories: (1) modeling of the chemical effects and (2) modeling of the electrical effects. The modeling of chemical effects includes the identification of reactions and mass transfer for the precursor and of diffusion, thermophoretic movement, and deposition of the product species. Reaction engineering techniques can have a major impact here as revealed by some recent studies in this area. The modeling of the electrical effects is needed in order to determine the electron density(concentration) and electron energy levels(plasma physics). These plasma parameters are then used in a proper model of chemical reactions driven by the electron activation of relatively inert species. Thus, the modeling of the glow discharge needs to be coupled with the classical chemical reaction engineering methodology (plasma chemistry).

The proposed research is aimed at developing a model for plasma reactors which is both detailed and computationaly effective.

B. Research Objectives

1. To determine self-consistent models of one-dimensional dc discharges used in plasma processing and solve them by mixed numerical and analytical methods. Specifically we are seeking:
    - Development of a two-region model with generalized ambipolar approximation for the negative glow region and the numerical integration of the cathode sheath region.
    - Development of three- and four-region models which include in addition to the regions above the collisionless part of the cathode region (region very close to the cathode) and the anode sheath, respectively.

2. Calculation of electron and ion densities, electron temperature, and electric field with spatial dependence in dc plasmas.
    - Numerical integration by Gear's routine for the collisional part of the cathode region.
    - Development of approximate analytical experssions for the bulk plasma region and the collisionless cathode region.
3. Developement of a mass transfer model, by incorporating the electronegative and neutral species into the discharge model, and computation of deposition rate for mass transfer model.
4. Verification of the model using suitable experimental data.

C. Research Accomplishments

A two region model has been developed which simplifies the computations for a dc glow discharge plasma between two parallel plates. The model consists of equations for electron and ion continuity, Poisson's equation for the electric field, and electron energy. The glow discharge is divided into a cathode sheath and a bulk plasma. The anode sheath is ignored in the computations. The bulk plasma is assumed quasineutral and supports ambipolar diffusion. To link the sheath region and the bulk region, the classical ambipolar analysis is modified to include a net total current in the plasma. In the sheath region the plasma variables are determined by numerical integration of an initial-value problem by Gear's routine. The sheath region solution is obtained by integrating from the cathode toward the anode, with the ion current fixed and with the cathode electric field iterated upon until a complete solution is found. The sheath-bulk boundary occurs at that distance from the cathode where the the electron and ion densities are nearly equal; matching conditions on the plasma varibles are imposed here.

The second region in the computation is the bulk plasma where the approximation of electroneutrality leads to an analytical solution. The matching of the electric field, particle densities and the electron temperature at the cathode sheath - bulk plasma interface completes the problem and also leads to a direct prediction of sheath thickness. In addition, as the total current is fixed, the continuity of fluxes of ions and electrons is automatically satisfied at this point. The model leads to prediction of electron and ion densities, electron temperature and electric field with the total current density and the interelectrode gap as the input variables (see figures). Exploration of discharge properties was also performed and the effect of pertinent parameters was qualitatively calculated.

Figure 1 is the plot of the ion and electron densities. The electron density is almost zero in the sheath and both ion and electron densities peak in the bulk. In the bulk region, following the ambipolar approximation, the values of the ion and electron densities are equal. The electron density is the order of magnitude smaller in the sheath than its value in the bulk, but the Gear's routine calculates it sufficiently accurately. This is one of the advantages of the initial value method used here. The method resolves a widely different concentration range for ions and electrons. The electron temperature distribution in the sheath is shown in figure 2. The temperature rises almost linearly close to the cathode due to the acceleration of the electrons by the electric field. As the endothermic ionization starts to take place the temperature starts to drop off. An average electron temperature is computed in the bulk. This temperature is calculated from balancing the energy requirements between the sheath and the bulk. Figure 3 represents the spatial dependence of the electric field. The field increases linearly in the cathode sheath; then it becomes almost zero in the bulk and finally positive as it gets close to the anode sheath. Since the effect of the anode region is neglected, the solution of the electric field is only valid up to the 0.1 centimeter of the anode (0.1 centimeter is chosen as the anode sheath thickness for lack of better information). For the region near the cathode (collisionless sheath) analytical solutions are possible (Mobility Limited model). This region is assumed to be collisionless and therefore the fluxes of ions and electrons are constant. There are strong electric field effects in this region and therefore the migration term is dominant and the diffusional effects are neglected. In figures 4 (a), (b), and (c) one may compare the mobility limited model with the initial value problem approach. Since the ionization is very small in the initial portion of the cathode sheath, up to 0.03 centimeter (for our computations) from the cathode, there is good agreement between this two approaches. Therefore it could be advantagous to use the analytical apporoach of the mobility limited model for calculation close to the cathode sheath. Thus the numerical solution is needed only for the collisional part of the sheath.

One of the advantages of the multi-zone model is the possible incorporation of additional important phenomena (e.g. addition of the equations for the negative and neutral species) in the model and ease of numerical stability analysis as opposed to that for the global simulation. The two-region model aids our understanding of the physics of the discharge and can be coupled with the chemistry to complete the picture of glow discharge modeling.

D. Future Work

1. Addition of excitation reactions to the existing model.
2. Incorporation of negative ions and neutral species in the model.
3. Expanding the model to predict the deposition rates of thin films in plasma reactors.

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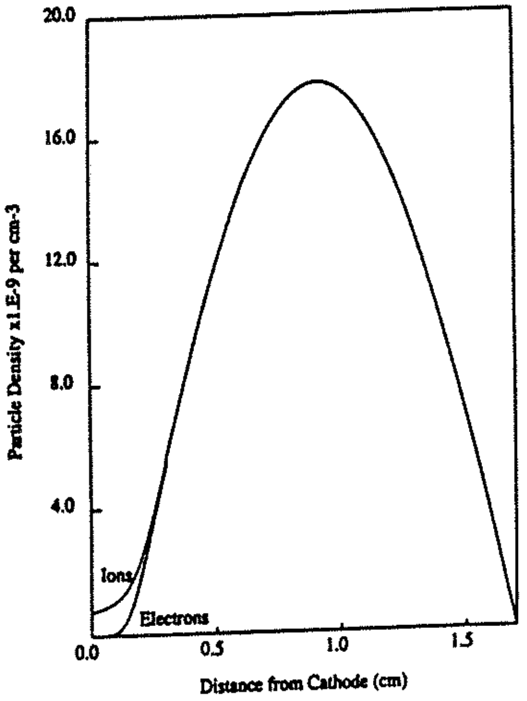

Figure 1: The global profile of the particle density for the entire plasma.

