

Report

June, 1986 - May, 1987

CHEMICAL REACTION ENGINEERING LABORATORY

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## INTRODUCTION

This report describes the major events and research activities in the Chemical Reaction Engineering Laboratory (CREL) from June 1, 1986 through May 31, 1987. During this period we have further confirmed our commitment to quality graduate student education and have strengthened the existing research areas and have expanded our research in new promising directions.

We believe that chemical reaction engineering will play a central role in modern chemical engineering in manufacture of new materials and specialty chemicals and by achieving more rapid, reliable and large scale-up factors in manufacture of fuels and commodity chemicals. We are making certain that our students get a full appreciation of the changing chemical engineering world and that they are capable of meeting the challenges imposed by new technologies. What then are the trends to which our students should be exposed?

Chemical reaction engineering (CRE) is now a mature discipline. It evolved in the 1940's from the ideal reactor concepts on one side and the systematic treatment of transport-kinetic interactions on catalyst particles on the other. Mathematical approaches of the early 1960's established the foundation on which the principles of CRE dealing with transport-kinetic interactions can be applied to a vast variety of fields. The unification of CRE approaches has been achieved. Increased computerization allows its application in complex problems. What of the future then? What will be the research directions and where, i.e. in which field, will the major industrial impact be felt?

Many would argue that the future of CRE is in high technologies. However, one must be careful to define what one means by high technology. Often biotechnology, high performance composites, semiconductor materials,

high performance ceramics, optical fibers technology, pharmaceuticals, etc., are understood to be high technology. That is not necessarily so since, for example, a fully automated modern steel plant may involve much more sophistication, control and automation than a primitive autoclave for production of bio-cells. Really, what is often meant by high-tech is high-value added products, i.e. relatively new technologies that produce specialty, often low volume, products the price of which is an order of magnitude above their manufacturing costs! We have no argument with the premise that CRE will be needed and will prosper by advancing high technology products. However, we are not at all convinced that it will play a significant role in development of high-value added products unless they also happen to be high technology products. The reason for this is simple and has nothing to do with science or engineering but with economics. In producing a high value added product (a miracle drug, a super fast semi-conductor chip, etc.) the bottle-neck is in the science. Once a bench scale scientist makes a breakthrough, scale-up factors required are small, and the efficiency of manufacturing is not critical since the profit margin is huge. This is the reason why the demand for CRE specialists in biotechnology has failed to materialize so far. Very specific, low volume products are being sought and engineering involvement is small and secondary to that of scientists. This will change when competitiveness in this area increases and/or when large scale biomass conversion is attempted.

The CRE research directions in the U.S. invariably follow the funding trends. Therefore in the short term future (5 years) one can expect increased emphasis on:

- aerosol reactors in production of ceramics and optical fibers,

- batch processing, control and optimization,
- biotechnology,
- chemical vapor deposition in preparation of semiconductor materials such as MOCVD of gallium arsenide, etc.,
- combustion and generation of particulates,
- reaction engineering of composite materials,
- reaction engineering in microgravity
- reaction engineering of specialty polymers
- zeolite catalysts, catalyst preparation and quantification, modifications with transition metals, studies of configurational diffusion.

Over the long run we well know that trends are cyclic in nature. The energy problem has not been solved permanently. Eventually petroleum based products will need replacement and synthetic fuels, renewable energy sources, new materials will be needed. The currently dormant research on:

- coal gasification and liquefaction,
- methanol synthesis,
- methanol to chemicals conversion,
- multiphase reactors,
- synfuels from various sources, etc.,

will be resurrected in addition to the currently popular areas.

All of the above areas seem to be more process oriented than the CRE research in the 1960's and 1970's that concentrated on analysis of various reactor types. The trend of remarrying CRE concepts with process chemistry is probably here to stay. It is of course possible to make further dramatic improvements in our understanding and "a priori" design of various multiphase reactor types that are today designed based on

empirical relations. The tools necessary to achieve this are available and consist of improved non-invasive technology for monitoring flow patterns and concentration profiles (gamma cameras and sources, x-ray and positron emission tomography, optical fibers, etc.) and of supercomputers that make difficult flow calculations possible. However, it is unlikely that any society will in the present climate allocate the resources necessary to tackle with the best available tools a problem such as fluidized bed or trickle-bed "a priori" design. If these breakthroughs happen, and they are possible based on our currently available arsenal of tools, they will occur in relation to the development of a particular technology that relies on such a reactor type. Research funding will be directed towards the development of improved data bases in treatment of hazardous chemicals, for processes for hazardous chemicals elimination, for expert systems for reactor safety, etc.

In the near future we can expect chemical reaction engineers to develop a second specialty (a "minor" so to speak) in a scientific discipline such as microbiology, electronics, ceramics, materials, etc. Then they will work very effectively together with scientists in early stages of the development of new processes. Capable managers with technical backgrounds will realize that productivity and success rate in developing new processes can be increased dramatically by letting chemical reaction engineers work with scientists on a new process or new materials from the very conception of new ideas. Thus, we will see significant involvement of CRE in new areas such as materials, semiconductors, ceramics, specialty polymers, food and feed, etc. Major industrial impact will be in scale-up and design of flexible processes that can meet changing customers' needs rapidly. All high technology areas will benefit from CRE and that

includes both "old" technologies, large scale commodity and specialty chemicals, petroleum processing and all the new high value products where a high level of competition exists.

Since reaction engineering is considered a mature discipline it is clear that higher returns are expected by application of the CRE principles in new emerging technologies than by further advancement of these principles. It is often argued that traditional approaches in studying a specific reactor type in a general sense bring now diminishing returns and incremental improvements in our knowledge base. This might be true if one insists on using old fashioned experimental and mathematical tools. However, as argued earlier, our scientific base in instrumentation and large scale computation has reached a new dimension. If we would bring these new tools to bear on multiphase reactor problems, advances paralleling those in medicine would be possible. The limiting factor at present is lack of funds since generic reactor analysis cannot be compared in appeal to health care. Nevertheless, research of various reactor types will continue with increased emphasis on novel devices that combine reaction and adsorption in one unit (e.g., reactive distillation, chromatographic reactor, supercritical reaction and separation, etc.). We should also remember that unexpected breakthroughs are possible at any time in any areas. Who could after all predict the timing of Danckwerts residence time distribution concepts and their impact on CRE that lasted several decades? All we can say is that CRE will remain a vital field, a fund field to do research in and to practice in industry. Steady progress will be made, more science will be brought back to CRE and major breakthroughs are possible. These seem also to be the conclusions of our recent Engineering Foundation Conference on reaction engineering held in Santa Barbara, California, March 8-13, 1987.

In summarizing, we can say chemical reaction engineering is a mature discipline that has emerged from the treatment of petroleum related catalytic reaction problems and has been broadened to the point that the word chemical should be dropped from its title. Reaction engineering principles deal with the transport phenomena - kinetic interactions and are general in nature and applicable to all types of processing and all phenomena where, in conversion of raw materials to useful products or to energy, reactions occur. Reaction engineering as a discipline has profited immensely from the availability of increased computational power and from the existence of data base management. Its further evolution is expected to make its dependence on various sciences (chemistry, bio-chemistry, materials, etc.) even stronger and possibly result in formation of various CRE subdisciplines.

Reaction engineering will continue to prosper in the future by relying more on basic chemistry in reaction pathway development and by incorporating basic hydrodynamic principles in reactor design. Empirical correlations will gradually be replaced by relations based on first principles. In spite of all these predicted specific advances the most valuable resource will remain the reaction engineering methodology itself. Perhaps the ultimate achievement will be the development of expert systems for reaction engineering which will combine the fundamental approaches of science with the experience, instinct and intuition of many great reaction engineers. These systems will then be able to lead us in design of safe, optimal reactors based on a minimum data set necessary.

We are trying to provide for our graduate students in CREL a research atmosphere within which they can develop into modern reaction engineers in line with our views of future needs which are outlined above. At the same time we firmly believe that a close and productive academic-



industrial relationship is essential for many companies to assure competitiveness in a number of new technologies. Pooling of resources in maintaining a firm reaction engineering base is particularly valuable and we are deeply indebted to the participating companies for their unwavering support of CREL. It is a pleasure to announce that Mobil and Sohio have joined in 1987 our group of participating companies in supporting CREL. It is by now evident that CREL at Washington University plays a special and unique role in keeping reaction engineering vital by:

- having a critical mass of faculty of the required expertise,
- concentrating resources from participating organizations to allow research continuity in certain areas,
- having a stimulating and stable group of graduate students to exchange ideas on a variety of projects,
- having a well balanced research program between old and new technologies, experimental and modeling work,
- emphasizing the use of fundamentals in problems of practical significance,
- establishing "a priori" design and role of CRE in new technologies.

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

We still classify our research in three broad generic areas of multiphase reactors, gas-solid noncatalytic reactions, and new materials, modeling, control and expert systems. A better classification is probably in order and will be attempted next year.

In the area of multiphase reactors we continue to work on better

quantification of various transport effects in trickle-beds, bubble columns, centrifugal packed beds, and slurry reactors. Easier scale-up and safer design are our overall goals. Here are some recent highlights. A new methodology for interpreting tracer data and for deciphering the causes of trickle-bed reactor malfunction are currently investigated (E. Beaudry). Experimental confirmation of this technique is planned (P. Hanratty). A new model for assessing the nature and configuration of the liquid in trickle-beds has been developed (R. Holub). A test has been successfully conducted on our medical school's PETT-II to confirm that positron emission tomography can resolve the nature of liquid structure (films, rivulets, etc.) and yield its three dimensional distribution in trickle-beds. Funds are being sought to implement this technique which could revolutionarize our understanding of trickle-beds.

Supporting experimental and theoretical evidence is sought (N. Devanathan) for the novel "elevator-mixing cell" model developed for bubble columns in CREL. This involves the development of a new approach in calculating liquid recirculation profiles. A single radioactive particle detection facility is being planned which will allow us to map the velocity and turbulence field in the bubble column as function of operating conditions. The theory for liquid flow, gas-liquid and liquid-solid mass transfer in centrifugal packed-bed gas-liquid contactors was developed and experimentally confirmed (S. Munjal). Further progress is being made (A. Basic) in predicting mass transfer coefficients in these devices. A novel experimental electrochemical technique will be used to determine liquid holdup. Growth of magnetic iron oxide particles is studied in a slurry reactor (D. O'Connor). Operating parameters that affect the size and shape of the crystallites, which are vital to their

application, are being identified.

In gas-solid noncatalytic reactions we have concentrated on understanding silicon production via silane pyrolysis. A working model of a fluidized bed reactor has been developed (S. Lai). Model predictions are in good agreement with the existing industrial data. The key parameters that affect reactor performance have been identified. Possibilities of growing silicon particles larger than 100  $\mu\text{m}$  in an aerosol reactor are being investigated (Y. B. Yang).

Our activities in the area of new materials, modeling and control continue to be numerous. We are expanding our joint efforts with our Materials Science Laboratory (Dr. J. L. Kardos) in modeling the cure cycle of composite materials from thermosetting materials (R. Dave, S. J. Choi) to thermoplastic materials (I. S. Yoon, S. J. Choi). Degassing of the composite and consolidation during cure are being quantified. Our efforts in modeling the temperature distribution and stress levels in Czochralski grown crystals (R. K. Srivastava) have received international attention. With good progress being made in modeling the hydrodynamics and mass transfer in melts (D. Dorsey) we are well on our way to document that improved multivariable control of CZ-growth is possible for a number of materials e.g. silicon, gallium arsenide, etc. The systematic study of the differences in performance of the three basic types of electrochemical cells, caused by differences in flow fields in the capillary gap, rotating electrolyser and pump cells, is nearing completion (B. Thomas). Significant progress has also been made in understanding the physics of plasma reactors (S. Pirooz).

All active research projects are summarized in Table I and are described in this report. It should be mentioned that S. Munjal completed

his D.Sc. thesis on "Fluid Flow and Mass Transfer in Rotating Packed Beds with Countercurrent Gas-Liquid Flow" and accepted employment with the Dow Chemical Company in Freeport, Texas. R. Dave successfully defended his thesis on "Computer Aided Processing of Composites" and is currently with the Michigan Molecular Institute in Midland, Michigan.

In the future more CREL projects will be initiated in the areas of new technologies where either transport effects need to be quantified or new control tools can be applied. We are indebted to Monsanto Chemicals for the donation of a \$500,000 TAP (Transient Analysis of Products) instrument. This, recently patented device, allows CREL to enter the world of catalytic research in the most meaningful way. The effect of changes in actual catalyst preparation or formulation on their performance will be investigated in the TAP device. The relationship between TAP performance (vacuum) and operation of laboratory scale reactors will be sought. Metal oxides, zeolites and other catalysts will be studied. In addition projects are contemplated in the areas of

- cyclic processes (integration of exothermic and endothermic reactions in a periodic operational mode)
- catalysis and trickle-bed operation in oxidation of hazardous wastes
- manufacture of high performance ceramics and ceramic composites
- production of aerosols and flame reactions

General principles will be sought and illustrated through experimental work on well selected test systems.

In pursuing some of the new projects and seeding the ideas for future work we often rely on input from our industrial advisors. Our gratitude

goes to all who have provided valuable input for a number of research projects. We are thankful to: F. X. Mayer and B. L. Tarmy of Exxon, G. Robertson of Hughes Research, F. Krambeck of Mobil, L. Bosanquet, R. E. W. Jansson and P. L. Mills of Monsanto, H. Hensley from Phillips, L. Clomburg from Shell, P. Wanser of Sohio, D. Dau and P. R. H. Martin from 3M Company, J. Cropley from Union Carbide. Special thanks are in order to R. E. W. Jansson and P. L. Mills of Monsanto for their efforts in enhancing the Monsanto-CREL interaction.

CREL remained active in professional meetings. Numerous papers were presented at the AIChE Annual meeting and at the World Chemical Engineering Congress in Japan. In addition, Drs. Duduković and Ramachandran together with Dr. F. Krambeck from Mobil organized and successfully conducted the 2nd Engineering Foundation Conference on Reaction Engineering, March 8-13, 1987 in Santa Barbara. The conference provided a unique forum for open exchange of views and drew over 100 participants from academia and industry.

The funding for CREL remained stable and new NSF grants have been approved for the next year. Industrial funding and EPRI funding is maintained. Active fund raising is planned in 1987/88 for our PET and SRPT facilities. Help and cooperation from participating companies will be greatly appreciated.

We are again planning our annual review meeting with industrial advisors for Wednesday, October 14, 1987. The whole day meeting will be held on Washington University campus. Since this is a unique occasion that enhances interaction with our students it is hoped that all industrial participants will plan to stay for the evening activities.

We are looking forward to seeing you all again in Fall 1987 (October 14) on our campus.

M. P. Duduković

TABLE I

## Active Projects in the Chemical Reaction Engineering Laboratory, June 1986 - May 1987

## AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results
<p>1. Trickle-Bed Reactor Performance and Scaleup</p> <p>Relevance: Generally accepted troubleshooting methods for trickle-beds are lacking. We attempt to develop a procedure by which the cause of reactor malfunction can be identified.</p>	Industrial	<p>M. P. Duduković P. A. Ramachandran P. L. Mills E. Beaudry P. Hanratty</p>	<p>A technique is developed for interpretation of results obtained by adsorbing and nonadsorbing tracers in order to identify liquid flow departure from the pilot plant flow pattern. The method identifies whether liquid maldistribution or catalyst deactivation is the culprit or reactor malfunction.</p>
<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 scaleup and this project attempts to fill the existing gap</p>	Industrial	<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. A preliminary test on a medical school PETT-2 device provided encouraging results.</p> <p>b) A general model is developed to predict, based on measured pressure drop, liquid structure in trickle-beds.</p>

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1986 - May 1987

AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results
<p>3. Hydrodynamics of Bubble Columns</p> <p><u>Relevance:</u> Complete description of liquid recirculation and backmixing would lead to more predictable designs of bubble columns.</p>	Industrial	M. P. Duduković P. A. Ramachandran N. Devanathan	<p>a) A computer aided radioactive particle tracking facility (CART) has been designed to yield velocity and turbulence fields in the column as a function of operating conditions.</p> <p>b) A model is developed for prediction of liquid recirculation.</p>
<p>4. Hydrodynamics and Mass Transfer in Centrifugal Packed-Bed Contactors</p> <p><u>Relevance:</u> 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 scaleup and use in gas-liquid and gas-liquid-solid operations.</p>	Exxon Foundation 3M Monsanto	M. P. Duduković P. A. Ramachandran A. Basic S. Munjal	<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) Experimental method for measurement of liquid holdup has been designed.</p>



TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1986 - 1987

AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results
<p>5. Iron Oxide Crystal Growth in a Three Phase Slurry Reactor</p> <p><u>Relevance:</u>                      Ferric hydroxide crystals are a precursor of magnetic iron oxide particles used in recording devices. Quantification of process variables that affect crystal size and shape is need for further process improvements.</p>	<p>Industrial</p>	<p>M. P. Duduković                      P. A. Ramachandran                      D. O'Connor</p>	<p>a) Literature search of the current understanding of the chemistry has been completed. Variables that may affect crystal size and phase are identified.</p> <p>b) Experimental procedure for evaluation of crystal size and shape is developed.</p>

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1986 - May 1987

AREA II: GAS SOLID NONCATALYTIC REACTIONS

Project	Funding	Investigators	Major Results
<p>1- Modeling of Fluidized-Bed Reactors and                      2. Aerosol Reactors for Manufacture of Silicon from Silane</p> <p><u>Relevance:</u>                      Silane pyrolysis in fluidized-beds and aerosol reactors is an attractive route for Si production. A model that accounts for all complex phenomena occurring is needed.</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 and Union Carbide experimental data is good. The ability to predict conditions that favor formation of fines has been demonstrated.</p> <p>e) Model of the aerosol reactor has been formulated.</p>

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1986 - May 1987

AREA III: NEW MATERIALS, MODELING AND CONTROL

Project	Funding	Investigators	Major Results
<p>1. Computer-Aided Processing of Thermosetting and Thermoplastic Composites</p> <p><u>Relevance</u> Curing or thermo-setting and thermoplastic composites 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>	<p>Industrial DOD</p>	<p>J. L. Kardos M. P. Duduković R. Dave S. Choi I. S. Yoon</p>	<p>a) Conditions that prevent void formation in thermosets have been identified.</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 of thermosets has been developed.</p> <p>d) A model for evolution and degassing of volatiles in thermoplastic materials has been formulated.</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. This work leads to procedures for accurate calculation of selectivity</p>	<p>Monsanto</p>	<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. It is shown that tracer responses and velocity profiles give quantitative information about mixing and transport near the electrodes.</p> <p>b) A complete model for the prediction of the electrochemical reactor performance has been formulated.</p>

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1986 - May 1987

AREA III: NEW MATERIALS, MODELING AND CONTROL

Project	Funding	Investigators	Major Results
of electroorganic processes based on quantified hydrodynamic effects.			
3. Temperature Distribution and Stresses in Czochralski Crystal Growth  Relevance: 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 control of the process.	EPRI	P. A. Ramachandran M. P. Duduković R. K. Srivastava	a) A finite element computer code is developed for calculation of reflected radiation, convection and conduction heat transfer in the crystal enclosure.  b) Simpler models that relate pull rate, crucible temperature and interface shape are developed for use in control.  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.  d) Radiation view factors for short crystals are calculated.  e) Residual stresses are calculated.
4. Hydrodynamics, Heat and Mass Transfer in the Czochralski process	EPRI	P. A. Ramachandran M. P. Duduković D. Dorsey	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.

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1986 - May 1987

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 thermocapillary 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. Modeling Plasma Effects 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	<p>a) A preliminary model that decouples plasma physics and chemistry has been developed and is tested on selected CVD systems.</p>

## AREA I: MULTIPHASE REACTORS

### Project I.1. Trickle-Bed Reactor Performance and Scale-Up

#### A. Problem Definition

The performance of a plant-scale trickle-bed reactor is often much poorer than the pilot-plant reactor from which it was designed. This can be due to one or a combination of three possible reasons: global liquid maldistribution, particle-scale incomplete contacting, and catalyst deactivation. Nonvolatile impulse tracer studies provide a measure of the combined effects of global liquid maldistribution and particle-scale incomplete contacting. Even when particle-scale contacting is complete, liquid maldistribution can be obscured by the contribution to the impulse tracer response curve (the E-curve) of the tracer while it is diffusing inside the porous particles. The goal of this project is to decouple the contribution to the E-curve of the tracer while it is in the particles. The resulting E-curve represents the distribution of residence times of the liquid external to the particles. This information can then be used to quantitatively assess whether global liquid maldistribution or catalyst deactivation affected the reactor's performance for a first-order, liquid-limiting reaction.

