

Report

June, 1985 - May, 1986

CHEMICAL REACTION ENGINEERING LABORATORY

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## INTRODUCTION

This report describes the major events and research progress in the Chemical Reaction Engineering Laboratory (CREL) from June 1, 1985 through May 31, 1986. During this period significant research progress was made on ongoing projects, new research ideas have been nucleated, and the laboratory was well represented through numerous scientific contributions at major national and international meetings. Most gratifying was the continued support of participating companies which remains firm in spite of various economic and organizational dislocations in a number of industries.

Our basic goals remain unchanged. We strive to provide a unique and the best possible environment for education of graduate students in chemical reaction engineering and to maintain a leading role in our selected research areas. We firmly believe that reaction engineering, dealing with quantification of transport-kinetic interactions, dynamics and control of reaction systems, is vital to the success of chemical engineering as a discipline. Reactor design often determines the success of the whole process since the reactor (the cost of which per se need not be a major component of the total cost) by its performance dictates the load on all separation units in the process and hence affects their size and cost. Therefore, the proper application of reaction engineering principles is essential in experimentation, scale-up and design for all processes, whether they are chemical, biochemical, petroleum, electrochemical or of other type.

We believe that the current and next decade present unprecedented opportunities for significant impact of reaction engineering on the development of numerous new technologies. Reaction engineering undisputably played

conductor manufacturing operations. By having a critical mass of people, and by exposing them through our regular weekly meetings to a variety of problems, we do educate well rounded individuals. Our students, while focussing in depth on their own problem, develop an appreciation for the underlying science of reaction engineering and the ability to use it in many diverse applications. It is extremely important to have individuals well trained to carry on petroleum and petrochemical processing, especially now when at many major companies there is a dangerous age gap developing among technical personnel. For example, some companies have not added chemical engineering expertise at a Ph.D. level since 1981! It is at least equally important to illustrate how successful application of reaction engineering principles can be in manufacture of specialty chemicals, new materials, etc. We do educate and train people in these areas who are capable of becoming leaders in the field. This should help in regaining and establishing the competitive edge for these new industries.

We are able to accomplish the above important tasks only due to the support of participating companies. We are indebted for that support which represents an essential cornerstone in our ability to maintain continuity of research projects.

Our research can be classified in three broad generic areas: multiphase reactors, gas-solid noncatalytic reactions, and new materials, modeling and control.

In the area of multiphase reactors we continue to work on the better quantification of various transport effects in trickle-beds, bubble columns and centrifugal, packed-beds. Trickle-beds and bubble columns are used in a variety of applications from the petroleum to the biochemical industry. Advancing the understanding of complex phenomena that occur

and design of the rotating packed-bed have also been outlined. Currently we are studying the use of the device for non-Newtonian fluids and in oxygenation reactions (A. Basić).

In gas-solid noncatalytic reactions our emphasis has shifted from coal gasification to chemical vapor deposition. Unfortunately, DOE has curtailed further funding of both moving bed gasifiers and of new gasification concepts. We believe that much remains to be learned. However, we have a new gasification concept (REGAS) developed that we will save for a better climate. In chemical vapor deposition our work was oriented towards manufacture of silicon by silane pyrolysis both in fluidized bed reactors (S. Lai) and in Siemens decomposers (Y.B. Yang). This is one of the key steps in making semiconductor grade silicon for the electronic and photovoltaic industry. A comprehensive model developed for the fluidized-bed is the first of its kind. It relies on inputs from many fields (homogeneous silane pyrolysis kinetics, homogeneous nucleation, heterogeneous gas-solid reactions, fluidized bed hydrodynamics, fluidized bed filtering of small particles, etc.). Preliminary comparison of model predictions with the limited available data is very encouraging.

Our activities in the area of new materials, modeling and control have expanded. Together with our Materials Science Laboratory (Dr. J. L. Kardos) we (R. Dave) have developed a first quantitative model for optimizing the cure cycle of thermosetting composite materials. The model contains our unique approach to describing void formation and resin flow during the cure. Further work is planned in modeling both thermosetting and thermoplastic composite materials. We have established our group (R. K. Srivastava) as a leader in modeling Czochralski growth of single crystals and are on

thesis entitled "Liquid Phase Mixing in Churn-Turbulent Bubble Columns" in January, 1986. He spent the spring semester with us as an instructor teaching transport phenomena and completing the papers from his thesis. Kevin was the recipient of the Exxon Foundation Teaching Fellowship during his last three years of graduate studies. He has received job offers from industry and universities and is currently deciding between an academic and industrial career. Steven Lai and Ed Beaudry successfully defended their D.Sc. thesis proposals, Steven in the area of fluidized-bed reactor modeling for silane pyrolysis, and Ed in the field of trickle-bed reactors. Sarat Munjal is in the process of writing his thesis on centrifugal packed-bed gas-liquid contactors, and Raju Dave is completing his work on modeling of the cure cycle for thermosetting composites. For his work under Drs. Kardos' and Duduković's direction he has received the SAMPE 2nd place award for \$2,000 in recognition of the most innovative graduate student paper. He is also one of the six graduate student finalists for the 1986 Sherwin-Williams Award of the ACS Division of Polymeric Materials. The winner will be selected at the ACS Anaheim meeting. As already mentioned, Kevin Myers, Sarat Munjal, Ed Beaudry and Steven Lai presented their work at the Chicago AIChE meeting in November, 1985. All of these presentations were well received. S. Munjal, K. Myers, R. Dave, B. Thomas, S. Lai and R. K. Srivastava also presented papers based on CREL work at the One Day AIChE Symposium in St. Louis in April, 1986. A paper was also presented based on B. Thomas' work on electrochemical reactor modeling at the Seattle AIChE meeting in August, 1985.

The new graduate students in CREL are: N. Devanathan, J. Mehta, D. O'Connor and S. Pirooz. Narasimhan Devanathan completed his M.S. at

for the Engineering School receive each year this award. This was the fifth time in ten years that he has been so honored. He also received a Burlington Northern Faculty Achievement Award for teaching and a \$5,000 prize. Two such awards were given this year at Washington University. Dr. B. Joseph spent a year on sabbatical at Berkley where he immersed himself into mastering the concepts of artificial intelligence (AI) and expert systems (ES). We are all looking forward to his return after his current lecturing tour in India, when we hope for CREL to profit from his newly acquired experience. Dr. Joseph also used his sabbatical to complete some writing in gasification and control. In spite of the recognition that he has received for his work on control, we hope that CREL will provide him with the opportunity to gain additional deserved visibility. Dr. P. A. Ramachandran is one of the pillars of CREL. He has had a very productive year in teaching, student advising, fund raising and writing of papers. He was instrumental in our ability to establish a firm base in multiphase reactors where his book remains the leading text of this field. Dr. Ramachandran was a key factor in our rapid development of CZ models and in acquiring EPRI funding for this work. He also developed a new course in Processing of Electronic Materials on which we intend to capitalize in the future. The strength of CREL continues to rely on these three faculty members who can so effectively work together.

Finally, it is especially gratifying to report that our industrial support has remained strong. The industrial participation plan is vital to the CREL very existence and our interactions with industry are invaluable in promoting the professional growth of our students. Our gratitude goes to all our industrial advisors who have expressed the



October 15. However, if everyone's schedule is crowded due to the World Congress of Chemical Engineering in late September and an early November AIChE Annual meeting, we will consider early September or December as alternative possibilities for the CREL meeting. Your feedback with regard to preference would be helpful.

We are looking forward to seeing you all again in Fall 1986 on Washington University Campus.

M. P. Duduković

TABLE I (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1985 - May 1986

AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results
<p>2. Hydrodynamics in Trickle-Bed Reactors</p> <p>Relevance: Fundamental description of flow patterns in trickle-beds and interpretation of pressure drop, holdup and flow transitions based on first principles is lacking. This information is essential for proper scale-up and this project attempts to fill the existing gap.</p>	<p>Industrial</p>	<p>M. P. Duduković P. A. Ramachandran R. Holub</p>	<p>a) Position Emission Tomography (PET) equipment is being designed to study noninvasively liquid distribution in trickle-beds as a function of operating conditions. Particle scale resolution is expected based on preliminary calculations.</p> <p>b) Particle scale flow models are set up.</p>
<p>3-4. Liquid Phase Mixing in Churn-Turbulent Bubble Columns and Hydrodynamics</p> <p>Relevance: Bubble columns are used extensively but liquid back-mixing is described based on a physically unrealistic axial dispersion model. Here we attempt to develop</p>	<p>Industrial Exxon Foundation</p>	<p>M. P. Duduković P. A. Ramachandran N. Devanathan K. Myers</p>	<p>a) A new, physically realistic model for liquid backmixing in churn-turbulent bubble columns has been developed. The key model parameter can be related to the available information on dispersion coefficients.</p> <p>b) Tracer studies for model verification have been completed. It has been shown that the model can be related to the dispersion model by either steady state or transient measurements.</p> <p>c) Model predictions for dissolved oxygen concentration profile are found to be</p>

TABLE I (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1985 - May 1986

AREA II: GAS-SOLID NONCATALYTIC REACTIONS

Project	Funding	Investigators	Major Results
<p>1- Modeling of Fluidized-Bed Reactors and Siemens Decomposers for Manufacture of Silicon from Silane</p> <p>Relevance: Silane pyrolysis in Siemens decomposers and fluidized-beds is an attractive route for Si production. A model that accounts for all complex phenomena occurring is needed for quantification of JPL and Union Carbide data. It is necessary to find the operating conditions that suppress formation of fines.</p>	<p>JPL</p>	<p>M. P. Duduković P. A. Ramachandran S. M. Lai Y. B. Yang</p>	<p>a) Homogeneous and heterogeneous reaction pathways for silane pyrolysis are identified and a simplified reaction scheme that accounts for CVD and homogeneous decomposition is proposed.</p> <p>b) A CSTR model for production of Si is developed that accounts for silane homogeneous and heterogeneous decomposition, homogeneous nucleation of Si, coagulation and growth of fines and capture of fines by large particles.</p> <p>c) A two-phase bubbling bed model is developed that accounts for the grid region and all of the kinetic and hydrodynamic phenomena.</p> <p>d) Model comparison with JPL experimental data is good. The ability to predict conditions that favor formation of fines has been demonstrated.</p> <p>e) Model of the siemens decomposer has been formulated and optimal operating conditions identified.</p>

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1985 - May 1986

AREA III. NEW MATERIALS, MODELING AND CONTROL

Project	Funding	Investigators	Major Results
<p>leads to procedures for accurate calculation of selectivity of electroorganic processes based on quantified hydrodynamic effects.</p>			<p>b) A complete model for the prediction of the electrochemical reactor performance has been formulated.</p>
<p>3. Simulation of Temperature Distribution in Crystals Grown by Czochralski Method</p> <p><u>Relevance:</u> Czochralski method is used to grow almost 90% of the single crystal silicon for the semi-conductor industry. The project will lead to an improved understanding of the process.</p>	<p>JPL EPRI</p>	<p>P. A. Ramachandran M. P. Duduković R. K. Srivastava</p>	<p>a) A finite element computer code is developed for calculation of reflected radiation, convection and conduction heat transfer in the crystal enclosure.</p> <p>b) Simpler models that relate pull rate, crucible temperature and interface shape are developed for use in control.</p> <p>c) It is demonstrated that jet cooling effects can be beneficial in control of diameter and interface shape and may also lead to higher productivity.</p> <p>d) Radiation view factors for short crystals are calculated.</p>
<p>4. Simulation of the Hydrodynamics, Heat and Mass Transfer in Czochralski Melts</p>	<p>JPL EPRI</p>	<p>P. A. Ramachandran M. P. Duduković D. Dorsey</p>	<p>a) A finite element code is developed for flow simulation using nine noded elements. Preliminary simulation of the flow pattern in Czochralski melts shows excellent agreement with previous results in the literature.</p>

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1985 - May 1986

AREA III: NEW MATERIALS, MODELING AND CONTROL

Project	Funding	Investigators	Major Results
<p>6. Modeling Plasma Effect in Deposition Processes</p> <p><u>Relevance:</u> The need to quantify plasma effects in CVD, sputtering, optical fiber production and other manufacturing of new materials.</p>	Industrial	P. A. Ramachandran M. P. Duduković S. Pirooz	a) A preliminary model that decouples plasma physics and chemistry has been developed and will be tested on selected CVD systems.

respect to gas were reported and experimentally verified (1,2). During this year we have extended this model for a more realistic case of reactions that exhibit a fractional order behavior (between zero and one) with respect to the gas reactant and are zeroth order with respect to the liquid reactant. The model is important in interpreting reactor performance under partial wetting conditions which arise at liquid mass velocities below  $3 \text{ kg/m}^2\text{s}$ .

The new model was then tested on the data of Ruiz et. al. (3) for the hydrogenation of maleic acid in water. They have determined in a completely wetted trickle-bed reactor that this reaction is 0.6 order in the hydrogen partial pressure (reactant A) and 0.08 order (essentially zero order) in the maleic acid concentration (reactant B). When conducting the reaction at lower liquid mass velocities (i.e., under partial wetting condition) they observed in a differential trickle-bed reactor a substantial decrease in the reaction rate with the decrease in the inlet concentration of maleic acid. They were unable to explain these experimental observations. Using the intrinsic and apparent kinetics given by Ruiz et. al. (3), the wetting efficiency correlation derived previously in CREL (4), and the liquid-solid mass transfer correlation of Tan and Smith (5), the reaction rate predicted by our new model is compared to the actual experimental points of Ruiz et. al. (3) in Figure 1. The model predictions which are based on entirely independently estimated parameters, give the correct trends and are able to explain the observed phenomena. The agreement between the model and experimental data is remarkable considering that the details of the experimental data were not available to us. This provided further support of the model's validity in explaining the reduction in reaction rate in partially wetted trickle-bed reactors at low concentrations of the zero-order, nonvolatile liquid reactant.

times more concentrated than the dissolved hydrogen, reactant A. However, the reduction in reaction rate according to the model is very slight below a fractional conversion of 0.2. Both of these findings have been confirmed experimentally.

3. A general, nonisothermal trickle-bed reactor model was developed for simulating a single, first-order, gas-limiting reaction at steady state. The model accounts for the effects on reaction rate due to external partial wetting of the catalyst. The model assumes plug flow of liquid and gas and equilibrium between liquid and vapor at each axial point in the reactor except for slightly soluble gases which can be assumed to have a finite gas-to-liquid mass-transfer rate.

The model requires as input parameters: inlet concentrations and flow rates, inlet temperature and pressure, kinetic rate constants, catalyst and reactor dimensions and porosities, and liquid and vapor components' molecular weights, densities, viscosities, specific heats, reference enthalpies and equilibrium relations. The model allows for the presence of a volatile solvent and an inert gas and makes it possible to investigate their role in reactor performance.

4. In summary, the work done during the past year completes our systematic treatment of liquid and gas limiting reactions under conditions of partial wetting and in close to isothermal reactors. The findings will be summarized in a guide for practitioners that will be helpful in identifying the particular regime and taking appropriate corrective action.

#### D. Further Research Plan

1. Investigate the role of fines in gas-limited reactions.
2. Extension of models to systems first-order in a liquid-limiting reaction and first-order in both gas and liquid reactants.

## Project I.2. Hydrodynamics in Trickle-Bed Reactors

### A. Problem Definition

Flow regime, liquid distribution and liquid-solid contacting all affect reactor performance and are not, as yet, understood phenomena due to the complex interactions between the phases present. Prediction of flow regimes is still of an empirical nature, and the attempts of others at quantifying this prediction have exposed some inconsistencies in the current view of the nature of liquid flow. Current models for liquid distribution are based on an assumed film flow configuration on the particle scale and conform ultimately to a diffusion type model on a reactor scale. These types of models offer no hope of predicting any major flow maldistribution even though this problem is observed in industrial reactors. Some flow distribution models have been developed which define a packing structure, and then apply simple mixing rules to govern the liquid distribution. While some of these models do predict liquid maldistribution, generally, the mixing rules are very simple and designed to ensure this possibility. The film flow assumption in most models implies complete liquid-solid contacting, a phenomenon which is not experimentally observed, and no models to predict incomplete wetting have been developed other than the empirical correlations for the wetting efficiency. Thus, both particle scale incomplete wetting and reactor scale liquid coring require further quantification.

Often flow regimes in trickle-beds are expected to conform to two-phase flow regimes in pipes and tubes. This belief is entrenched in the practice of using capillary two-phase annular flow models as building blocks for trickle-bed models. Figure 1 and 2 clearly illustrate that flow regimes in a capillary (Figure 1) are completely different, even reversed, than those observed in trickle beds (Figure 2). When plotted on the



the Washington University Medical School around 1975 to obtain quantitative reconstructions of the brain [4], and our device will be similar to the original prototype but with several improvements to enhance the resolution. Two factors make this method viable only at Washington University. First, the radioisotopes needed are rather short-lived so a cyclotron to produce them must be nearby (our physics department operates a cyclotron with the required capabilities). Second, many researchers in the electrical engineering and radiology departments of Washington University are actively working on this device at a more advanced level than we require, and their interaction has been informally ensured. The device will be used to observe the differences of the rivulet and film flow and liquid flowrates, surface tension, porous vs nonporous packing, regions of decreased or increased porosity, flow redistributors, liquid distributors and collectors, etc.).

2. A finite element code for solving the Navier-Stokes equations in two phase flow fields in complex geometries with surface tension effects has recently been obtained and work is proceeding on the particle scale models.

3. A doctoral proposal on the above project is near completion and an NSF equipment proposal will be submitted for the required hardware.

#### Nomenclature in this Section

$U$  = superficial velocity

$\rho$  = density

#### Subscripts

$N$  = nonwetting phase = air

$W$  = wetting phase = water

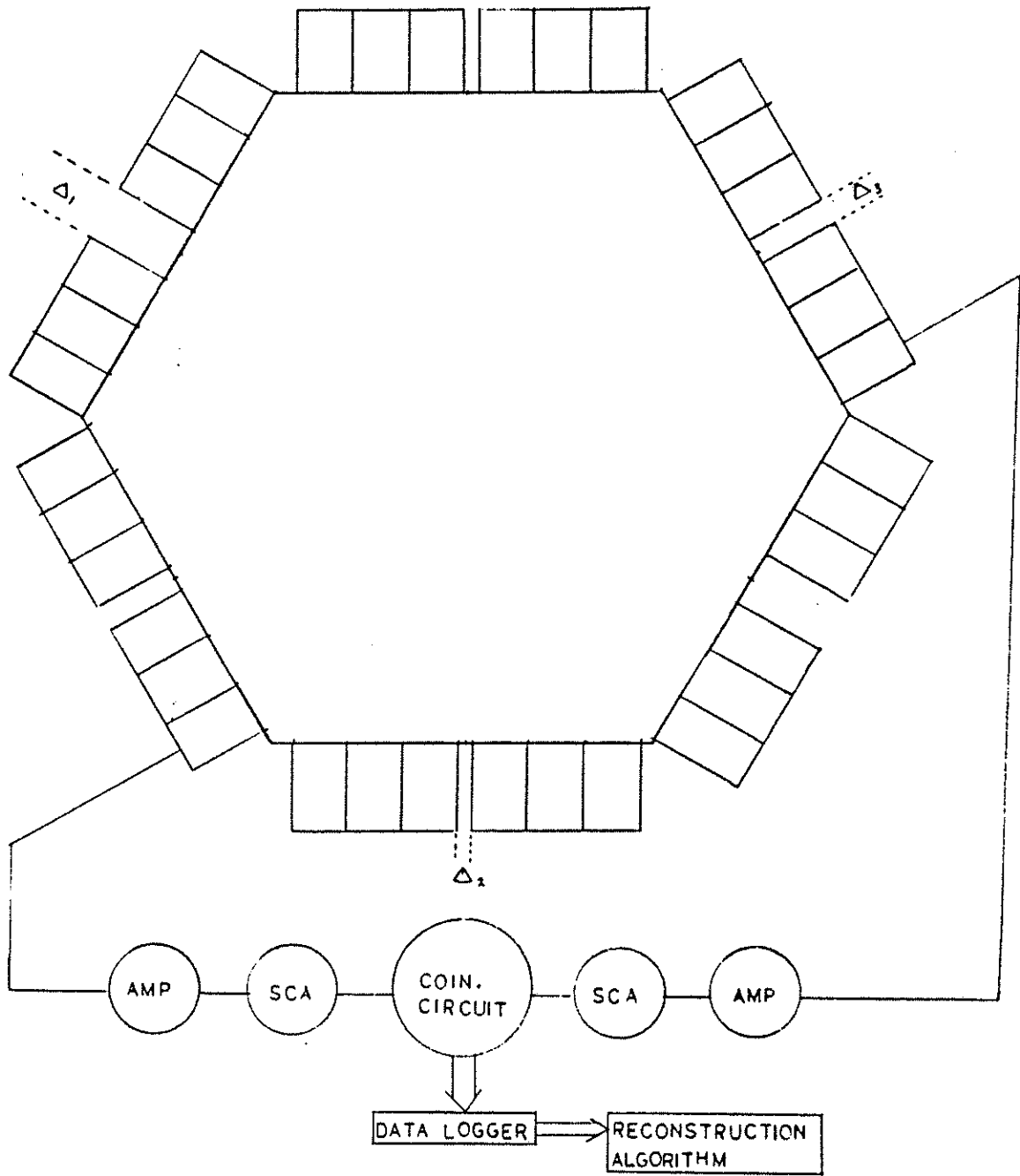


FIGURE 3 SCHEMATIC OF DETECTION SYSTEM

## Project I.3. Liquid-Phase Mixing in Churn-Turbulent Bubble Columns

### A. Problem Definition

Design of bubble column reactors operating in the churn-turbulent flow regime is typically based upon employing the axial dispersion model to describe the mixing of the gas and liquid phases. Presently there is no valid justification for applying the axial dispersion model to liquid-phase mixing in the churn-turbulent regime. Also, the axial dispersion model leads to species conservation equations of the two-point boundary-value type which are computationally complex, particularly in reacting systems. For these reasons an alternative model to describe the behavior of churn-turbulent bubble columns is desired. This model should be firmly based upon the characteristics of churn-turbulent flow and should be computationally efficient.