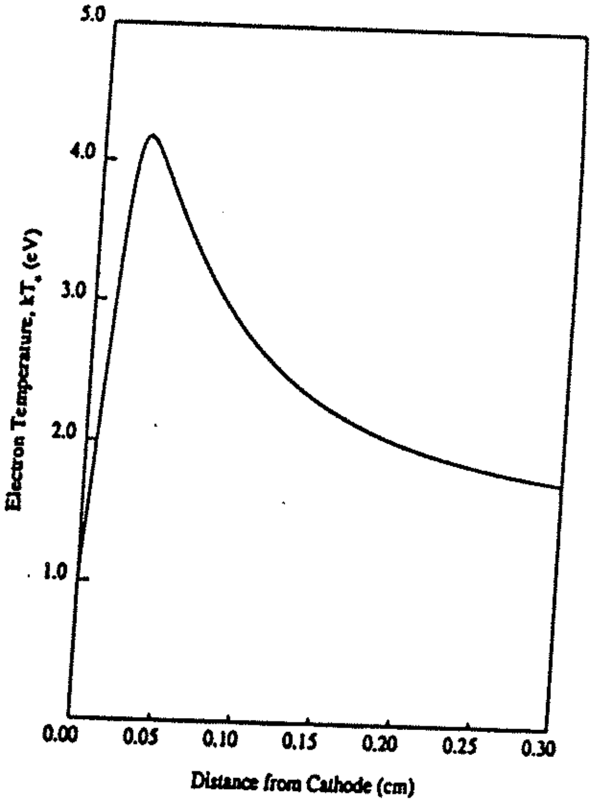

Figure 2: The electron temperature in the sheath

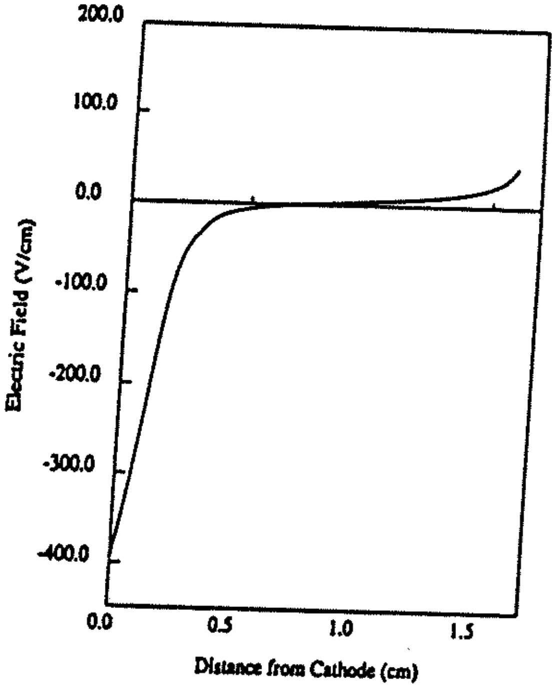

Figure 3: The global profile of the electric field for the entire plasma.

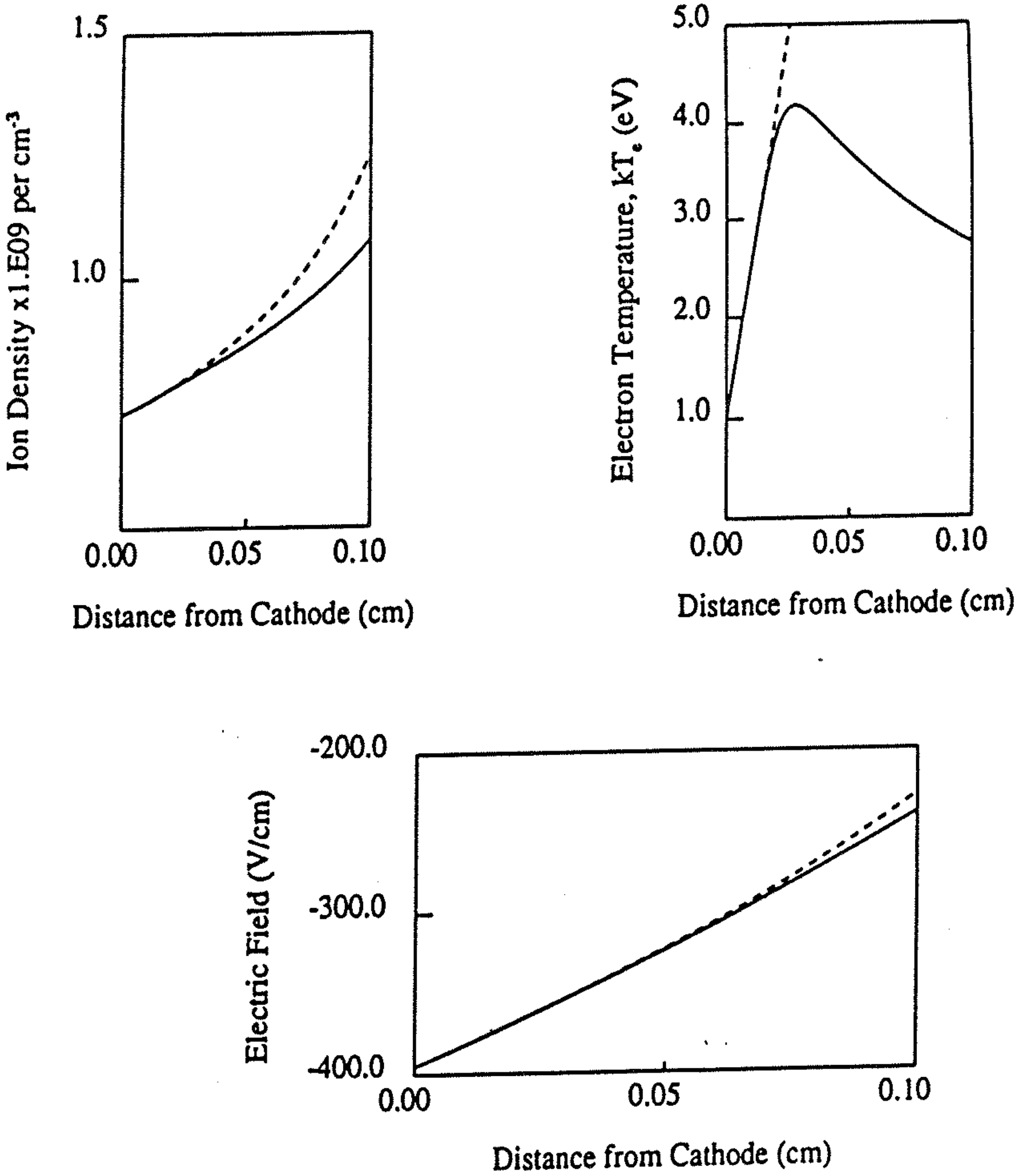

Figure 4: Comparision of Gear's (IVP) method (solid line) and the mobility limited method (dotted line), (a) Match of ion density profiles, (b) Match of electron temperature distribution,(c) Match of the electric field.

Modeling Devolatilization of Thermoplastic (Polyimide) Composites

A. Problem Definition

High performance structural composite materials, containing continuous fibers and polymer matrices, are in demand in the structural engineering industry. The occurrence of voids and undesirable resin composition gradients in the final part are the most frequent manufacturing problems and causes of part rejection.

In the case of thermosetting resin composites, the void phenomena occur during the curing-consolidation process and involve heat, mass, and momentum transfer with simultaneous chemical reaction in a multiphase system with time-dependent material properties and boundary conditions. Modeling of such thermosetting resin composite processes, based on engineering principles, was reported(1,2,3).