#### B. Research Objectives

1. Development of particle-scale transfer functions based on a tracer mass balance in assumed particle models.
2. Selection of the particle-scale model that gives the most consistent results.
3. Applying the analysis to actual industrial trickle-bed reactors.

#### C. Research Accomplishments

1. The procedure and software for decoupling the intraparticle diffusion contribution from the overall E-curve was established, based on the work of

Villiermaux (1) in liquid chromatography. The procedure is diagramed in Figure 1 and a description follows. Given the E-curve that resulted from a pulse of a nonvolatile, nonadsorbing tracer, the data is converted into the Laplace domain, where  $s$  is the Laplace transform variable. This Laplace domain curve of  $\bar{E}(s)$  vs.  $s$  is then replotted as  $\bar{E}(p)$  vs.  $p$  where  $p = s + k_{ex}H(s)/\epsilon_L$ . The term  $k_{ex}H(s)/\epsilon_L$ , which will be further described below, represents the contribution to the E-curve of the tracer when it was in the particles. The resulting curve of  $\bar{E}(p)$  vs.  $p$  is then inverted back into the time domain and represents the E-curve that would have been obtained had the tracer not diffused into the particles. This E-curve, which represents only the external liquid, can be quantitatively analyzed for global liquid maldistribution (bypassing, stagnant zones, etc.).

Determining the proper model or form describing the tracer while it is within the particles ( $k_{ex}H(s)/\epsilon_L$ ) is the key to the procedure. The term  $k_{ex}$  is the exchange coefficient between the external liquid and the liquid within the particles. The liquid holdup outside of the particles is  $\epsilon_L$ , and  $H(s)$  is the particle-scale transfer function describing what happened to the tracer during the time it was in the particle. This transfer function  $H(s)$  is based on a tracer mass balance in assumed models for the porous particle. The proper transfer function can be shown theoretically to be the one which correctly predicts the conversion of a nonvolatile, first-order reactant and which gives the same  $\bar{E}(p)$  vs.  $p$  curve for both an adsorbing and a nonadsorbing tracer.

Five transfer functions were derived based on five particle-scale models. The models were: 1.) spherical catalysts that are approximated for internal and external partial wetting by the suggestion of Sakornwimon and Sylvester (2), 2.) infinite slab catalysts that are approximated for internal and external wetting by the suggestion of Dudukovic (3), 3.) dry,

half-wetted, and fully wetted slabs as given in a previous CREL Annual Report (4), 4.) spherical catalysts completely engulfed in a large stagnant sphere of liquid as suggested by Koros (5), and 5.) a weighted combination of Models 1 and 4.

The transfer function for Model 1, assuming all pores are liquid filled, is:

$$H(s) = \frac{\frac{D_e}{k_s R} \left[ \left( \frac{\epsilon_p s}{D_e} \right)^{1/2} R \coth \left\{ \left( \frac{\epsilon_p s}{D_e} \right)^{1/2} R \right\} - 1 \right]}{1 + \frac{D_e}{k_s R} \left[ \left( \frac{\epsilon_p s}{D_e} \right)^{1/2} R \coth \left\{ \left( \frac{\epsilon_p s}{D_e} \right)^{1/2} R \right\} - 1 \right]} \quad (1)$$

where:

$$R = \frac{3(1-\epsilon)}{a_p f} \quad k_{ex} = k_s a_p f$$

The effective diffusivity ( $D_e$ ) is calculated using the Wilke-Chang correlation for the molecular diffusivity and assuming a tortuosity of 3.0. The liquid-solid mass-transfer coefficient ( $k_s$ ) was obtained from the correlation of Tan and Smith (6). The fraction of wetted catalyst external surface area ( $f$ ) was obtained from the  $\eta_{ce}$  correlation developed in our laboratory (7). The other values are assumed to be known: the pellet porosity ( $\epsilon_p$ ), the bed porosity ( $\epsilon$ ), and the external particle surface area per volume of empty reactor ( $a_p$ ). This is the same model that was used by Kennedy and Jaffe (8) but with complete external wetting ( $f=1.0$ ).

2. The five models were tested on simultaneous tracer and hydrodesulfurization data kindly supplied by Exxon. An example of one analysis using Model 1 is shown in Figures 2 - 5. Figure 2 is the E-curve for a pilot-plant reactor. Qualitatively, it appears to be in plug flow, with the spread of the response curve due to the diffusion of tracer into the particles. Transforming this E-curve into the Laplace domain yields the dashed line in Figure 3 of  $\bar{E}(s)$  vs.  $s$ . This curve is then replotted as  $\bar{E}(p)$  vs.  $p$ , where  $p = s + k_{ex}H(s)/\epsilon_L$  with  $H(s)$  given by Equation (1) and



the external liquid holdup determined from the first moment of the E-curve. This curve of  $\bar{E}(p)$  vs.  $p$  is the solid line in Figure 3 (marked external) and represents the response of a tracer residing only in the external liquid. This response is nearly identical to that of a plug-flow reactor with the same external liquid holdup, as shown by the nearly coincident line in Figure 3. Figure 4 is the E-curve from a plant-scale trickle-bed reactor, clearly not in plug flow. The dashed line in Figure 5 is  $\bar{E}(s)$  vs.  $s$  using the E-curve of Figure 4, and the solid line marked external is the plot of  $\bar{E}(p)$  vs.  $p$ . This solid line clearly deviates from a line showing what the response of a plug-flow reactor (pfr) would have been.

The consistency of the transfer function was tested by comparing conversion predictions vs. measurements. The intrinsic kinetic rate constant per particle pore volume ( $k_p$ ) is found from the conversion ( $X$ ) measured in the pilot-plant reactor:  $X = 1 - \bar{E}(p)$  where  $p = k_{ex} H(k_p) / \epsilon_L$ . This rate constant was then applied to the data of the plant reactor and predicted a conversion of 92%, which was above the actual plant measurement of 85% and below the prediction of 99% which assumes plug flow.

3. Some preliminary generalizations were drawn from the analysis. Models 1, 2, and 3 provided very similar behavior, and all overpredicted the conversions measured in the plant reactors. This could be due to not having the correct transfer function, different states of catalyst activation in the pilot-plant and plant reactors, tracer volatility, poor estimates of transport properties, or some other possibilities. Model 4 required impossible liquid holdups and also gave unrealistic conversions. Model 5 requires too many parameters (size and number of stagnant pockets) and was not found to be better than Models 1, 2, and 3.

#### D. Further Research Plans

1. Check the consistency of the transfer functions using adsorbing and nonadsorbing tracers. Both tracers will give the same  $\bar{E}(p)$  vs.  $p$  curve when the correct transfer function is used.
2. Selection of a transfer function for general use.

#### E. Bibliography

1. Villiermaux, J., Multiphase Chemical Reactors Vol. II - Design Methods, Sijthoff and Noordhoff, (A. E. Rodrigues and D. Tondeus, Eds.), 107 (1981).
2. Sakornwimon, W., and N. D. Sylvester, Ind. Eng. Chem., Process Des. Dev., 21, 16 (1982).
3. Dudukovic, M. P., AIChE J, 23, 940 (1977).
4. CREL Annual Report, June 1, 1984 - May 31, 1985, 'Project I.1'.
5. Koros, R., Multiphase Chemical Reactors Volume II - Design Methods, Sijthoff and Noordhoff, (A. E. Rodrigues and D. Tondeus, Eds.), 429 (1981).
6. Tan, C. S., and J. M. Smith, AIChE J, 28, 190 (1982).
7. El-Hisnawi, A. A., M. P. Dudukovic, and P. L. Mills, ACS Symp. Series No. 196, 421 (1982).
8. Kennedy, C. R., and S. R. Jaffe, Chem. Eng. Sci., 41, 845 (1986).

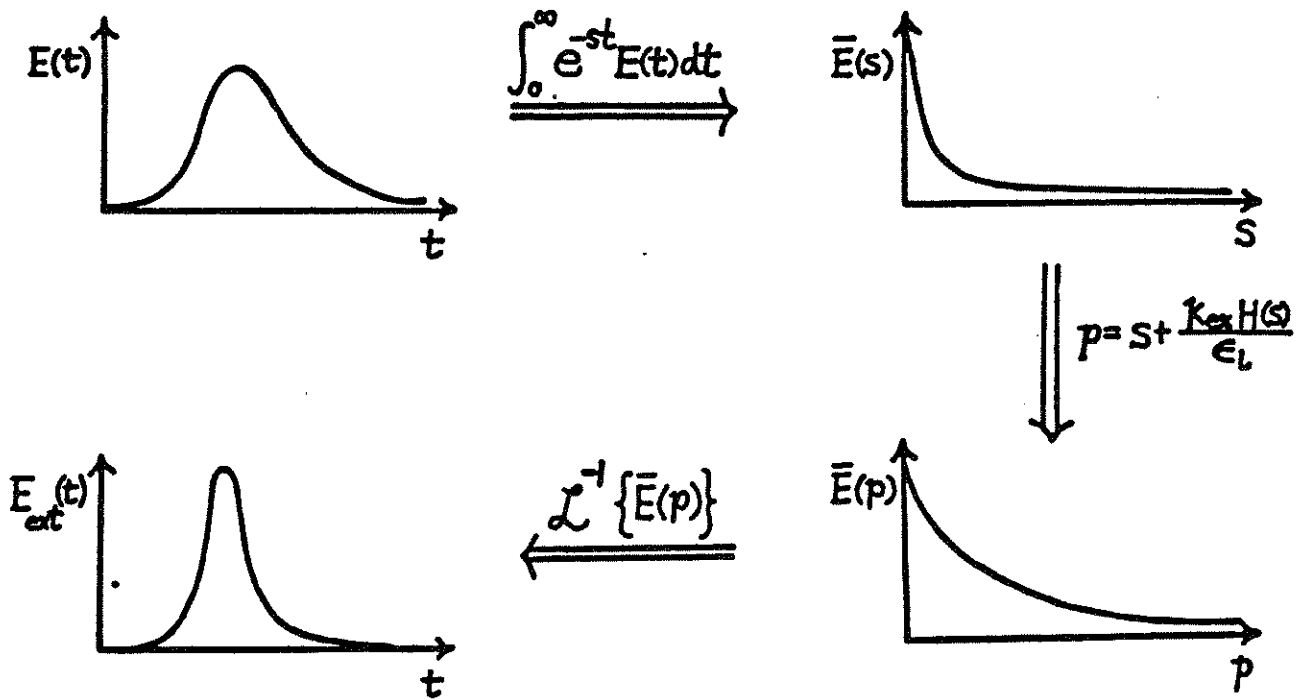


Figure 1. Procedure for Extracting the E-Curve of the External Liquid

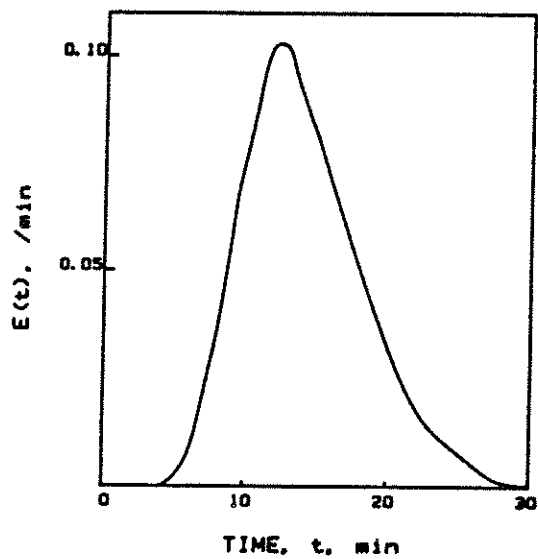


Figure 2. Pilot Plant E-Curve

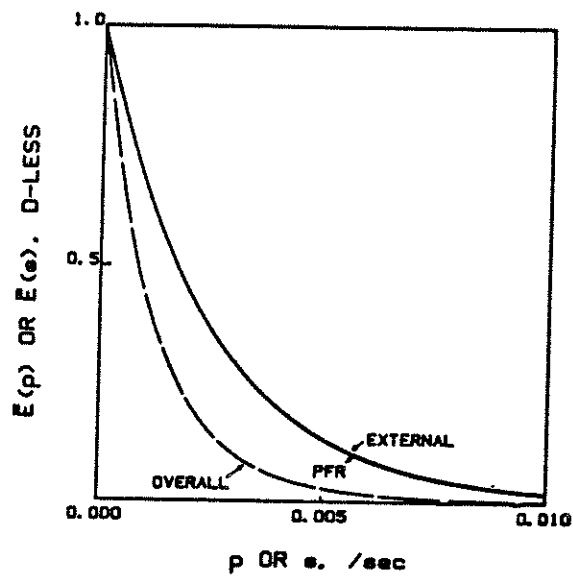


Figure 3. Laplace Domain of the Pilot Plant E-Curve

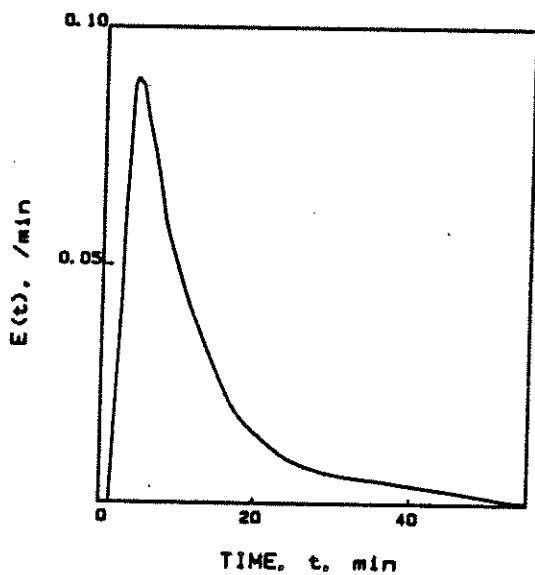


Figure 4. Actual Plant E-Curve

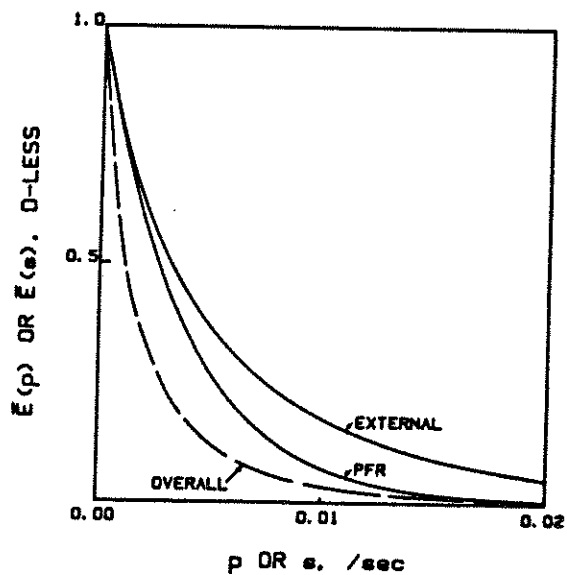


Figure 5. Laplace Domain of the Actual Plant E-Curve

## 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 three phases present. The prediction of flow regime is accomplished using empirically developed maps from relatively small diameter beds. Attempts at predicting the observed flow regime transition from trickle to pulsing flow are just appearing in the literature and an unifying theory is still lacking. On the particle scale, liquid distribution in trickle beds is currently viewed as films flowing over the packing with the gas flowing in the remaining voids. The bed scale distribution is accounted for by two basic models, diffusion or random walk models and structural models. The diffusion models assume uniform packing structure and always predict a uniform liquid distribution at some critical bed depth. These models never predict flow maldistribution. The structural models attempt to model the stochastic nature of packed beds and allow for nonuniform packing structure. These models can predict liquid maldistribution, but a knowledge of how liquid flows on the particle scale and what factors determine whether a particle is completely wetted is required. Even these fundamental concepts are not rigorously defined in a trickle-bed. Thus, both particle scale incomplete wetting and reactor scale liquid maldistribution 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 flow annular models as building blocks for trickle-bed models. Figures 1 and 2, [1,2], 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 same basis, almost no overlap exists.

Due to the inherent difficulties of measuring particle scale incomplete wetting, and then relating this to the bed scale via a structural model, many investigators have taken the approach of modelling the important bed parameters such as pressure drop, holdup, and incomplete wetting with Ergun type phenomenological models or correlations [3]. An important consideration here is that the phenomena upon which the models are based has never been measured in a nonintrusive manner. For this reason, the validity of some assumptions in the models is unknown. Therefore, 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 and build a nonintrusive holdup measuring device to visualize the liquid distribution in trickle beds and confirm, or disprove, the assumptions behind the models used

in objective 2.

2. Using currently available phenomenological models of two phase flow hydrodynamics in trickle beds, model the flow distribution, pressure drop, and effect of bed scale nonuniformities on the reactor scale wetting.

### C. Research Accomplishments

Progress has been made in both objectives.

1. A nonintrusive method for viewing the flow field has been decided on and the preliminary design and equipment proposal completed (see Figures 3 to 5). The method will be based on POSITRON EMISSION TOMOGRAPHY, PET, 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 (6 to 8 millimeter resolution is expected). The device was first developed at Washington University Medical School around 1975 to obtain quantitative reconstructions of blood flow in the brain [4]. Our device will be similar to the original prototypes but with several improvements to enhance the resolution. Two factors make this method viable only at Washington University. First, the design and construction of these devices is done here, and hence a proven design as well as the necessary construction equipment is readily available. 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 liquid distribution and the effect of surface tension, porous vs. nonporous packing, regions of decreased or increased porosity, flow redistributors, liquid distributors and collectors, etc.. This information will then be incorporated into the phenomenological models.

2. Some questions were raised as to the ability of PET to resolve liquid saturated zones among the background radiation from other zones of the bed which are not saturated with liquid. To answer this question, a static phantom test (see Figure 6) was performed on an existing device at the Washington University Medical School (note: size and time constraints prevented actual bed operation). Liquid saturated zones of different sizes were artificially placed in the bed by constraining portions of the bed with tubing which were sealed at the bottom. These tubes were then filled with radioactive  $^{11}\text{C}$  isotope (a positron emitter) at a concentration of 1.0 microcurie per cubic centimeter. The same isotope solution was then poured over the packing and allowed to drain, leaving a background radiation due to static holdup in the bed. The results of the scan prove the ability of the method in resolving regions of different liquid holdup and are shown in Figure 7. Note that zones from 1/2 inch to 1/8 inch were used and the device could not quantitatively resolve the 1/8 inch zone, as was expected.

3. A predictive model based on observed pressure drops in trickle-beds has been developed which predicts the occurrence of liquid maldistribution, and quantitatively calculates the



important characteristics of the maldistributed flow. The model is called the THREE ZONE MODEL since it divides the bed into three noninteracting zones called the Film, Dry, and Rivulet zones. The accessibility of each phase to each zone is shown in Figure 8. The model was tested using the experimentally observed pressure drop hysteresis [5,6,7, and Figure 9] which has been attributed to liquid maldistribution in the case of the lower leg for increasing liquid flow rate. The curve for decreasing liquid flow rate has been attributed to entirely film flow. The results of the model, as tested on two such hysteresis loops available in the literature, are shown in Figure 10 in the form of the fraction of the bed occupied by each zone. As can be seen, the model does predict a large deviation from film flow for the increasing liquid flow rate curve, and predicts that most of the bed is in film flow for the decreasing liquid flow rate curve. The same trends as shown for the increasing liquid flow rate were also measured by Charpentier [8] with electrical conductivity probes, but his results are only qualitative due to the intrusive nature of the measurement.

#### D. Further Research Plans

This research is proceeding on three fronts.

1. The PET device is in the funding stage. When funding is obtained, the device will be built and used in the described manner.
2. Other nonintrusive methods, such as gamma scintillation photography, are being investigated as alternatives to PET to

give semi-quantitative information from which the validity of the phenomenological models to be used can be ascertained. Still the quantitative nature of PET makes it the best method, by far, for the flow visualization studies.

3. The modelling of the bed is proceeding in a more rigorous manner in an attempt to predict not only the current parameters, but also the pressure drop, given only the bed properties and flow rates. The model equations will be re-evaluated based on the experimental flow visualization studies when completed.