### B. Research Objectives

1. Develop an alternative phenomenological model to describe liquid-phase mixing in churn-turbulent bubble columns.
2. Numerically examine the behavior of the proposed mixing model for a variety of nonvolatile, nonreactive tracer studies and compare the behavior of the proposed model with that of the axial dispersion model.
3. Perform a series of pulse tracer experiments and compare these experimental results with the proposed mixing model.
4. Demonstrate how the proposed liquid-phase mixing model can be extended to consider the effects of interphase mass transfer and liquid-phase chemical reaction, thus providing a complete model of churn-turbulent bubble column behavior.

2. The behavior of the proposed model was examined for a number of standard tracer studies. First, a steady backmixing experiment in which a continuous stream of a nonvolatile, nonreactive tracer is injected into the liquid phase near the liquid overflow is simulated. The tracer concentration profile that develops along the length of the column due to backmixing can be employed to characterize the mixing of the liquid phase.

Simulation of the slug and cell model for this steady backmixing experiment indicated that the proposed model predicts an exponentially-decaying tracer concentration profile similar to that predicted by the axial dispersion model and observed experimentally (1). The rate of decay of this tracer concentration profile was found to be dependent upon the magnitude of the unknown exchange parameter  $Y$ . With the proper choice of the parameter  $Y$  the behavior of the slug and cell model could thus be 'equated' to that of the axial dispersion model under a given set of operating conditions. In this manner a correlation for the unknown exchange parameter can be developed by equating the behavior of the two models under a variety of operating conditions while relying upon some readily available literature correlation to predict the behavior of the axial dispersion model. When the axial dispersion coefficient correlation of Baird and Rice (2) is employed, the following power-law correlation for the unknown parameter  $Y$  is obtained.

$$Y = 0.449 N^{-0.0679} D^{-0.331} U_G^{0.207} \quad (1)$$

$N$  is the number of cells along the column length (dimensionless),  $D$  is the column diameter (in cm), and  $U_G$  is the superficial gas velocity (in cm/s). This comparison of the two mixing models was performed for column length to diameter ratios in the range of 6 to 37 (86 in one extreme case),

pass through the system. The behavior of the slug and cell model was simulated for a number of simple kinetic schemes (zero, half, first, inverse first, second, and third-order and Michaelis-Menten kinetics; all irreversible). Figure 3 illustrates the necessity of accounting for the nonideal mixing of the liquid phase when high reactant conversions are desired. This figure demonstrates that the volume required by a completely backmixed system,  $V_{CBM}$ , can be many times greater than that required when the nonideal mixing of the liquid is accounted for by the slug and cell model,  $V_{SCM}$ .

Consideration of interphase mass transfer with the slug and cell model of churn-turbulent bubble column behavior requires quantification of gas-phase mixing which is a simple matter since the behavior of the gas has previously been taken into account as it affects liquid-phase mixing. Like the liquid, the gas is divided into a fraction that travels upwards with the slug and a stationary fraction which is trapped within the turbulence and circulation of the liquid in the cells. The gas in the slugs is further divided into a large central bubble and smaller entrained bubbles and an exchange of the small bubbles entrained with the slug and those trapped within the cells is permitted. All gas bubbles are taken to be spherical and the bubble sizes and mass transfer coefficients can be estimated from available theories.

Figure 4 presents a comparison between experimental data of Deckwer et. al. (3) for the absorption of oxygen into water with predictions of the axial dispersion model and the slug and cell model. The axial dispersion model prediction is a best fit between the model prediction and the experimental data. The predictions of the slug and cell model are for various values of the parameter  $P$  which is the fraction of the gas in the rising

$V_c$	- cell volume
$V_{SCM}$	- reactor volume of completely backmixed model
$V_{LDF}$	- volume of liquid downflow from cell to cell
$V_{LE}$	- volume of liquid exchanged between a slug and a cell
$V_{SCM}$	- reactor volume of slug and cell model
$V_{LUF}$	- volume of liquid upflow with slug
$W, X, Y, Z$	- dimensionless model parameters (refer to Table 1 for definitions)
$z$	- axial position
<u>Greek</u>	
$\epsilon_c$	- cell gas holdup
$\theta$	- dimensionless time

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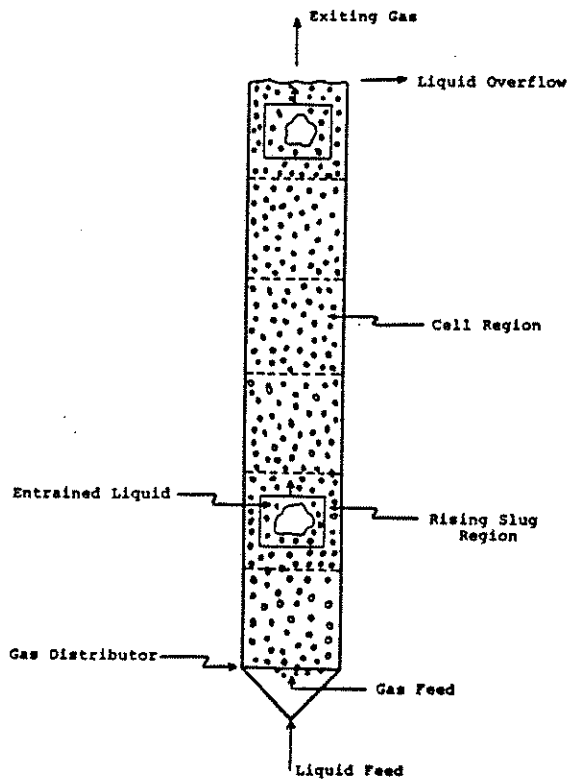


Figure 1. Schematic of the Physical Model of Churn-Turbulent Bubble Column Operation

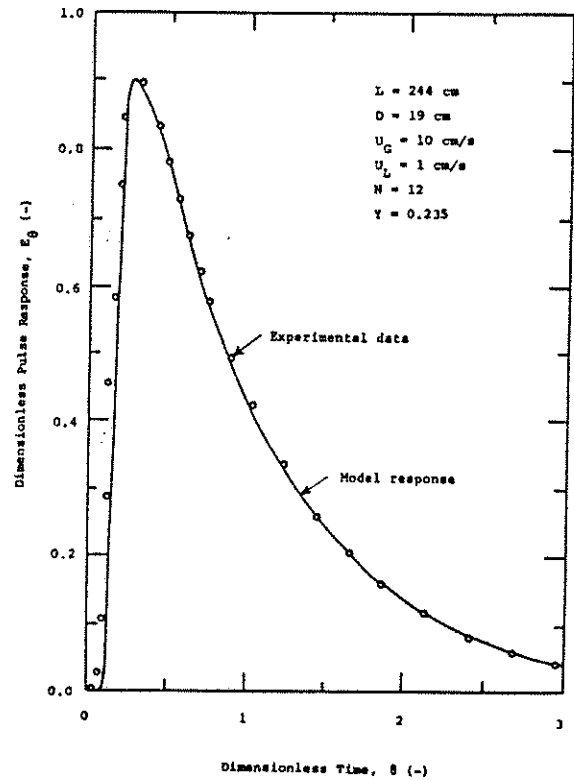


Figure 2. Comparison of an Experimental Pulse Response with that of the Slug and Cell Model

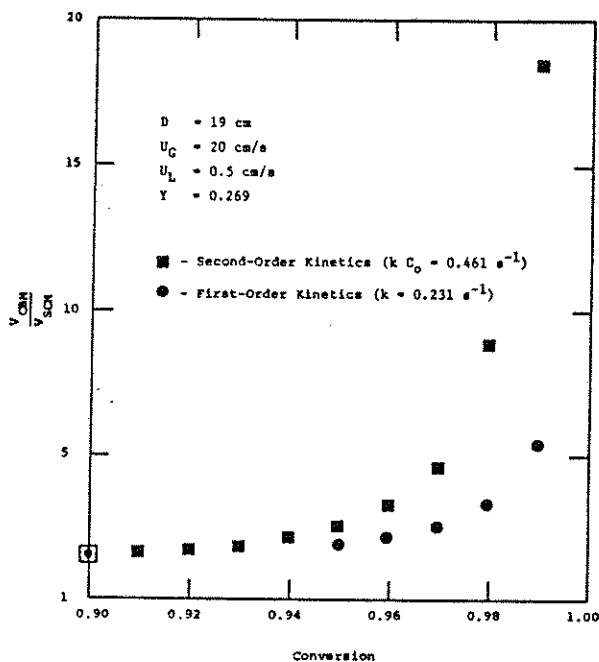


Figure 3. Comparison of Reactor Volumes of the Slug and Cell Model and the Completely Backmixed Model

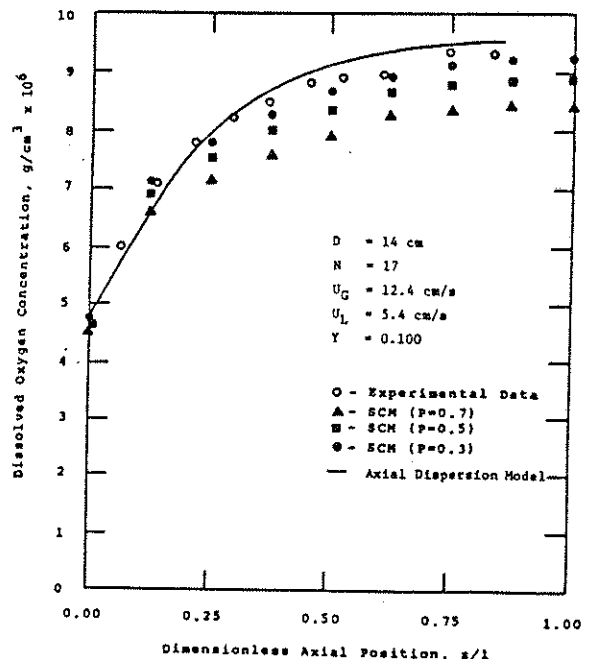


Figure 4. Comparison of the Slug and Cell Model and the Axial Dispersion Model with Experimental Data for the Absorption of Oxygen in Water

5. Measure transient voidage profiles by successive activation gamma-ray tomography and compare results with predictions from 4 above.

#### C. Research Accomplishments

The project has just been initiated. Literature survey is in progress. The pseudohomogeneous liquid circulation model has been formulated. This model will be solved numerically in the first instance. Experiments are being planned for voidage and liquid velocity measurements. The existing bubble column will be used for this purpose. The work will lead to improved understanding of bubble columns on a fundamental basis.



water at Traverse City, Michigan Air Base. Toulene at 150 to 500 ppb and benzene at 50 to 200 ppb in ground water, at a flow rate of 70 to 120 gpm, are reduced to less than 1 ppb by stripping with air at a flow rate of 600 to 1600 scfm.

Discussion of the rotating packed beds in open literature is very limited. ICI, the only company to study them extensively, has published very limited data. Moreover they have made no attempt to explain the phenomena at the fundamental level. It is necessary to verify the validity of the Sherwood's flooding correlation because it can explain the dramatic reductions in the equipment size. It is also necessary to determine the increase in the mass-transfer coefficients and the interfacial area as functions of the rotational speed, liquid flowrate, etc. Such information is needed for the design and scale-up of the rotating packed bed and for its potential use as a gas-liquid contactor or a reactor-separator in heterogeneous catalysts. The objective of this study is to provide such information.

#### B. Research Objectives

We want to fully quantify the behavior of the rotating packed-bed so that its design or scale-up can be readily accomplished for any desired operation. We also want to develop a better understanding of the behavior and structure of liquid films in centrifugally accelerated flows.

#### C. Research Accomplishments

##### 1. Equipment

The rotor was fabricated at the Washington University workshop. Figure 1 shows the vertical section of the rotor. The packed bed is 1 inch high. The inside radius of the packed bed can be varied from 3 cm to 5 cm and the outside radius can be varied from 7 cm to 8.7 cm. Figure 2 shows

### 3. Mass-Transfer Correlations

Approximate correlations for gas-liquid mass transfer coefficient,  $k_L$ , and liquid-solid coefficient,  $k_S$ , in a rotating bed, were developed based on Davidson's statistical model (5) for the gravity-flow packed bed. He extended the  $k_L$  correlation for a gravity-driven laminar film flow on an inclined flat surface to a correlation for a packed bed by assuming that the packed bed consists of randomly-oriented flat surfaces with complete liquid mixing (i.e. surface renewal) at the junction of the flat surfaces. For the rotating packed bed, we first developed  $k_L$  and  $k_S$  correlations for laminar film flow on a rotating blade, Figure 4, and a rotating disk, Figure 5. Penetration theory and asymptotic film velocity (6,7) were used to develop the approximate analytical expressions. These correlations for the flat surfaces were then extended to the packed bed using a statistical model. The final form of the correlations is:

$$k_L = 2.6 \left( \frac{Q_w}{\Delta X} \right) (Sc)^{-1/2} (Re)^{-2/3} (Gr)_{avg}^{1/6} \quad (1)$$

and

$$k_S = 2.8 \left( \frac{Q_w}{\Delta X} \right) (Sc)^{-1/2} (Re)^{-8/9} (Gr)_{avg}^{2/9} \quad (2)$$

Here

$$\begin{aligned} Q_w &= \text{volumetric flowrate per unit width of the packed surface} \\ &= (\pi L / 2 a_e \rho_L) \end{aligned}$$

$$Re = \text{Reynolds number} = 4Q_w \rho_L / \mu_L$$

$$\Delta X = \text{surface renewal distance} = d_p \text{ at low } Re, \quad d_p/2 \text{ at high } Re$$

$$(Gr)_{avg} = \text{Grashof number} = \frac{R_{avg} \omega^2 (\Delta X)^3}{(\mu_L / \rho_L)^2}$$

$$Sc = \text{Schmidt number} = (\mu_L / \rho_L) / D$$

Reynolds number is approximately 100 and therefore  $\Delta X = d_p$  is an appropriate choice. The predicted values of  $k_L$  are fairly close to the experimental values. However,  $\Delta X = 0.86 d_p$ , gives a better fit of the experimental data. Also shown in the figure are the predicted values of  $k_L$  for the gravity flow by Davidson's model.  $k_L$  for the rotating bed is approximately 2 times higher.

#### 6. Liquid-Solid Volumetric Mass-Transfer Coefficients

Liquid-solid volumetric mass-transfer coefficients have not been reported in the literature so far. These values will be required if this device is to be used as a three-phase reactor. Dissolution of naphthalene in water was used to determine the  $k_S a_S$  values in the rotating packed bed. Non-spherical particles had to be used in these tests because spherical naphthalene particles of  $d_p = 3$  mm could not be obtained. The average particle diameter was 3.38 mm.

Figure 8 shows the measured values of  $k_S a_S$  as a function of  $\omega$  for two bed volumes.  $k_S a_S$  increases with  $\omega$ . Also shown in the same figure is the experimental value of  $k_S a_S$  in gravity flow for the same  $d_p$  and the same liquid superficial flowrate estimated from the values reported by Goto et. al. (9).  $k_S a_S$  in the rotating bed are 4 to 6 times higher than those in gravity flow. Further, if we assume  $a_e/a_p = a_s/a_p$ , then experimental  $k_S$  values can be estimated by using the  $a_e/a_p$  given in Figure 6. These experimental  $k_S$  values are within 25% of those predicted by Equation 2.

#### D. Future Work

We are now planning our next phase of research. There are many interesting possibilities, of which some are as follows:

1. Flow of Bingham plastic fluids. Above a certain yield stress, a Bingham plastic fluid will not flow in the gravity-flow packed beds. The limiting yield stress in the rotating bed will be much higher. Removal of monomer from a polymer may be a typical application.

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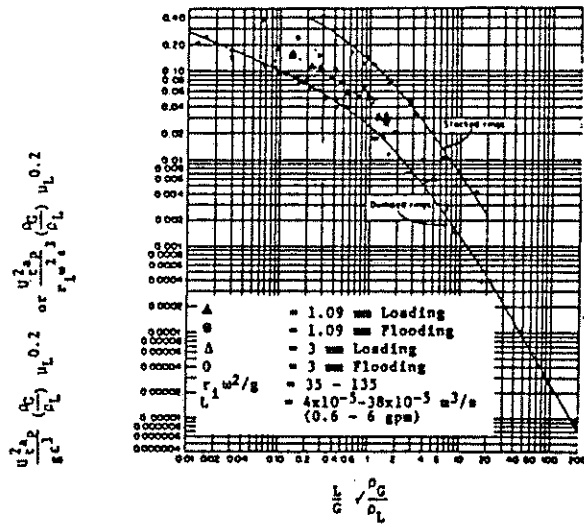


Figure 3. Empirical Correlation of Flooding and Loading Data with Sherwood Correlation

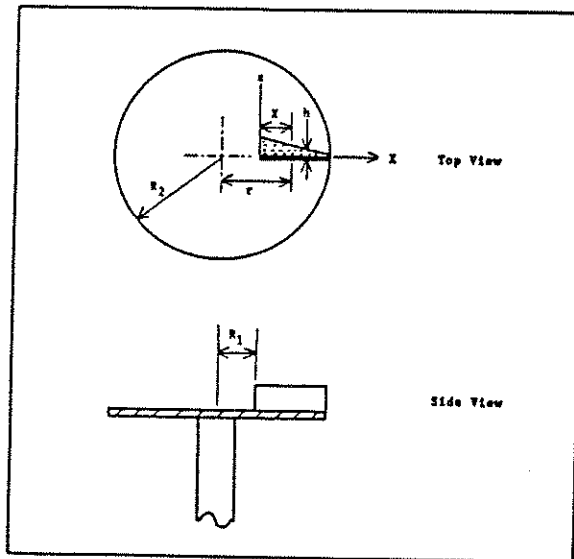


Figure 4. Rotating Blade Model

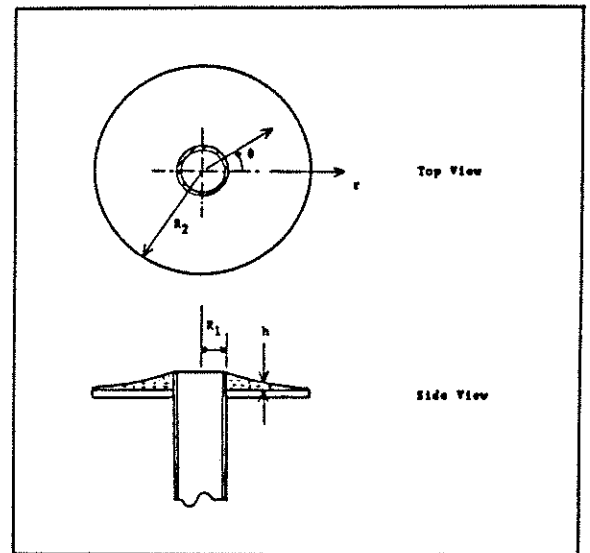


Figure 4. Rotating Disk Model

## Project I.6. Three Phase Reaction Systems in Centrifugal Contactors

### A. Problem Definition

Investigation of the possibilities of use of the HIGEE device described in Project I.5, as a three-phase reactor has been initiated. In order to establish some relation between the possible performance of the HIGEE as a reactor and the phenomena that are believed to govern it, a theoretical analysis of a three phase reaction system in the centrifugally induced liquid flow was undertaken.