Thermoplastic composites have several advantages over thermosetting composites. Some of them are: high thermal decomposition temperature, high mechanical strength, and shorter processing cycles. However, fiber reinforced thermoplastic composite processing technology is very immature compared to thermoset technology. Unlike the thermosetting composite process, where environmentally absorbed water is a critical factor in the formation of voids, in the thermoplastic (polyimide) process, absorbed moisture is only a minor contributor to the formation of voids. "Avimid" K-III polymers are amorphous, linear chain, condensation polyimides. "Avimid" K-III polyimides are produced from polyimide precursor solutions by the reaction of an aromatic diethyl ester diacid with an aromatic diamine in N-Methyl-2-Pyrrolidinone(NMP) solvent. The presence of the solvent in the initial prepreg material is necessary to ensure the wettability and adherence of the resin to the fibers. The reaction proceeds with loss of water, ethyl alcohol, and solvent to form the imide ring. Multiple volatile species are continuously being evolved as reaction by-products as well as from the solvent present in the precursor solution. The polymerization chemistry of "Avimid" K-III polyimide is given in Fig. 1a.

During the initial temperature ramp of the processing cure cycle, while the resin viscosity drops rapidly, evolution of volatiles can take place. The process that produces voids during the initial heating period must be subjected to certain process conditions so that voids are eliminated before resin viscosity rises and prior to the end of the consolidation process. Additional difficulty arises during the devolatilization of thermoplastic composites due to the presence of the fibers. Clearly describing this process from the first principles of transport phenomena is difficult but necessary, if progress is to be made.

B. Research Objectives

Modeling of the devolatilization process for thermoplastic (polyimide) composites requires the scientific understanding of the physical phenomena, such as the mass transfer at the interface between the liquid and the vapor phase and the transport phenomena inside the composite laminates. This model is to be based on general scientific principles so that it will be applicable to any thermoplastic composite system involving the evolution of volatiles.

The purpose of the current work is to present the framework of a model(or models) for devolatilization of polyimide composites as a function of the cure cycle used and to demonstrate its usefulness for scale-up and cure cycle selection. The specific objectives of the research are:

- Develop model equations for the devolatilization process of thermoplastic (polyimide) matrix composite system.
- Predict the effect of the major variables such as the composite thickness and heating rate, and the major model parameters such as the gaseous phase permeability and the mass transfer coefficient at the interface between the liquid and the vapor phase.
- Verify the proposed model with the experimental results.

C. Research Accomplishments

The type of system under consideration is a porous medium consisting of three phases as shown in Fig.1b. An inert solid phase is impregnated with gas and liquid phases. In modeling the devolatilization of thermoplastic (polyimide "Avimid" K-III) composites, the system phases and their components are as follows;

Solid Phase: Carbon Fiber bed
Liquid Phase : "Avimid" K-III (Polyimide)
Diamine
Diacid
N-Methyl-2-Pyrrolidinone(NMP)
Ethyl Alcohol
Water
Gas Phase : N-Methyl-2-Pyrrolidinone(NMP)
Ethyl Alcohol
Water

Each phase represents a continuum, and its behavior can be predicted by application of the appropriate laws of physics which are the well-known transport equations of heat, mass, and momentum in continuous media. The complex geometry of the porous medium makes it difficult to solve these transport equations. A different set of governing point equations will arise for each phase and there is no way of knowing a priori in which phase an arbitrary point lies and, therefore, which set of equations is appropriate. In order to achieve solvable governing equations which are valid throughout the composite the point equations need to be volume averaged to include the effect of each phase on the whole. Whitaker (4,5) has developed the methods for performing this volume averaging for drying processes. Thus, the method of local volume averaging is a convenient starting point for modeling the devolatilization process.

Due to the length of the composite part compared to its thickness, a one-dimensional model can be employed. The mathematical model was developed for one dimensional heat, mass, and momentum transfer utilizing this method of local volume averaging in modeling devolatilization of thermoplastic composites. The schematic diagram for this geometry is shown in Fig. 1c.

The devolatilization process of thermoplastic (polyimide) matrix composites involves several transport steps. The phase change of volatile components in porous media is an essential phenomenon for mass and energy transfer. The study of phase change in porous media can be approached in two different ways(6,7). The first is the mass transfer limited model. The second is the equilibrium model. Either the equilibrium model or the mass transfer limited model is suggested as a constitutive relation for the rate of phase change of the volatile component. For the volatile migration mechanism, the Darcy's flow model or the diffusion model is proposed.

Model equations were first solved for a simple case of a single volatile component in order to make sure that the model is heading in the right direction. In this particular demonstration of the model, ethanol is chosen as the single volatile component, since it is one of by-products of the polymerization reaction of the polyimide. The mass transfer limited model was used as a constitutive relation. The rate of phase change of the ith volatile component , m_i ,is assumed to be given by:

$$m_i = Km_i \, A_l \, (\gamma_i \, x_i \, P_{\gamma i}{}^{*} - P_{\gamma i})$$

The FEM computer program was developed for the simple case of a single volatile component and is used for the computation of the following results.

In the devolatilization process we are interested in knowing the mass flux of volatile components at the bleeder surface. Also, we want to know the temperature and pressure profiles as a function of space and time.

Fig. 2a shows the temperature profile for a heating rate of 1 °C/min starting at room temperature and ramping up to 300 °C. The origin of the abscissa corresponds to the tool surface, and the right hand side end point corresponds to the laminate-bleeder interface. The heating rates are indicative of the change in temperature of the tool surface.

Fig. 2b shows the solvent removal rate at the bleeder(which is set to be equal to the laminate surface) for the temperature ramp of 1 °C and 2 °C per minute at a value of $K_m A_l$ (volumetric mass transfer coefficient) = 1.5×10^{-5} [g/cm^3 min atm] and for the total composite thickness of 0.5 cm. The other variables are shown in the figure legends. A change of 1 ^{o}C/min in heating rate results in nearly a 100 minute change in the time at which the maximum evolution of ethanol occurs. The higher heating rate of course yields the shorter time.

The time for the appearance of the maximum mass flux is reduced by doubling the value of K_m A_l at the same composite thickness as shown in Figs. 2b and 2c. Unlike the composite thickness effect, where doubling the thickness at the same K_m A_l results in doubling the mass flux, doubling the value of K_mA_l does not result in doubling the mass flux, even though it increases the mass flux and reduces the time for the appearance for the maximum mass flux.

Fig. 2d depicts the gas phase pressure profile for a heating rate of 1 ^{o}C/min and $K_mA_l = 1.5 \times 10^{-5}$ [g/cm^3 min atm]. Note that the pressure (for example, at the tool surface) first rises quickly and then decreases. It is this initial quick rise which provides the driving force for convective mass transfer.

D. Further Research Plan

1. The computer program, which at present handles only the case of a single volatile component, will be modified and expanded to include the general case of multiple volatile components and new polymer systems.

2. Model input parameters, which at present are not available, will be obtained or estimated.

3. Experimental studies will be done to verify the developed model. Because of the lack of information dealing with the devolatilization rate during the thermoplastic(polyimide) matrix composite processing, this experiment is to be carried out to obtain the data on the mass flux rate vs. time at the bleeder surface with different sets of major variables, such as heating rate, the composite thickness, and vacuum pressure.