#### E. Nomenclature

U = superficial velocity of the subscripted phase

$\rho$  = density of the subscripted phase

L = superficial mass flux of liquid

G = superficial mass flux of gas

#### Subscripts

N = nonwetting phase = gas

W = wetting phase = liquid

#### F. Bibliography

1. Biswas, J. and P. F. Greenfield, Int. J. Multiphase Flow, 11, 553, (1985).
2. Charpentier, J. C. and M. Favier, AIChE J., 21, 1213, (1975).
3. P. A. Ramachandran and R. V. Chaudhari, Three Phase Catalytic Reactors, Gordon and Breach Science Publ., NY, (1983)

4. Ter-Pogossian, M. M., M. E. Phelps, E. J. Hoffman, and N. A. Mullani, Radiology, 114, 89, (1975)
5. Kan, K. and P. F. Greenfield, Ind. Eng. Chem. Proc. Des. Dev., 17, 482, (1975).
6. Levec, J., A. E. Saez, and R. G. Carbonell, AIChE J., 32, 353, (1986).
7. Christensen, G., S. J. McGovern, and S. Sundaresan, AIChE J., 32, 1677, (1986).
8. Charpentier, J. C., C. Prost, W. van Swaij, and P. Le Goff, Chim. Ind., Gen. Chim., 99, 803, (1968).

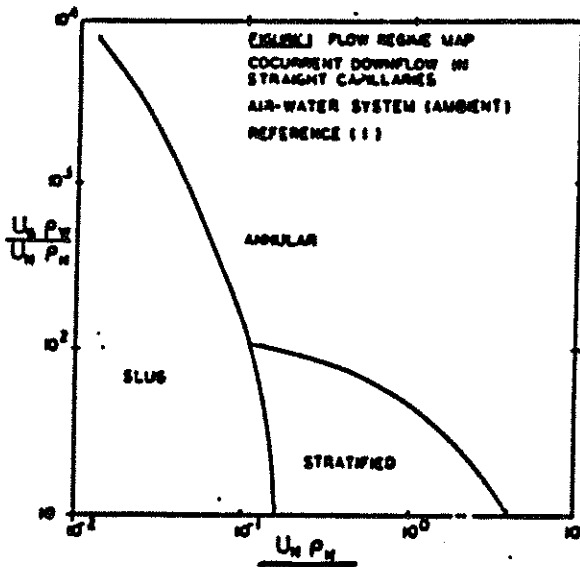


Figure 1. Flow Regime Map for Capillaries.

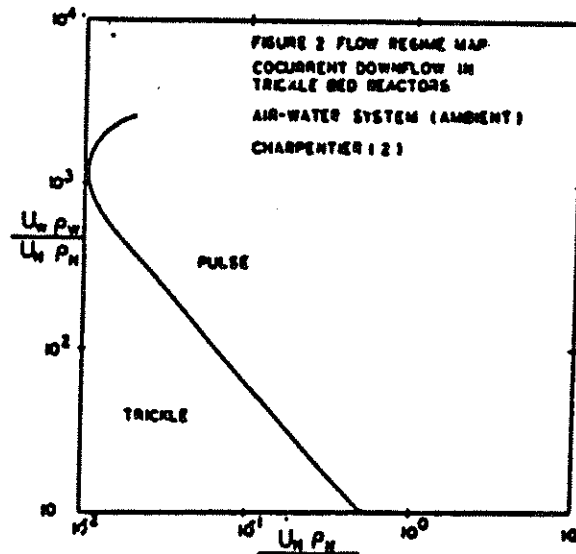


Figure 2. Flow Regime Map for Trickle-Beds.

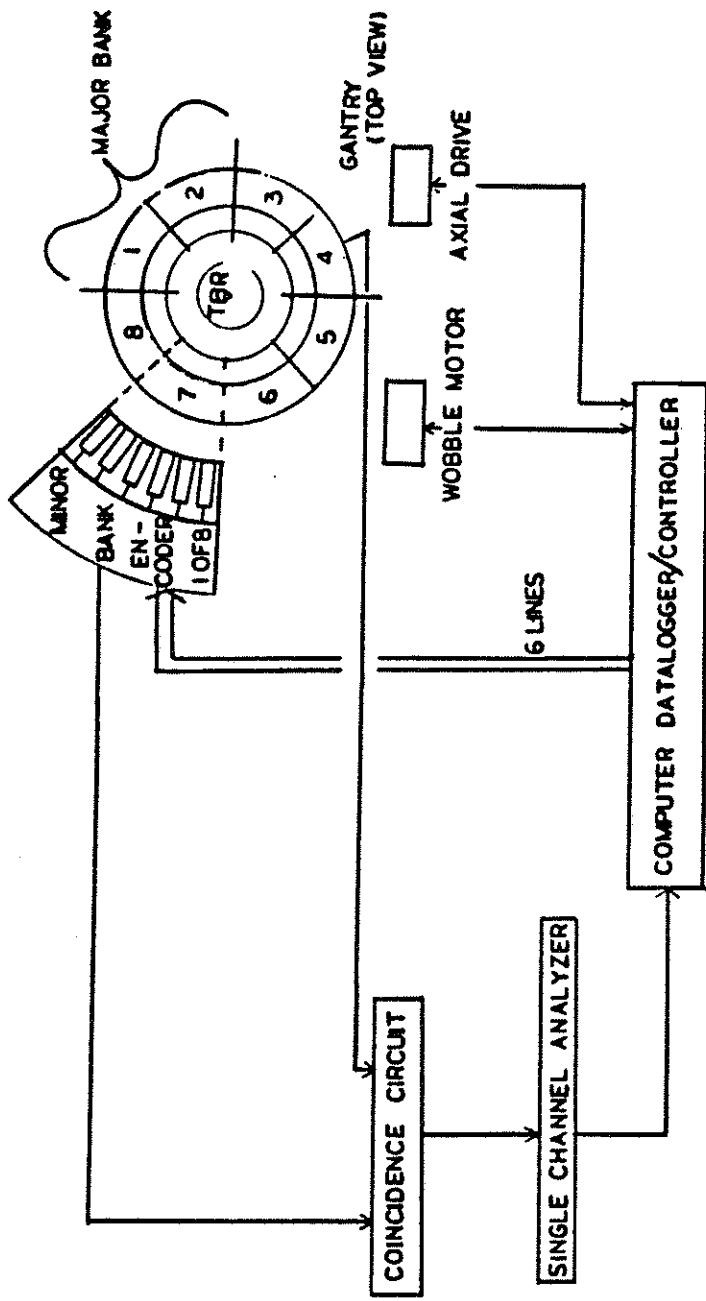
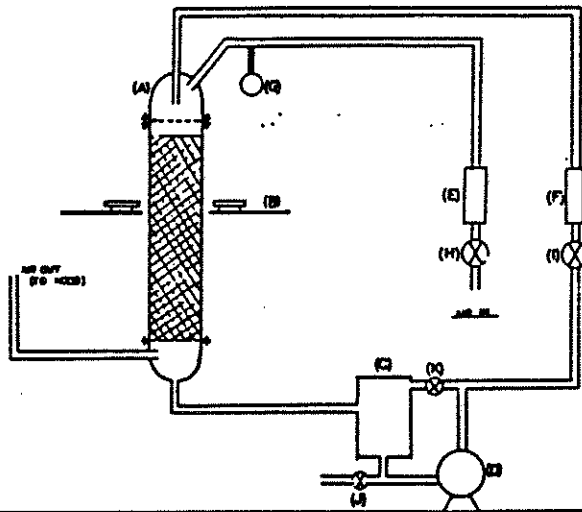


Figure 3. Schematic of the Gantry and Detection System.



KEY TO FIGURE 4

- (A) Trickle Bed Reactor
- (B) Coincident NaI(Tl) detectors (36 total) and support platform mounted for rotation and axial movement.
- (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 the System

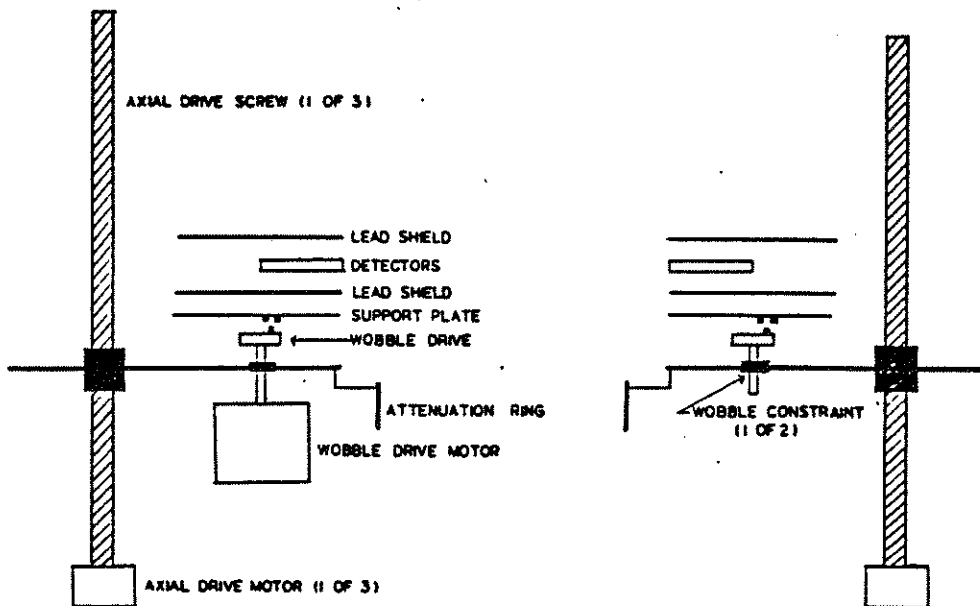


Figure 5. Expanded Cross-Section of the Gantry

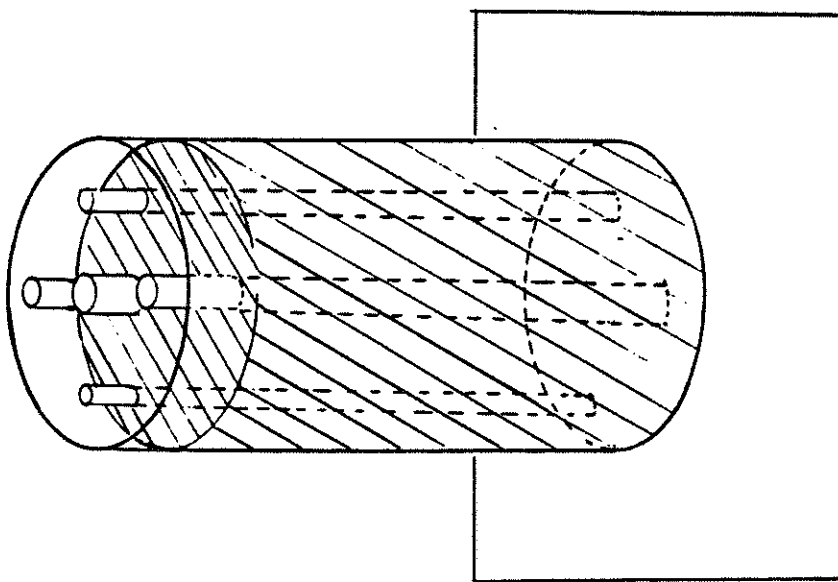


Figure 6. Schematic of the Test Phantom. Approximate rivulet position and size shown.

WASHINGTON UNIVERSITY SCHOOL OF MEDICINE --- SUPER PETT II (HEAD)

SUBJECT ID  
PHANTOM

DATE: 1/14/87

PUN:

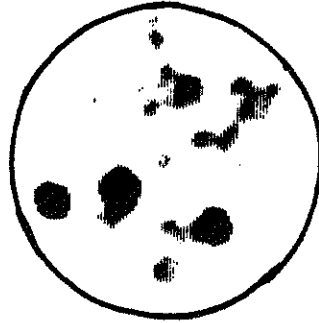
SLICE: 2

NUCLIDE: C11

COMPOUND:

SCAN TIME: 3565 SECS.

TOTAL COUNTS: 2,281,045



3010

1595

Figure 7. Phantom Test Results. Poor copy. Actual quantitative resolution = 4 mm. Saturated zones appear black. Static holdup appears gray. Actual rivulet position shown. Phantom wall sketched in for reference.

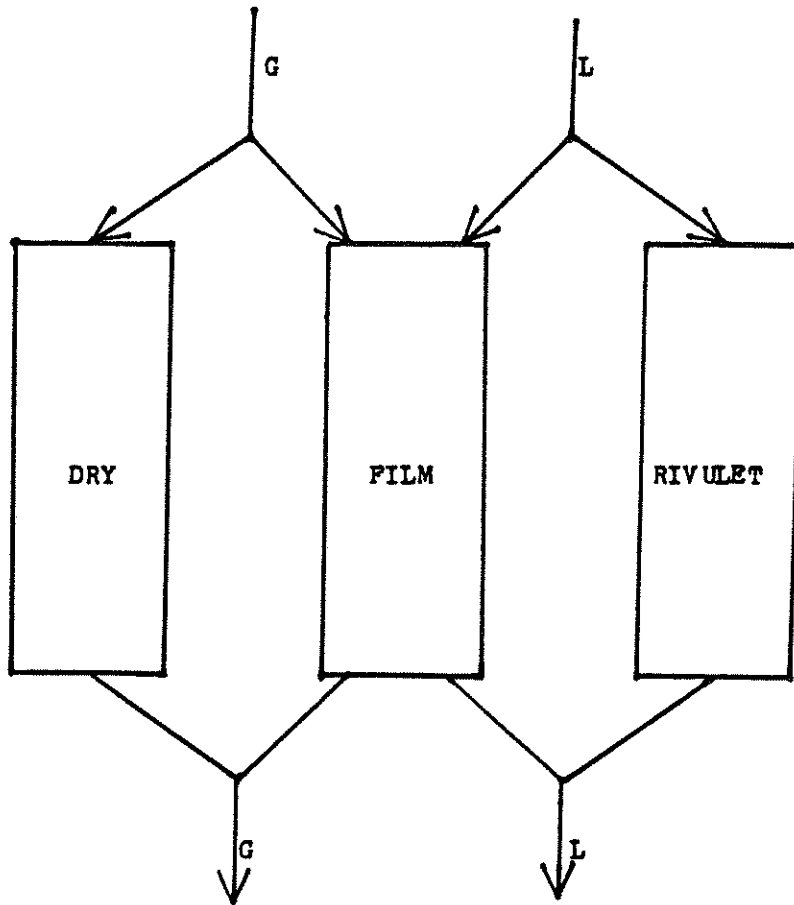


Figure 8. The Three Zone Model. The accessibility of each zone to each phase is shown.

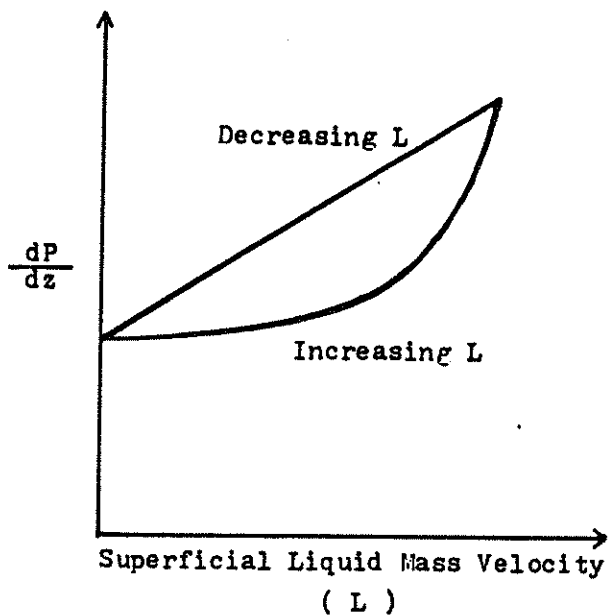


Figure 9. Schematic of a Pressure Drop Hysteresis Loop seen in TBR's.  $G$  is constant. Lower leg is seen upon increasing  $L$  to pulsing from zero. Upper leg is seen upon decreasing  $L$  from pulsing.

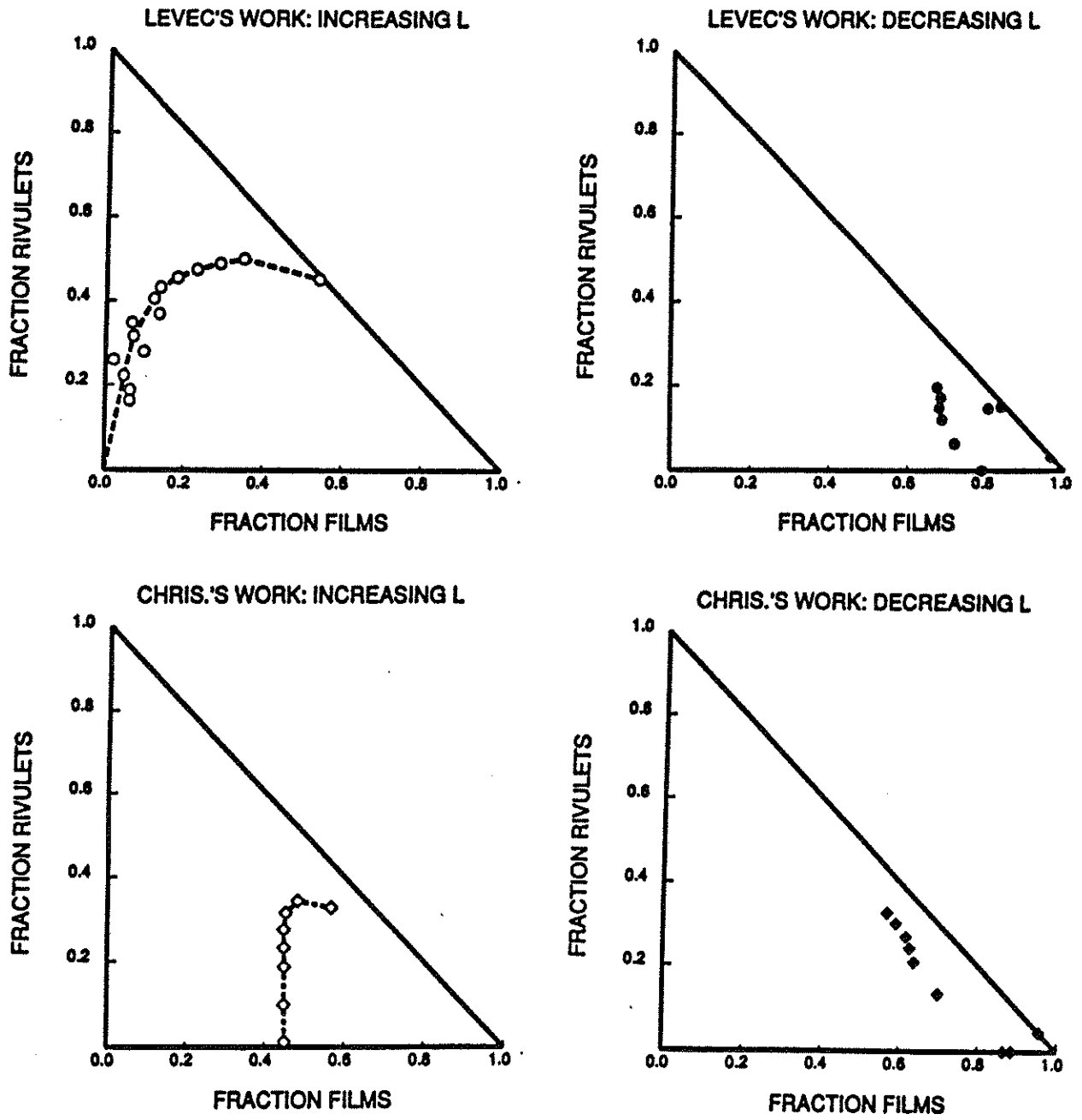


Figure 10. Test Results from the Three Zone Model. Plot titles give the reference from which the data was taken.



Project I.3 Hydrodynamics of Bubble Columns - Investigations Using A  
Computer Aided Radioactive Tracking [CART] Facility

A. Problem Definition

Liquid circulation or 'Gulf stream effect' is a phenomenon commonly encountered in bubble columns caused by nonuniform holdup profiles. It contributes to liquid phase mixing, and also affects bubble coalescence and heat transfer to the wall or immersed tubes. The accurate design and scaleup of bubble columns is contingent upon our ability to quantify liquid circulation.