The system considered was a reaction between the dissolved gas and a liquid reactant, taking place on the solid surface of the flat rotating plate over which the liquid flows in a thin film. Apart from the advantages in better understanding of the HIGEE reactor performance, this study also has some fundamental merit.

### B. Research Objectives

This study has been recently initiated. As is the practice of CREL, the student participates fully in problem formulation and definition of research objectives. The overall objectives is to gain a better understanding of the conditions when HIGEE could be a viable three phase reactor with particular attention being paid to some oxidation systems.

### C. Research Accomplishments

A model was set up for a liquid containing a reacting solute flowing over a rotating disk. Starting at some radial position, the disk is coated with a catalyst that induces an infinitely fast reaction between the liquid reactant and the gaseous species taken up from the gas above the liquid free surface. Liquid is introduced with the saturation concentration of the gaseous species.

### 1. Liquid Holdup and Residence Time Distribution Determination

The inaccessibility of the packed bed core of the HIGEE rotor defies a straightforward use of any technique that has been devised for the liquid holdup measurement and RTD determination in gravity packed beds. Work will be done in designing experiments that will overcome the mechanical difficulties, as well as the end effects present in the small HIGEE unit of our Laboratory. At this point, the most promising methods seem to be electroconductivity measurements and residence time tracing with electrolytes.

### 2. A Model Reaction System

The distinguishing characteristics of the HIGEE device: high liquid throughputs, hence very short residence times and greatly enhanced gas-liquid mass transfer hint at the kind of reaction system that would benefit from the use of this device. A very fast reaction that is gas to liquid mass transfer limited is sought. A possible candidate is probably to be found in the area of water purification, or specialty chemicals. As to the use of porous packing, it seems that for any reasonable particle sizes, the internal diffusion resistance make the liquid recycling mandatory in order to achieve any appreciable conversion.

A suitable reaction system will be chosen and the reaction run in our unit. Data will be collected on its performance, that then can be compared to the conventional way of running the reaction chosen. Evidence will be sought in support of the presumed advantages of HIGEE in overcoming the mass transfer limitations.

### 3. Theoretical Analysis

Further numerical analysis of the three phase reaction systems in the centrifugal field will be carried. The model already briefly described

## AREA II: GAS-SOLID NONCATALYTIC REACTIONS

### Project II.1. Modeling of Fluidized-Bed Reactors for Manufacture of Silicon from Silane

#### A. Problem Definition

Production of polycrystalline silicon particles for semiconductor and solar applications via silane pyrolysis in fluidized bed reactors is economically attractive. Fines can form by homogeneous nucleation at high silane concentration and are considered a loss to the process. In a fluidized bed reactor, fewer fines are generated because: i) less free space is available for homogeneous nucleation, ii) the seed particles scavenge the fines and incorporate them into the deposition growth. Therefore, a fluidized bed can be operated at a much higher silane concentration than a Siemens decomposer and the process economics can be improved. However, the phenomena occurring in a fluidized bed with growing seed particles and fines remain to be fully quantified.

Experimental work is going on at JPL and Union Carbide to quantify the relationships between particle growth and operating conditions. It is necessary to develop an appropriate model to interpret, quantify and unify the available experimental data. Successful scale-up of the process can be achieved only through a well tested fundamental model.

#### B. Research Objectives

1. Development of a mathematical model for fluidized bed pyrolysis of silane that relates production rate and product silane properties (such as size, size distribution, presence and absence of fines) with fluidized bed size and operating parameters (such as wall temperature, feed concentration, gas flow rate, seed size, etc.) and with bed grid design.
2. Comparison of model predictions and experimental data and parameter sensitivity studies.



fluidization conditions. It is clear that the CSTR model can give a lower estimate on fines formation and an upper bound on deposition rate. At higher temperatures FBBR predictions can deviate significantly from CSTR behavior due to increased production of fines. This is to be expected for two reasons. The homogeneous decomposition has a higher activation energy than the CVD reaction and is favored at higher temperatures. At the same time bubble expansion is more drastic at higher temperatures and the gas bypassing problem is aggravated.

The effect of the  $f_{jb}$  factor on FBBR performance is illustrated in Table 2. At higher rates of jet-emulsion exchange the CSTR performance is approached. Unfortunately, there is no reliable model for the grid region based on which the exchange coefficients could be accurately estimated. However, the results indicate the importance of grid design and gas-solid contacting in the grid region on reactor performance. It can be shown that increased residence time in the jets, large jet-emulsion exchange coefficients are all beneficial to good performance and suppression of fines.

The FBBR model can be modified by a more physically realistic description of the bed hydrodynamics which considers the bubble behavior to vary along the bed and with the operating conditions, i.e. with the gas superficial velocity. This is the so called Cells-in-Series model. Table 3 shows the product comparison between these two models. The refined model can converge to certain values when increasing the number of cells. We can estimate the  $f_{jb}$  value for the FBBR model by matching the results with the new model. Since the refinement is constructed by using a detailed bubble distribution, the improvements can only be good when reliable correlations are used for bubble behavior, e.g. bubble size, bubble void fraction, and bubble rise velocity.

Table 1. Comparison of the CSTR and FBR Model Predictions and Experimental Results for Two JPL Runs

	Silicon Seed		Experimental Conditions			
	Weight (Kg)	$\bar{d}_p$ ( $\mu\text{m}$ )	Silane Concn. (%)	Bed temp. ( $^{\circ}\text{C}$ )	Total gas flow rate (moles/min)	Duration (min)
Example 1 (Run 1)	10.50	227	20	650	3.0	90
Example 2 (Run 2)	11.34	212	80	650	2.5	173

PRODUCT COMPARISON

	Experimental Data		Model Predicted (CSTR)		Model Predicted (FBR)	
	Production rate (Kg/hr)	$\bar{d}_p$ ( $\mu\text{m}$ )	Production rate (Kg/hr)	$\bar{d}_p$ ( $\mu\text{m}$ )	Production rate (Kg/hr)	$\bar{d}_p$ ( $\mu\text{m}$ )
Example 1 (Run 1)	0.87	235.5	1.00	237.4	0.91	236.5
Example 2 (Run 2)	3.50	241.5	3.34	260.2	2.68	253.0

Reactor Specifications: Bed diameter 15.4 cm (6.065" I.D.); Number of orifice holes in distributor: 4,500.

Orifice area: 0.02 cm<sup>2</sup>; Distributor temperature: 200°C; Entering gas temperature: 200°C.

Table 2. Comparison of the FBR Model at Different Levels of Jet-Emulsion Exchange and the CSTR Model. (Run 1: 20% SiH<sub>4</sub> in the feed)

	FBR			CSTR
	$f_{jb}=10$	$f_{jb}=50$	$f_{jb}=100$	
Silane Conversion (%)	99.50	99.21	99.15	99.04
Fines Elutriation (%)	30.9	8.1	1.6	0.0
Deposition Rate (kg/h)	0.696	0.922	0.986	1.002

Table 3. Product Comparison Between Different Hydrodynamic Behaviors of Fluidized Bed Model. (Run 1: 20% SiH<sub>4</sub> in the feed)

	Modified Two-Phase Model		Cells-in-Series Model	
	$f_{jb}=10$	$f_{jb}=50$	N=5	N=10
Silane Conversion (%)	99.6	99.2	99.9	99.9
Fines Elutriation (%)	34.9	6.9	14.7	12.3
Deposition Rate (kg/h)	0.66	0.93	0.86	0.89

3. Investigate the maximum packing density of rods. Perform a parameter sensitivity study and optimize the decomposer operating condition.
4. Design an experiment in a tubular reactor to determine the conditions of  $\text{SiH}_4$  pressure and temperature at which homogeneous nucleation occurs.

### C. Research Accomplishments

Preliminary work has been done in the past nine months. The thermodynamics and kinetics of silane pyrolysis have been reviewed and studied. A first order CVD reaction and a first order reversible reaction as well as homogeneous nucleation theory have been incorporated into the reactor model. A computer program has been developed for solving the model equations which include all mass transfer and heat transfer equations and a stiff ordinary differential equation arising from the AC current heating of the rod. Eddy current effects of alternating current have been studied for different frequencies and different rod diameters at various surface temperatures. Figure 1 and Figure 2 illustrate these effects, i.e. the higher the relative frequency is, the more current will flow near the rod surface, the more uniform temperature distribution is inside the rod. Therefore, high frequency is preferred because it prevents the hot spot in the center of the rod.

The high temperature mass transfer limitation on reaction rate is explained by the model. The percentage of mass transfer resistance is illustrated in Figure 3 as a function of the  $\text{SiH}_4$  molar fraction in the feed. All important operating variables such as inlet composition, rod surface temperature, flow rate, etc., are related to the growth rate, conversion of silane, exit gas temperature as well as to the homogeneous nucleation rate. The conversion as function of growth rate and rod temperature is shown in Figure 4. It can be seen from this figure that

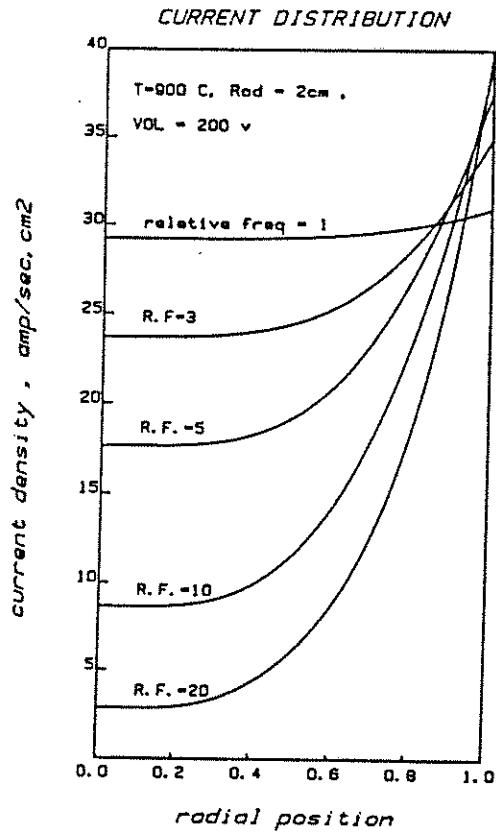


Figure 1. Current Density Distribution as a Function of Relative Frequency.

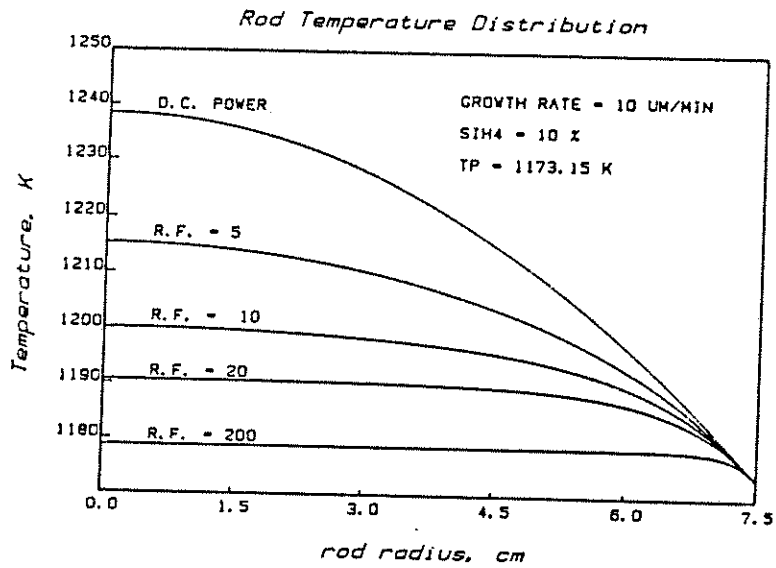


Figure 2. Radial Temperature Profile in a Silicon Rod as a Function of Relative Frequency.

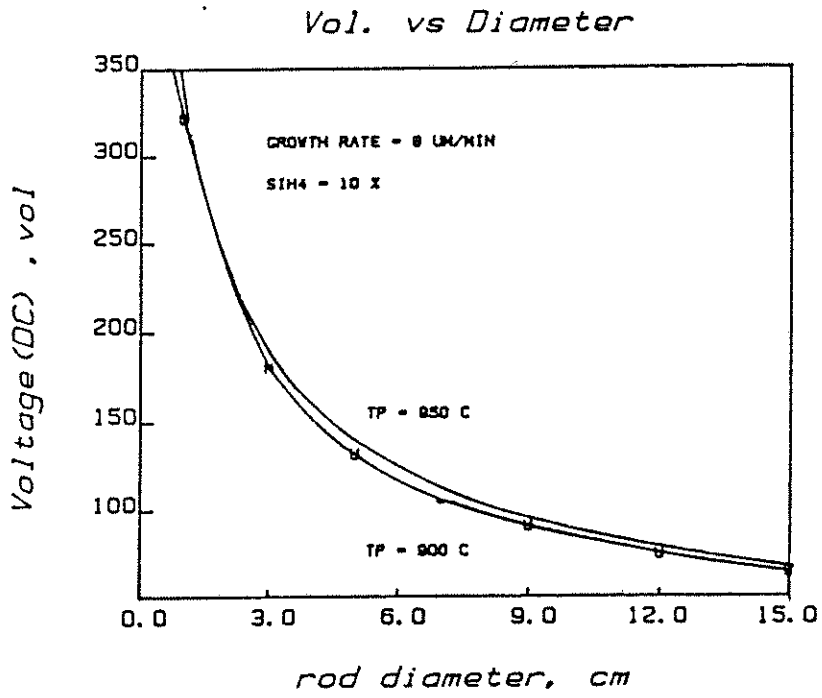


Figure 5. Required Voltage for Desired Surface Temperature.

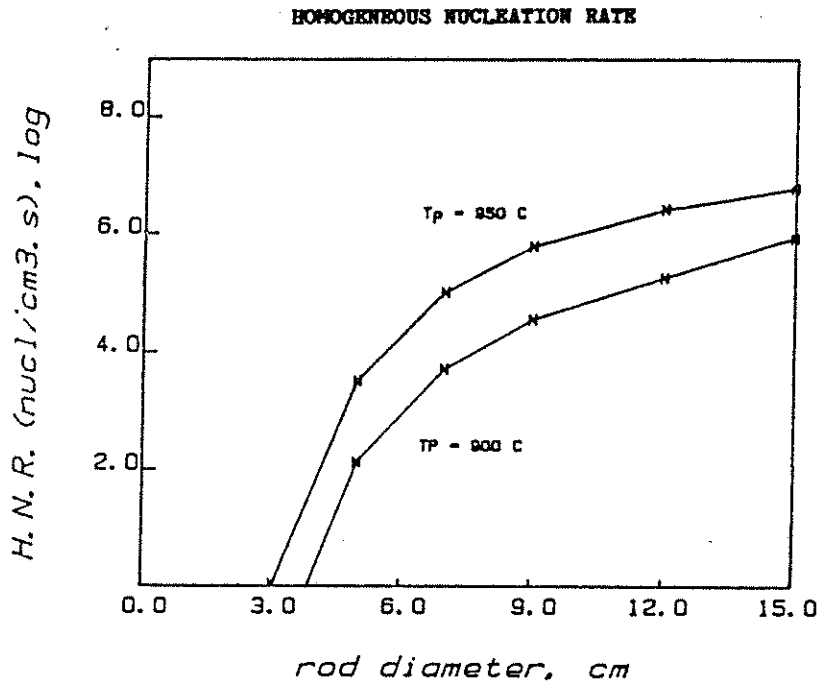


Figure 6. Homogeneous Nucleation Rate.

2. A pressure-temperature stability equation as a function of humidity exposure, has been developed which identifies the resin pressure values for each temperature below which void growth is possible and above which voids cannot grow but rather tend to collapse.
3. A generalized three-dimensional model and attendant computer code for resin flow during composite processing has been developed. The model is based on a theory of consolidation and flow through a porous medium, which considers that the total force acting on a porous medium is countered by the sum of the opposing forces, including the force due to the spring-like effect of the fiber network and the hydrostatic force due to the pressure of the liquid within the porous medium. The flow in the laminate is described in terms of Darcy's Law for flow in a porous medium, which requires a knowledge of the fiber network permeability and the viscosity of the flowing fluid. Unlike previous resin flow models, this model properly considers the flows in different directions to be coupled and provides a unified approach in arriving at the solution. Comparison of numerical solutions with the closed form analytical solution, which is obtainable for some simple test cases, shows good agreement. Comparison of predicted results for the resin mass loss and the average final thickness per ply with experimentally determined values shows good agreement.
4. Finally, combining the model for void growth with the models for transport of void and resin (which incorporates resin kinetic and viscosity models), guidelines are proposed for the selection of an optimum autoclave cure cycle.

discs), even though the overall geometry is the same, vastly different hydrodynamic regimes are encountered.

The effect of the hydrodynamics on certain electrochemical reaction pathways has been investigated (1,2) and has been shown to be a crucial step in obtaining desired yields and efficiencies. In addition, from economic indicators (3,4), electrochemical processes are becoming more competitive with existing, more conventional routes, even without rigorous reactor design considerations. If relationships between hydrodynamics regime and cell performance could be quantified, the electrochemical synthesis may become the preferred route. Therefore to exploit the electrochemical pathways and hopefully to popularize the electrochemical applications, an important component is to develop a (semi) quantitative electrochemical reactor model. The model would have to include effects due to:

1. Convection
2. Diffusion
3. Electric field
4. Electron-transfer reactions
5. Homogeneous chemical reactions

#### B. Research Objectives

1. Solve the velocity profiles for the three cells.
2. Solve the convective-diffusion of tracer for bulk and wall-generated inert tracer (this will provide a meaningful commentary on the overall mixing characteristics of the system).
3. Construct an electrochemical reaction model, including all of the above listed phenomena: convection, diffusion, migration, heterogeneous/homogeneous reactions) based on dilute solution theory.

4. Develop simplified models for the inert tracer problem as well as for the overall electrochemical model.

#### C. Research Accomplishments

The velocity profiles were solved for assumed steady state flow in the capillary gap cell and the rotating electrolyser for Reynolds number at 100 and a Taylor number ( $\alpha = a (\omega/\nu)^{1/2}$ ) of 7 in the co-rotational case. The pump cell solution experienced convergence problems and work is continuing to resolve them.

From the numerical results to date time dependent phenomena seem probable (5,6,7) and therefore to investigate higher Reynolds number a transient code must be constructed. These time dependencies are apparent for all three cell types.

Once the velocities are available, the convective diffusion of inert tracer may be solved, assuming a decoupled system; the Peclet number is about  $10^5$  and therefore this approach should introduce very little error. This was done for the Capillary Gap cell and the Rotating Electrolyser for both bulk and wall-generated tracer. The main information available from these two simulations pertained to interelectrode mixing: the wall generated tracer remained in the immediate region of the electrode in the co-rotational case, whereas greater mixing was observed in the stationary case. These results are supported by the observed axial velocity profiles. The same program can then be used for the pump cell once the velocities are available.

The general electrochemical reactor model (disc geometry) has been coded and is presently being debugged and tested. This model results in a set of nonlinear partial differential equations which are solved using orthogonal collocation in the z direction and standard integration in r.



#### D. Future Research Plan

Within the next four to six months the following will be accomplished:

1. Transient Navier-Stokes solution will be obtained.
2. General Electrochemical Reactor model will be completed and applied to simple competing reaction systems (oxidation of styrene, methoxylation of Furan).
3. Gas evolution effects will be investigated and possibly incorporated (in a pseudo-homogeneous manner) into the reactor model.