Nomenclature

m_i : The rate of phase change of the ith volatile component
Km_i : The mass transfer coefficient at the interface between the liquid and vapor phases
A_l : The interfacial area for mass transfer per unit volume of the composite
γ_i : The activity coefficient of the ith volatile component in the liquid phase
x_i : The mole fraction of the ith volatile component in the liquid phase
$P_{\gamma i}^*(T)$: The saturation vapor pressure of the ith volatile component at temperature T
$P_{\gamma i}$: The partial pressure of the ith volatile component in the gaseous phase

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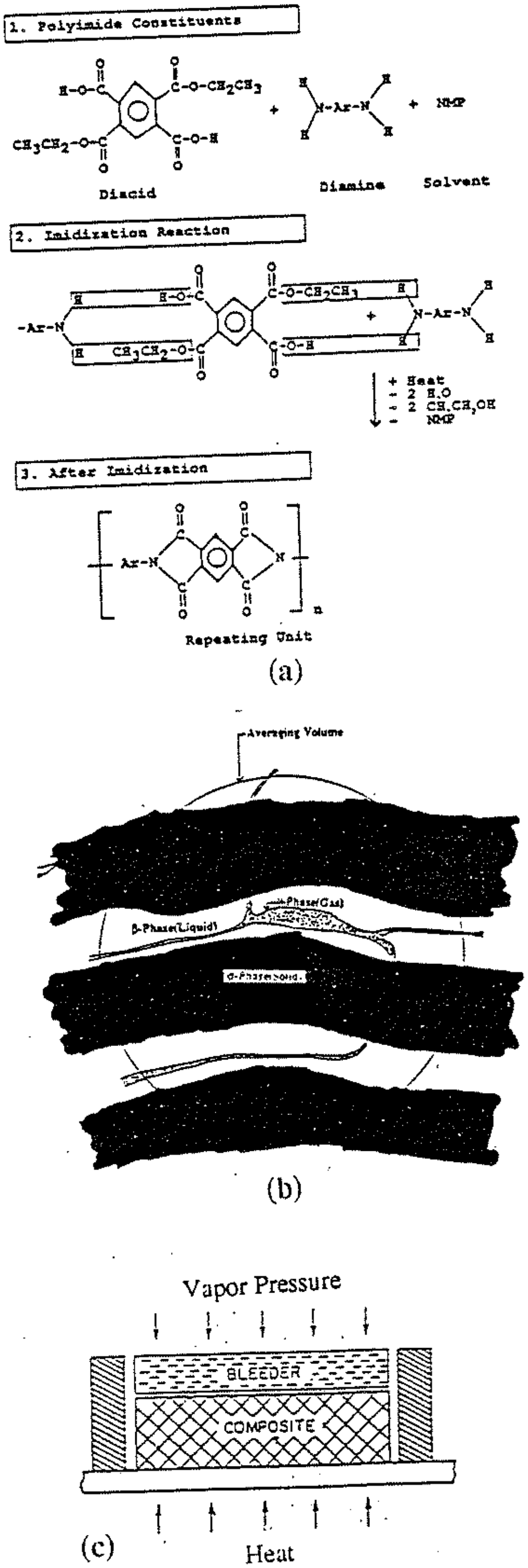
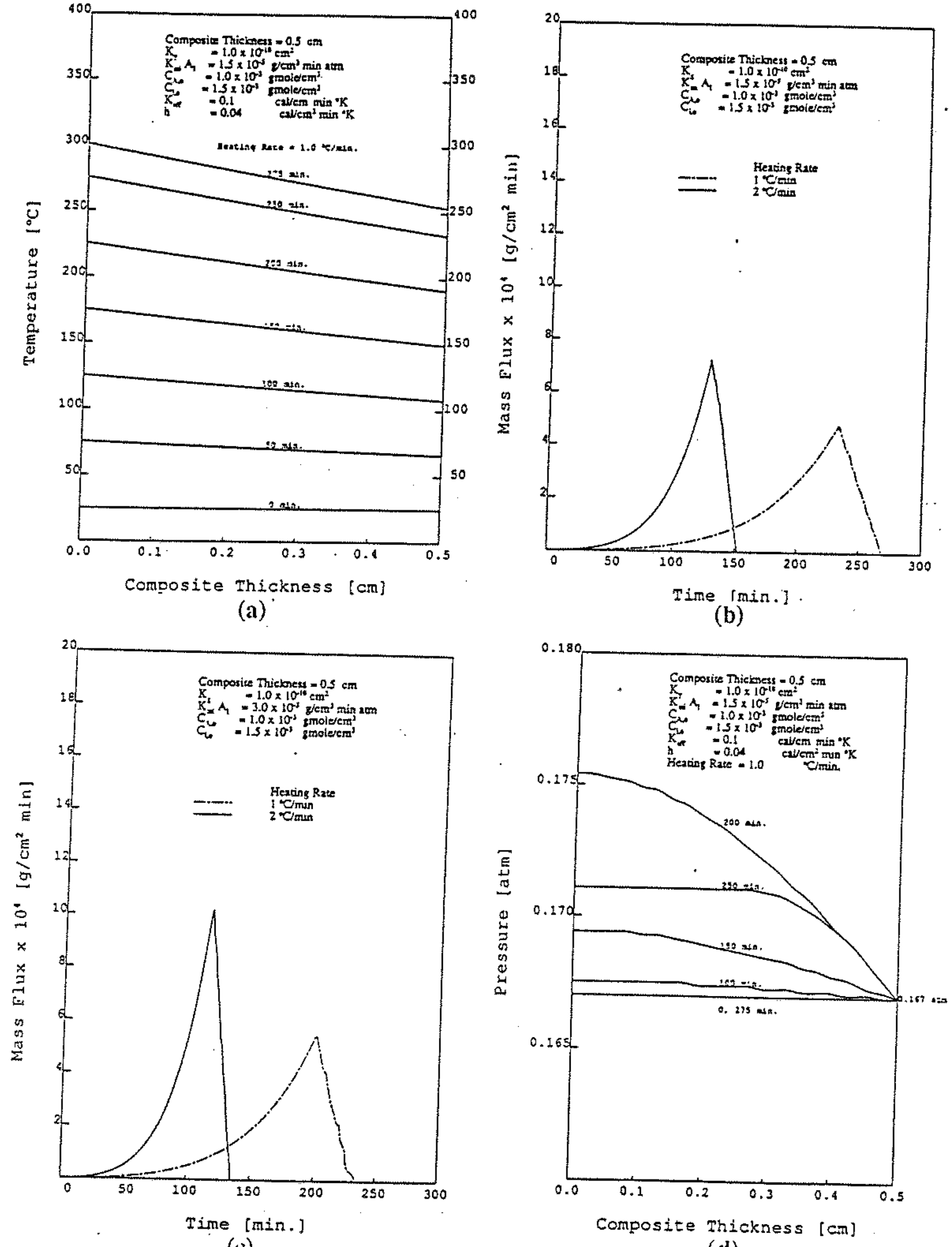


Fig.1 a) Polymerization Chemistry of Polyimide
b) System Phases in a Composite Laminate during the Devolatilization Processing
c) Schematic Geometric Diagram of 1-D Model



(a) (b)

(c) (d)

Fig.2 a) Temperature Profile
b),c) Solvent Removal Rate at the Top of the Composite Laminate
d) Pressure Profile

MODELING THE PROCESS CYCLE OF THERMOPLASTIC COMPOSITES WITH EXPERIMENTAL VERIFICATION

A. Problem Definition

In order to fabricate a thermoplastic polyimide (Avimid[1] K-III) composite of high quality, models describing the process (so-called master model) are required for understanding and controlling the process. The master model includes submodels involving kinetics, viscosity, devolatilization, heat transfer, consolidation, and void formation and growth.