There is a considerable disagreement between the various theoretical approaches suggested for liquid circulation. The 2-D inviscid models, (Whalley and Davidson, 1974, Joshi and Sharma, 1979) make use of the principle of minimization of the maximum vorticity which has no physical basis. In addition these models neglect the body force term in the momentum equations. The 1-D models (Ueyama and Miyauchi, 1979) which are based on the momentum equations for the liquid phase, have a limited range of applicability. These models require suitable constitutive equations for the Reynolds stresses and the gas-liquid interaction forces for proper closure. In addition, none of the models are able to predict the void profiles a priori. Hence a unified treatment of circulation is necessary. This includes a systematic experimental investigation of liquid circulation and its dependence on column geometry, operating conditions and liquid physical properties.

Liquid mixing in churn-turbulent bubble columns is traditionally described using the 1-D axial dispersion model, which has no physical basis for this situation. A novel phenomenological model, which considers most of the features of churn-turbulent flow, was developed in this laboratory (Myers et al., 1986) as an alternative to the axial

dispersion model. In the present approach, we propose to describe mixing by a 2-D conservation equation, with the velocity profiles and dispersion coefficients as input to the model. This latter information will be provided by theory and experiment.

Wall heat transfer coefficients are correlated using single phase flow correlations (such as the Seider and Tate correlation) by empirically adjusting the constants. It is necessary to develop a basic surface renewal model which can predict the heat transfer coefficient if liquid velocity profiles are available.

### B. Research Objectives

#### Experimental:

1. Design and implement a COMPUTER AIDED RADIOACTIVE TRACKING [CART] facility for measuring local instantaneous liquid velocity profiles.
2. Use CART to describe the liquid circulation as a function of column geometry (distributor type, diameter), liquid physical properties (viscosity, surface tension) and operating conditions (superficial gas velocity).
3. Perform a backmixing experiment by introducing liquid radioactive tracer in a batch column and monitoring its spread with the aid of scintillation detectors.
4. Measure time averaged holdup profiles by gamma ray tomography. The results will be used as input to the 2-D model.

#### Theoretical:

1. From experimental measurements extract various turbulence parameters such as Reynolds stresses, eddy viscosity, dispersion coefficients and correlation coefficients. Develop a theoretical basis for predicting the eddy viscosity and turbulent dispersion in terms of easily measurable quantities.

2. Develop a simple 1-D model for circulation which can predict both liquid velocity and holdup profiles by incorporating suitable constitutive equation for the slip velocity.

3. Formulate and solve a 2-D pseudohomogeneous model for the liquid velocity profiles. The experimentally determined holdup and eddy viscosity profiles will be an empirical input to this model. Model predictions will be compared to the actual liquid velocity profiles.

4. Solve a 2-D model for the spread of a nonvolatile tracer. The experimental velocity profiles and turbulent dispersion coefficients will be an empirical input to this model. The results will be compared to those of the backmixing experiment.

#### C. Research Accomplishments

1. The experimental section of this project will be carried out at Florida Atlantic University with Dr. Davood Moslemian, who will serve as a coinvestigator in this project.

The CART has been designed and will be set up in the next few months. Its principle is as follows. The motion of a single radioactive particle, emitting gamma radiation at a constant energy level and which is neutrally buoyant in the liquid will be monitored using an array of 16 scintillation detectors arranged in an optimum configuration around the column. Using preestablished intensity vs. distance calibration, the distance of the tracer from each detector will be determined. The redundancy of data from multiple detectors will be used to locate the instantaneous position of the tracer. The displacements can be time differentiated to yield instantaneous velocities. If the column is divided into a number of sampling compartments, the repeated appearance of a tracer in a sampling compartment enables the ensembled average velocity profiles to be determined. Figure 1 shows the detector

arrangement and a schematic of the data acquisition system is shown in Figure 2. The details of the experiment are summarized in Table 1.

Theoretical estimates of errors due to void fluctuations have been obtained. The attenuation, buildup, effect of solid angle and detector efficiency have been taken into account in these computations. Figure 3 shows the photon countrate as a function of distance from the detector. The maximum error is about 25% at a countrate of 2500. This represents the worst possible scenario. Since calibration experiments will be insitu, the effect of void fluctuations is likely to be negligible. This will be confirmed by our preliminary experiments.

2. A simple 1-D model for liquid circulation has been developed. The model assumes steady axi-symmetric flow, no end effects and constant eddy viscosity. The voidage variation with holdup is expressed by two parameters,  $\epsilon_{\max}$ , the centerline voidage and  $n$ , a constant.

$$\epsilon/\epsilon_{\max}=1-(r/R)^n$$

The overall momentum equation (gas+liquid) is solved with appropriate boundary conditions to yield the velocity profiles. Wall shear stress is obtained from the liquid continuity. A constitutive equation for the slip velocity has been proposed using the two phase drift flux theory. This, in conjunction with gas continuity, yields the holdup profile. The only empirical parameter, the eddy viscosity, is correlated in terms of column diameter and superficial gas velocity ( $U_G$ ). Figure 4 shows the predicted and observed velocity profiles for  $U_G = 0.095$  m/sec. The agreement is reasonable. Ueyama and Miyauchi's model overpredicts the velocity close to the centerline. Figure 5 compares the holdup profiles. Using the present model, a value of  $n = 3.825$  was obtained. Ueyama and Miyauchi's model assumes  $n = 2$  for all columns which clearly overpredicts the voidage close to the centerline.

Although the model predictions are reasonable, the applicability of the model is limited by the empirical correlation for eddy viscosity and the constitutive equation for the slip velocity which are valid in a limited range of operation. Our current efforts are directed towards predicting the eddy viscosity using turbulence theory and the holdup profiles using the principle of minimum entropy production at steady state.

#### D. Future Work

1. The experiments will be conducted in stages. In the first stage, the CART facility will be constructed and some proof of concept experiments will be carried out. These include the assesment of: a) the effect of void fluctuations, b) uniqueness of intensity vs. distance relation, and c) the capability of CART to follow a prescribed trajectory.
2. The pseudohomogeneous 2-D model for liquid circulation and the 2-D model for tracer dispersion have been formulated and they will be solved using FIDAP/ PROTRAN finite element codes.

#### E. Bibliography

1. Hills, J. H., Trans. Inst. Chem. Engrs., 52, 1 (1974)
2. Joshi, J. B. and Sharma, M. M., Trans. Inst. Chem. Engrs., 57, 244 (1979).
3. Myers, K., Dudukovic, M. P. and Ramachandran, P. A., Chem. Eng. Sci., 1986, in press.
4. Ueyama, K. and Miyuachi, T., AIChE J., 25, 234 (1983)
5. Whalley, P. B. and Davidson, J. F., Proc. Symp. Two Phase Flow Systems, Inst. Chem. Engrs. Symp. Ser., 38, paper J5, 1974.

Table 1. Summary of experimental details.

Column material	Plexiglass
Column diameter	19 cm.
Column height	122 cm
Wall thickness	0.64 cm
Distributor	Porous plate
Liquid	Water
Gas	Air
Tracer particle	0.5 mm ion exchange polystyrene
Radioactive source	Cs-137, 0.662 MeV
Source strength	200 $\mu$ Ci
Detectors (16 Nos.)	2' by 2' NaI crystal/PMT
Sampling rate	30 Hz.
Duration of experiment	2-3 hrs

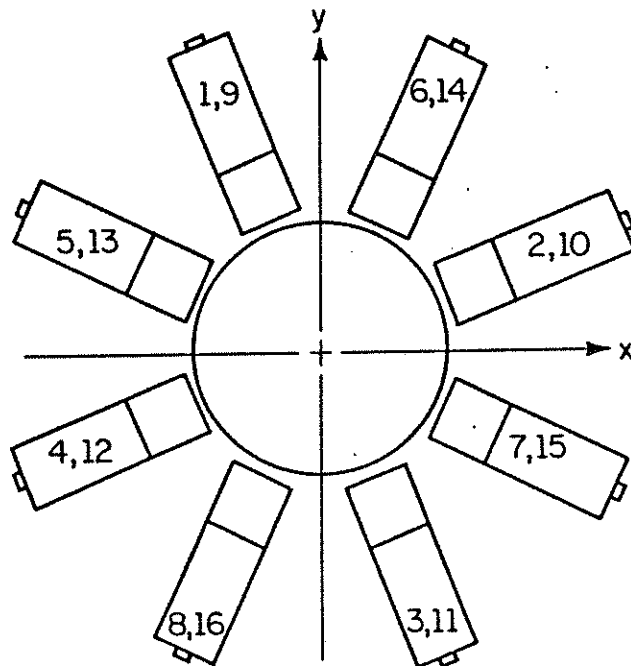


Figure 1. Arrangement of detectors; z- Coordinates: Crystals 1,2,3,4: 106.75 cm; Crystals 5,6,7,8: 76.25 cm; Crystals 9,10,11,12: 45.75 cm; Crystals 13,14,15,16: 15.25 cm.

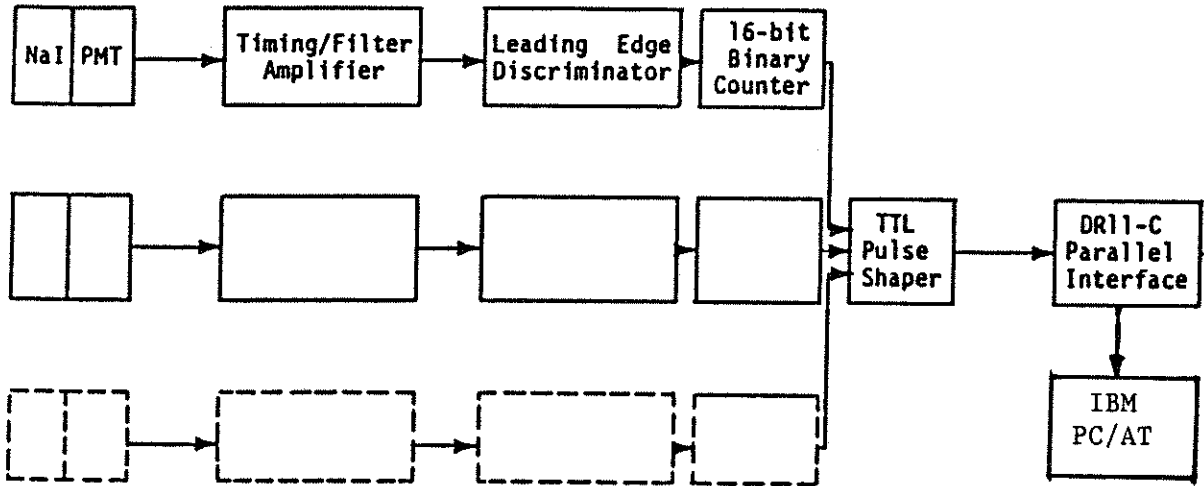


Figure 2. Schematic of the data acquisition system.

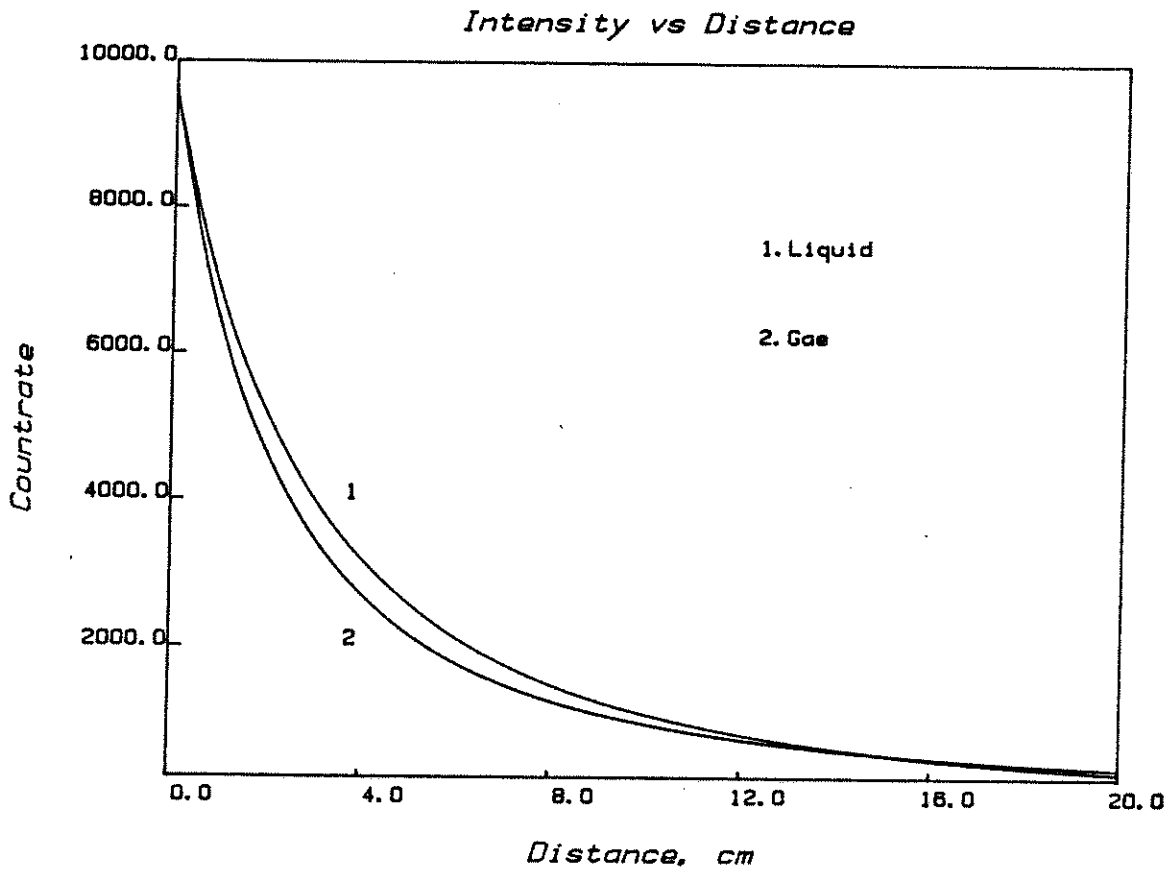


Figure 3. Intensity vs. distance relation for source along axis.

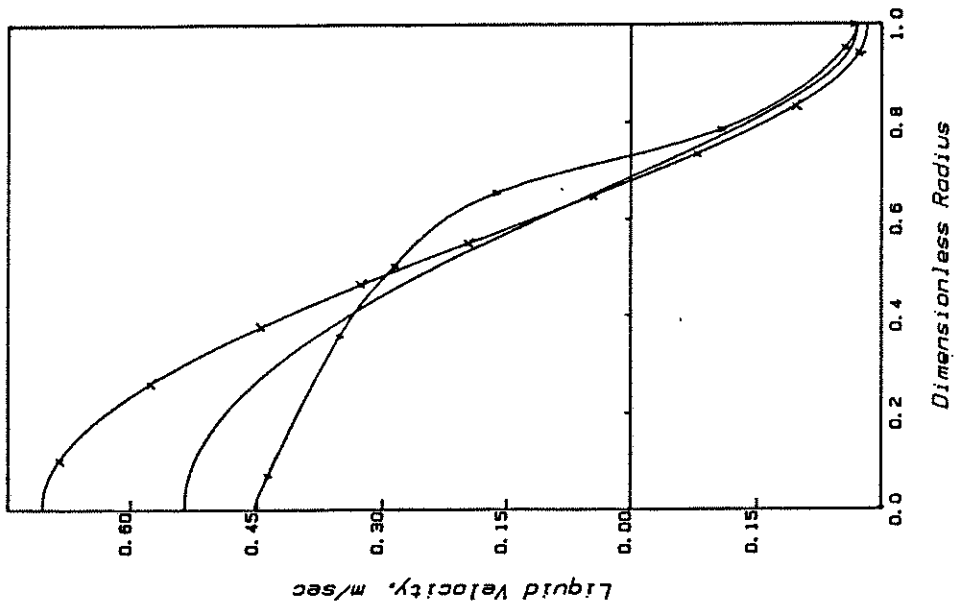


Figure 4. Liquid velocity profiles;  
 —x— Experimental data of Hills (1974).  
 — Model predictions.  
 —x— Ueyama and Miyuchi's model (1979).

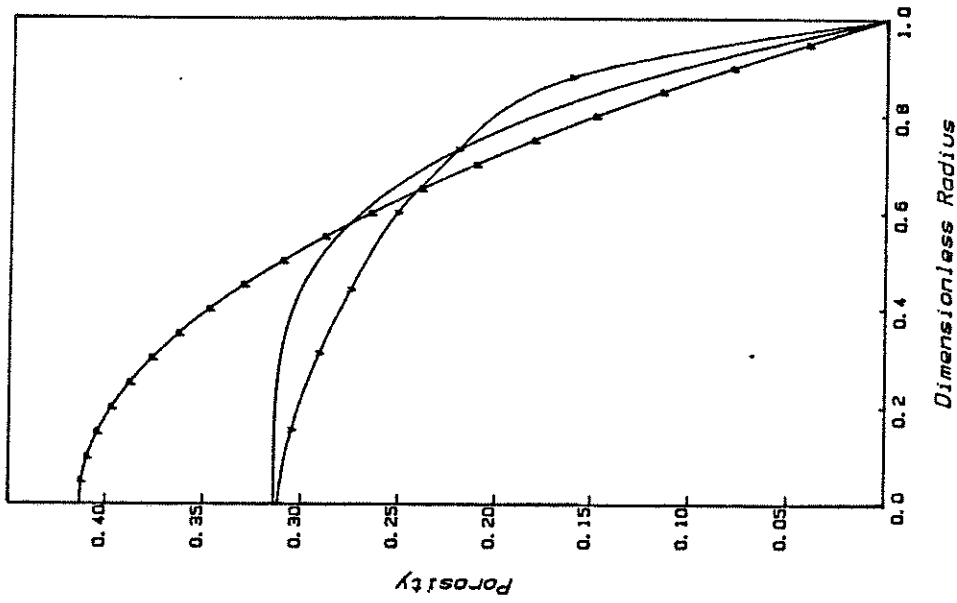


Figure 5. Voidage profiles;  
 —x— Experimental data of Hills (1974).  
 — Model predictions.  
 —x— Ueyama and Miyuchi's model (1979).



Project I.4 Hydrodynamics and Mass Transfer in Centrifugal Packed  
Bed Contactors

A. Problem Definition

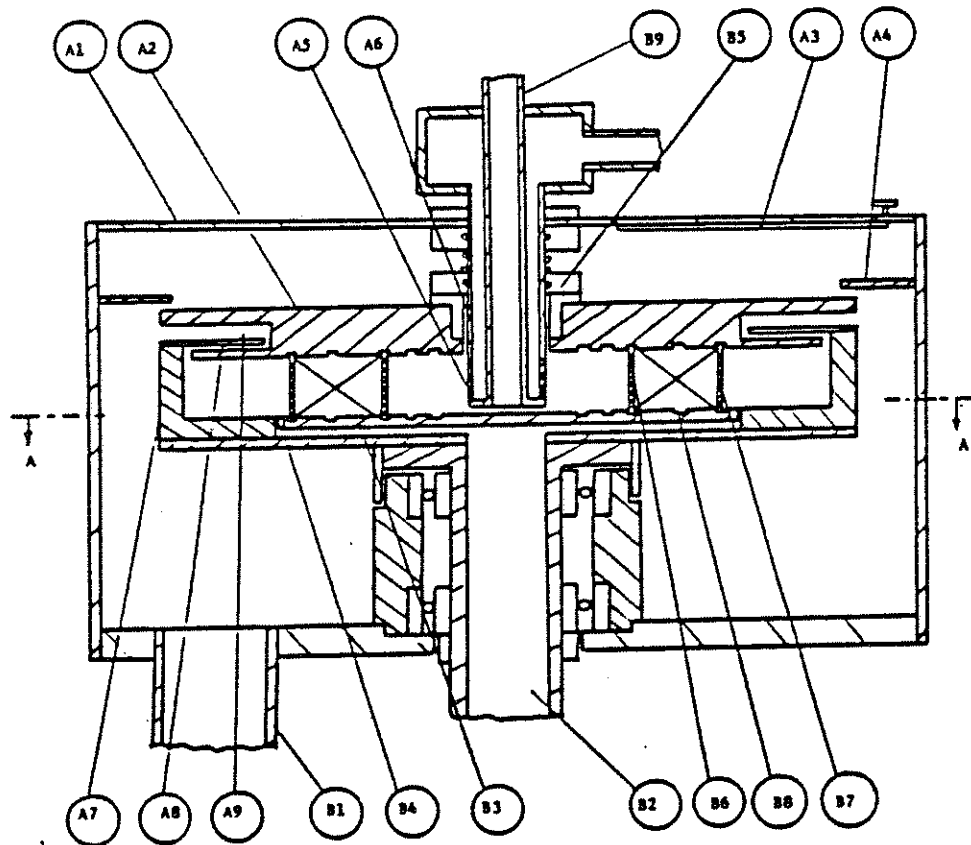
Centrifugal gas-liquid contactor (HIGEE) is a device in which centrifugal force is employed as an adjustable drive for flow of liquid through a porous medium. A cross section of the centrifugal contactor constructed in our Laboratory for counter-current flow of gas and liquid phases is shown in Figure 1.