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number of experiments unless experimental results are interpreted through an appropriate model of the system. The problem of calculating the temperature profile in the crystal is coupled with the temperature profiles in the melt, and hence, a complete analysis of the system (crystal + melt) is necessary. The temperature profile in the melt is in itself coupled with the flow field due to the interaction of forced and natural convection. Further complexity arises due to the fact that the melt crystal interface as well as crystal growth rate cannot be fixed a priori and are determined as part of the solution.

#### B. Research Objectives

1. To develop a complete model and an efficient algorithm for the CZ process to predict the temperature distribution in the crystal including the interface shape and the growth rate.
2. To develop simple models for the CZ process which can be used on-line to control the crystal growth process.
3. To investigate the effects of jet cooling on the CZ growth.
4. To develop software using finite element analysis to calculate thermal stresses in the crystal of proper geometry, i.e., nonplanar interface shape, neck and shoulder portion. The predicted temperature field will be used directly to calculate the thermal stresses.
5. To develop an algorithm for the transient simulation of the CZ process and develop new strategies for the control of both diameter and the interface shape. Investigations will also be made to control the entire thermal history of the growing crystal.

#### C. Research Accomplishments

A computer model has been developed for the calculation of temperature field in the crystal and the melt including the crystal-melt interface

### Project III.3. Simulation of Temperature Distribution in Crystals

#### Grown by Czochralski Method

##### A. Problem Definition

The Czochralski process (CZ) is one of the most important methods for the growth of single silicon crystals. The crystal growing apparatus consists of a quartz crucible, a graphite heater, and a graphite susceptor assembly. In the CZ process, pure polycrystalline silicon and dopant materials (e.g., boron, antimony, etc.) are placed in a crucible and heater is turned on. A molten bath is thus established and then a single crystal seed of the appropriate crystallographic orientation is contacted with the melt. At this point, the melt temperature and the pulling rate are manipulated to grow a good quality crystal of a desired diameter.

The position and shape of the crystal-melt interface during the growth process and the temperature distribution in the crystal are important factors in determining the crystal quality. Adverse thermal gradients may result in crystal-melt interface instabilities or in excessive thermal stresses leading to poor quality of the crystal. Thus, heat transfer plays an important role in the growing process and control of thermal gradients greatly influences the overall process performances. The heat transfer process in the CZ process is affected by many variables such as:

- i) geometric variables including crucible shape, enclosure shape, heater position and shape, etc.
- ii) controllable operating variables such as pulling rate, crystal rotation rate, crucible rotation rate, gas flow rate, etc.
- iii) process variables such as melt depth, crystal diameter, etc.

Due to the complex interaction among these variables their inter-relationship cannot be understood in a quantitative sense through any

and the growth rate. The heat transfer in the melt is assumed to be by conduction only. The model accounts for the detailed direct and reflected radiation heat transfer among the various 'surfaces' present in the pulling apparatus. The model was extensively used for investigating the effects of various process parameters on the growth rate and the interface shape (1).

The detailed analysis of the radiative heat transfer requires the knowledge of configuration view factors between the various surfaces. The closed form expressions for the view factors are not available in the literature for the short crystal lengths, i.e., when the crystal top is within the crucible. The procedure for calculating the view factors during this initial stage of growth was developed and has also been submitted for publication (2).

Based on the analysis of the results obtained from the aforementioned detailed model, simple models have been proposed. These simple models establish a direct relationship between the important process and operating variables affecting the CZ process. The important variables describing the CZ process are the growth rate ( $v$ ), the crucible temperature ( $T_c$ ), the melt level ( $h$ ) and the height of the exposed portion of the crucible wall ( $h_c$ ). For the crystal of radius  $R$ , the growth rate is given by

$$v = \frac{A}{R} - \frac{h_c \Delta t}{R} - \frac{C\Delta T}{h} \quad (1)$$

where  $\Delta T = T_c - T_m$ ,  $T_m$  is the melting point of the silicon.

$A$ ,  $B$  and  $C$  are empirical constants and can be determined from the experimental data or from the results obtained from the rigorous model. The interface shape is characterized as follows:

$$\begin{aligned}\Delta r &= z(r=0) - z(r=R) \\ &= z_{\text{center}} - z_{\text{edge}}\end{aligned}\tag{2}$$

In terms of  $\Delta r$  the equation for the interface in the form of a parabola can be written as follows:

$$z_I(r) = \Delta r \left[1 - \left(\frac{r}{R}\right)^2\right]\tag{3}$$

It is shown that at constant crucible temperature ( $T_c$ ), the relationship between  $\Delta r$  and  $R$  is as follows:

$$\Delta r = C_1 R - C_2 R^2 \quad (\text{constant } T_c)\tag{4}$$

Similarly at constant crystal radius  $R$ , the effect of changes in the crucible temperature on the interface shape can be described by the following relationship:

$$\Delta r = a - b\Delta T \quad (\text{constant } R)\tag{5}$$

where

$$\Delta T = T_c - T_m$$

$C_1$ ,  $C_2$ ,  $a$  and  $b$  are empirical constants.

The detailed results are presented in a recently published article (3).

The concept of cooling the crystal in the vicinity of the crystal-melt interface by means of a gas blowing jet was investigated. The idea is to increase the growth rate and further control the crystal diameter or interface shape by manipulating the gas velocity through the jet. It was discovered that both the crystal diameter and the interface are more stable in the presence of jet cooling and moreover an additional degree of freedom (manipulated extent of jet cooling by changing the gas velocity) is now available to facilitate a simultaneous control of crystal diameter and the interface shape [4].

#### D. Future Research

1. To develop software using finite element analysis to calculate thermal stresses.
2. Investigate transient effects in the CZ growth and develop new strategies for the global control of CZ grown crystals.

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Project III.4. Simulation of the Hydrodynamics, Heat and  
Mass-Transfer in the Czochralski Process

A. Problem Definition

Single crystals of silicon with uniform electrical properties are needed for many electronic and photovoltaic applications. To achieve uniformity, dopants must be evenly distributed within the crystal, and contaminants must be kept below prescribed levels. Additionally, a low density of structural defect (dislocation) is required.

A large majority of the single crystal silicon used in the semiconductor industry is grown by the Czochralski (CZ) process. In this process a single-crystal, cylindrical ingot is grown from a melt which is held in a quartz crucible. Crucible and dopants are added to the melt before growth begins. Crystal can be rotated to favorably effect the hydrodynamics. Uniform diameter crystals can be obtained by adjustments in the heating rate of the melt or in the pull rate of the crystal. Slow corrosion of the crucible walls by the molten silicon will introduce contaminants (mainly oxygen) into the melt, which can subsequently be incorporated into the crystal.

An improved knowledge of the hydrodynamics, heat and mass-transfer in the CZ process would be of great use for optimization of the process. Scant experimental data are available in the open literature for this system due to the harshness of the molten silicon environment. Experiments are also expensive due to the high cost of materials and to the large amount of time required to grow the crystals (typically 1-2 days). For this reason, the value of a numerical simulation of the process becomes obvious.

## B. Research Objectives

The purpose of this work is to develop rigorous computer models to predict the hydrodynamics, heat and mass-transfer during the CZ process. The model for heat-transfer in the crystal has already been developed (see, 84-85 report), and is in a form where it can easily be coupled with a simulation for the melt to obtain an overall model for the process.

The goals of the present work are therefore:

1. Develop a program to solve for the hydrodynamics and heat-transfer in the melt.
2. Couple the above code with the existing program for the crystal to obtain a full simulation of the process.
3. Develop rigorous mass-transfer models for the transport of dopants, oxygen and carbon in the melt.
4. Investigate the effect of an applied magnetic field on the transport phenomena in the melt.
5. Determine favorable operating conditions for crystal growth through parametric studies with the rigorous models.
6. Using the results of the rigorous mass-transfer model, develop simple correlations relating the final dopant and impurity distributions in the crystal to the operating conditions and system geometry.

## C. Research Accomplishments

A preliminary finite element code was developed and verified by comparison with a commercially available package for solving fluid dynamic problems by the finite element method (FIDAP). FIDAP was also used to determine that the steady-state code is generally inadequate for simulating practical growth conditions, as the solution is often oscillatory.



Four individual flow mechanisms were isolated and the resulting flows are shown in Figures 1-4. The lines shown within the melt are streamlines, which correspond to the individual fluid particle paths in the case of a steady-state flow. Positive values of the stream function correspond to a counter-clockwise flow, and negative values to a clockwise flow. Each flow mechanism is briefly described below.

Figure 1 depicts the flow resulting from natural convection. Hotter fluid rises at the heated crucible wall and cooler fluid descends beneath the crystal.

Figure 2 represents the flow pattern associated with rotating the crystal. The fluid is accelerated radially outward by the rotating crystal, and drawn up from the center of the melt to conserve mass. Note that the flow is much stronger at the top surface of the melt than elsewhere within the crucible.

Figure 3 shows the flow resulting from rotation of the crucible. Fluid is accelerated radially outward at the crucible bottom, causing a counter-clockwise vortex to form. This vortex has a greater extent than that observed from crystal rotation.

Figure 4 illustrates thermocapillary flow or the Marangoni effect. The temperature difference across the melt free surface produces a surface tension gradient. Fluid at the surface flows from region of low surface tension (the hot crucible wall) to regions of higher surface tension (the cooler crystal). A counter-clockwise vortex develops.

#### D. Future Research Plan

The existing finite element code for the melt will be coupled with the program for the crystal to obtain a full simulation of the process. A finite element program to simulate the mass transfer in CZ

melts will be developed. Case studies will be performed to find favorable operating regimes for crystal growth, and to obtain rigorous results for use in developing simple mass-transfer models.

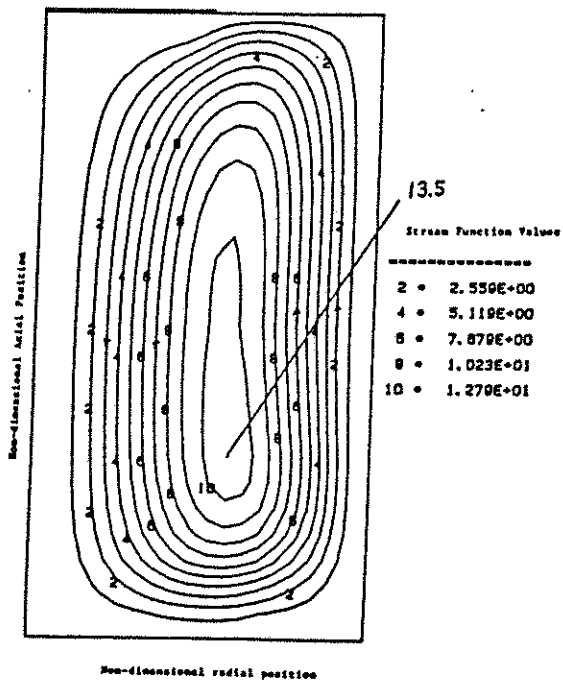


Figure 1. Natural Convection  
GR = 20,000

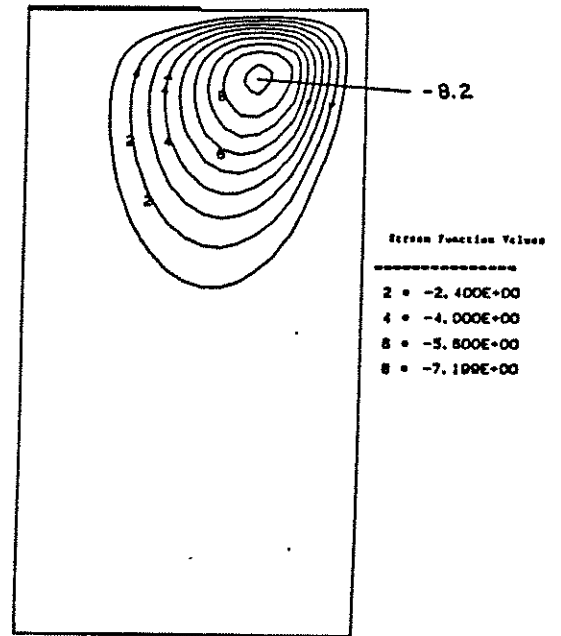


Figure 2. Crystal Rotation,  
Re = 200

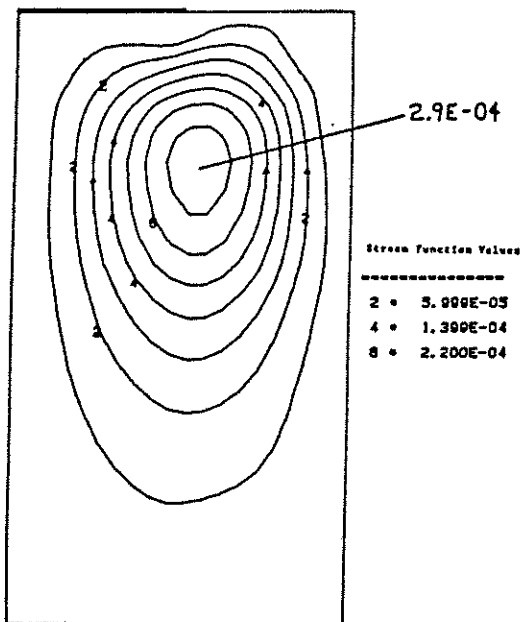


Figure 3. Crucible Rotation,  
Re = 1

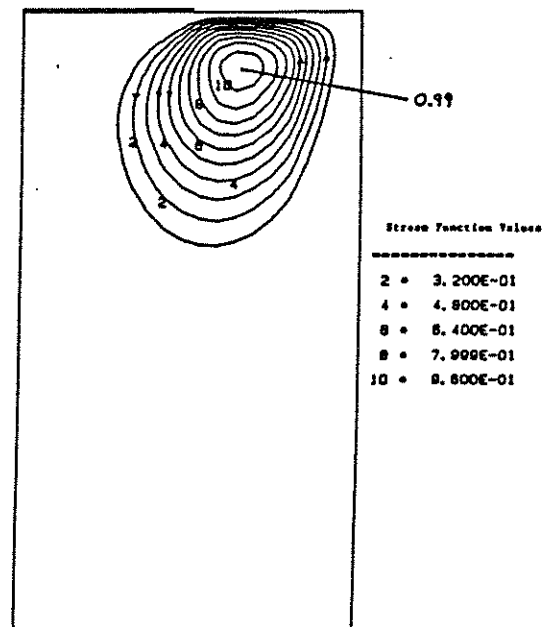


Figure 4. Thermocapillary Flow

## Project III.5. On-Line Optimization of Chemical Processes

### A. Problem Definition

The escalating costs of raw materials and energy have increased the incentives for operating chemical plants at their optimum efficiency. Due to changing process variables and market conditions it is necessary to continuously revise the processing conditions to maintain peak efficiency. Current strategies, based upon steady state models, are limited by the inherent transient nature of the problem and the lack of adequate process models. New approaches proposed in the literature consist of identifying an adequate process model, using on-line data and then using these models to compute the optimum operating conditions. The problems here are related to the large dimensionality and nonlinearity of the process models.

### B. Research Objectives

The objectives of this research are:

1. Develop methodology to solve the problem of on-line identification and optimization of integrated chemical process systems.
2. Build an experimental facility to study the on-line optimization of ethylene-oxidation.
3. Implement and test on-line estimation and control strategies on the experimental reactor system.
4. Based on experimental results suggest suitable modifications to the algorithms and test them on simulated industrial scale systems.

### C. Research Accomplishments

#### 1. Steady State On-line Optimization:

For fast processes, steady state control strategies are useful. The control algorithm termed the Two-Phase Approach has been applied to a simulated ethylene oxide reactor [1]. Fig. 1 shows that optimal steady

states of this system can be found using this approach.

## 2. Dynamic On-Line Optimization:

As the two-phase approach is applied to slow processes, the following dynamic algorithms are proposed:

- i) use the very recent data to update the process model,
- ii) use the updated model to find the new optimal operating state,
- iii) the manipulated variables should be varied in such a way that the process can reach the new operating state as soon as possible,
- iv) the period taken into account cannot be too long so that the effect of disturbances can be considered in time,
- v) on-line identification and on-line optimization work in tandem.

This dynamic algorithm has been applied to a two-CSTR system [2].

Fig. 2 shows that this method can successfully track optimal operating conditions under the effect of different concentration of the reactant in the feed stream. The on-line identification algorithm, we proposed, has been compared with a well-known on-line estimation method - Kalman Filter Theory [3]. We found that the Horizon Search, our algorithm, is superior to the extended Kalman Filter. The result is shown in Fig. 3. On the regulatory level, once again, the Two-Phase approach works much better than other on-line schemes as we applied this algorithm to control a one-CSTR system [4]. A good comparison is shown in Fig. 4.

Currently, we are using the Two-Phase Approach to control a simulated industrial scale binary distillation column. Preliminary results show that this approach is a good strategy to bring down the operating cost and simultaneously satisfy operating constraints (compositions of both top and bottom products are greater than 0.95) as shown in Figure 5.

#### D. Future Research Plan

We will continue our work on the binary distillation column example. In the future, this approach will be extended to control of a multi-component column.

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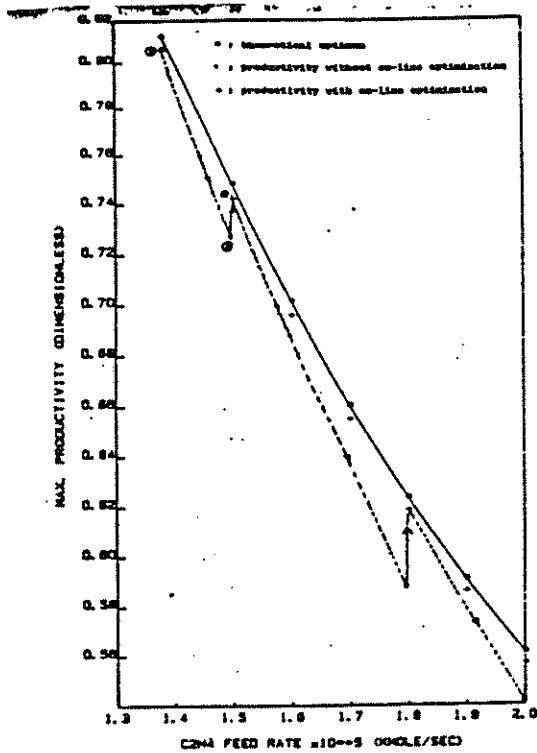


Figure 1. Maximum Productivity vs:  $C_2H_4$  Feed Rate

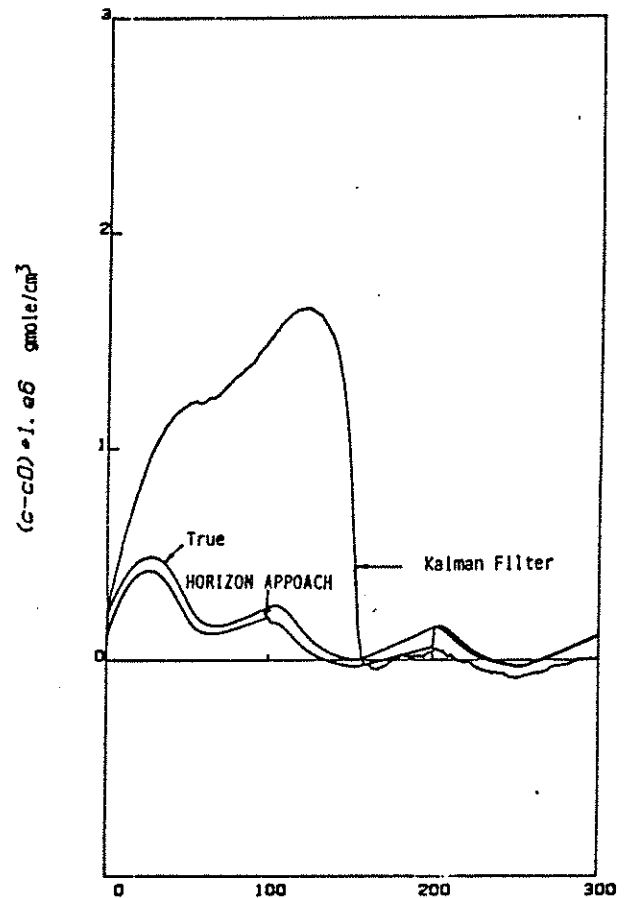


Figure 3. Simultaneous Estimation of  $C, T, \alpha$  Noisy Measurements of  $T$ .