A submodel for describing the devolatilization of thermoplastic polyimide composites has been proposed (1). It is assumed that the mass transfer limited model and Darcy's Law are valid in the development of the governing equations for the devolatilization model. A submodel for the consolidation process has also been proposed using soil consolidation theory (2).

This project addresses the problems of devolatilization and consolidation of thermoplastic polyimide composites in terms of modeling and experimental verification.

B. Research Objectives

1. Address the crack formation and healing phenomena. Develop and experimentally verify a submodel for crack formation and healing.
2. Experimentally verify a submodel for devolatilization.
3. Experimentally verify a submodel for resin flow (consolidation).
4. Address gas diffusion at the later stages of processing.

C. Research Accomplishments

It is proposed that morphological changes, high processing temperature and consolidation pressure can lead to crack formation and healing. Figure 1 shows a processing cycle for the Avimid K-III composite material and temperature ranges where the devolatilization and the consolidation process and the phenomena such as imidization, crystallization, melting of the crystallite, and crosslinking occur. The formation of cracks can be verified by the scanning electron microscopy studies of the composites with different extents of reaction. Also, computer-aided X-ray

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[1] Trademark of Du Pont Co.

tomography scanning will be used to have three-dimensional structural information inside the laminate.

The preliminary results of simulation show that the proposed devolatilization model might predict the devolatilization rate if the assumptions of the mass transfer limited model and Darcy's Law are proven acceptable. In order to verify whether or not the mass transfer limited model is correct, the gas pressure in the laminate has to be measured as a function of time and position. Figure 2 shows the schematic of the designed apparatus for measurements of the gas pressure. In conjunction with the mass transfer limited model, the method for determining the volumetric mass transfer coefficient is proposed which involves thermogravimetric analysis (TGA).

The resin flow model is based on soil consolidation theory. The experimental apparatus for measuring the resin pressure is shown schematically in Figure 3. The miniature pressure transducers will be used. Commercially available carbon fibers and Avimid K-III neat resin will also be used. It is known that the applied pressure, bleeder resistance, presence of dams, and thickness of the laminate are important factors to the resin pressure distribution.

It is proposed that in the later stage of processing, the mechanism by which the volatiles are removed becomes diffusion-controlled.

D. Future Research Plan

1. Completion of TGA/Mass Spectroscopy experiment.
2. Verification of crack formation and healing.
3. Completion of measurements of gas pressure and temperature.
4. Verification of a consolidation submodel.
5. Demonstration of usefulness of the verified model in selection of a desireable process cycle.

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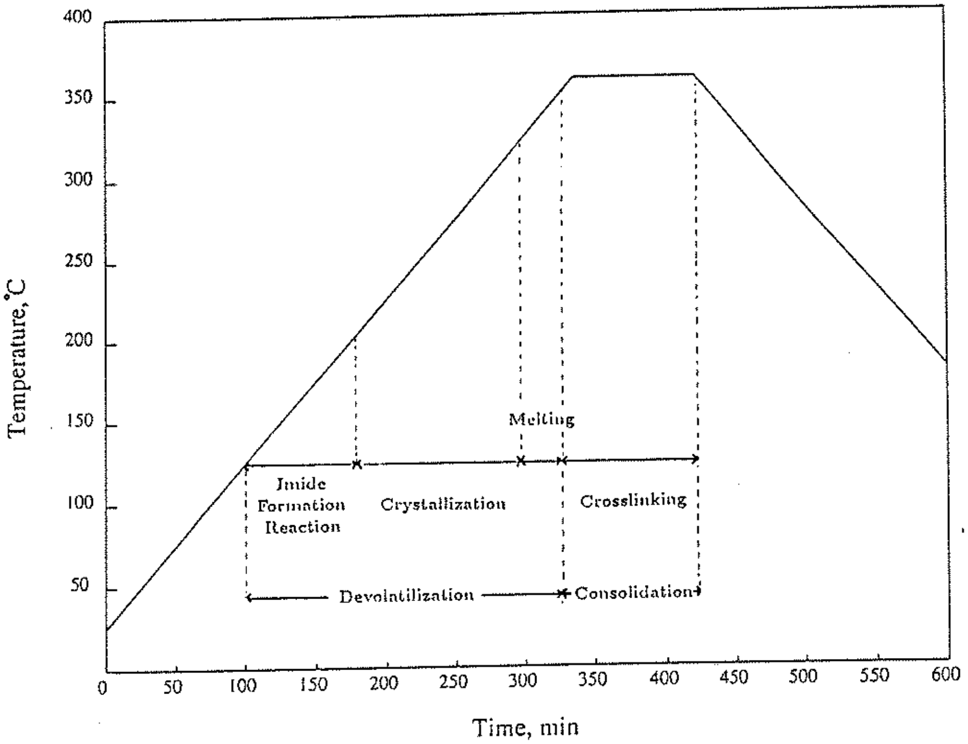
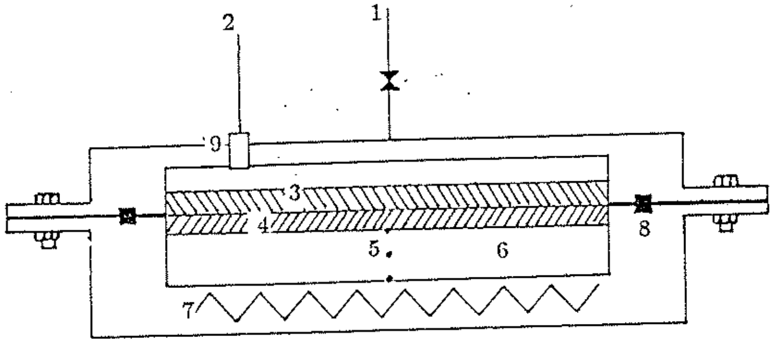


Figure 1 A typical process cycle for the Avimid K-III including temperature ranges of various processes



1 to Vacuum Pump
2 to Pressure Recorder
3 Porous Plate
4 Bleeder
5 Miniature Pressure Transducer
6 Avimid K-III Neat Resin or Prepreg
7 Heater connected to the Temperature Controller
8 Rubber Gasket
9 Vacuum Gage