Interphase transport of momentum and mass in a porous medium when centrifugal force as the body force are the phenomena that govern the performance of centrifugal contactors in any of their possible applications. An understanding of these processes is indispensable for developing a theoretical basis for description of centrifugal contactors. Such a theory should explain the high performance of the HIGEE device that has been noted in separation operations (Ramshaw and Mallinson, 1981). It should also indicate the feasibility of using centrifugal contactors in other processes (for example, such as involve three phase systems with chemical reaction). Finally, such a theory should provide a sound basis for reliable design and scale up of the rotating packed bed contactor.

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

B. Research Objectives

This project is a continuation of the work on this problem that has already been done in our Laboratory (Munjaj, 1986).



A1. Rotor Casing

A2. Rotor Cover

A3. Wiper

A4. Splash Shield

A5. Liquid Inlet Holes

A6. Stationary Double-Pipe

A7. Rotor Wall

A8. Liquid-Seal Lip

A9. Liquid-Seal

B1. Liquid Exit Pipe

B2. Hollow Shaft

B3. Gas Inlet

B4. Gas Inlet Holes

B5. Gas Seal

B6. Inner Packing Support

B7. Outer Packing Support

B8. Packing Support Grooves

B9. Gas Exit Pipe

Figure 1

So far, the concept of liquid films has been used to model the hydrodynamics and mass transfer in the porous packing of the rotating packed bed. This approach is further exploited in this project. A 'liquid film model' is introduced. Qualitatively, it can be described as liquid being present only in form of thin films that coat the solid surface of the packing. To develop this model two lines of approach are used.

On one hand, a simple theoretical model of liquid film flowing under the influence of the centrifugal force is considered. On the other hand, experimental work is proposed for gathering the information on holdup and the actual state of distribution of the liquid phase in the rotating packed bed.

The theoretical model for liquid flow is based on liquid film flow on a rotating disk. Hydrodynamics of the film and gas-liquid mass transfer with and without heterogeneous chemical reaction at the disk surface are modeled.

Experimental evidence regarding liquid holdup and liquid distribution is necessary to confirm the assumptions of the liquid film model. It is suggested to gather such evidence by measurement of the electrical resistance of the rotating packed bed with a solution of an electrolyte as the liquid phase.

The objective of this project is to use the results of the theoretical and experimental work in establishing the liquid film model. The following specific studies are planned:

- Obtain solutions for the problems of hydrodynamics and mass transfer on the rotating disk.

- Obtain the information on liquid holdup and the state of distribution of the liquid phase in the rotating packed bed by

experimental measurements.

- Devise a statistical model for the distribution of total liquid flow rate through the rotating packed bed to the random surfaces of the packing; then apply the theoretical results of the rotating disk problem to this random surfaces.

### C. Research Progress

Solutions to several aspects of the rotating disk problem have been obtained. Figure 2 is the schematic of the physical situation considered. Only the region of well developed film flow is considered. In this region the boundary layer extends across the entire thickness of the film. An approximate solution to the hydrodynamic problem is obtained by the momentum integral method of the classical boundary layer theory. Figure 3 illustrates the effect of different initial conditions on the dimensionless film thickness. The figure illustrates that the approach to the asymptotic film thickness is very rapid in this region, even when the initial film height is a factor of two higher or lower than the asymptotic height at the starting point.

Dissolution of a gaseous species in the film of lean liquid was considered in two limiting cases: no chemical reaction and an infinitely fast chemical reaction at the solid surface of the disk. Analytical solutions were obtained for these two problems in the region of asymptotic film thickness under some simplifying assumptions (Basic, 1987). These solutions were compared to the approximate solution based on the penetration theory (Munjaj, 1986). Curves 1, 2 and 3 in Figure 4 give the radial dependence of the solute gas flux at the interface for the cases of: no chemical reaction on the disk surface (curve 1), the penetration theory solution (curve 2) and with an infinitely fast

surface reaction (curve 3). To ensure that mass transfer takes place in the region of asymptotic film thickness, for which an analytic solution is possible, lean liquid was assumed exposed to the dissolving gas only for dimensionless radii larger than 2.5. From the form of curves in Figure 4 one can conclude that there exists a narrow region of validity of the penetration theory, in which this solution is representative of both other cases. After this region, the situation changes. Due to asymptotic thinning of the liquid film, the flux in the case of infinitely fast reaction tends to infinity. On the contrary, the flux in the physical dissolution problem tends to zero, due to saturation of the film. Curves 1 and 3 become widely separated, and the penetration theory solution (curve 2) cannot represent either.

For experimentally determining holdup and distribution of the liquid phase in the rotating packed bed, a method is suggested which is based on measurement of apparent electrical resistance of the packing. This method is based on the work of Achwal and Stepanek (1975) and Prost and Le Goff (1964) who related the apparent electrical conductance of a d packed bed to its liquid holdup. The anisotropy of liquid distribution is accounted for by introducing a tortuosity factor, following the idea of the latter authors.

The method relies on measurement of electrical conductance of the rotating packed bed in the radial and axial direction. A set of working equations has been developed by which this data can be used to check for the effects of anisotropy of the liquid distribution and to calculate the liquid holdup (Basic, 1986).

Figure 5 represents the cross section of the upper part of the rotor of the rotating packed bed of our Laboratory, with electrodes inserted into the packing. It shows the way in which leads used to

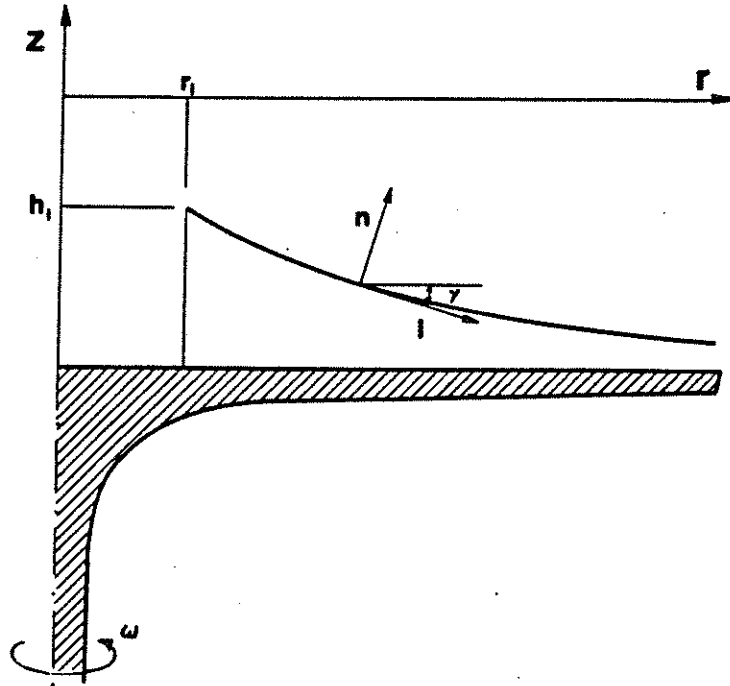


Figure 2

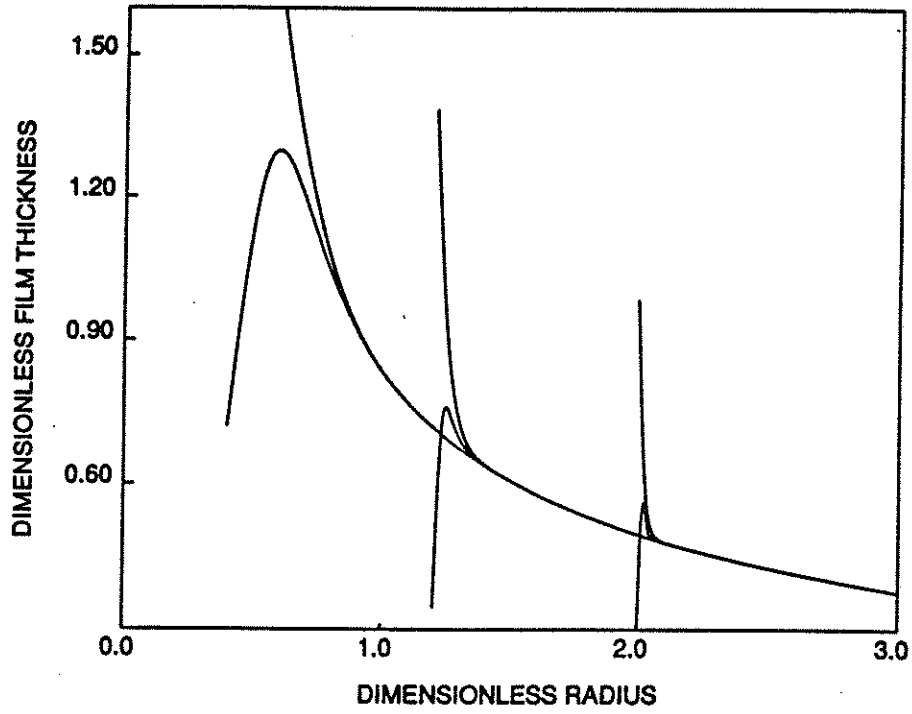


Figure 3

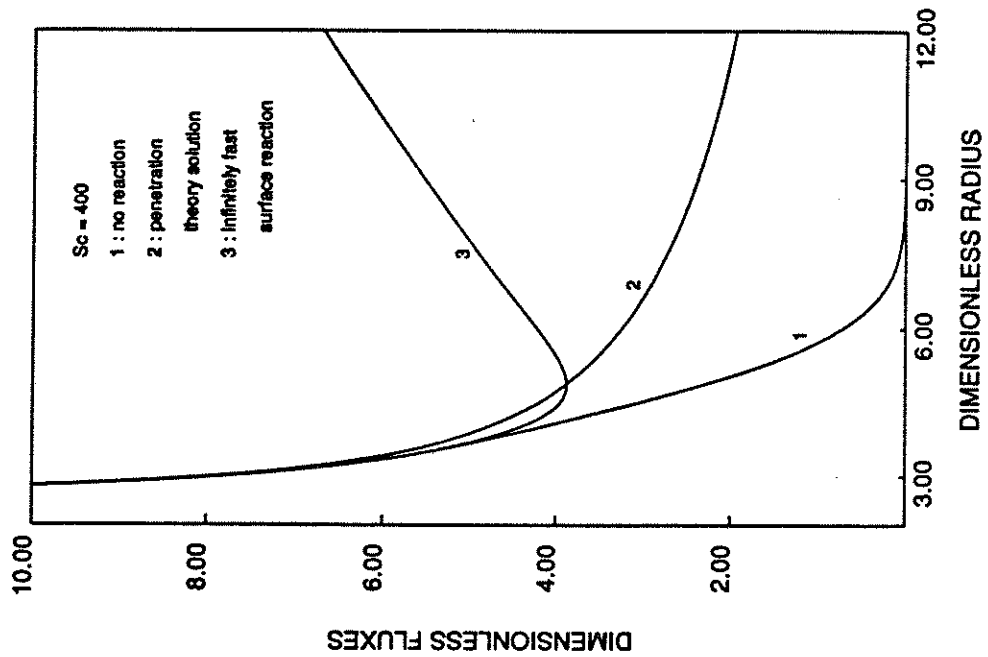


Figure 4

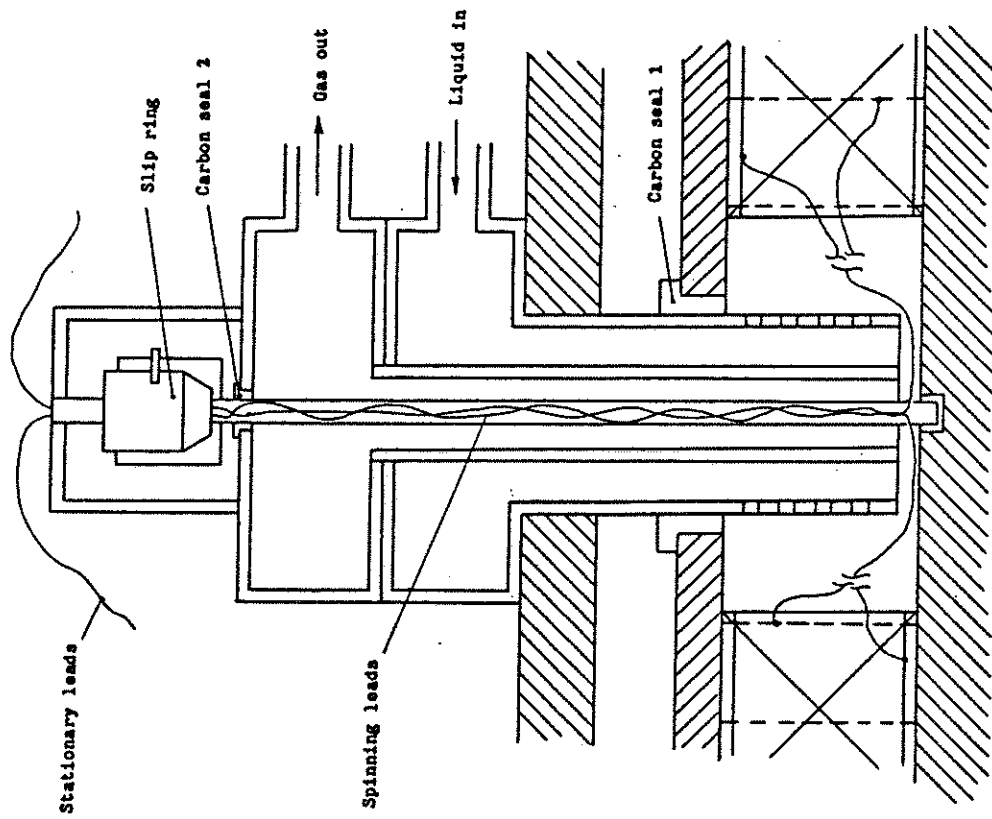


Figure 5

measure voltage drop across the bed are introduced into the rotating part of the unit.

#### D. Further Research Plan

In the theoretical part of this project which is concerned with the rotating disk problem, it remains to model the entry region. This is the part of the flow field in which the boundary layer exists together with a zone of potential flow. A correlation of the length of this region with initial conditions will be sought.

Solutions to the problem of mass transfer with heterogeneous reaction with a reaction rate of a general magnitude will be obtained numerically. Chemical enhancement of gas absorption will be examined as a function of the reaction rate and the radius of the disk.

Measurements of electrical resistance of the bed will be made. It is planned to complement this method by measurement of electrical capacitance. These two electrical measurements should provide sufficient information for determining unambiguously both liquid holdup and the state of distribution of the liquid phase. Results of these experiments will either confirm the physical situation that was assumed by the liquid film model or indicate the need for a different approach.

#### E. Nomenclature

dimensionless film thickness	film thickness on the z scale.
dimensionless flux	flux divided by $C^*D((v/\omega)^{1/2})$ , ( $C^*$ - saturation concentration, D - diffusivity).
dimensionless radius	see r.
$h_i$	initial film thickness (dimensionless).



l	direction tangent to the liquid surface.
n	direction of the normal to the liquid surface.
Q	liquid flow rate.
r	dimensionless radius: radius divided by $Q/((\nu/\omega)^{1/2})$ .
$r_i$	initial radius (dimensionless).
Sc	Schmidt number.
z	dimensionless axial coordinate: distance perpendicular to the disk divided by $(\nu/\omega)^{1/2}$ .
$\gamma$	angle between directions r and l.
$\nu$	kinematic viscosity.
$\omega$	rotation speed.

#### F. References

- Achwal, S. K. and J. B. Stepanek, 'An Alternative Method of Determining Liquid Holdup in Gas-Liquid Systems', Chem. Eng. Sci., **30**, 1443 (1983).
- Basic, A., D.Sc. Proposal, Washington University in Saint Louis, 1986.
- Munjal, S., D. Sc. Thesis, Washington University in Saint Louis, 1987.
- Prost, C. and P. Le Goff, 'Etude, par conductivite electrique, des filets liquides coulant dans une colonne a garnissage avec contre-courant ou contre-courant de gaz', Chim. ind., Gen. chim., **91**, 6 (1964).

Project I.5 Iron Oxide Crystal Growth in a Three Phase  
Slurry Reactor

A. Problem Definition

One method of producing iron oxide particles used in the manufacture of magnetic media (tapes, disks, etc...) is to produce  $\alpha$ -FeOOH particles in a slurry reactor. These particles are then dried, reduced, and re-oxidized in a series of gas-solid reactions to form  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. Since the shape and size distribution of the crystals are determined in the slurry reactor, and these properties are of major importance to the final properties of the magnetic tapes, the experimental and modelling efforts of this research are focused on the slurry reactor.

In a batch slurry process, ferrous hydroxide is first precipitated from sodium hydroxide and ferrous sulfate solutions at a high pH and in the absence of oxygen. After the precipitation, air is bubbled through the slurry to oxidize the precipitate to form hydrated, acicular, ferric hydroxide crystals ( $\alpha$ -FeOOH). The crystals are on the order of 1 micron long with an aspect ratio ratio of 5 - 10.

B. Research Objectives

The proposed objectives of this work are as follows:

1. Develop a better understanding of the mechanisms by which the particles are formed.
2. Determine the variables which are important to the

particle morphology.

3. Develop an experimentally verified model of the crystallization process which will predict the size distribution of the particles based on a defined set of operating conditions.
4. Propose an appropriate reactor design based on the crystallization model.

### C. Research Accomplishments

A review of the literature reveals that although the oxidation of ferrous hydroxide precipitate and related reactions have been described, very little quantitative modelling of the process has been documented. However, a qualitative description of the process (ref. 1, thanks to H. Buttery, 3M Company, who provided the translated version) documents that the morphology of the initial ferrous hydroxide precipitate is hexagonal platelets versus the acicular structure of the  $\alpha$ -FeOOH product. Based on this information, it seems the final  $\alpha$ -FeOOH crystals grow to form a new phase as the oxidation of the precipitate proceeds.

Additional properties of the system based on experimental observation (1,2), show the oxidation rate of the ferrous hydroxide to be limited by the rate of oxygen mass transfer into the solution. Finally, based on experiments (1), the rate at which the precipitate oxidation is performed can influence the crystal growth of the  $\alpha$ -FeOOH phase.

Currently, work is being done to develop sample preparation techniques for the electron microscope. This will allow the acicular  $\alpha$ -

FeOOH crystals to be viewed at different stages of their development. Also, different methods of direct particle size distribution measurement are being sought. Two aspects which make this problem difficult are the size range and acicular shape of the crystals.

#### D. Future Research Plans

Work will be done to experimentally verify and clarify the qualitative observations described above. Once this is complete, a model of the particle growth will be developed and a reactor design will be proposed.

#### E. References

1. W. Feitknecht, Z. fur Elektrochemie, 63, 34-43 (1959)
2. S. Miyamoto, Bull. Chem. Soc. Japan, 3, 137 (1928)

## 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: 1) less free space is available for homogeneous nucleation, 2) 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.

A great deal of experimental effort was expended on this project both at JPL and Union Carbide. 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 silicon properties (such as size, size distribution, presence and absence of fines) with fluidized bed size and operating parameters (such as bed 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 study.

### C. Research Accomplishments

Three models for the fluidized bed pyrolysis of silane have been developed. The first model, the backmixed reactor (CSTR) model, based on an ideally mixed reactor assumes perfect gas-solid contacting, no spatial gradients in temperature or composition in the reactor and no gradients between particles and gas. The other two models, developed for the bubbling fluidized bed (FBBR) to assess the effect of hydrodynamic uncertainties on predictions of reactor performance, are based on the two-phase theory. The modified two-phase (FBBRME) model acknowledges the presence of the jetting (grid) region, bubbles and emulsion phase in the bed. Average bubble characteristics and the complete well-mixedness in the emulsion phase are assumed. The two-phase plug flow (FBBRPE) model assumes that small bubbles form already at the grid and rise in plug flow while growing. The emulsion phase is assumed in plug flow also and the variation of bubble characteristics along the reactor is considered. All 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.