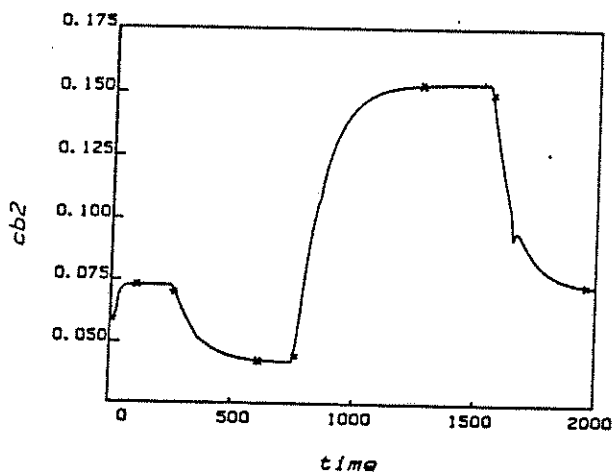


Figure 2. Tracking of the Optimum in Presence of Constantly Changing Input Disturbance. Points at which On-line Optimizer is Turned On or Off are Shown with an x.

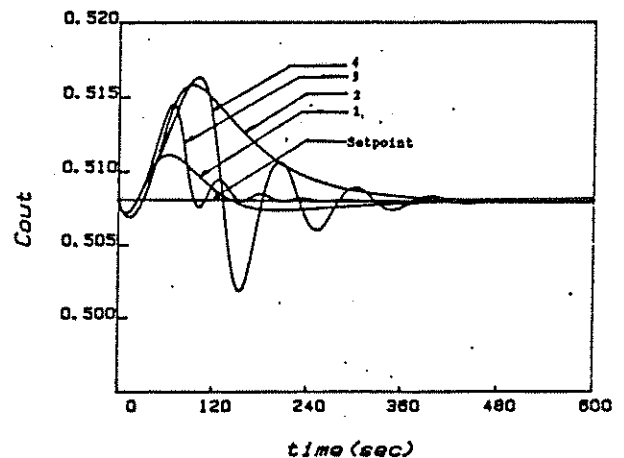


Figure 4. Comparison of Different Control Strategies on the Regulatory Control of the CSTR Example (1: Two-Phase Approach, 2: PID, 3: Adaptive (Self-Tuning) Control  $n=3, m=5, b_0 = -0.5, \lambda=0.95$ , 4: Adoptive Control,  $n=3, m=2, b=4, b_0 = -0.8, \lambda=0.97$ ).

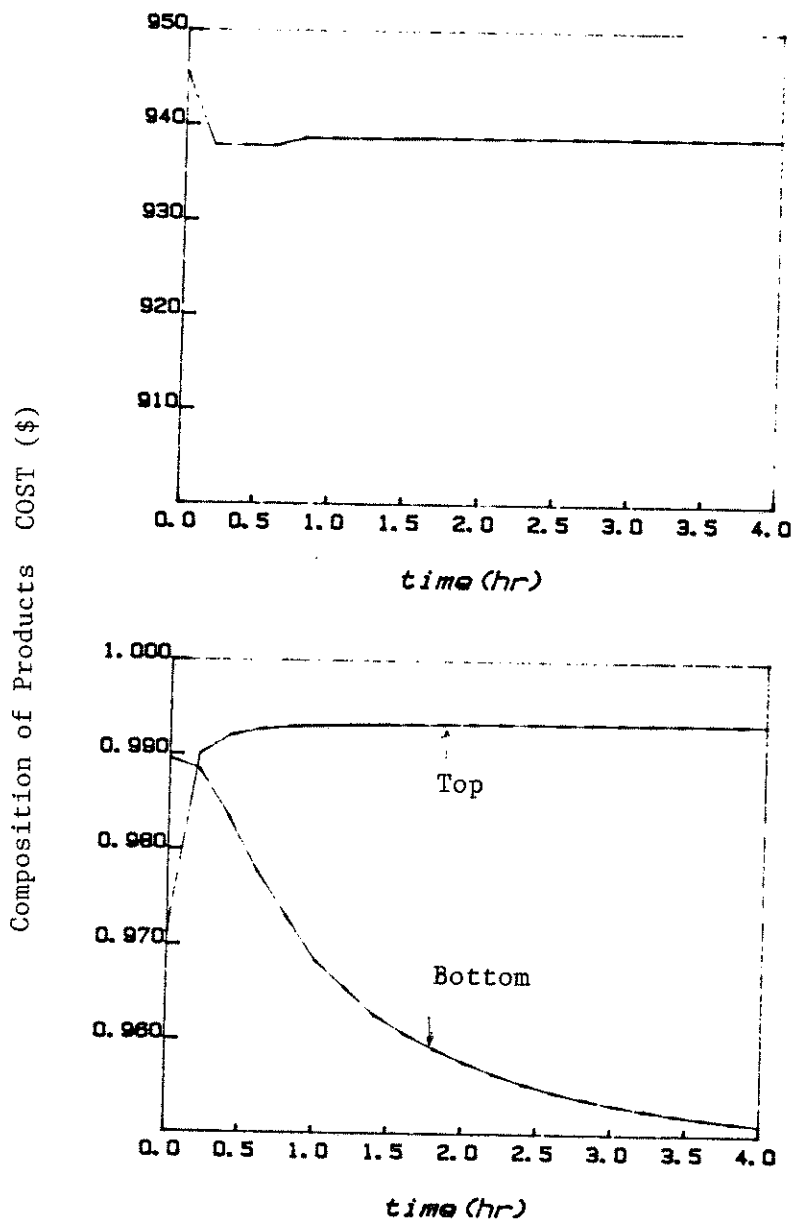


Figure 5. On-Line Optimization Control of Benzene-Toluene Distillation Column.

$$(\text{Cost} = \int_0^T Q dt, C_b, C_t \geq 0.95)$$



## Project III.6. Modeling Plasma Effects in Deposition Processes

### A. Problem Definition

A glow discharge plasma can be defined as a region of relatively low pressure and low temperature gas in which a degree of ionization in a quasineutral state is sustained by the presence of energetic electrons. When an electric field is applied to an ionized gas, energy is transferred more rapidly to the electrons than to the ions. Furthermore, the transfer of kinetic energy from an electron to a heavy particle (atom, molecule, or ion) in an elastic collision is proportional to the electron-to-heavy particle mass ratio and therefore very small ( $\sim 10^{-5}$ ). Consequently, at low pressures (low collision frequency) the free electrons can accumulate sufficient kinetic energy as that they have a high probability of producing excitation or ionization during the collisions that they make with the heavy particles. The production of these excited species, and their interactions with surfaces and growing coatings, is the reason that low pressure glow discharge plasmas are assuming an ever-increasing role in micro-electronic fabrications, optic fibers, and materials processings. Some of the advantages of plasma enhanced deposition processes are: low temperature of the gas which avoids excessive heating of the substrate, heterogeneous reactions on the walls which minimizes soot formation, and the ease of process control.

Even though the kinetics of plasma processes can greatly be enhanced, (due to the fact that reactions of excited species have lower activation energy) the complex environments in a plasma reactor are far from being well understood. To date there are no quantitative models that predict the reaction performance as a function of operating and design variables. There is a need to develop fundamental models to describe these phenomena. For this both, plasma physics and plasma chemistry, need to be put together.

## B. Research Objectives

The aim of this study is to investigate the plasma enhanced chemical vapor deposition and the plasma sputtering processes. The objectives are:

1. Start with a simple diffusion-convection model of zero order generation of active species. Electric field is implicitly incorporated within the kinetic rate constant. In this manner the plasma chemistry and plasma physics are decoupled.
2. Add the effect of migration due to electric field to predict the local electron concentrations and electron energies distribution. This will achieve the necessary coupling of the plasma physics with the chemistry.
3. Apply the above models to practical systems such as production of amorphous silicon, production of optical fibers, etc.

## C. Research Accomplishments

The work has been underway for a short time. A simple model for the mass transfer analysis of zero order generation of active species followed by wall deposition was derived. The plasma reactor is modelled in three zones: a central zone with electron impact dissociation, diffusion and convection and two lateral zones with only diffusion and convection. The generation term,  $R_A$ , is a function of electron density and electron temperature.

Zones I and III

$$0 = \left[ \frac{\partial^2 C}{\partial z^2} + \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right] - V_z(r) \frac{\partial C}{\partial z}$$

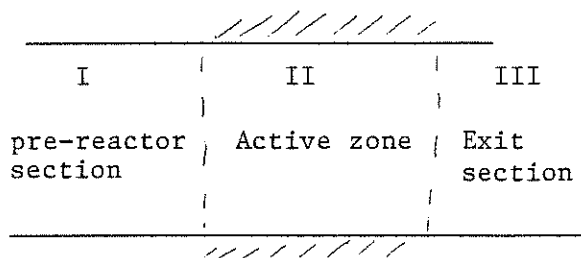


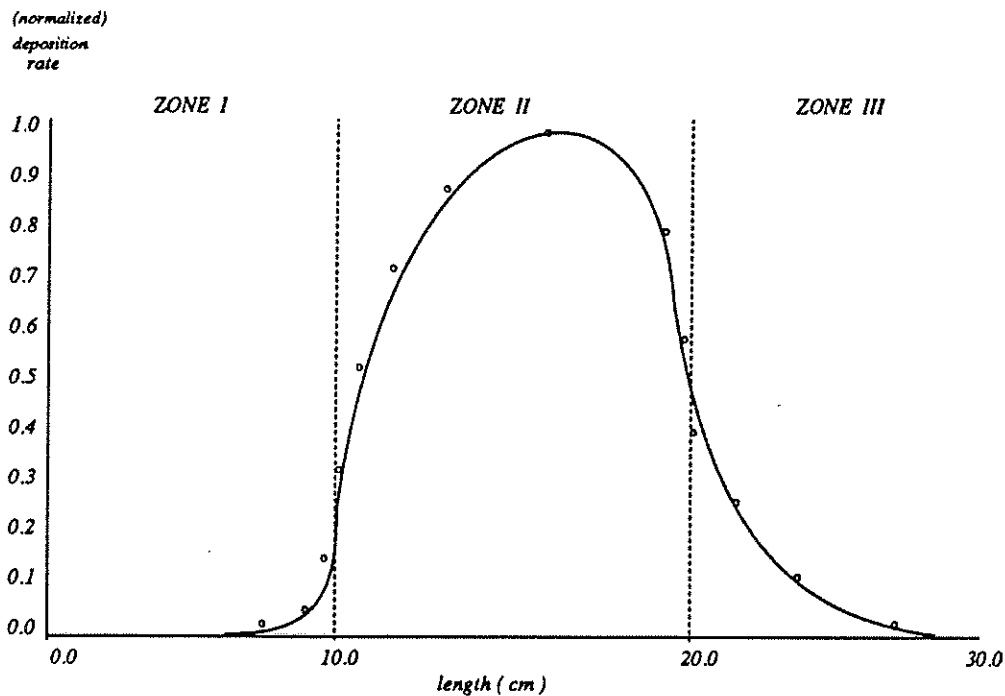
Figure 1. Plasma Reactor

Zone II

$$\left[ \frac{\partial^2 C}{\partial z^2} + \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right] - V_z(r) \frac{\partial C}{\partial z} = R_A$$

where  $R_A = f$  (electron concentration) =  $f$  (power, operating parameters)

With this model we are able to explain the deposition profiles of some industrially important species such as silicon nitride films obtained from a gaseous mixture of  $\text{SiH}_4$  and  $\text{N}_2$ ,  $\text{SiO}_2$  films or amorphous silicon by glow discharges in  $\text{SiH}_4$ . Both analytical and numerical results have been obtained. Numerical results are necessary when  $R_A$  depends in a non-linear manner on a precursor concentration and when the electron concentration profiles are not constant in the reactor.



Zones I and III - generation of active species

Zone II - active plasma zone.

Figure 2. Shows the position profiles predicted by simple mass transfer model. The open circles represent experimental results of Turban and Catheine (J. Thin Solid Films 48, 57, 1978) for deposition of silicon nitride.

By moving the reaction zone, a uniform deposition along a length of interest can be obtained and this procedure is used in plasma assisted

production of optical fibres. Strategies for process control and film thickness control can be accomplished by using a detailed model of the process which will be developed. The modelling of a DC discharge reactor has just been started. The model will consist of equations for electron and ion continuity, Poisson's equation for the self-consistent electric field, and an equation for the electron energy.

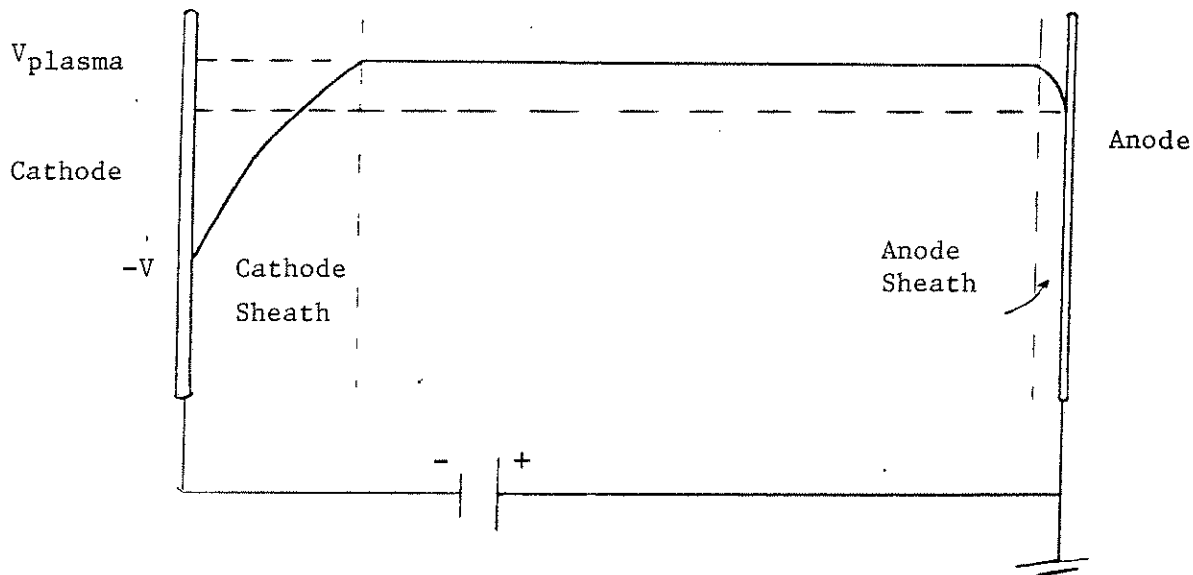


Figure 3. Voltage distribution of a DC glow discharge in a sputtering process.

#### D. Further Research Plan

In the next few months the complete set of equations pertaining to electron and ion distributions, electron energy and field strength will be solved for a DC discharge with application to sputtering. The results will then be compared to some experimental data available. The analysis of the tubular plasma reactor will be strengthened by incorporating the field equations.

### CURRENT FUNDING

The external support of the laboratory during the period covered in this report (June 1, 1985 through May 31, 1986) was derived from various sources.

Industrial participation fees supported the research in all areas and amounted to \$120,000.

Modeling of silane pyrolysis in fluidized bed reactors and associated work were supported by the last continuation of the now expired JPL grant at \$34,000. (The total grant was for \$85,000).

Modeling of CZ growth was supported by the 2nd year continuation of the JPL grant at \$55,000/year and a newly initiated EPRI contract for \$210,428/three years.

Proposals are pending in a variety of areas with NSF, DOE and DARPA.

## CURRENT STAFF

During the period covered by this report (June 1, 1985 through May 31, 1986) the following individuals have been associated with the various projects in the laboratory.

### A. Faculty

Dr. Milorad (Mike) Dudukovic, Professor and Director

Dr. Babu Joseph, Associate Professor (on sabbatical at UC-Berkley 85/86)

Dr. P. A. Ramachandran, Associate Professor

Dr. R. Srivastava, Research Associate

Mr. C. Hwang, Visiting Scholar

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N. Devanathan

D. Dorsey

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S. S. Jang

S. Lai

J. Mehta

S. Munjal

K. Myers - Exxon Educational Foundation Fellowship Recipient

D. O'Connor - Shell Fellowship Recipient

S. Pirooz

B. Thomas - Monsanto Electrochemical Fellowship Recipient

Y. Yang

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P. L. Mills	Monsanto
B. L. Tarmy	Exxon

## PUBLICATIONS AND PRESENTATIONS

### A. PAPERS AND CHAPTERS

1. Chaudhari, R. V., M. G. Parande, P. A. Ramachandran, P. H. Brahe, H. G. Vadgaonkar and R. Jaganathan, "Hydrogenation of Butynediol to Cis-Butenedial Catalyzed by Pd-Zn-C<sub>2</sub>CO<sub>3</sub>; Reaction Kinetics and Modeling of a Batch Slurry Reactor", AIChE J. 31 (1985): 1891-1903.
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## B. PRESENTATIONS

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16. Myers, K., M. P. Duduković and P. A. Ramachandran, "Liquid-Phase Mixing in Churn Turbulent Bubble Columns", AIChE Annual Meeting, Chicago, November 10-15, 1985. Paper 98b.
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24. Thomas, B., P. A. Ramachandran and M. P. Duduković, "Simulation of Radial Flow Electrochemical Cells", AIChE One Day Symposium, St. Louis, April 23, 1986.

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b) Seminars

M. P. Duduković

Louisiana State University  
University of Arkansas  
University of Florida  
University of Pittsburgh  
University of Rochester

B. Joseph

UC - Berkeley  
UC - Santa Barbara

P. A. Ramachandran

Lawrence Livermore National Laboratory  
University of Waterloo (2)

C. THESES

Myers, K. J., "Liquid-Phase Mixing in Churn-Turbulent Bubble Columns".  
D.Sc. Thesis, Washington University, St. Louis, May 1986.



4. Develop simplified models for the inert tracer problem as well as for the overall electrochemical model.

#### C. Research Accomplishments

The velocity profiles were solved for assumed steady state flow in the capillary gap cell and the rotating electrolyser for Reynolds number at 100 and a Taylor number ( $\alpha = a (\omega/\nu)^{1/2}$ ) of 7 in the co-rotational case. The pump cell solution experienced convergence problems and work is continuing to resolve them.

From the numerical results to date time dependent phenomena seem probable (5,6,7) and therefore to investigate higher Reynolds number a transient code must be constructed. These time dependencies are apparent for all three cell types.

Once the velocities are available, the convective diffusion of inert tracer may be solved, assuming a decoupled system; the Peclet number is about  $10^5$  and therefore this approach should introduce very little error. This was done for the Capillary Gap cell and the Rotating Electrolyser for both bulk and wall-generated tracer. The main information available from these two simulations pertained to interelectrode mixing: the wall generated tracer remained in the immediate region of the electrode in the co-rotational case, whereas greater mixing was observed in the stationary case. These results are supported by the observed axial velocity profiles. The same program can then be used for the pump cell once the velocities are available.

The general electrochemical reactor model (disc geometry) has been coded and is presently being debugged and tested. This model results in a set of nonlinear partial differential equations which are solved using orthogonal collocation in the z direction and standard integration in r.

## Project III.2. Modeling of Radial-Flow Electrochemical Reactors

### A. Problem Definition

Of the many electrochemical cells which are in use, the parallel-plate cell has received much attention. However, even though the potential distribution is good and the mixing conditions can be altered to satisfy most requirements, the space time yield is less than adequate as is the energy efficiency. These concerns have incited the development of other cell designs, three of which are the capillary-gap cell, pump cell and the rotating electrolyser.