Figure 2 Schematic of the apparatus for measurements of the gas pressure

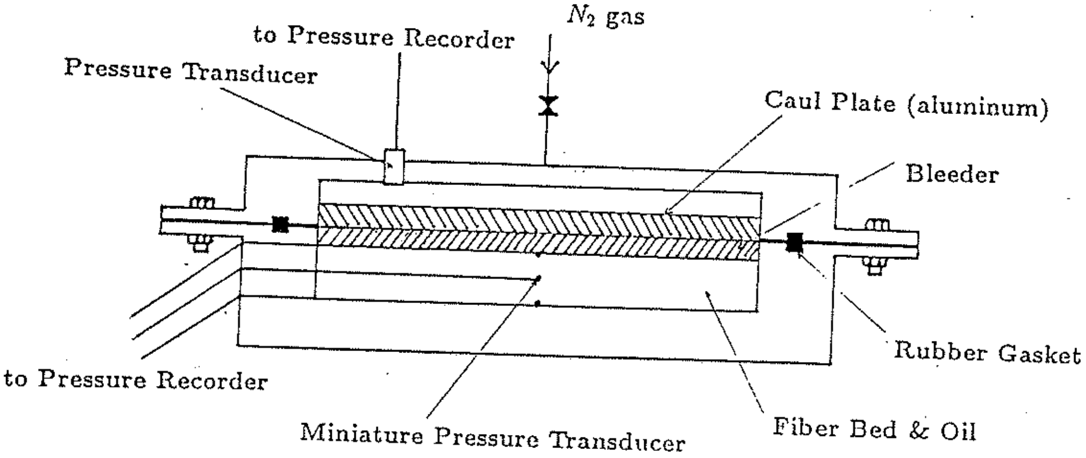


Figure 3. Schematic of the miniclave for measurement of the resin pressure and gas pressure

INTELLIGENT PROCESSING OF COMPOSITES: CONTROL OF THE PULTRUSION PROCESS

A. Problem Definition

Traditionally, the manufacture of composites has been very labor intensive and quality control has been difficult. Automation, on the other hand provides the necessary process stabilizations and built-in quality control to produce advanced composite components for high volume, price-sensitive applications in a cost effective way. The recent advances in computer technology in the form of more powerful hardware and advances in artificial intelligence hold the promise of improving the automation of the composite manufacturing process. Recent advances in process control methodology exploit the power of new process control computers by using on-line process models to guide the control actions.

Among all the composite manufacturing processes, pultrusion, which has seen considerable growth recently is chosen as the focus of this research for its continuous processing nature. The concepts that we develop and prove will be applicable to other types of composite manufacturing methods as well. The research will lead to cost reductions in composite manufacturing through more consistent quality control of products, reduced waste and increased throughput.

The pultrusion technique is a process used by the reinforced plastics industry to produce constant cross section shape products. A scheme of the pultrusion process is given in Figure 1. The process involves pulling resin impregnated fiber filaments through a heated die to cure the resin and then cutting the reinforced materials to desired length (Hollaway, 1986).

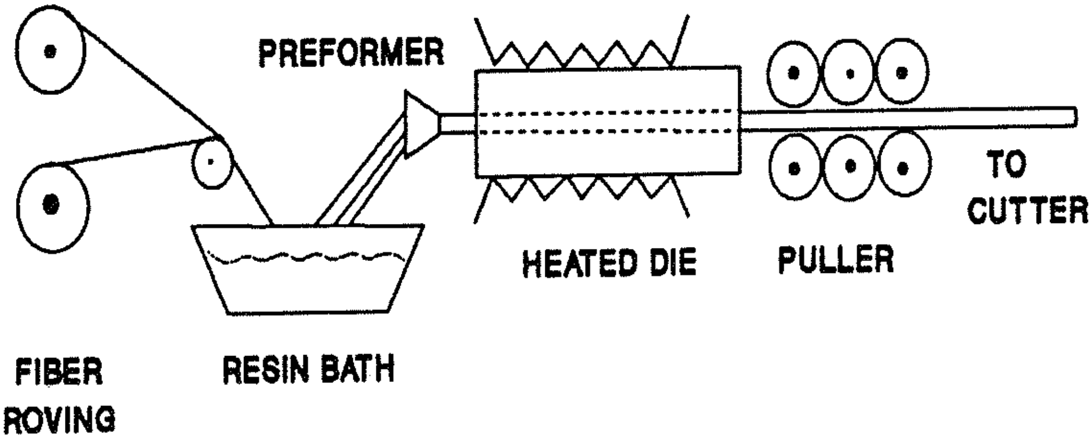


Figure 1. Pultrusion Process

B. Research Objectives:

The objective of this research project is to synthesize, implement and test intelligent process control strategies in the manufacture of polymer composites via the pultrusion process. Specifically, research will focus on the following:

1. Develop mathematical model for numerical simulation of the process.
2. The development of appropriate phenomenological models suitable for on-line computations.
3. Identify the type and placement of on-line sensing needed.
4. Model adaptation to fit changing processing requirements.
5. Develop on-line control and optimization strategies.
6. Use expert systems technology to capture the knowledge base needed for improved automation.

C. Research Accomplishments:

So far, the focus of this project has been on obtaining a good understanding of the pultrusion process through the development of a process model and numerical simulation using this model. The heat transfer and curing reaction model given by Han et al. (1986) in the pultruded materials has been extended to simulate the unsteady state response of the process and a similar model for heat transfer in the die is also added to the model. The mathematical model, based on an empirical kinetic model, can predict the dynamic variation in the temperature profile and the resin conversion in both radial and axial directions in the composite.

D. Future Research plan:

The prospective goals of this project are:

1. Extend the simulation study to heat transfer in the body of the die.
2. Extract control strategies by conducting numerical experiments using the simulation program.
3. Formulate a phenomenological model which will be more suitable for on-line process control.

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MONODISPERSE PARTICLE PRODUCTION BY VAPOR CONDENSATION IN NOZZLES

This project represents part of J.R. Turner's M.S. thesis which was completed at UCLA under the supervision of Prof. S.K. Friedlander. The work has been documented in: J.R. Turner, T.T. Kodas and S.K. Friedlander, (1988) J. Chem. Phys., 88, 457-465; and J.R. Turner (1987) M.S. thesis, Chemical Engineering Department, University of California, Los Angeles.

A. Problem Definition

Submicrometer particles are desirable for industrial and research applications such as the production of ceramic parts from powders and the growth of thin films. Many applications require nearly monodisperse particles of high purity. Particle production methods include communition, liquid phase processes (e.g. sol-gel and solution-precipitation) and vapor phase processes (e.g. flames, plasmas, aerosol reactors and condensation reactors). Submicrometer particles are difficult to form by communition, and the resulting particle size distribution is usually very broad. Liquid phase processes, which are currently the industry standard for monodisperse particle formation, feature high monodispersity at the expense of less-than-ideal purity and low mass production rates. High product purity is often achievable by vapor phase processes. Powders produced by flames (e.g. carbon black) are suitable only if relatively large degrees of polydispersity can be tolerated. Aerosol reactors and condensation reactors show potential for producing monodisperse particles. They are distinguished by the type of driving force for particle formation. In an aerosol reactor, the driving force for gas-to-particle conversion is a chemical, photochemical or thermal reaction which generates the condensable species; the driving force in a condensation reactor is an axial temperature gradient which reduces the condensable species' equilibrium vapor pressure.