The unknown jet-emulsion exchange coefficient in the FBBRME model can be estimated using the bubble-emulsion exchange profile in the FBBRPE model based on the equivalent enhanced exchange in the entrance region. The  $f_{jb}$  value in the FBBRME model, which is the ratio relating jet-emulsion exchange to bubble-emulsion exchange, can then be calculated by the following equation:

$$\int_0^{L_f} (K_{be} - \bar{K}_{be}^{FBBRPE}) dz = (f_{jb} - 1) \bar{K}_{be}^{FBBRME} h_j \quad (C1)$$

Enhanced exchange  
in the FBBRPE model
Enhanced exchange  
in the FBBRME model

where  $L_f$  is the expanded bed height,  $h_j$  is the jetting height,  $\bar{K}_{be}^{FBBRPE}$  and  $\bar{K}_{be}^{FBBRME}$  are the asymptotic  $K_{be}$  value of the FBBRPE model and the average  $K_{be}$  value of the FBBRME model, respectively. The calculated equivalent jet-emulsion exchange coefficients and the  $f_{jb}$  values in the FBBRME model are shown in Figure 1 for various grid designs. It can be seen that the  $f_{jb}$  value decreases, but the jetting height increases, with increasing orifice diameter, i.e.  $d_{or}$  or  $A_{or}$  values. By using equivalent values of exchange coefficients in the entrance region the differences in predictions of the two models can be mainly ascribed to the assumption made with regard to the backmixing of the gas in the emulsion phase. The FBBRME model assumes perfectly mixed emulsion gas and the FBBRPE model assumes plug flow. Table 1 shows the comparison of model predictions for various grid designs based on the above approach. It is found again that with the grid design, that enhances the exchange coefficient in the grid region, the FBBRME model always gives better reactor performance, and the results at very high  $f_{jb}$  values approach the CSTR behavior, i.e. the homogeneous nucleation can be almost suppressed. However, the FBBRPE model predictions are not that sensitive to the bubble-emulsion exchange in the entrance region and the elutriation of fines stays within a certain range in cases of all grid designs.

The FBBRME model always predicts less elutriation of fines and the higher deposition rate than the FBBRPE model for all grid designs. Since the two models bracket the state of emulsion gas backmixing, it is

expected that the real performance should lie between the predictions of the FBBRME and FBBRPE models when the two are based on the equivalent enhanced exchange in the entrance region.

The sequence of determining the key reactor and operating conditions for this process is shown in Figure 2. Although the reactor size dominates the hydrodynamic behavior, and thus affects the reactor performance significantly, it is usually determined first based on the process demand or economics. Reactor diameter of 6 inches or 15 inches is normally used for the pilot plant and for a commercial unit the reactor diameter can be as large as 48 inches. The grid design can influence the bubble size distribution, especially in the entrance region, and thus affects the formation of fines somewhat. It is essential in the grid design to maintain the gas distribution so as to produce uniform tiny bubbles. This can be achieved either by using a distributor with small openings or a multilayer screen. In order to ensure a sufficient pressure drop to achieve equal flow through the openings, thereby preventing the formation of defluidized zones within the bed, the distributor is designed for the selected operating conditions, e.g. pressure and gas superficial velocity, etc. (1). After the reactor specifications are decided, the operating conditions can then be chosen based on the requirements for the final product. The reactor performance, e.g. deposition rate, percentage of fines elutriated, the quality of fluidization and product morphology, is mainly determined by the first three operating parameters: inlet silane concentration, inlet gas flow rate and bed temperature. The starting diameter of seed particles and the starting bed weight or height are important when the final diameter of seed particles, the duration time and the maximum expanded bed height are considered. Finally, some



operating conditions need to be adjusted during the process when the particles grow larger, e.g. the withdrawal of product is necessary if the increased bed height exceeds the maximum expanded bed height and the inlet gas flow rate needs to be increased periodically to maintain the quality of fluidization.

The primary goal of this process has been the production of a marketable size product (1000 microns diameter) with minimal final powder formation. It is then necessary to test the ability of the model to simulate the long duration runs. Most of the JPL experiments with the 6 inch FBR were of short duration only up to 4 hours (2). The long duration runs were conducted by a 6 inch diameter fluidized bed process development unit (PDU) at the Union Carbide Corporation (UCC) (3). One of their successful runs, i.e. J-02, in which particles grew to 1000 microns in 58 hours from seeds of mean size of 300 microns, is selected for model comparison. The predicted curve for the particle growth as a function of time is compared with the experimental data of UCC Run J-02 and is shown in Figure 3. It is found that the FBRPE model shows very good agreement with UCC experimental data for the particle sizes up to 700 microns. However, as the particles grow larger than 700 microns, the FBRPE model overpredicts the elutriation of fines resulting in the smaller growth rate compared with the UCC results. According to the criterion proposed by Catipovic et al. (4), the particle size for the transition of flow regime from fast bubbles to slow bubbles is about 700 microns for this case. It is believed that the increased error in model predictions for the particle sizes over 700 microns is due to the inadequacy of modeling the slow bubble regime by the two-phase theory, which is also noted by Park et al. (5). However, a general and complete model for the slow bubble regime is yet to be developed.

#### D. Future Research Plan

This project has been completed and no further work is planned. However, models should also be developed for continuous mode of operation, which is more practical for commercial operations. In this mode, the mean particle size in the reactor would remain constant with respect to time. Coarse particles would be preferentially withdrawn as product, while seed particles would be introduced into the bed. Population of particles of different initial size should be treated also.

#### E. Bibliography

1. Kunii, D. and O. Levenspiel, Fluidization Engineering, Wiley, N.Y. (1969).
2. Rahatgi, N.K., Silicon Production in a Fluidized Bed Reactor: Final Report, DOE/JPL-1012-123, Jet Propulsion Laboratory, April 1986.
3. Flat Plate Solar Array Project, Fluid Bed Silane Decomposition R D, Final Report for the Period July 1982 - April 1986 by Union Carbide Corporation, August 1986.
4. Catipovic, N.M., G.N. Jovanovic and T.J. Fitzgerald, 'Regimes of Fluidization for Large Particles', *AIChE J.*, 24, 3 (1978).
5. Park, D., O. Levenspiel and T.J. Fitzgerald, 'Plume Model for Large Particle Fluidized-Bed Combustors', *Fuel*, 60 (1981).

Table 1. Comparison of the Modified Two-Phase (FBBRME) and Two-Phase Plug Flow (FBBRPE) Model Predictions Based on the Equivalent Enhanced Exchange in the Entrance Region  
(Parameters: 20% Silane in the Feed,  $T_0=650^{\circ}\text{C}$ )

	Grid 1	Grid 2	Grid 3
Orifice Diameter (cm) ( $d_{or}$ )	0.16	1.13	2.52
Orifice Area (cm <sup>2</sup> ) ( $A_{or}$ )	0.02	1.0	5.0
No. of Orifice Holes ( $N_d$ )	4500	90	18
Calculated $f_{jb}$ value	126.0	9.4	2.6
Silane Conversion (%)			
FBBRME	99.18	99.23	99.26
FBBRPE	99.98	99.90	99.80
Fines Elutriation (%)			
FBBRME	0.24	1.77	6.71
FBBRPE	8.60	6.90	10.50
Deposition Rate (kg/h)			
FBBRME	1.000	0.986	0.936
FBBRPE	0.924	0.940	0.902

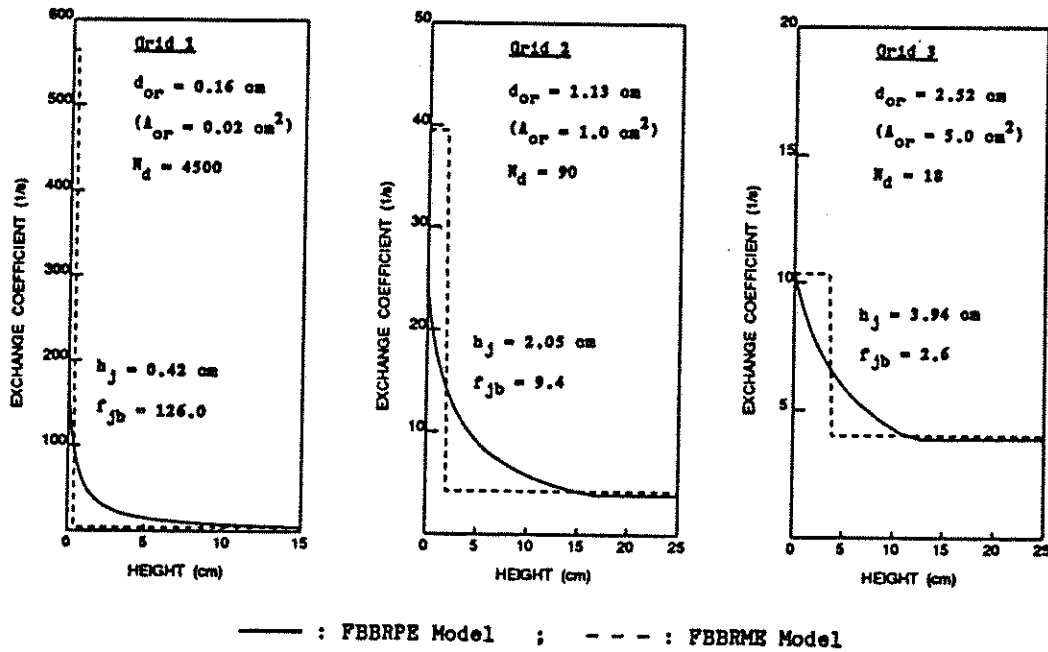


Figure 1. Calculated  $K_{je}$  and  $f_{jb}$  in the Modified Two-Phase (FBBRME) Model based on the Equivalent Enhanced Exchange, Eq. (C1)

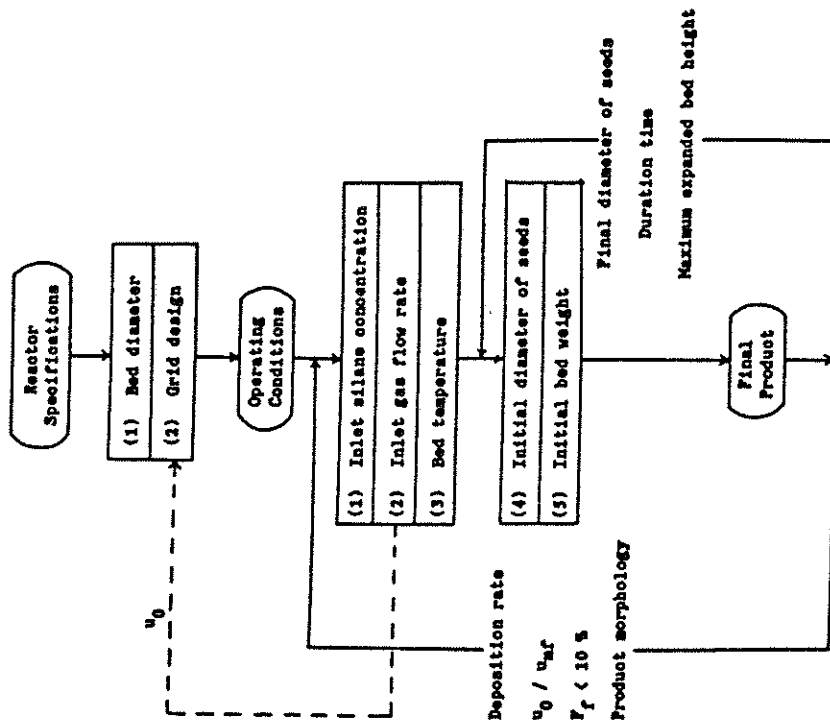


Figure 2. Sequence of Determining the Key Reactor and Operating Conditions for Fluidized Bed Silicon Production from Silane

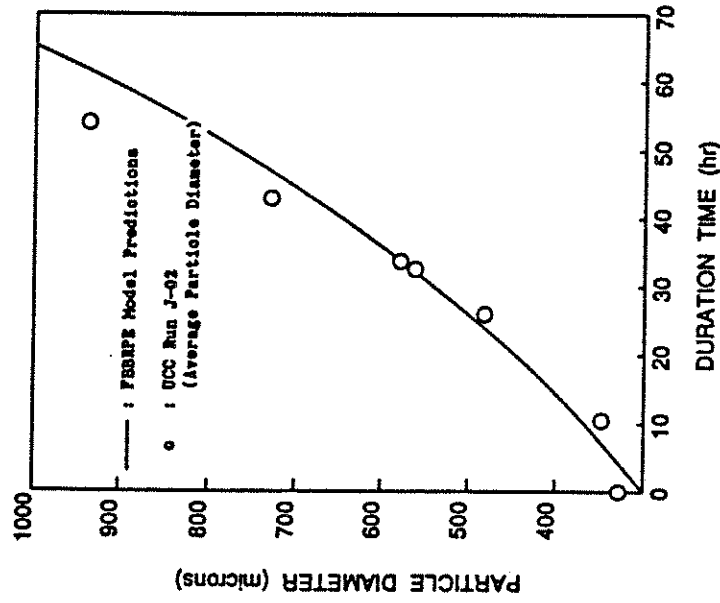


Figure 3. Comparison of the Two-Phase Plug Flow (FBRPE) Model Predictions and the UCC Experimental Results for the Particle Growth as a Function of Time

Project II.2. Modeling of the Aerosol Reactor  
for Production of Polycrystalline Silicon

A. Problem Definition

One attractive approach to produce bulk silicon, with the possibility of conveying silicon particles to the Czochralski's crystal growth apparatus, is by homogeneous gas phase pyrolysis of silane in an aerosol reactor. Particle size as large as 10  $\mu\text{m}$  in diameter was produced in the laboratory scale reactor with seed particles of 0.1  $\mu\text{m}$  in diameter at Caltech. If the particles can be grown to even bigger sizes, for example 50 to 100  $\mu\text{m}$ , this aerosol reactor would provide a very desirable means for commercial production of polycrystalline silicon. In order to accomplish this goal, two steps are required: (1) Establish a basic theory of particle growth, construct a laboratory scale reactor, and experimentally demonstrate the feasibility of growing large size particles. (2) Apply the theory of particle growth along with the reaction kinetics and transport effects to set up a detailed reactor model. An appropriate model could provide the necessary information on how to improve the laboratory reactor to grow the aerosol to super-micron size, and should present guidelines for design of large scale reactors.

Small particles are grown by the following major mechanisms: (1) coagulation among fines and seed particles, (2) condensation of silicon vapor on particle surface, and (3) CVD reaction on particle surface. Successful growth of the aerosol requires that the seed particles scavenge effectively the fines formed by homogeneous nucleation at a maximum decomposition rate of silane. Previous work on modeling aerosol

reactors neglected the coagulation of the aerosol which is important for the system of interest. Therefore a model accounting for coagulation has to be developed.

#### B. Research Objectives

The purpose of this research is to study the transport-kinetics effects in production of polycrystalline silicon. Specifically it is desired to model the aerosol reactor and to investigate the possibility of growing larger particles for commercial application. The following tasks are proposed:

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

#### C. Research Accomplishment

Preliminary work has been performed in identifying the growth mechanisms from the experimental results. A rough aerosol model based on the experimental data has been developed to estimate the various process rates. Model prediction are illustrated in Figure 1, showing that the

aerosol growth is mainly due to the condensation on the particles and to the capture of fines formed by homogeneous nucleation. CVD reaction on the reactor wall consumes less than 10 % of total silane feed. The cell model developed by Alam and Flagan has been modified to study the effect of silicon vapor condensation on the average nucleation rate. The results show that the condensation on particles quenches the nucleation rate. The average nucleation rate can be calculated by using the bulk concentration of silicon vapor because the vapor sink only affects about 2 % of the total cell volume as illustrated in Figure 2.

A detailed model for the aerosol reactor has been formulated which includes mass balance equations for silane and silicon vapor and two population balances for both fines and seed particles. The coagulation among the seed particles and fines is taken into account in the model, allowing the seeds to capture the fines. The integral-differential equations of the population balances are reduced to differential equations by using the method of moments. The resulting model consists of 8 coupled ordinary differential equations.

#### D. Further Research Plan

- 1) Solve the model equations for the plug flow model. This consists of 8 coupled ODEs and represents an initial value problem.
- 2) Investigate other approaches to simplify the population balance equations beside the method of moments approximation.
- 3) Discuss the implications of model simulations.

### E. References

- 1) Ray, J.R. and S.K. Iya, 'Silane Pyrolysis in a Free space Reactor', IEEE Photovoltaic Specialists Conference, June 1981, PP 565-568
- 2) Pesthy, A., R. Flagan and Seninfeld, 'The effect of a Growing Aerosol on the Rate of Homogeneous Nucleation of a Vapor', J. Colloid Science, **82**, 465-479, (1982)
- 3) Alam, M. K. and R. Flagan, 'Simultaneous Homogeneous Nucleation and Aerosol Growth', J. Colloid Science, **97**, 232-246, (1984)
- 4) Alam, M. K. and R. Flagan, 'Controlled Nucleation Aerosol Reactor: Production of Bulk Silicon', Aerosol Sci. Tech., **5**, 237-248, (1986)
- 5) Pratsinis, S.E. T.T. Kotas M.P. Dudukovic and S.K. Friedlander, 'Aerosol Reactor Design: Effect of Reactor Type and Process Parameters On Product Aerosol Characteristics', Ind. Eng. Chem. Process Des. Dev. **25**, 634-642 (1986)
- 6) Friedlander, S.K., Smoke, Dust and Haze, John Wiley and Sons, New York, (1977)
- 7) Hulburt, H.M. and S.L. Katz, 'Moments Equation and Laguerre Polynomial', Chem. Eng. Sci., **19**, 555-574 (1964)