Figure 1

#### Capillary-Gap and Pump Cell

#### Configuration

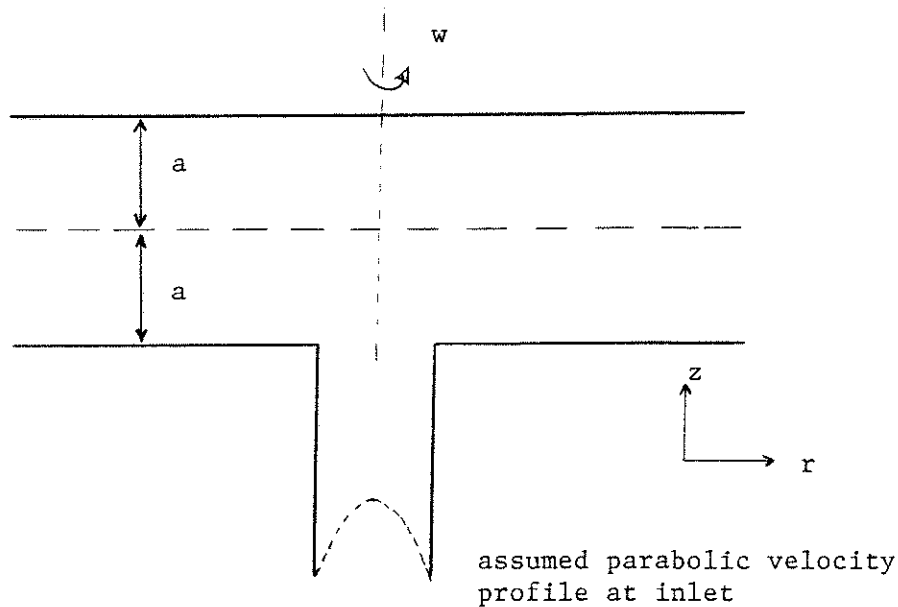


Figure 1 shows the form of these cells, they being two parallel discs with radial outflow. In the capillary-gap cell both discs are stationary whereas in the rotating electrolyser, both discs are rotated at the same speed. The pump cell has only one disc rotating. Due to the different rotational arrangements (stationary, single disc rotating, co-rotational

AREA III: NEW MATERIALS, MODELING AND CONTROL

Project III.1. Computer-Aided Processing of Thermosetting Composites

... automating the autoclave composite curing process could result in estimated savings of hundreds of millions of dollars over the next 20 years ....

Aviation Week & Space Technology

May 14, 1984

A. Problem Definitions

Fiber-reinforced epoxy resin composite laminates are used in cans, aircrafts, pipes, etc. The fabrication of composite laminates consisting of a thermosetting resin matrix is a complex process. It involves simultaneous heat, mass, and momentum transfer along with chemical reaction in a multiphase system with time-dependent material properties and boundary conditions. Two critical problems, which arise during production of thick structural laminates, are the occurrence of severely detrimental voids and gradients in resin concentration. In order to efficiently manufacture qualify parts, on-line control and process optimization are necessary, which in turn require a realistic model of the entire process.

B. Research Objectives

1. Develop a model that predicts conditions which lead to bubble formation and growth and verify experimentally.
2. Develop a quantitative model for the squeezing flow of resin. Determine the required model parameters by a set of independent experiments and check model validity against available data.

C. Research Accomplishments

1. A model and attendant computer code has been constructed to describe time-dependent void growth and stability for any processing cure cycle.

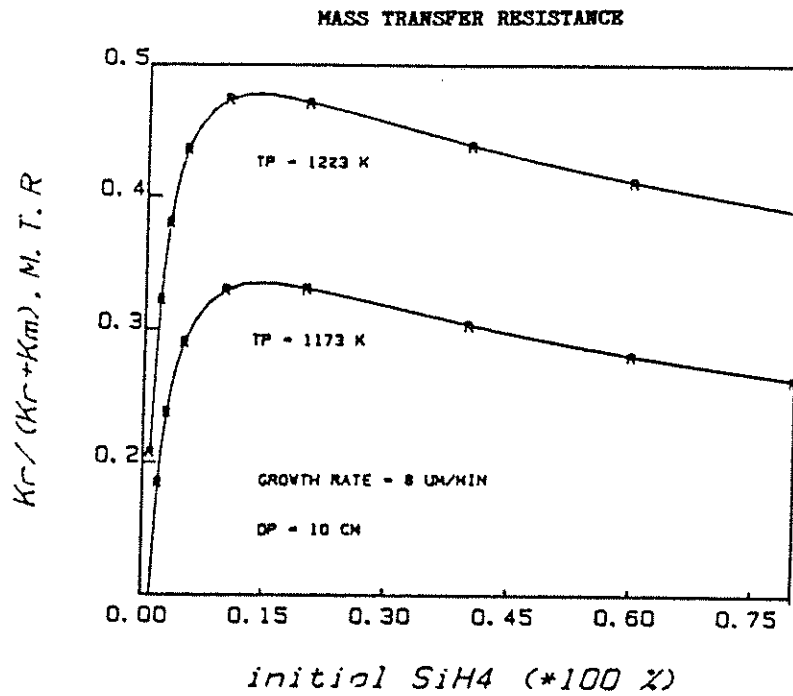


Figure 3. Fraction of Process Resistance due to Mass Transfer.

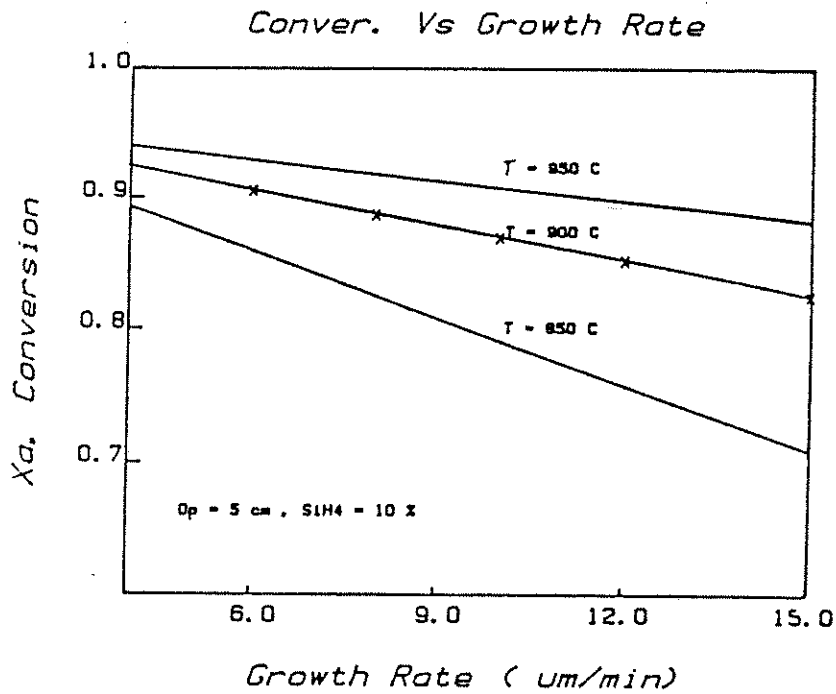


Figure 4. Silane Conversion as a Function of Growth Rate.



the operating temperature should be around 900°C and the growth rate 4 to 10  $\mu\text{m}/\text{min}$ . The voltage required, as a function of rod diameter, to keep the rod surface temperature constant is shown in Figure 5. Since the current resistance decreases and the heat loss increases as the diameter increases, the applied voltage needs to decrease almost exponentially. The homogeneous nucleation rate based on the classical theory as a function of rod diameter and surface temperature is plotted in Figure 6. Because the temperature in the gas phase increases very fast as the diameter increases, the strongly temperature dependent nucleation rate increases exponentially.

The results obtained from the model suggest as the optimal operating region the temperature around 900°C, growth rate from 4 to 8  $\mu\text{m}/\text{min}$  and the initial silane composition about 10%. These conditions are essentially in agreement with the Japanese patents' data.

#### D. Further Research Plan

1. Study the hydrodynamics in details for both the conventional and Japanese modified decomposers. Compile suitable literature correlations for various heat and mass transfer parameters.
2. Study the homogeneous nucleation from the kinetic point of view and CVD reaction in details through literature search. Modify the current model and do the magnitude analysis of different rate forms.
3. Compare the model results with the tubular experiments for the homogeneous nucleation rate and update the reactor model.

## Project II.2. Modeling of Siemens Decomposers for Production of Bulk Silicon

### A. Problem Definition

Siemens decomposers have been traditionally used for more than two decades in industry for production of bulk polycrystalline semiconductor grade silicon. From this material single crystal silicon is grown by Czochralski's method or by the float zone method. The process is a gas-solid reaction on a silicon rod which leads to formation of a solid film, i.e. chemical vapor deposition (CVD). Very pure compounds of silicon such as chlorosilane and silane are reacted on electrically heated seed silicon rods. Ultra-pure silicon is slowly deposited on a cherry red rod, that grows up from about 6 mm to 150 mm in diameter at the speed of 4 to 15  $\mu\text{m}/\text{min}$ . This is a high temperature, slow, semi-batch process and the product of polysilicon is expensive, which is primarily due to the large amount of energy consumption.

While numerous experimental studies have been reported, modeling work seems to be far behind mainly because the hydrodynamics and reaction kinetics in the process are not entirely understood. Nevertheless, just like in other complex chemical processes, chemical engineering approach can be used successfully to model the Siemens process and to optimize the process parameters. A model is needed to relate kinetic, mass and heat transfer effects to product quality and process efficiency.

### B. Research Objectives

1. Review the thermodynamics and kinetics of chlorosilane and silane systems. Obtain simple but good approximate CVD rate forms, homogeneous reaction rate forms and also homogeneous nucleation rate.
2. Study the alternating current effects of silicon rod heating and the hydrodynamics of decomposer. Develop a detailed model which will include all the heat and mass transfer terms.

#### D. Future Research Plan

Model sensitivity studies can be performed further to investigate the effect of the following variables:

1. Kinetics of silane pyrolysis
  - (i) rate of silane heterogeneous CVD
  - (ii) rate of silane homogeneous decomposition
  - (iii) rate of Si vapor homogeneous nucleation
2. Hydrodynamics behavior in the fluidized beds
  - (i) effect of gas expansion
  - (ii) effect of bubble behavior
  - (iii) effect of grid design

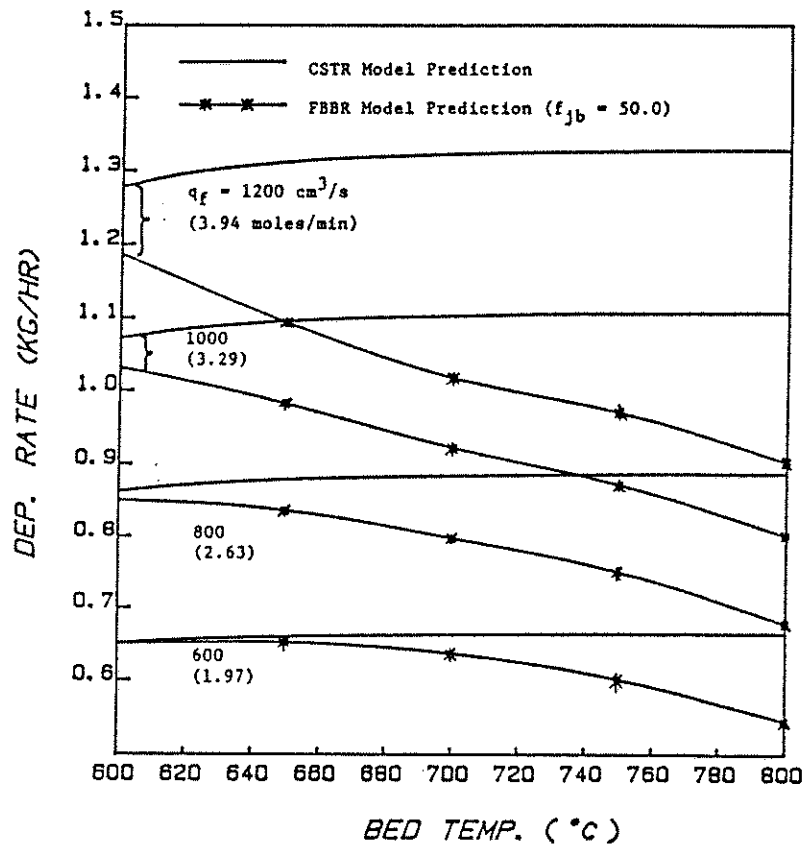


Figure 1. Comparison of CSTR and FBBR Model Predictions for Deposition Rate (Conditions of Run 1 of Table 1,  $r_i = 0.01135$  cm, with Homogeneous Nucleation).

### C. Research Accomplishments

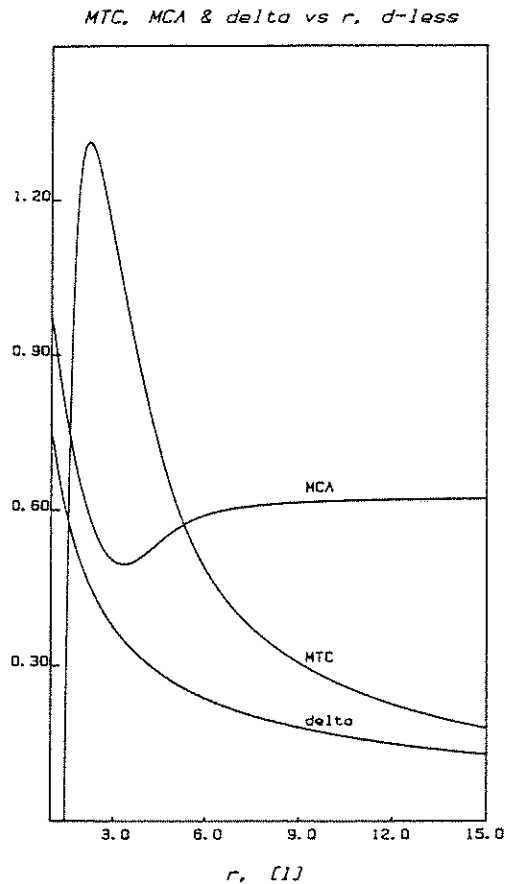
Two models for the fluidized bed pyrolysis of silane have been developed. The first one based on an ideally mixed reactor (CSTR) assumes perfect gas-solid contacting, no spatial gradients in temperature or composition in the reactor and no gradients between particle and gas. The second model (FBBR) based on the modified two-phase theory acknowledges the presence of the jetting (grid) region, bubbles and emulsion phase in the bed. Both models account for homogeneous and heterogeneous decomposition, homogeneous nucleation, coagulation and growth by diffusion of fines, scavenging of fines by large particles, elutriation of fines and CVD growth of large seed particles.

Model predicted results are compared with two JPL experimental runs in Table 1. Both models predict reasonably well the production rate and final particle size. Because the duration of the runs was too short to achieve substantial growth of seeds experimental accuracy is not sufficient to justify adjusting the only unknown parameter of the FBBR model, i.e.  $f_{jb}$ , which is the multiple by which emulsion-bubble exchange is enhanced in the grid region. The values of Table 1 are computed at  $f_{jb} = 50$ , i.e. under the assumption that jet-emulsion exchange is 50 times faster than bubble-emulsion exchange.

The comparison of CSTR and FBBR ( $f_{jb} = 50$ ) predictions for deposition rate with 20%  $\text{SiH}_4$  in the feed and as a function of bed temperature and gas flow rate is illustrated in Fig. 1. At low bed temperatures and at low gas flow rates (i.e. close to minimum fluidization conditions) CSTR and FBBR predictions are close. While mathematically this is to be expected, it is doubtful that CSTR behavior can be achieved in practice since solids circulation would not be vigorous enough at close to minimum

will be extended, and more complete numerical solutions will be sought for it. This analysis may be extended to the flow of liquid on rotating inclined surfaces ('rotating cups').

An approximate solution for the well developed film flow regime of liquid was obtained by single point orthogonal collocation technique. The results (the most important of which: liquid film thickness ( $\delta$ ), dissolved gas mixing cup concentration (MCA), and the mass transfer coefficient (MTC) are shown in the enclosed figure in the dimensionless form) were in accordance with the intuitive expectations.



#### D. Further Research Plan

The work envisaged for the characterization of the HIGEE device in terms of the chemical reactor theory, at this point, is seen to fall under three general headings:

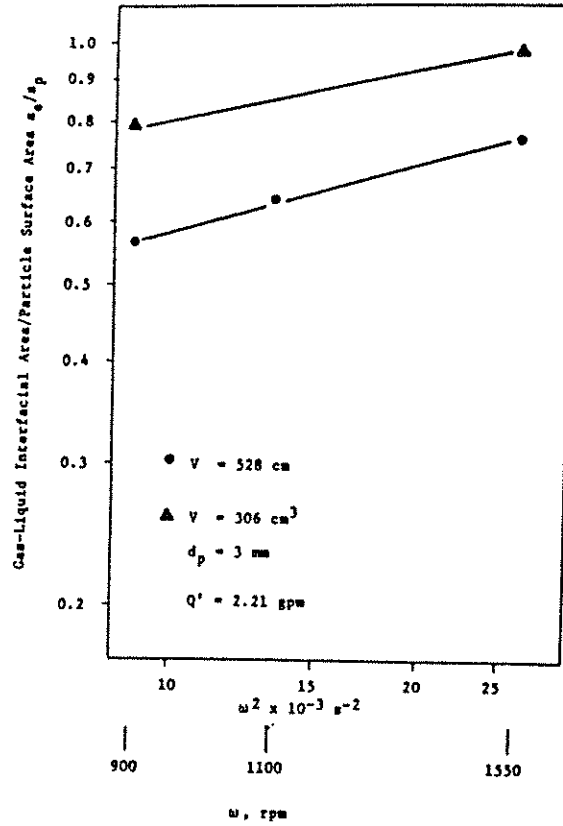


Figure 6. Effect of Rotational Speed on  $a_e/a_p$ .

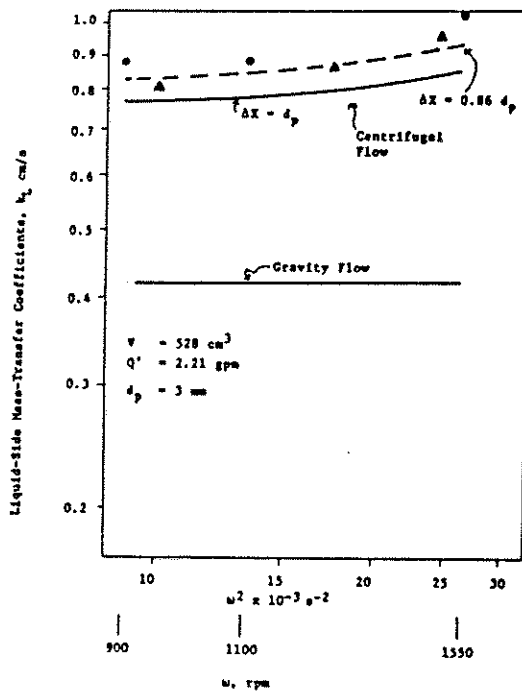


Figure 7. Effect of Rotational Speed on Liquid-Side Mass-Transfer Coefficient.

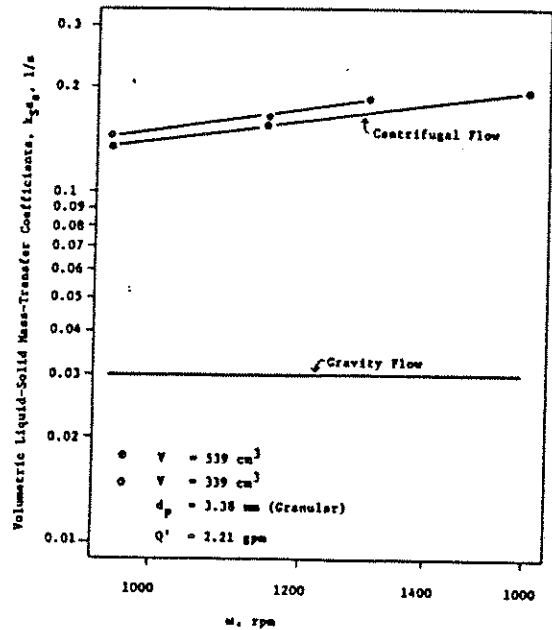
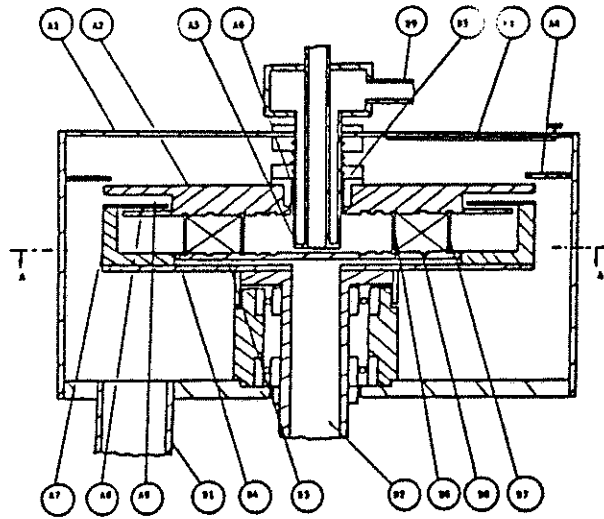


Figure 8. Effect of Rotational Speed on Liquid-Solid Volumetric Mass-Transfer Coefficient.