Models have been developed to describe the performance of isothermal aerosol reactors in terms of the leading moments of the particle size distribution (Pratsinis,et al.,1986a,b). Unfortunately, for operating conditions which yield monodisperse particles, conventional reactor configurations still suffer from low mass production rates and may have trouble competing against liquid phase processes with respect to economic viability.

B. Research Objectives

The purpose of this project was to investigate novel methods to manufacture monodisperse particles. The criteria developed for monodisperse particle formation in isothermal tubular aerosol reactors (Kodas an Friedlander, 1988) suggest that a nozzle may be an attractive method. When a gas containing a condensable vapor expands from a reservoir through a subsonic or supersonic nozzle, the gas is cooled and the vapor can condense to form particles. A nozzle is a tubular flow reactor with varying cross section, and in this case operates as a condensation reactor. Nozzles also feature high throughputs in a relatively small system. Our goal was to develop a theoreical framework to describe particle formation and growth in subsonic nozzles. The governing equations were subsequently solved to determine the dependence of final product powder properties on system operating conditions.

C. Research Accomplishments

C.1 Nozzle Flow System

The proposed nozzle flow system can be divided into two sections – a reservoir and a condensation zone. The reservoir acts as a source of monomer and carrier gas for the expansion process. The condensation zone consists of a nozzle and if necessary, a straight section to increase the residence time. Coupled eqautions were set up and solved to obtain information about the aerosol properties.

C.2 Basic Equations

The gas dynamics for steady one-dimensional flow with condensation are described by a set of equations for the conservation of mass, momentum and energy and an equation of state. The aerosol dynamics were developed by extending the model of Pratsinis, et al. (1986a) to account for the non-isothermal expansion effects. The complete model for the gas and aerosol dynamics consists of a set of ten coupled ordinary differential equations.

C.3 Key Parameters

For a given carrier gas and condensable species, there are six independent variables: four operating conditions (exit Mach number and reservoir temperature, pressure and degree of supersaturation); and the nozzle shape (area distribution and length). The governing equations were integrated to calculate the performance indices used to characterize the product aerosol (number concentration, average particle diameter, width of the size distribution and process yield).

C.4. Conclusions

Calculations, based on theory, for aluminum sec-butoxide (a precursor to alumina powder) show that approximately uniform submicrometer particles can be produced at high mass flow rates by subsonic nozzle expansion. Two modes of nozzle operation are predicted. In one case nucleation is confined to the nozzle while in the other case nucleation occurs both in the nozzle and in a straight section following the nozzle. Nearly monodisperse particles can be produced for a wide range of operating conditions for both types of nozzle operation. Particle properties are less sensitive to operating conditions, however, when the conditions are chosen so that nucleation is confined to the nozzle.

D. Future Research Plan

1. Further studies would be needed to characterize the formation of particles from condensable species with properties different from aluminum sec-butoxide.
2. The actual performance of the system should be experimentally verified using a small prototype nozzle.

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ANTICIPATED FUTURE DIRECTIONS FOR CREL

As already mentioned CREL's focus is on education of graduate students and development of general (generic) methodologies for handling transport-kinetic interactions in a variety of reaction engineering problems. The current trends in industrial practice are oriented towards making specific high value products with any available technology. The order of priority is product, technology, methodology. Although we still maintain that the proper role of CREL is the development of methodology, we wish to serve the needs of our industrial participants in developing a link of such methodology to particular technologies and products.

Envisioned future directions for CREL (shown in Table 3) can be summarized as a commitment to:

1. Maintain and increase the strength of current research in multiphase reactors, modeling and control.
2. Establish a knowledge base for new related areas of materials preparation; develop new experimental techniques, new reactor devices, expert systems for reaction engineering problems, novel processing for high performance materials, etc.

In the first category we will emphasize:

i) Unique, sophisticated, state-of-the-art instrumentation.

ii) Comprehensive computational models based on first principles.

In the second category we perceive of developing some of the following areas:

i) Catalyst preparation, testing and scale-up. Applications in specialty chemicals and hazardous waste abatement.

ii) Thin film deposition via CVD, PLE, PPCVD, etc. Applications to semiconductors, superconductors, high performance ceramics.

iii) Preparation of fine particles. Applications to magnetic recording devices, ceramics, etc.

We would appreciate feedback from our industrial participants as to which areas are of most long term interest to them.

TABLE 3

THE FUTURE DIRECTION AND CREL OBJECTIVES ARE

- TO MAINTAIN STRENGTH IN TRADITIONAL AREAS OF MULTIPHASE REACTORS BY
  - INTRODUCING MODERN NON-INVASIVE INSTRUMENTATION FOR STUDIES OF THESE SYSTEMS
  - DEVELOPING IMPROVED THEORIES FOR UNDERSTANDING FLOWS IN SUCH SYSTEMS
- TO ESTABLISH AN INCREASED OVERLAP WITH PERTINENT SCIENCE IN SPEEDING UP PROCESS OR PRODUCT DEVELOPMENT E.G.

  TAP DEVICE + CONVENTIONAL LAB REACTORS
  (SURFACE CHEMISTRY-CRE OVERLAP IN CATALYST DEVELOPMENT AND CHARACTERIZATION)
- TO UTILIZE CRE PRINCIPLES IN DEVELOPMENT OF HIGH-TECH MATERIALS E.G. AEROSOLS
- TO UTILIZE CRE PRINCIPLES IN DEVELOPMENT OF NEW REACTOR TYPES OF PROCESS SCHEMES E.G. RPB
- TO UTILIZE THE ADVANCES OF AI AND EXPERT SYSTEMS IN CRE E.G. SAFE REACTOR DESIGN

CURRENT FUNDING

The external support of CREL during the period covered by this report (June 1, 1987 through May 31, 1988) was derived from various sources.

Industrial participation fees were essential in supporting the research in both main areas. They amounted to $120,000.

Modeling of Czochralski crystal growth was supported by the 3rd year of the EPRI contract at $70,000/year.

Trickle-bed and rotating packed-bed research was supported by two NSF grants totaling $123,880/year.

Control and expert system project was supported by an NSF grant of $65,000/year.

CURRENT STAFF (1987/88)

During the period covered by this report (June 1, 1987 through May 31, 1988) the following individuals have been associated with the various projects in the laboratory.

A. Faculty

Dr. Milorad (Mike) Duduković, Professor and Director
Dr. Babu Joseph, Associate Professor
Dr. P. A. Ramachandran, Associate Professor
Dr. G. Gao, Visiting Scholar
Dr. R. Srivastava, Research Associate

B. Graduate Students

A. Basić
S. J. Choi
N. Devanathan
D. Dorsey
P. Hanratty
R. Holub
D. O'Connor
S. Pirooz
J. Turner
H. T. Wu
Y. B. Yang
I. S. Yoon

INDUSTRIAL ADVISORY BOARD (1987/88)

L. P. Bosanquet	Monsanto
L. Clomburg	Shell Development
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F. Krambeck	Mobil
F. X. Mayer	Exxon
P. L. Mills	Monsanto
B. L. Tarmy	Exxon
P. Wanser	British Petroleum

CREL PUBLICATIONS AND PRESENTATIONS

A. PAPERS AND CHAPTERS

1. "Recent Advances in the Analysis and Design of Trickle Bed Reactors", P. A. Ramachandran, M. P. Duduković and P. L. Mills, Sadhana 10, 269-298 (1987).