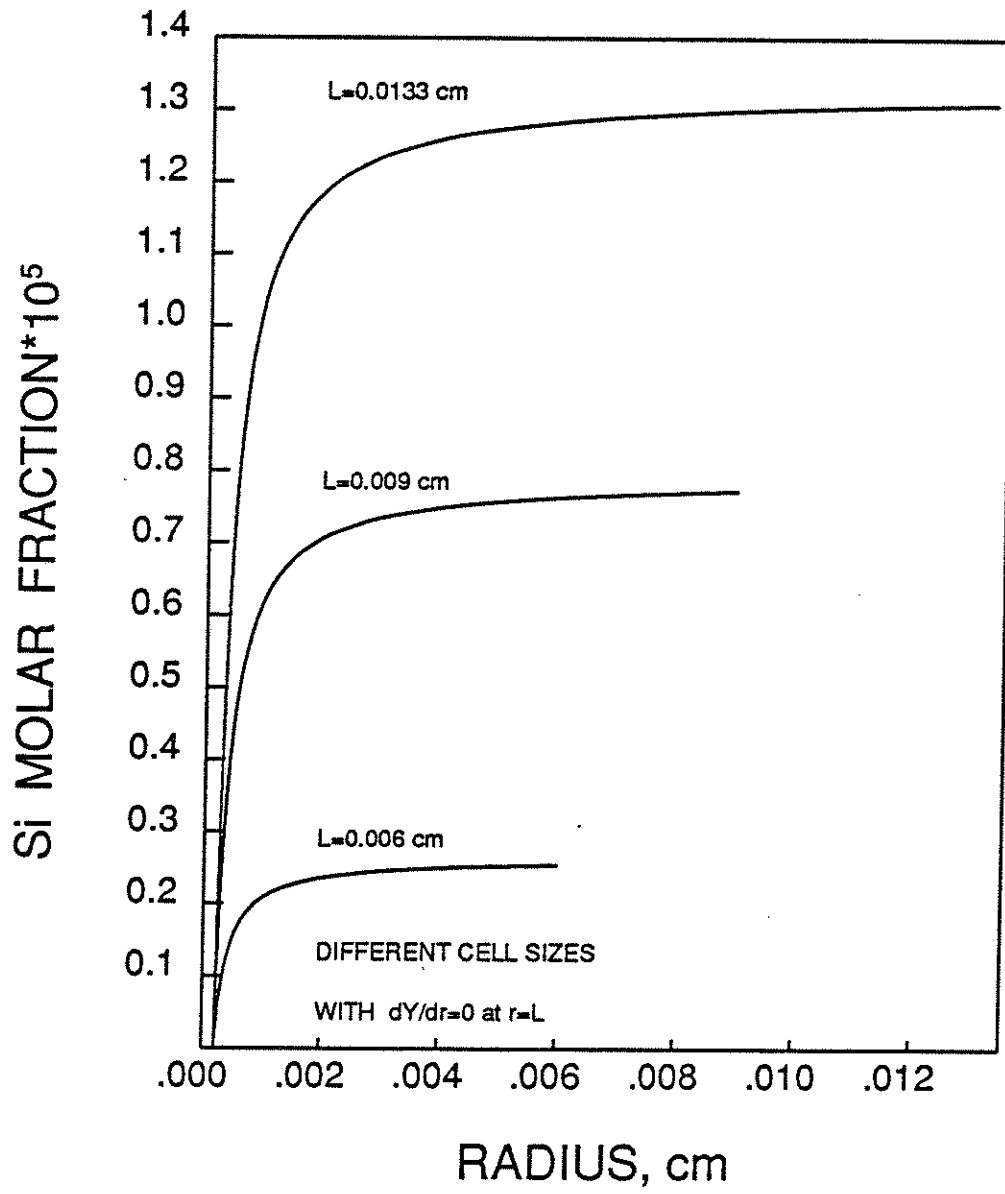


Figure 2 Silicon Vapor Concentration  
Around a Spherical Particle

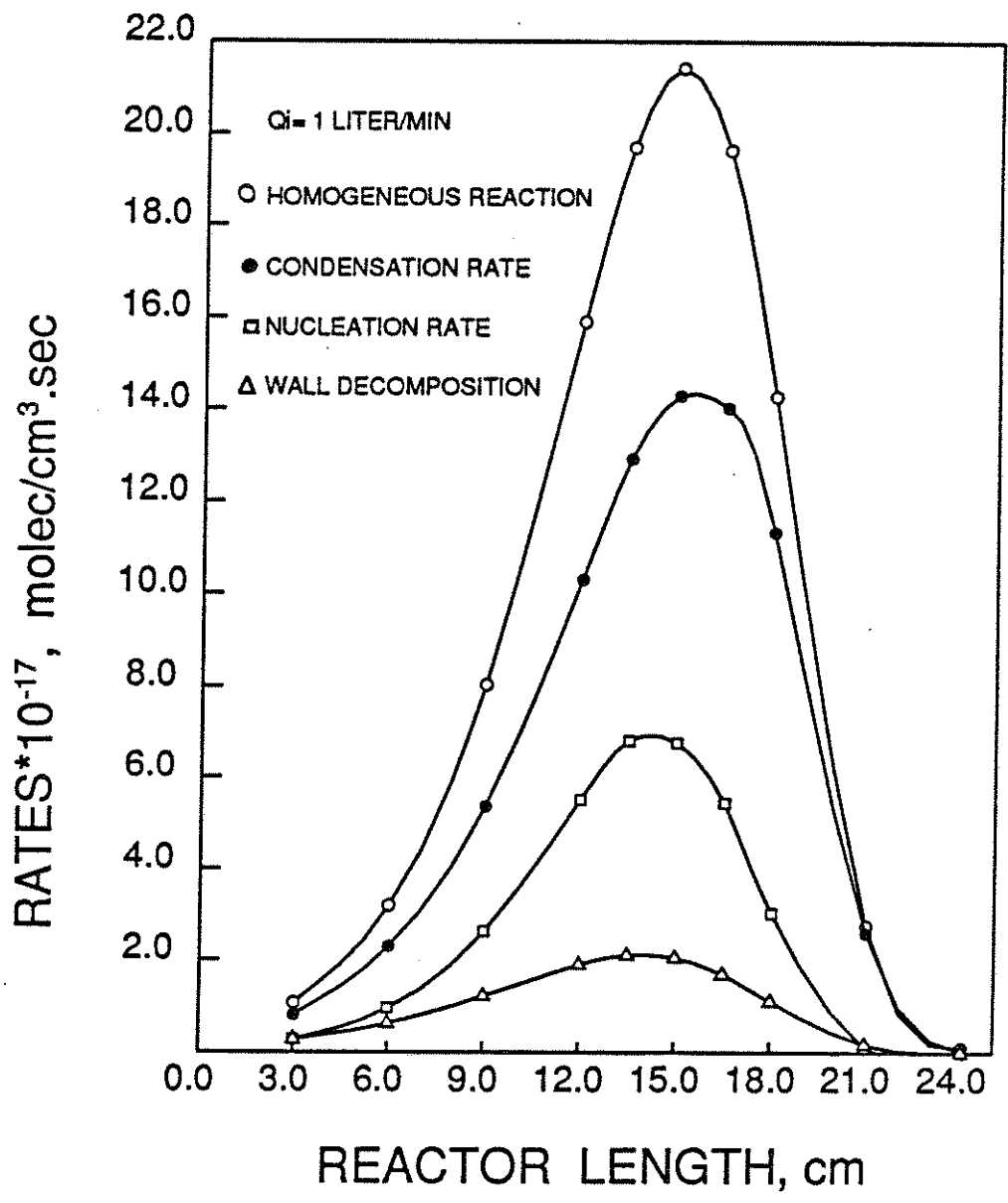


Figure 1 Comparison of Various Rates

Project III.1. Computer-Aided Processing of Thermosetting  
and Thermoplastic Composites  
(Joint Project with Materials Science Laboratory)

A. Problem Definition

A key question now facing the U.S. composite material industry is how to manufacture large, continuous fiber, high performance structural parts at a globally competitive cost. Underlying this question are the problems of part rejection due to voids and gradients in resin content, as well as costly process development due essentially to trial and error learning curves. Our objective is to approach these problems in a systematic way starting from first principles as much as possible. The ultimate goal is to develop a master model that will allow a selection of an optimal cure cycle given physical properties and kinetic behavior of the resin, properties of the fibers and size and shape of the part to be manufactured. For experimental verification of this general approach we have selected two test systems: As-4 fibers/Hercules 3502 epoxy resin system as a representative of thermosetting materials and M-6 fibers/Dupont Avamid K-111 resin system as a thermoplastic material.

B. Research Objectives

1. Develop a model that predicts void formation during cure of thermosetting composites and identify conditions necessary for prevention of void growth.
2. Develop a model for the squeezing flow of the resin during cure of thermosetting composites to determine resin pressure profiles during cure and the residual resin content profile.
3. Develop a model for quantification of degassing of the thermoplastic materials during cure.

## C. Research Accomplishments

### 1. Thermosetting Composites

The first two research objectives with regard to the thermosetting materials have been accomplished in a recent D.Sc. thesis (1). It was shown that voids are water vapor, the source of which is water adsorbed by the resin during the layup of the prepreg at uncontrolled temperature, and relative humidity conditions. If one monitors the conditions of humidity and temperature during prepreg layup and assumes that equilibrium between humid air and the resin is reached then void formation can be prevented. In order to accomplish this it is necessary at each temperature during the cure cycle to keep the resin pressure at each point of the composite above the vapor pressure of dissolved water. This requires the knowledge of the resin pressure profiles which is obtained from the resin flow model. This model rests on the assumption that the autoclave pressure is partly taken up by the fibers, which behave like a nonlinear spring (the spring characteristics can be determined via independent experiments) and partly by the resin which then, due to the pressure gradient, flows into the bleeder bag. The squeezing resin flow, calculated by the above model, is in good agreement with experimental data obtained at McDonnell Douglas. The details of these models and guidelines for selection of optimal cure cycles are presented in a series of publications (2-12).

### 2. Thermoplastic Composites

A transport phenomena based model has been formulated for prediction of devolatilization rates of the inert solvent (NMP) and reaction byproducts (ethanol and water) as function of laminate thickness and selected temperature pressure cure cycle.

## D. Future Research Plans

It is expected that the model for cure of thermoplastic materials will

be expanded to include resin flow and cure kinetics and that model results will be compared to data.

E. Bibliography

1. R. S. Dave, Computer-Aided Processing of Composites, D.Sc. Thesis, Washington University, St. Louis, MO 63130, December 1986 (2-12).
2. J. L. Kardos, M. P. Duduković, E. L. McKague and M. W. Lehman, "Void Formation and Transport During Composite Laminate Processing - An Initial Model Framework", ASTM Special Tech. Publ., 797, Productivity and Quality Assurance of Composite Materials, (C. E. Browning, ed.), pp. 96-109 (1982).
3. J. C. Halpin, J. L. Kardos and M. P. Duduković, "Processing Science: An Approach for Prepreg Composite Systems", Pure & Applied Chemistry, 55(5), 893-906 (1983).
4. J. L. Kardos, M. P. Duduković and R. Dave, "Void Growth and Resin Transport During Processing of Thermosetting-Matrix Composites", Advances in Polymer Science (K. Dusek, ed.) 80, 101-123 (1986).
5. R. Dave, J. L. Kardos and M. P. Duduković, "A Model for Resin Flow During Processing of High Performance Composites", Polym. Mater. Sci., 55, 334-338 (1986).
6. R. Dave, J. L. Kardos and M. P. Duduković, "A Model for Resin Flow During Composite Processing: Part 1 - General Mathematical Development", Polymer Composites, 8, 29-38 (1986).
7. R. Dave, J. L. Kardos and M. P. Duduković, "A Model for Resin Flow During Composite Processing: Part 2 - Numerical Analysis of Unidirectional Graphite/Epoxy Laminates", Polymer Composites, 8, 123-132 (1987).
8. R. Dave, J. L. Kardos and M. P. Duduković, "Process Modeling of Thermosetting Matrix Composites: A Guide for Autoclave Cure Cycle Selection", Proc. Amer. Soc. Composites, Technomic Publ. Co., Lancaster, PA (1986). pp. 137-145.

9. J. L. Kardos, M. P. Duduković and R. Dave, "Resin Flow and Voids Formation During Curing of Reinforced Graphite Composites", World Congress III Chem. Eng., Keio Plaza Hotel, Sept. 21-25, 1986; Vol. VI, 499-502, paper 11a-354.
10. R. Dave, J. L. Kardos and M. P. Duduković, "A Model for Resin Flow During Processing of High Performance Composites", ACS NATO Meeting, Anaheim, CA, Sept. 1986.
11. R. Dave, J. L. Kardos, S. J. Choi and M. P. Duduković, "Autoclave vs Non-Autoclave Composite Processing", Proc. 32nd Nat. Symp. SAMPE, Anaheim, CA, April, 1987.
12. R. Dave, J. L. Kardos and M. P. Duduković, "Autoclave Processing of Thermosetting Matrix Composites: Models for Automation and Cure Cycle Selection", Proc. 1987 Annual Technical Meeting Soc. Plastic Engineers, Los Angeles, CA, May, 1987.

## 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 (CG), the Pump cell (PC) and the Rotating Electrolyser (REL).

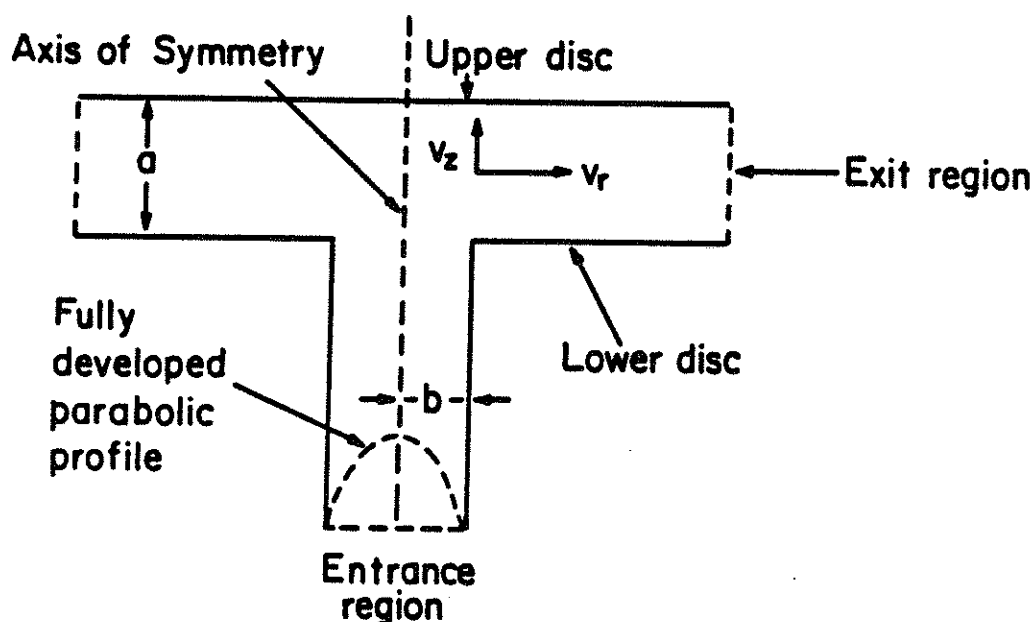


Figure 1 Geometry of Radial Flow Cells

Figure 1 shows the geometry of these cells, they being two parallel discs with radial outflow. In the CG cell both discs are stationary whereas in the REL, both discs are rotating at the same speed. The PC has only one disc rotating. Due to the different arrangements (stationary, single disc rotating, co-rotational discs), even though the geometry is identical, 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 the hydrodynamic regime and cell performance could be quantified, the electrochemical routes may eventually be preferred. 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 equation 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. Make some performance comparisons between the four electrochemical reactor types based on model heterogeneous and



homogeneous reaction schemes. The fourth reactor, in addition to the three radial flow cells, is the parallel plate cell (PPER).

5. Complete the preliminary design of experimental radial flow equipment for tracer and electrochemical reaction work.

### C. Research Accomplishments

As mentioned in last year's annual report the velocity profiles in the CG cell and the REL had been resolved over quite a broad range of parameter values (flowrate, gapwidth and rotational speed in the case of the REL). Convergence of the flow field simulation was enhanced somewhat by changing from 8 to 9 noded elements in the Finite Element program and by altering the Pump cell boundary conditions. Still the nonlinearity of the PC flow field continued to be a major problem especially at larger radii. A semi-analytical perturbation solution was therefore developed for the PC which gave a reasonable estimate for the three velocity components: radial, axial and azimuthal. The range of applicability is limited to Taylor numbers less than about 2.5 in order to maintain accuracy of about 10 % compared to the rigorous FEM solution. Figures 2 and 3 show a comparison of radial velocities for flowing Reynolds numbers of 1 and 50 at a rotational speed of 100 rpm. The axial and azimuthal velocities were of similar accuracy. With these results, the velocity profiles for the three radial cells, in laminar flow, are now available.

Convective-diffusion of inert tracer has been modeled for the CG cell and the REL. With the PC velocities now available the existing computer code can be used to quantify the mixing characteristics of the Pump cell. This will be finished during the summer of 1987.

A detailed electrochemical reactor model was constructed, using

dilute solution theory, incorporating all phenomena enumerated in the problem definition. To date two copper winning reaction systems have been simulated: one from an HCl solution and another from a sulphuric acid solution. Figure 4 provides a comparison between a previous model (5) and this work for the PPER using the first system (HCl solution) , consisting of the following reactions

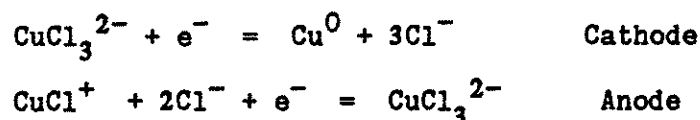


Figure 5 reports a comparison for the PPER, CG and the REL at a flowrate of  $3.6\text{E}-08 \text{ m}^3/\text{s}$  with an applied voltage of 0.400 V (the rotational speed of the REL corresponded to a rotational Reynolds number of  $1.0\text{E}05$ ). Due to the high axial velocities present in the PC its solution is more difficult and one may have to apply FEM to resolve these difficulties (rather than the Orthogonal Collocation method which was developed for this work). Nevertheless, using the actual radial velocity profiles but zero axial velocities, an average current density of  $129 \text{ A/m}^2$  was computed compared to 52.6, 52.8 and  $57.7 \text{ A/m}^2$  for the PPER, the CG and the REL respectively. Note that this result for the PC was based on the cell emptying into a large tank of reactant concentrations the same as the electrolyte feed. For electrowinning applications this should be acceptable.

#### D. Future Research Plan

Within the next four months the following will be accomplished:

1. The generic Electrochemical reactor code will be applied to a homogeneous and heterogeneous reaction scheme exhibiting a competing reaction pathway.
2. Preliminary design of experimental apparatus will be

completed.

3. Convective-Diffusion work will be completed for all three cells and a simplified tracer model will be finished.

#### E. Nomenclature

Q - volumetric flowrate ( $m^3/s$ )

Re - flowing Reynolds number ( $Q*a/(\pi b^2 \nu)$ )

$\alpha$  - Taylor number ( $a^2*\omega/(4*\nu)$ )<sup>1/2</sup>

X - co-ordinate parallel to electrode - axial distance for PPER and radial distance for the radial cells.

Z - axial distance (normal to electrode). Both the X and Z co-ordinates are dimensionless.

#### F. Bibliography

1. Ghoroghchian, J. , R.E.W. Jansson and D. Jones, 'The Production of Hypobromite and of Propylene Oxide in an Electrochemical Pump cell', J. of Appl. EChem., 7, 1977, pp. 437-443.
2. Jansson, R.E.W. and M. Fleischmann, 'Effect of Cell Design on Selectivity and Conversion in Electroorganic Processes', AICHE Symp. Ser., No. 185, Vol. 75, 1979, pp. 2-7.
3. Jansson, R.E.W., 'Organic Electrosynthesis', C and EN., Nov. 19, 1984, pp. 43-57.
4. Jansson, R.E.W., 'The Industrialization of Electrochemical Reactions', Phil. Trans. R. Soc. Lond., A 302, 1981, pp. 285-295.
5. Nguyen, T.V., C.W. Walton, R.E. White and J. Van Zee, 'Parallel Plate Electrochemical Reactor Model', J. of EChem. Soc., Vol. 133, No. 1, 1986, pp. 81-87.

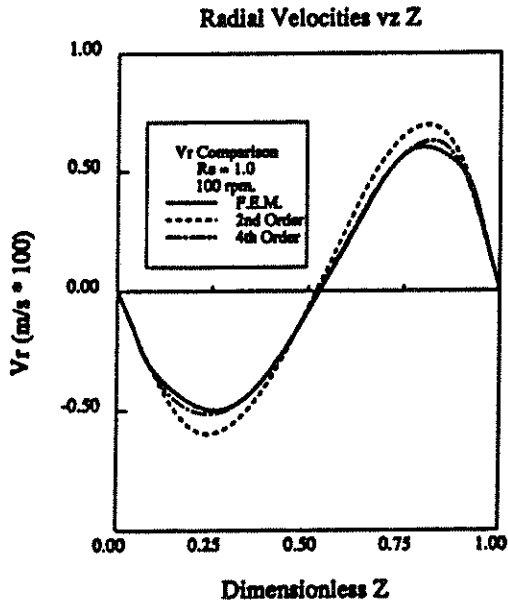


Figure 2 Pump Cell Radial Velocities : Comparison of Semi-analytical to FEM. Flowing Re of 1 and 100 rpm.

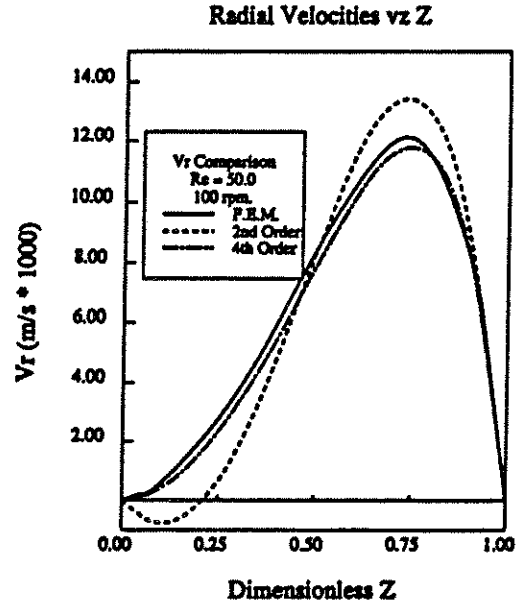


Figure 3 Pump Cell Radial Velocities : Comparison of Semi-analytical to FEM. Flowing Re of 50 and 100 rpm.

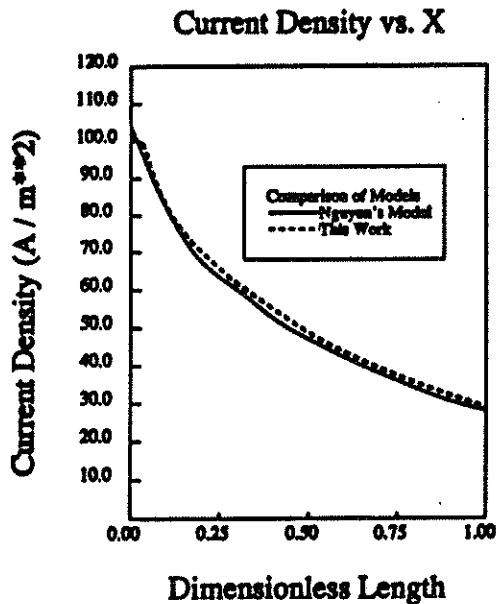


Figure 4 Comparison of Current Density for the PPER : this model versus previous model of Nguyen et al.