- |                            |                             |
|----------------------------|-----------------------------|
| A1. Rotor Casing           | B1. Liquid Exit Pipe        |
| A2. Rotor Cover            | B2. Hollow Shaft            |
| A3. Wiper                  | B3. Gas Inlet               |
| A4. Splash Shield          | B4. Gas Inlet Holes         |
| A5. Liquid Inlet Holes     | B5. Gas Seal                |
| A6. Stationary Double-Pipe | B6. Inner Packing Support   |
| A7. Rotor Wall             | B7. Outer Packing Support   |
| A8. Liquid-Seal Lip        | B8. Packing Support Grooves |
| A9. Liquid-Seal            | B9. Gas Exit Pipe           |

Figure 1. Vertical Section of the Rotor Assembly

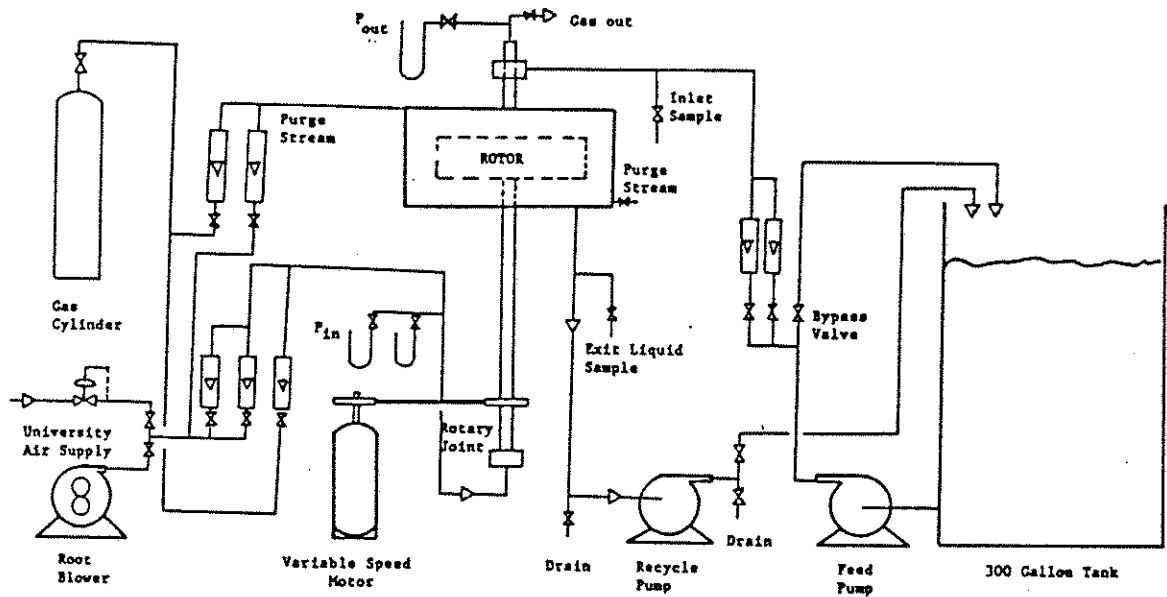


Figure 2. Flow Diagram of the Rotating Bed Experimental Set-up.



2. NSF proposal for studying liquid film flow on a rotating blade and a rotating disk is pending.

3. We are looking for a suitable, mass-transfer limited, fast reaction system which could be used to demonstrate the usefulness of this device.

Industrial participants can provide a useful input in this selection.

#### Nomenclature in this Section

$a_e$	- effective gas-liquid interfacial area, $\text{cm}^2/\text{cm}^3$
$a_p$	- particle surface area, $\text{cm}^2/\text{cm}^3$
$a_s$	- effective liquid-solid interfacial area, $\text{cm}^2/\text{cm}^3$
$d_p$	- particle diameter, cm
$D$	- diffusivity of gas in liquid, $\text{cm}^2/\text{s}$
$g$	- acceleration due to gravity, $\text{cm}/\text{s}^2$
$k_L$	- liquid-side (gas-liquid) mass-transfer coefficient, cm/s
$k_S$	- liquid solid mass-transfer coefficient, cm/s
$Q'$	- total liquid flowrate, $\text{cm}^3/\text{s}$
$L$	- superficial liquid flowrate, $\text{g}/\text{cm}^2/\text{s}$
$r_i, R_1$	- inside radius of the packed bed, cm
$R_2$	- outside radius of the packed bed, cm
$R_{\text{avg}}$	- $(R_1 + R_2)/2.0$ , cm
$u_t$	- superficial gas velocity, cm/s
$V$	- volume of the packed bed, $\text{cm}^3$

#### Greek

$\rho_L$	- liquid density, $\text{g}/\text{cm}^3$
$\mu_L$	- liquid viscosity, $\text{g}/\text{cm}/\text{s}$
$\omega$	- rotational speed of the rotor, radian/s

The above correlations show that both  $k_L$  and  $k_G$  are expected to increase with the rotational speed,  $\omega$ .

#### 4. Gas-Liquid Interfacial Area

The chemical method was used to determine the effective gas-liquid interfacial area,  $a_e$ . In this method, the absorbed gas reacts with a species in the liquid. For fast reactions, under certain conditions, the amount of absorption gives  $a_e$ . NaOH-CO<sub>2</sub> was chosen for our studies because its reaction kinetics are well known, it is easy to dispose after use, and it is economical.

Figure 6 shows the measured values of  $a_e/a_p$  as a function of rotational speed for 3 mm spherical glass beads. Two bed volumes,  $V = 528 \text{ cm}^3$  and  $V = 306 \text{ cm}^3$  were used. The figure shows that  $a_e/a_p$  increases with  $\omega$  and this indicates that rotation helps in increasing the gas-liquid interfacial area. In a gravity-flow packed bed,  $a_e/a_p$  at the same superficial liquid flowrate and for the same particle diameter was estimated to be approximately 0.2 to 0.3. In this case, the values in the rotating bed are approximately 2 to 3 times higher than those in gravity flow.

#### 5. Liquid-Side Mass-Transfer Coefficients, $k_L$

The chemical method was used to determine the  $k_L$  values also. Mass transfer in the rotor casing is absent because the absorbed gas (CO<sub>2</sub>) has reacted with NaOH in liquid. The chemical method at high Hatta number gives  $a_e$  and at Hatta number close to unity gives  $k_L$ . This is not an entirely desirable technique for determining  $k_L$ , but in this case it seems that it is more accurate than the physical method.

Figure 7 shows the measured values of  $k_L$  as a function of  $\omega$  for  $d_p = 3 \text{ mm}$  and  $V = 528 \text{ cm}^3$ .  $k_L$  increases with  $\omega$ . The predicted values of  $k_L$  by Equation 1 are also shown in the same figure. In our case the

the flow diagram of the experimental set-up. A complete description of the rotor and the auxiliary equipment is described elsewhere (4).

The rotor has been operating for the past 18 months without any major maintenance problem.

## 2. Flooding

The Sherwood correlation, if valid for the rotating packed-bed, explains two main reasons for using this device. If the acceleration due to the gravity force,  $g$ , in the ordinate group of the Sherwood correlation, Figure 3, is replaced by the driving force in the centrifugal packed bed,  $r_i \omega^2$ , it is easy to see that either packing area per unit volume,  $a_p$ , or gas superficial velocity,  $U_t$ , may be increased. Higher  $a_p$  and  $U_t$  result in dramatic size reductions compared to gravity flow.

Flooding point was determined by visual observation. It was indicated by: (1) appearance of an opaque mist in the eye of the rotor, (2) heavy water spray in the gas exit pipe, and (3) wide fluctuations in the pressure drop and flow meter readings. Flooding initiates at the inside edge of the packed bed because at this edge  $U_t$  is maximum and centrifugal force is minimum. Loading point was also determined during the flooding experiments. It was determined from the pressure drop versus the gas flowrate curves and it was defined as the gas flow rate at which the slope of the log-log plot was equal to 2.0.

Figure 3 shows the comparison of the flooding and the loading data in the rotating bed against the Sherwood's curve for gravity flow. The comparison shows that the correlation for dumped rings in gravity flow underpredicts the loading point in a rotating bed by 40% and the flooding point by 40% to 70%. From a practical point of view, the prediction by Sherwood's correlation is satisfactory, since it is conservative.

## Project I.5. Centrifugal Packed-Bed Contactor

### A. Problem Definition

Mass transfer in a rotating packed bed with countercurrent gas-liquid flow is a recent development (1). The device consists of a rotating packed bed in the shape of a torus (or doughnut). The liquid is sprayed on the inside edge of the packed bed and is thrown outwards by the centrifugal force. The gas is introduced from the outside and due to the imposed pressure gradient flows inward countercurrently to the liquid.

A rotating packed bed can achieve dramatic size reductions in gas-liquid mass-transfer operations (2). This size reduction results from a combination of two factors. First, the flooding limits are very high and this leads to a small gas-flow area (or cross-sectional area). Second, higher volumetric mass-transfer coefficients results in a lower total volume for the packed bed. Hence, a combination of small cross-section and a small total volume leads to a compact mass-transfer device.

There are many advantages of using this device. The compact size requirement makes it useful for the space-limited applications like offshore processing facility. It is easily portable and easy to winterize. Smallness and simplicity would allow fabrication from more costly materials, such as titanium, with special properties. The same qualities may also be advantageous in designing for the high pressure service. The unit reaches equilibrium quickly and can be shut down quickly, features that might be useful for batch pharmaceutical processing. This device can achieve an excellent turndown by using a variable speed motor. It is also well suited for microgravity applications.

There is one known commercial rotating packed bed in operation (3). This device is currently being used to strip aviation fuel from ground

## Project I.4. Hydrodynamics of Bubble Columns

### A. Problem Definition

Liquid circulation, often termed as the 'Gulf stream effect', is commonly encountered in gas-liquid bubble columns and gas-liquid-solid three phase fluidized beds. This circulation is caused by density differences due to non-uniform gas hold-up profiles in the column. Circulation contributes to backmixing and is, therefore, detrimental to reactor performance, especially at high conversions. The accurate design and scale-up of bubble columns is, in part, contingent upon the ability to quantify liquid circulation.

A number of theoretical approaches have been suggested to model circulation, but they are in disagreement. A unified treatment is necessary. In addition no information is available on bubble columns operating in churn-turbulent flow.

### B. Research Objectives

1. Formulate and solve a pseudohomogeneous liquid circulation model neglecting gas-liquid interaction, for the first level model. Incorporate gas-liquid interaction in a simple constitutive manner for a second level model.
2. Measure time averaged voidage profiles by gamma-ray tomography and use the results as input to the model.
3. Obtain local liquid circulation velocities experimentally by a novel computer-aided radioactive gamma particle tracking facility. Compare with the predictions of the model in 1 above.
4. Formulate rigorous model for liquid circulation allowing for gas-liquid interaction. Solve the continuity and momentum equations for gas and liquid to yield the pressure, velocity and voidage profiles.

Table 1. Summary of Proposed Model Equations

Overall Gas Balance  $U_G A = f_s V_s$

Overall Liquid Balance  $V_{LUF} = \frac{U_L A}{f_s} + V_{LDF}$

Species Conservation in Slugs  $C_{si} = (1-X)C_{s(i-1)} + X C_{ci}$

Species Conservation in Cells  $C'_{ci} = (1-Y-Z)C_{ci} + Y C_{s(i-1)} + Z C_{c(i+1)}$

Species Conservation in Bottom Cell  $C'_{c1} = (1-W-Z)C_{c1} + W C_o + Z C_{c2}$

Species Conservation in Top Cell  $C'_{cN} = (1-Y-Z)C_{cN} + Y C_{s(N-1)} + Z C_{sN}$

$$W = \frac{U_L A}{f_s V_c (1-\epsilon_c)}$$

$$X = \frac{V_{LE}}{V_{LUF}}$$

$$Y = \frac{V_{LE}}{V_c (1-\epsilon_c)}$$

$$Z = \frac{V_{LDF}}{V_c (1-\epsilon_c)}$$

slugs that is associated with the large central bubble. It can be seen that for a value of 0.3 for P that the slug and cell model describes the experimental data at least as well as the axial dispersion model.

#### D. Further Research Plan

The development of the slug and cell model as an alternative to the axial dispersion model for describing the behavior of churn-turbulent bubble columns has been completed. It has been demonstrated that the slug and cell model can describe essentially the same behavior as the axial dispersion model in all cases examined. The slug and cell model has also been extended to consider the effects of interphase mass transfer and chemical reaction. The basic advantages of the slug and cell model are its firm phenomenological basis and its computational simplicity which is due to its algebraic (in case of steady state) or initial-value (in case of transients) species conservation equations.

#### Nomenclature in this Section

A	- column cross-sectional area
$C_{ci}$	- liquid species concentration in cell i before slug passage
$C'_{ci}$	- liquid species concentration in cell i after slug passage
$C_{si}$	- liquid species concentration in a slug after it leaves cell i
$C_o$	- liquid species concentration in liquid feed
D	- column diameter
$E_\theta$	- dimensionless pulse response
$f_s$	- frequency of slug appearance
L	- column length
N	- number of cells in system
P	- fraction of slug gas volume associated with the large, central bubble
$U_G$	- superficial gas velocity
$U_L$	- superficial liquid velocity

column diameters in the range of 19 to 57 cm, and superficial gas velocities in the range of 10 to 30 cm/s.

The simulation of the slug and cell model for the steady backmixing experiment described above provided a basis for estimating the one unknown model parameter which would allow the behavior of the slug and cell model to be examined for other types of tracer experiments. In particular, the behavior of the slug and cell model was investigated for pulse tracer experiments under the same conditions as were studied for the steady backmixing experiment. It was found that if the behavior of the two mixing models was equated for the steady backmixing experiment, the dimensionless variance of the pulse responses of the two models would vary by no more than 1.3%. This indicates that the slug and cell model is capable of describing essentially the same behavior as the axial dispersion under both steady and transient mixing conditions. Further, these investigations clearly demonstrated the computational simplicity of the slug and cell model due to the algebraic nature of the equations involved.

3. A series of standard pulse tracer experiments were performed in a 19-cm diameter bubble column with an air-water system employing a methylene blue dye as the tracer. A comparison of an experimental pulse response with that of the slug and cell model is presented in Figure 2. The magnitude of the exchange parameter  $Y$  was determined by matching the dimensionless variance of the model response with that of the experimental response. It can be seen from Figure 2 that this variance matching provides very good time-domain agreement between the experimental and model responses.

4. Extension of the slug and cell model to consider homogeneous liquid-phase reactions is relatively straightforward since the model system simply appears as a series of batch reactors which exchange liquid as the slugs



### C. Research Accomplishments

1. A novel phenomenological model of liquid-phase mixing in churn-turbulent bubble columns has been developed. This model is descriptively termed the slug and cell model ("elevator-mixing cells" model is another possible alternative) and is schematically illustrated in Figure 1. The model system can be seen to be divided into two regimes. The gas-rich regions, termed slugs, periodically move through the system and entrain and transport liquid to various points within the system. The gas-lean regions, termed cells, are stationary and are vigorously agitated by the passage of slugs through the system. A number of cells of a characteristic size exist along the length of the column. Due to the turbulent nature of the flow there will be an exchange of liquid between adjacent cells and between the slugs and cells as a slug passes through the system. This physical model accounts for three of the basic characteristics of churn-turbulent flow: the periodic appearance of large, fast-rising gas bubbles, the presence of large-scale turbulence in the liquid, and the internal circulation of the liquid.

The model equations describing liquid-phase mixing in the absence of mass transfer and reaction are summarized in Table 1. The parameter  $W$  characterizes the liquid feed to the system, the parameters  $X$  and  $Y$  describe the exchange of liquid between the slugs and cells, and the parameter  $Z$  describes the exchange of liquid between adjacent cells. A number of the model parameters can be estimated based upon previous studies, physical reasoning, or simple experiments. In this way the model can be reduced to the single unknown parameter  $Y$ . As can be seen from Table 1, the model is of the initial-value type and the algebraic model equations are ideally suited for numerical computations.

KEY TO FIGURE 4

- (A) Trickle Bed Reactor
- (B) Coincident NaI(Tl) detectors (36 total) and support platform mounted for rotation and axial movements.
- (C) Surge tank
- (D) Liquid pump
- (E) Air rotameter
- (F) Liquid rotameter
- (G) Gas pressure gauge
- (H) Air flowrate control valve
- (I) Liquid flowrate control valve
- (J) System drainage valve to storage tank (not shown)
- (K) Recirculation loop valve for liquid pump

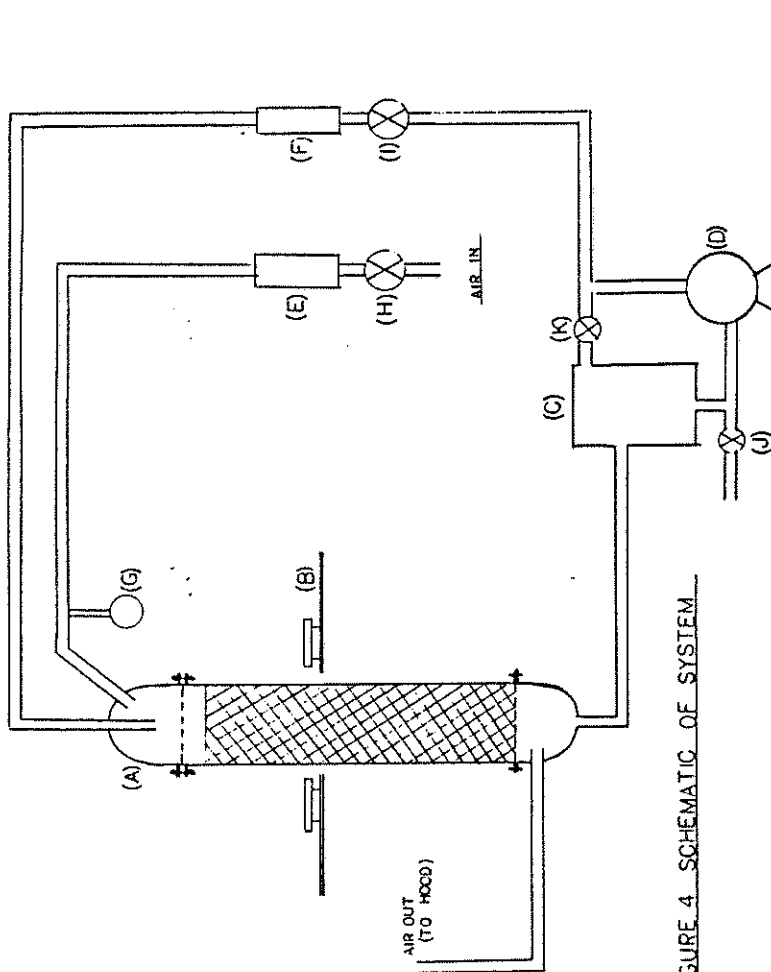


FIGURE 4 SCHEMATIC OF SYSTEM

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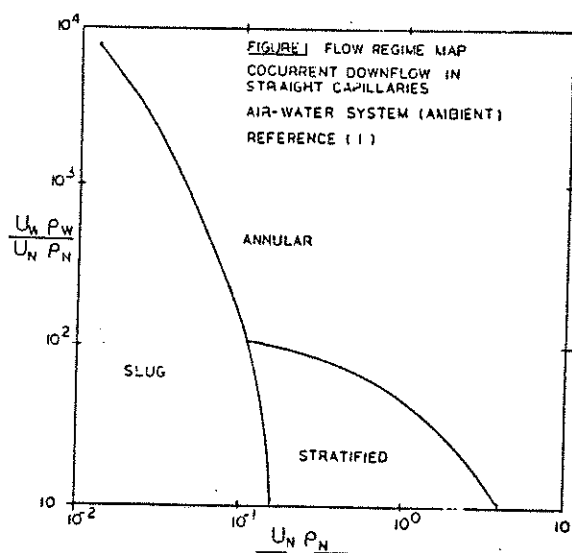


Figure 1. Flow Regime Map in Capillaries.