2. "Solution Methods for a Class of Linear and Nonlinear Diffusion-Reaction Equations with Mixed Boundary Conditions", P. L. Mills, S. Lai, M. P. Duduković and P. A. Ramachandran, The Chem. Eng. J., 36, 17-29 (1987).

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5. "Modeling Liquid Phase Chemical Reaction and Interphase Mass Transfer in Churn-Turbulent Bubble Columns", K. J. Myers, M. P. Duduković and P. A. Ramachandran, Chem. Eng. Sci., 42, 2757-2766 (1987).

6. "Simulation of Tracer Distribution in Radial Flow Electrochemical Cells", F. B. Thomas, P. A. Ramachandran, M. P. Duduković and R. E. Jansson, in Recent Trends in Chemical Reaction Engineering, B. D. Kulkarni et al., eds., Wiley Eastern Limited, 1, 343-356 (1987).

7. "A Model for Resin Flow During Composite Processing: Part 2 - Numerical Analysis of Unidirectional Graphite/Epoxy Laminates", R. Dave, J. L. Kardos and M. P. Duduković, Polymer Composites, 8, 123-132 (1987).

8. "Trickle-Bed Reactors: Liquid Diffusional Effects in Gas-Limited Reaction", E. G. Beaudry, M. P. Duduković and P. L. Mills, AIChE J., 33(9), 1435-1447 (1987).

9. "Comparison of Solution Methods for a Mathematical Model of Dilute Solute Mass Transfer with Chemical Reaction on a Nonuniform Surface", P. L. Mills, S. Lai, M. P. Duduković and P. A. Ramachandran, Comp. Math. Applications 14(2), 139-151 (1987).

10. "Chemical Reaction Engineering: Current Status and Future Directions", M. P. Duduković, Chem. Eng. Education, 21(4), 210-214 (1987).

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12. "A Numerical Study of Approximation Methods for Solution of Linear and Nonlinear Diffusion-Reaction Equations with Discontinuous Boundary Conditions", P. L. Mills, S. Lai, M. P. Duduković and P. A. Ramachandran, Comp. Chem. Eng., 12(1), 37-53 (1988).

13. "Determination of Binary Gas Diffusion Coefficients in Spherical Porous Media by Steady and Unsteady-State Analysis of Single Pellet Reactor Data", S. P. Waldram, P. L. Mills and M. P. Duduković, Mathl. Comp. Modeling, 11, 38-42 (1988).

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15. "A Finite Element Solution for Diffusion and Reaction in Partially Wetted Catalysts with Power-Law Kinetics", P. L. Mills, S. Lai, M. P. Duduković and P. A. Ramachandran, Ind. Eng. Chem. Res., 27, 191-199 (1988).

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17. "Control of Constrained Multivariable Nonlinear Processes Using a Two Phase Approach", S. S. Jang, B. Joseph and H. Mukai, Ind. Eng. Chem. Res., 26(10), 2106-2113 (1987).

18. "Reduced-Order Models for Staged Separation Columns - IV. Treatment of Churns with Multiple Feeds and Side-streams via Spline Fitting". R. K. Srivastava and B. Joseph, Comp. Chem. Engg., 11(2), pp. 159-164 (1987).

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20. "Simulation of Fixed-bed Gas-Solid Reactors Using an Adaptive-Spline Collocation Method", A. Bhattacharya and B. Joseph, Comput. Chem. Engg., 12(4), 351-353 (1988).

21. "Modeling Hysteresis Phenomena in Systems of Multiple Slits: Application of the Principle of a Minimum Rate of Entropy Production at Steady State", R. A. Holub, P. A. Ramachandran and M. P. Duduković, Mathl. Comput. Modeling, 11, 26-31 (1988).

B. PRESENTATIONS

1. "Computer Control of Processes", B. Joseph, 3-day Shourt Course in Computer-Aided Design Center, I.I.T., Bombay, June, 1987.

2. "Data Acquisition and Control Using Microcomputers", B. Joseph, 2-day Short Course (Part of AIChE Today Series); Boston, 1987; New York, 1987; New Orleans, 1988.

3. "On-Line Optimization Using Dynamic Process Models", S. S. Jang, B. Joseph and H. Mukai, Paper Presented at AIChE National Meeting, New Orleans, 1988.

4. "Modeling of Fixed-Bed Gasification Reactors", B. Joseph, Seminar Presented at Combustion Engineering Laboratory, Brigham-Young University, Provo, Utah (1987).

5. "The Undergraduate Design Course: Current Curricula and a Critical Evaluation", B. Joseph, U.S.-India Cooperative Seminar on Chemical Engineering Curricula, Bangalore, Jan., 1988.

6. "Reduced-Order Models for Separation Processes", B. Joseph, Paper Presented at the Sixth International Conference on Mathematical Modeling, St. Louis, August, 1987.

7. "Modeling Hysterisis Phenomena in Systems of Multiple Slits: Application of the Principle of a Minimum Rate of Entropy Production at Steady State", R. A. Holub, P. A. Ramachandran and M. P. Duduković, 6th Internt. Conf. on Mathematical Modeling, St. Louis, August, 1987.

8. "Determination of Binary Gas Diffusion Coefficients in Spherical Porous Media by Steady and Unsteady-State Analysis of Single Pellet Reactor Data", S. P. Waldram, P. L. Mills and M. P. Duduković, 6th Internt. Conf. on Mathematical Modeling, St. Louis, August, 1987.

9. "Modeling of Czochralski Growth: Implications for Control", M. P. Dudukovic, P. A. Ramachandran and R. K. Srivastava, AIchE annual Meeting, New York, November, 1987, Paper 122f.

C. D.Sc. THESES

1. E. G. Beaudry, "Modeling of Trickle-Bed Reactors at Low Liquid Flow Rates", D.Sc. Thesis, Washington University, St. Louis, MO, December 1987.

2. S. M. Lai, "Modeling of Fluidized Bed Reactors for Manufacture of Silicon", D.Sc. Thesis, Washington University, St. Louis, MO, August 1987.

3. F. B. Thomas, "Modeling of Laminar Flow Electrochemical Cells", D.Sc. Thesis, Washington University, St. Louis, MO, August 1987.

D. D.Sc. PROPOSALS

1. N. Devanathan, "Investigation of Liquid HYdrodynamics in Bubble Columns via a Computer Automated Radioactive Particle Tracking (CARPT) Facility", D.Sc. Proposal, Washington University, St. Louis, MO, March 1988.

2. R. A. Holub, "Maldistribution in Trickle-Bed Reactors", D.Sc. Proposal, Washington University, St. Louis, MO, April 1988.

3. I. S. Yoon, "Modeling the Process Cycle of Thermoplastic Composites with Experimental Verification", D.Sc. Proposal, Washington University, St. Louis, MO, May 1988.