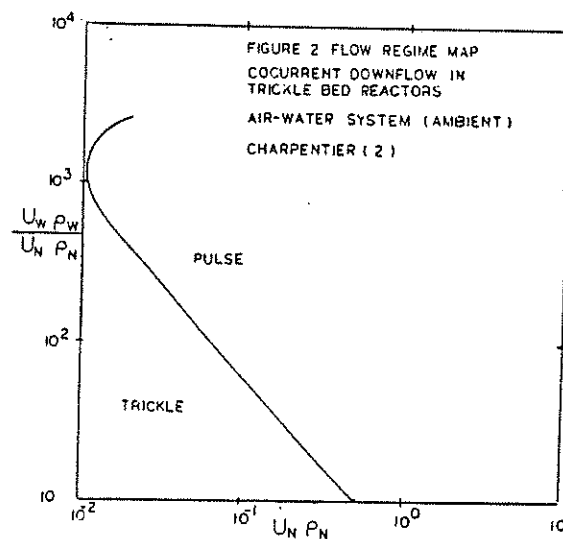


Figure 2. Flow Regime Map in Trickle-Beds.

same basis almost no overlap exists. Further, noninvasive flow visualization of liquid distribution in trickle-beds is necessary before correct phenomenological models can be developed.

#### B. Research Objectives

The objectives of this project are:

1. Develop a nonintrusive method of viewing the liquid flow field in a trickle-bed reactor.
2. Based on the observations, develop some simple particle scale models which are representative of the observations, but solvable by a finite element code currently available (e.g. film flow on an inclined string of spheres).
3. Correlate, if possible, the bed scale parameters required by percolation theory (fraction of accessible bonds) to the observed flow field and the dimensionless numbers representative of the system.
4. Relate the particle scale model predictions to the bed scale via percolation theory. Compare the predicted values of holdup and liquid-solid mass transfer coefficients, for example, to correlations existing in the literature [3].

#### C. Research Accomplishments

This project is in its initial planning stage.

#### D. Further Research Plans

1. A nonintrusive method for viewing the flow field has been decided on, and the preliminary design work completed (see Figures 3 and 4). The method will be based on POSITRON EMISSION TOMOGRAPHY and will allow the quantitative resolution of the liquid distribution on any cross-section of a six inch diameter trickle-bed down to less than one centimeter (7 to 9 millimeter resolution is expected). The device was first developed at

- Development of a generalized procedure for interpretation of tracer data on pilot plant and plant reactors and establishment of a diagnostic for determining whether reactor malfunction is caused by flow maldistribution or catalyst deactivation.

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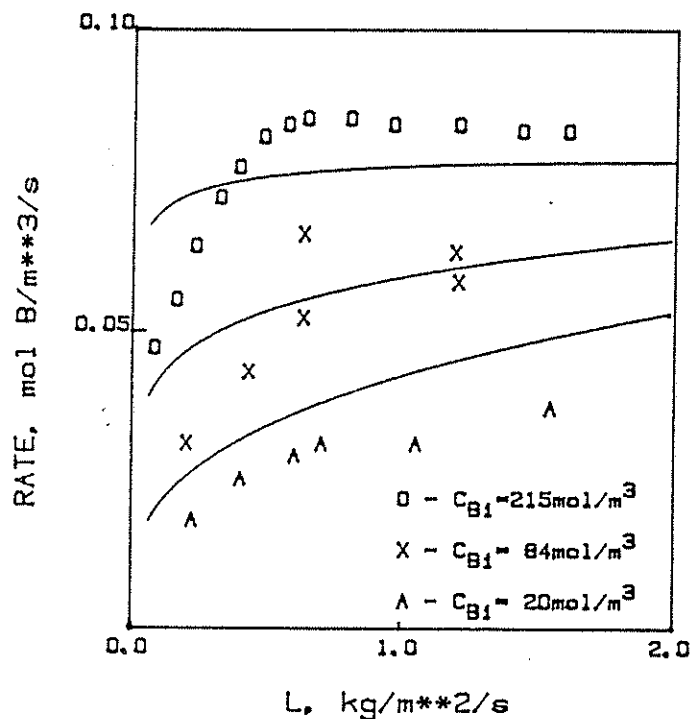


Figure 1. Experimental Data and Model Predictions for Data of Ruiz et. al. (3).

2. An approximate but useful criterion was developed which establishes the liquid reactant conversion,  $X_B$ , above which the reaction rate, otherwise zeroth order with respect to the liquid reactant, becomes affected by liquid reactant concentration.

$$X_B < 1 - 3 \phi_A \frac{D_{eA} b C_A^*}{D_{eB} C_{Bi}} \quad (1)$$

As long as liquid conversion is less than the right-hand side of Eq. (1) the nonvolatile reactant B will not reduce the rate of reaction in a partially wetted trickle-bed reactor. In the above expression  $D_{eA}$  and  $D_{eB}$  are the effective diffusivities of the dissolved gas reactant A and the nonvolatile liquid reactant B, respectively. The stoichiometric coefficient for reactant B is b. The equilibrium dissolved gas concentration is  $C_A^*$  and the inlet concentration of the nonvolatile reactant is  $C_{Bi}$ . The generalized Thiele modulus,  $\phi_A$ , is  $(V_p/S_A) \sqrt{k_v/D_{eA}}$ , where  $V_p$  and  $S_x$  are the volume and external surface area of a catalyst pellet, respectively, and  $k_v$  is the first-order rate constant based on pellet volume and  $C_A^*$ .

This criterion can be applied to our hydrogenation of  $\alpha$ -methylstyrene in n-hexane data. The Thiele modulus  $\phi_A$  was estimated in a stirred basket reactor to be 50 after the intrinsic rate constant,  $k_v$ , was measured in a slurry reactor. The ratio of the effective diffusivities,  $D_{eA}/D_{eB}$ , was assumed to be equal to the ratio of molecular diffusivities in the liquid and estimated to be 5. The concentration ratio, at the inlet,  $bC_A^*/C_{Bi}$ , was estimated to be 0.002. The right hand side of Eq. (1) is -0.5, which indicates that the nonvolatile, zero-order reactant B may be reducing the observed rate of reaction at the inlet, although it is 500

## AREA I: MULTIPHASE REACTORS

### Project I.1. Trickle-Bed Reactor Performance and Scale-Up (Gas-Limiting Reaction)

#### A. Problem Definition

In order to design and scale-up trickle-bed reactors properly, it is necessary to first be able to predict their performance for well understood test reactions. The goal of this project is to examine how well one can predict the performance of a trickle-bed reactor for a gas-limited reaction. The performance predictions are based on kinetics measured in a slurry reactor, effectiveness factor for a completely wetted pellet measured in a stirred basket reactor, and independently determined liquid-solid contacting efficiency measured by tracers.

#### B. Research objectives

1. Development of a model for an isothermal trickle-bed reactor with a gas-limiting reaction.
2. Comparison of model-predicted and experimental reactor performance.
3. Generalization of the model and extensions to nonisothermal systems.

#### C. Research Accomplishments

1. In the last CREL annual report (1) we presented a new model for explaining the observed effect of the liquid reactant concentration on trickle-bed performance for an apparent gas-limiting reaction. It was shown that under conditions of partial catalyst wetting liquid reactant may not diffuse rapidly enough towards the dry catalyst surfaces where the gas supply is abundant. This creates a zone depleted of liquid reactant close to dry catalyst surfaces and introduces an apparent additional mass transfer resistance for the gas reactant on dry surfaces, i.e. the diffusional resistance of the zone depleted of liquid reactant. Our findings for a reaction which is zeroth order with respect to liquid and first order with

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1985 - May 1986

## AREA III: NEW MATERIALS, MODELING AND CONTROL

Project	Funding	Investigators	Major Results
<p><u>Relevance:</u> Flow pattern in the melt influences the rate of heat removal from the system and therefore affects the crystal growth rate. In addition flow stability is an important parameter in governing crystal quality. A detailed description of flow including all known factors is also necessary to understand crystal growth in zero gravity systems.</p>			<p>b) Additional complexities such as thermo-capillary flow, dynamic meniscus shape, etc., have been added to the model. Work on improving the computational efficiency of the method is also in progress.</p> <p>c) The effect of nonplanar crystal-melt interface on velocity profiles in the melt has been quantified.</p> <p>d) A mass transfer model has been formulated.</p>
<p>5. On-Line Optimization of Chemical Processes</p> <p><u>Relevance:</u> Efficient use of computers in optimal reactor and plant operation.</p>	NSF	B. Joseph S. S. Jang	<p>a) Detailed dynamic model for ethylene oxide reactor was developed.</p> <p>b) Detailed studies of regulatory and optimizing control were made using this model.</p> <p>c) New techniques of nonlinear estimation, control and optimization were developed.</p> <p>d) A new approach to on-line optimization called two-phase approach is developed and applied to reactor problems.</p>



TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1985 - May 1986

AREA III: NEW MATERIALS, MODELING AND CONTROL

Project	Funding	Investigators	Major Results
<p>1. Computer-Aided Processing of Thermosetting Composites</p> <p><u>Relevance:</u> Curing or fiber reinforced epoxy resins is a key process in manufacture of new fiber reinforced materials. Quality control of the product requires precise resin content and elimination of all voids. This research is oriented towards such a goal.</p>	Industrial	<p>J. L. Kardos M. P. Duduković R. Dave</p>	<p>a) A model for bubble formation and growth has been completed.</p> <p>b) A model for squeezing flow of the resin during compression of the composite has been completed.</p> <p>c) A general procedure for selection of the optimal cure cycle has been developed.</p>
<p>2. Modeling of Radial Flow Electrochemical Reactors</p> <p><u>Relevance:</u> Mixing pattern of the electrolytes is of importance in electrochemical reactors. An accurate description of nonidealities in flow becomes especially critical since many of the ionic reactions are rapid. This work</p>	Monsanto	<p>P. A. Ramachandran M. P. Duduković B. F. Thomas R. E. W. Jansson</p>	<p>a) A detailed numerical solution is performed for the velocity distribution in the capillary gap cell, pump cell and the rotating electrolyzer using finite element methods. An analysis of convection and diffusion of a tracer in these systems has been investigated. Two situations: bulk marking and wall marking are analyzed separately since the nearly stagnant region near the walls needs to be accurately characterized for fast reactions. Tracer responses and velocity profiles give quantitative information about mixing and transport near the electrodes.</p>

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1985 - May 1986

## AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results
<p>an appropriate back-mixing description for bubble columns. Improvement of scale-up and reactor performance prediction is expected.</p>			<p>d) in good agreement with experimental data. Hydrodynamic models for bubble column have been developed.</p>
<p>5- Centrifugal Packed-Bed Contactor</p> <p>Relevance: A centrifugal rotating packed-bed is an efficient gas-solid contactor that offers unique advantages at normal and zero gravity conditions. Complete characterization is necessary for scale-up and use in gas-liquid and gas-liquid-solid operations. Potential for use in oxygen starved systems is considerable.</p>	<p>Exxon Foundation 3M Monsanto</p>	<p>M. P. Duduković P. A. Ramachandran A. Basić S. Munjal</p>	<p>a) A laboratory packed-bed centrifugal contactor has been built. Flooding tests indicate the validity of the Sherwood correlation. Mass transfer tests indicate increased volumetric mass transfer coefficients dependent on rotational speed.</p> <p>b) The theory for film flow in centrifugal contactors has been developed and used in theoretical prediction of mass transfer coefficients.</p> <p>c) Design procedure for rotating contactor has been outlined.</p> <p>d) Use of the rotating-bed in three phase systems is being investigated.</p>

TABLE I

## Active Projects in the Chemical Reaction Engineering Laboratory, June 1985 - May 1986

## AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results
<p>1. Trickle-Bed Reactor Performance and Scale-up</p> <p><u>Relevance:</u> Trickle-beds are used extensively in industry but generally accepted design and scale-up methods are lacking. This project attempts to show that the prediction of performance of an integral trickle-bed reactor when kinetics, operating conditions and liquid physical properties are known is possible. This should allow more rational trickle-bed design.</p>	Industrial	<p>M. P. Duduković P. A. Ramachandran E. Beaudry P. L. Mills</p>	<p>a) A model for performance of an isothermal trickle-bed reactor in case of a gas limiting reactant is developed and checked against experimental data for <math>\alpha</math>-methylstyrene hydrogenation in various organic solvents.</p> <p>b) By comparing experiments with theory it is established that the reaction can shift from gas limited to liquid limited at conditions of incomplete catalyst wetting. When this is accounted for model predictions are in excellent agreement with experimental results.</p> <p>c) The model is extended to treat non-first order reactions and is shown to predict the experimental trends observed in maleic acid hydrogenation. No previous model was able to account for these observations.</p>

interest and provided valuable input for a number of research projects. We are thankful for their time and help to: J. T. Hargreaves of Amoco, F. X. Mayer of Exxon Research and Development, B. L. Tarmy from Exxon Engineering, H. Hensley from Phillips, L. Bosanquet and P. L. Mills of Monsanto, D. Dan, G. Damerell and P. R. H. Martin of 3M Company, J. Cropley from Union Carbide and L. Clomburg of Shell Development. We are especially appreciative of Dr. R.E. W. Jansson's efforts. Dr. Jansson, in spite of his numerous duties at Monsanto, managed to find the time to teach an excellent course in electrochemical reaction engineering which enriched our CREL offering. He is also instrumental in guiding our electrochemical project.

The funding for CREL surpassed our goal of stabilizing it at last year's level. The funds came from the industrial participation fees (\$120,000); from the Jet Propulsion Laboratory (JPL) for modeling of silane pyrolysis (\$34,000); from JPL for modeling of Czochralski crystal growth (\$55,000); from the Electric Power Research Institute (EPRI) for modeling of CZ growth of large silicon crystals (\$210,000) and from the National Science Foundation (NSF) grant for on-line optimization (\$43,000). CREL operation is also supported by various industrial fellowships awarded to our Chemical Engineering Department for which our students are eligible. Currently, we have three fellows among the CREL group: Richard Holub is the recipient of the Amoco Fellowship, Dan O'Connor of the Shell Fellowship and Brent Thomas of the Monsanto Electrochemical Fellowship.

The Fall meeting with industrial participants held in the middle of October both in 1984 and 1985 has been successful and is now part of CREL tradition. This year we tentatively plan the meeting for Wednesday,

the University of Illinois at Chicago under Dr. Saxena's direction on coal gasification. He presented a paper based on his work at the Pittsburgh Gasification Meeting. At the moment he is involved in assessing novel ways of monitoring liquid backmixing in bubble columns and is developing a more sound approach to hydrodynamic modeling of these contactors. Jaimin Mehta joined us from I.I.T, Bombay, where he obtained his B.S. degree. He is implementing some new control strategies on existing experiments and in educating CREL personnel in fractals. We expect him to do characterization of gas-solid reactions using fractals and associated concepts. Dan O'Connor returned to his alma mater from industry. He is currently selecting a project in the area of multiphase reactors in preparation of specialty chemicals. Saeed Pirooz, who received his B.S. and M.S. here, decided to tackle a difficult problem of plasma reactor modeling for his D.Sc. project.

Our research associates remained very active. Dr. Rajesh K. Srivastava is rapidly establishing himself as an authority on Czochralski crystal growth. His relentless effort has been instrumental in establishing our CREL group as a leader in CZ modeling and in producing five papers for publication. Dr. G. Hwang, our visiting scholar from the Wuhan Institute in China, continued his systematic work in transferring the most recent achievements in nonlinear control theory to chemical engineering applications.

Our three faculty members remained very active in publishing and presenting their work, in teaching and advising students, and in pursuing funding for our numerous projects. A list of our publications and presentations for the period covered in this report is appended. Dr. M. P. Duduković received two special honors this spring. The graduating class of seniors elected him Engineering Professor of the Year. Two professors

our way (D. Dorsey) in surpassing the accomplishments of the leaders in the field of melt hydrodynamics. The first systematic quantification, via finite element analysis, of flow fields in three basic types of electrochemical cells is in progress (B. Thomas). Substantial additional research progress was made (S.S. Jang) in developing and applying the horizon, two-phase approach, in on-line control and optimization of reaction systems. This work represents the state-of-the-art in modern control.

This is a brief and incomplete summary of our research activity. Additional details are available in the report. All projects that have been active during the period June 1, 1985 through May 31, 1986 are summarized in Table I and described in the report.

There are many personal news about the group that could be reported and some selective highlights follow. CREL was represented by 10 (ten) presentations at the AIChE Annual Meeting in Chicago in November, 1985. Four of these were given by our graduate students (E. Beaudry, S. Lai, S. Munjal and K. Myers). We had 3 (three) presentations at the recent ISCRE9 (9th International Symposium on Chemical Reaction Engineering) in Philadelphia, May, 1986. Considering that ISCRE usually limits a research group to one paper, this is a considerable accomplishment. These papers have appeared in Chemical Engineering Science 41 (4), 1986. Our visibility at national and international meetings has certainly been remarkable and our graduate students have left an excellent impression.

Our graduate student population has reached the level beyond which we do not want to expand. This is an optimal size for the purpose of research interaction and exchange of ideas but somewhat burdensome in terms of the necessary funds' raising activities. The news concerning our graduate students are as follows. Kevin Myers completed his D.Sc.

in them is necessary in order to make scale-up and design easier and economical. In trickle-bed studies we have developed a methodology for the practitioner to follow in distinguishing and understanding gas and liquid-reactant limiting systems. A novel model (E. Beaudry) that quantifies previously puzzling effects of liquid feed concentration in a gas-reactant limiting situation has been developed. A new methodology for interpreting tracer data and in relating pilot and plant reactor data, using actual industrial data, is being currently tested. We (R. Holub) plan to develop PET (positron emission tomography), using the know-how from our medical school, to study noninvasively liquid flow structures in trickle-beds. If successful, this will be the first three dimensional picture of liquid flow. This study was motivated by the recent discovery that flow regimes in trickle-beds were dramatically different than those in single capillaries. Since single capillaries are building blocks for most trickle-bed models, clearly a proper flow visualization study is in order.

We (K. Myers) have developed a novel "elevator-mixing cells" model for scale-up of bubble columns operated in the churn-turbulent regime. Preliminary comparison with data for dissolved oxygen is very encouraging. Further quantification of this phenomenological model is in progress as well as a revisitiation of the hydrodynamic descriptions for bubble columns. We (S. Munjal) have also developed the theory for gas-liquid and liquid-solid mass transfer in rotating packed-bed contactors. Partial experimental confirmation of the theory has been obtained. This device yields substantially higher throughputs and mass transfer coefficients than gravity flow devices and has great potential for application to production of specialties and in micro gravity environment. The rules for scale-up

an important role in establishing the leadership of the American petroleum, petrochemical and commodity chemicals industry in the world. However, two major changes of the present decade demand further evolution in reaction engineering. On one hand, we have witnessed a slowdown in plant construction for large scale commodity chemicals and petrochemicals. Nevertheless, sometime in the future new large scale chemical and syn-fuel processes will be needed. In order to be built economically, they will require much larger scale-up factors and rapid and safe transfer of bench data to plant design. This places an increased demand for better quantification of complex phenomena in various reactor types, for reliable and computationally efficient reactor models and for proven control strategies. The current slow-down in traditional chemical engineering areas represent a great opportunity to implement current advances in physics, chemistry and computer sciences in better and new approaches for reactor design. On the other hand, a variety of novel processes are being developed in specialty chemicals, biotechnology, and new materials, such as ceramics, metals, polymers, optical fibers, semiconductors, composites, etc. Rapid introduction of reaction engineering principles and expansion of the discipline to meet the special demands of these new manufacturing areas is needed. In order for the economy to prosper we must meet these challenges of the future.

We believe that CREL plays a unique and special role in keeping reaction engineering a vital and growing discipline. We have three faculty members, two research associates and over a dozen graduate students involved in advancing the discipline. The blend of projects encompasses a wide spectrum of problems, from those related to the petrochemical and petroleum industry, to those of interest to specialty chemicals, materials or semi-