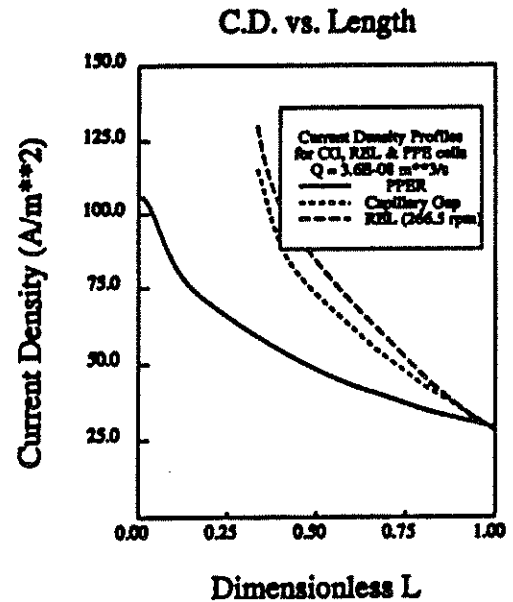


Figure 5 Current Densities for three Electrochemical cells. Gap width of 1mm, and Vapplied of 0.40 V.

Project III.3 Temperature Distribution and Thermally Induced Stresses  
in Czochralski Crystal Growth

A. Problem Definition

The Czochralski process (CZ) is one of the most important methods for growth of single crystals of a number of materials. Over 80% of single crystals of silicon of diameter larger than 6 inches are produced by the CZ method. The crystal growing apparatus (schematic shown in Figure 1) consists of a quartz crucible, a graphite heater, graphite susceptor assembly, pulling rod assembly and crystal enclosure purged with gas. In the CZ process, pure polycrystalline silicon and dopant materials (e.g. boron) are placed in a crucible and the heater is turned on. A molten batch is established and a single crystal seed of the appropriate crystallographic orientation is contacted with the melt. After the neck and shoulder growth a crystal of constant diameter is pulled by balancing heater input and pulling rate. Constant large diameter crystal free of dislocations and with uniform resistivity is required. Resistivity is a function of hydrodynamics and mass transfer in the melt that govern dopant arrival rates to the crystal. Dislocations can be created by excessive stresses which in turn are the result of excessive temperature gradients in the crystal. Therefore, prediction of temperature gradients in the crystal as a function of enclosure design and operating procedure is desirable.

B. Research Objectives

1. To develop a procedure for calculation of temperature profiles in the crystal during the growth process as a function of geometric variables (crucible and enclosure shape, heater position, etc.), operating variables (pulling rate, crystal rotation rate, gas purge rate,

etc.) and process variables (crystal diameter, melt depth, etc.).

2. To relate temperature gradients to thermally induced stresses.

### C. Research Accomplishments

1. A computer algorithm was developed for calculation of heat transfer in the CZ enclosure. Conduction in the crystal and reflected radiation among the crystal surface, melt surface and all surfaces of the enclosure are accounted for. The heat transfer program for the melt is coupled to the crystal program through the boundary condition at the crystal-melt interface that determines the position of that interface. Currently, conduction dominated heat transfer in the melt is assumed. The developed algorithm has been described in detail [1].

2. Using the linear thermoelasticity theory and the linear expansion coefficient for silicon, from the temperature gradients, displacements are calculated by a developed finite element program. The strain field, calculated from the displacement field, is related via Hooke's law to stresses in the crystal. These stresses are transformed to resolved shear stresses. These are the stresses that cause crystal slippage along certain planes and hence cause dislocations and twins. In silicon which is a face centered cubic structure there are 4 slip planes  $[111]$  and three slip directions  $[1\bar{1}0]$ . The total resolved shear stress is the sum of the twelve resolved shear stresses. It is assumed that the probability of dislocation occurrence is high only if the total resolved shear stress exceeds the yield stress. In Figure 2 the contours of equal total resolved shear stress are plotted across wafer surfaces, when the wafers are cut out at certain axial locations of the growing crystal. At no position is the yield stress exceeded and hence dislocations are unlikely in a silicon crystal grown under the above conditions. This

conforms to experimental evidence. The patterns of the RSS distribution in Figure 2 are in conformity with the results published by Kobayashi and Iwaki [2]. The RSS values are the highest at the center and at the outer edge and have the lowest values in between. Therefore, in system, where the yield stress is much lower, such as GaAs, we would expect a W pattern of dislocations, i.e. highest in the center and edges and lowest in the annular region, which is observed experimentally.

Our algorithm for evaluation of stresses is in preparation for publication.

#### D. Future Research

Research will be directed towards the development of improved multi-variable control schemes for CZ growth.

#### E. Bibliography

1. Srivastava, R. K., Ramachandran, P. A., Duduković, M. P., "Interface Shape in CZ Grown Crystals: Effects of Conduction and Radiation", J. Crystal Growth 73, 487 (1985).
2. Kobayashi, N., Iwaki, T., "A Thermoelastic Analysis of the Thermal Stress Produced in a Semi-Infinite Cylindrical Single Crystal During Czochralski Growth", J. Crystal Growth 73, 96 (1985).

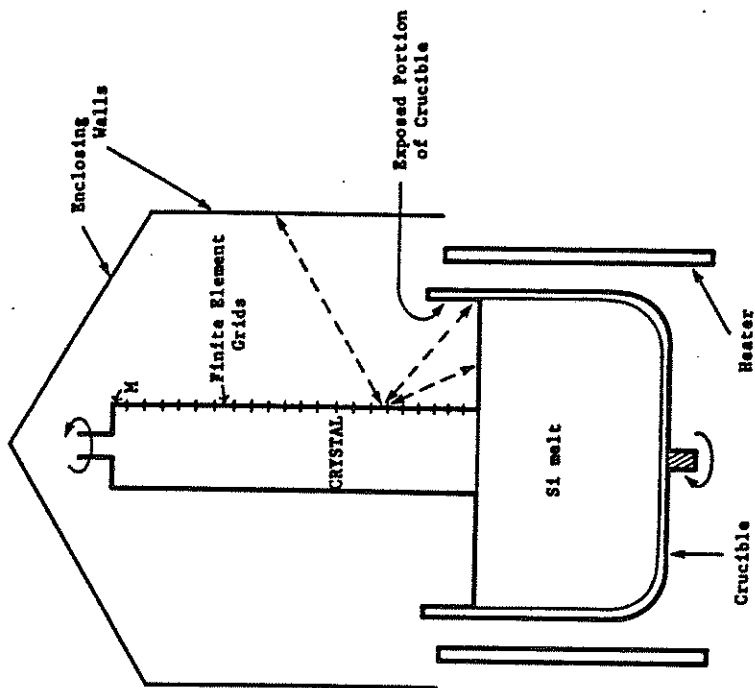
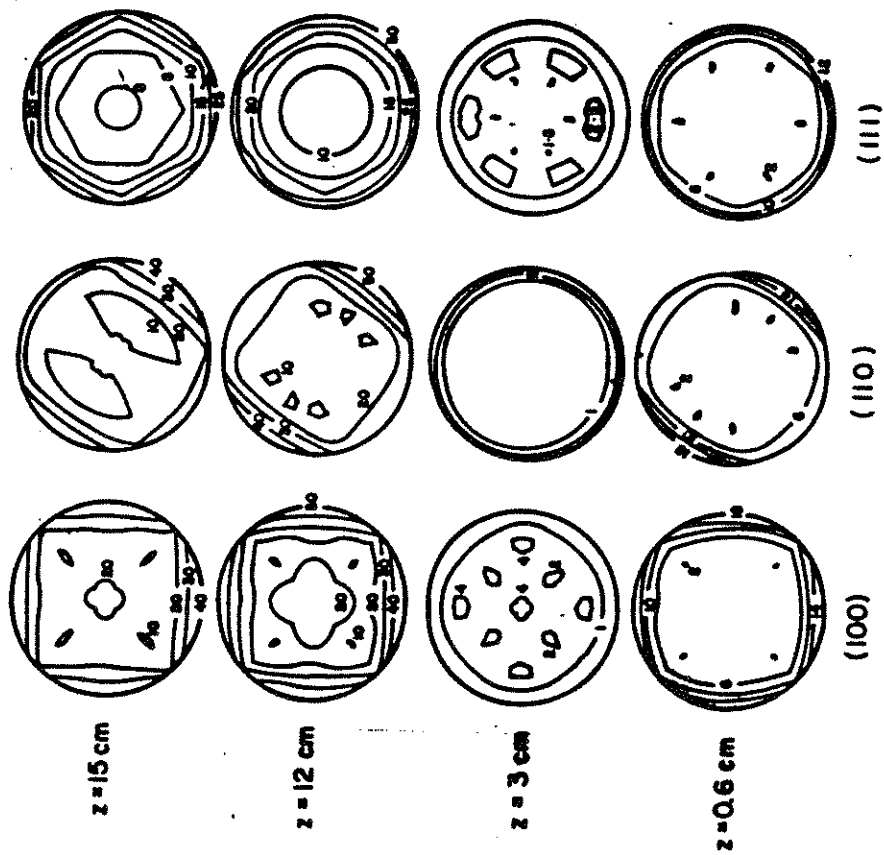


FIGURE 1. SCHEMATIC OF CZOCHRALSKI SINGLE CRYSTAL PULLING APPARATUS,

- - - INDICATES RADIATION INTERACTION

BETWEEN VARIOUS SURFACES.



DISTRIBUTION OF RESOLVED SHEAR STRESS  
 ( $RSS \times 10^7, \text{ dyne/cm}^2$ ) ON THE WAFER SURFACE AT  
 DIFFERENT AXIAL LOCATIONS

FIGURE 2



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

A. Problem Definition

Single crystal silicon with uniform electrical properties is required for many semiconductor applications. To obtain uniformity, dopants must be evenly distributed within the crystal. It is also necessary to keep the concentrations of contaminants (e.g. oxygen) below prescribed levels.

In the Czochralski(CZ) process, dopant distribution and contaminant concentrations in the grown crystal are functions of the mass-transfer in the melt during crystal growth. The mass-transfer is in turn dependent on the convection in the melt. As buoyant convection arises due to thermally induced density gradients, the heat-transfer in the melt must also be considered. An improved knowledge of the hydrodynamics, heat and mass-transfer in CZ-melts is therefore required to determine methods to improve the process.

Considerable work has been performed in recent years towards improving the CZ-process by growing the crystal in the presence of an externally applied magnetic field. The magnetic field has the effect of damping out flow oscillations which normally arise due to unstable natural convection. These flow oscillations result in fluctuations in the heat flux to the crystal. This causes a non-constant growth rate and can even result in periodic remelt of the grown crystal. These effects lead to axial striations in dopant concentration.

B. Research Objectives

The purpose of this work is to develop models for predicting the quality of grown crystals (in terms of dopant distribution, oxygen concentration, etc.) as a function of the geometric and operating para-

meters of the process. Computer models will be developed, where the aim will be to attain adequate physical rigor without exceeding our available computational resources. The results of case studies with the rigorous computer models will then be correlated to develop simple models for mass-transfer in CZ-melts.

### C. Research Accomplishments

#### C.1 Convergence Limits, Steady-State Hydrodynamics Code

Test cases were run using the previously developed steady-state hydrodynamics and heat-transfer code. The convergence limits are given in Table 1. The Grashof number ( $Gr$ ) is a nondimensional parameter which is a measure of the importance of natural convection. Order of magnitude results are given as the exact numbers are dependent on geometric factors (crystal and crucible radius, melt depth). The limit for natural convection is reached due to the onset of oscillatory (time dependent) flow. This result agrees with that of Crochet(1). Note that an order of magnitude increase in  $Gr$  is allowed in the presence of an axially applied magnetic field. This stabilizing effect is due to the velocity damping associated with the magnetic field.

For the case of crystal rotation, convergence was limited by our computational ability to discretize the very thin boundary layer ( $< 1mm$ ) where the velocity gradients are high. When an axial magnetic field is applied, the boundary layer is even thinner, and adequate discretization is even more difficult to achieve. This is why convergence has not yet been obtained for combined crystal rotation and applied magnetic field.

#### C.2 Thermal Boundary Conditions

Also studied was the sensitivity of the model to the thermal boundary conditions imposed along the crucible wall. In all of the previous simulations in the open literature, the effect of heating the

melt is approximated by setting the temperature at the side of the crucible to some constant value. The boundary condition along the crucible bottom, however, has been handled differently by different workers. These approximations are enumerated below:

1. Heated bottom (crucible bottom is the same temperature as the crucible side)
2. Insulated bottom (no heat flow through the crucible bottom)
3. Linearly varying temperature profile, decreasing from the side to the center of the crucible bottom

We prefer a quadratically varying profile over the linear profile as the linear case results in a discontinuity of heat flux at the axis of symmetry.

The cases of heated, insulated and quadratically varying boundary conditions were compared with all other parameters held constant. The results are given in Figure 1, in terms of the heat flux at the melt-crystal interface as a function of radius. This is an important quantity as it will have a large effect on the crystal growth rate. It can be seen from the figure that for this case there is about a factor of six difference in the heat flux between the heated and insulated cases. These results demonstrate the need for experimental data on the thermal environment in the CZ-enclosure.

### C.3 Preliminary Results, Applied Axial Magnetic Field

The model was updated in the previous year to include the effect of an axially applied magnetic field. An axial field is one that is oriented such that it is parallel to the axis of symmetry. Preliminary results are shown for the case of combined natural convection and thermocapillary flow. Figure 2 is a plot of the streamlines for the case of no applied field. The streamlines correspond to the paths that

the individual fluid particles traverse. The positive values for the stream function indicate that the flow is counter-clockwise in direction. The magnitude of the contour values is an indication of the velocity of the flow.

Figure 3 represents the flow in the presence of an axially applied magnetic field. The velocity of the flow is much reduced, as can be seen from the smaller contour values. Furthermore, there is a significant change in the structure of the flow. The single counter-clockwise eddy has split into two separate eddies. This occurs because the fluid is trying to align itself with the magnetic field.

#### D. Future Research Plan

1. Obtain solutions for realistic crystal and crucible rotation rates. Resolve the flow field in the boundary layers by either coordinate stretching or by patching a boundary layer solution with a finite elements solution for the flow in the bulk melt.
2. Develop a rigorous model for mass-transfer of dopants and oxygen in the melt.
3. Develop simple models for mass-transfer in the melt based on the results of the the rigorous model.

#### E. Bibliography

1. Crochet, M.J., Wouters, P.J., Geyling, F.T. and Jordan, A.S., J. of Crystal Growth, 65, 153, (1983)

Table I. Convergence Limits for the Steady-State Code

	Practical Values	No Applied Magnetic Field	Axially Applied Magnetic Field
Grashof number	$10^6-10^9$	$O(10^6)$	$O(10^7)$
Crystal Rotation Rate	5 - 20 rpm	2 rpm	—

CONTOUR VALUES

- 1 = 2.000E+01
- 3 = 6.000E+01
- 5 = 1.000E+02
- 7 = 1.300E+02

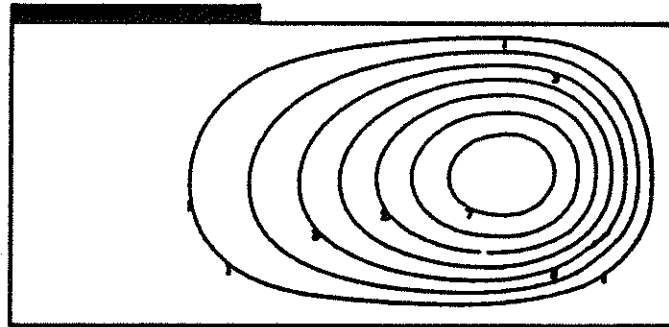


Figure 2. Meridional streamlines, no applied field

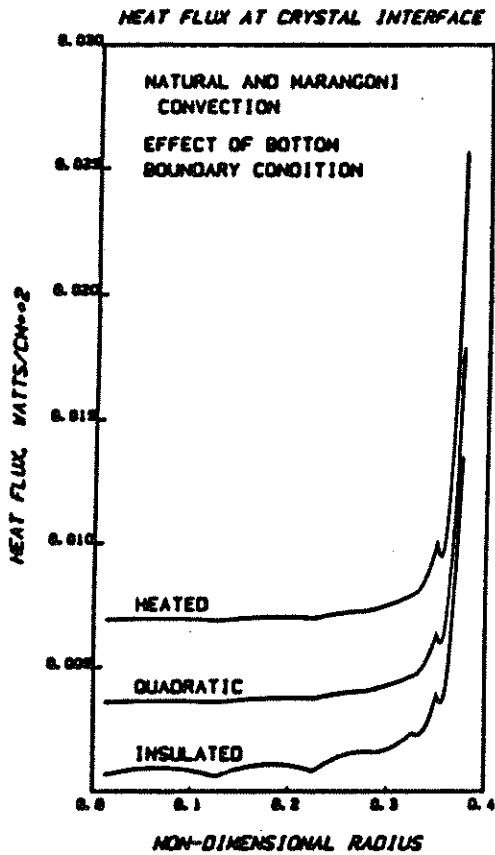


Figure 1.

CONTOUR VALUES

- 1 = 1.000E+00
- 3 = 1.700E+00
- 5 = 2.500E+00
- 7 = 3.400E+00
- 9 = 4.100E+00

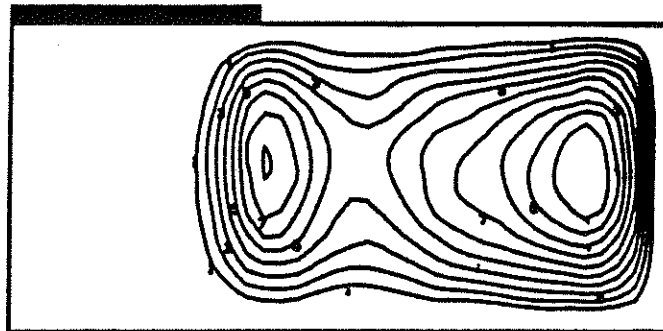


Figure 3. Meridional streamlines, applied axial magnetic field

## Project III.5 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 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 fabrication, optic fibers, and materials processing. Some of the advantages of plasma enhanced deposition processes are : low temperature of the gas which avoids excessive heating of 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 is 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. To formulate a global model for the DC-discharge and study the effects of different parameters.
2. Study the plasma-activated chemical vapor deposition process and construct a model to predict the effect of electric field strength on the deposition profile.
3. Apply the above models to practical systems such as production of amorphous silicon, controlled purity silica, etc.

C. Research accomplishments

One of the methods used for the preparation of optical fibers and fabrication of microelectronics is plasma-activated chemical vapor deposition.

A model for the mass transfer analysis of a zero order generation of active species followed by wall deposition was formulated. The plasma reactor is divided into three zones: a central zone with reaction (electron impact dissociation), convection and diffusion, and two lateral zones with only diffusion and convection.

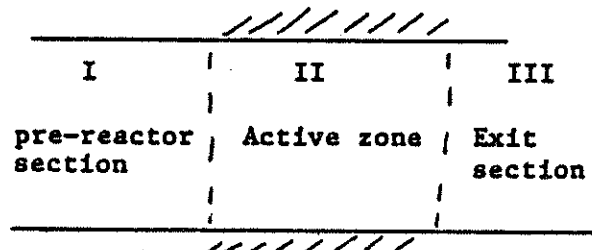


Figure 1. Plasma Reactor

### Zones I and III

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

### Zone II

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

The generation term,  $R_A$ , is a function of electron density and electron temperature. Both analytical and numerical results have been obtained. This model can predict the deposition rate of some industrially important species such as silica, silicon nitride films or amorphous silicon by glow discharges in  $\text{SiH}_4$ .

By moving the plasma zone, superposition of deposition profiles occurs and a uniform deposition along a length of interest can be obtained. Gas velocity, Peclet and Damkoeler number are the most important parameters. Model predictions depend on an assumed kinetics (fig. 2). In order to have a realistic kinetics form, a model predicting electron concentrations and energy levels is required.

For this reason, the modelling of a DC discharge reactor is under way. The model consists of equations for electron and ion continuity, Poisson's equation for the electric field, and electron energy equation. The reactor is divided into three zones : bulk, cathode pre-sheath, and cathode sheath. In this manner we can enhance our understanding of physics and chemistry of the process by considering the relative importance of various terms in different zones.

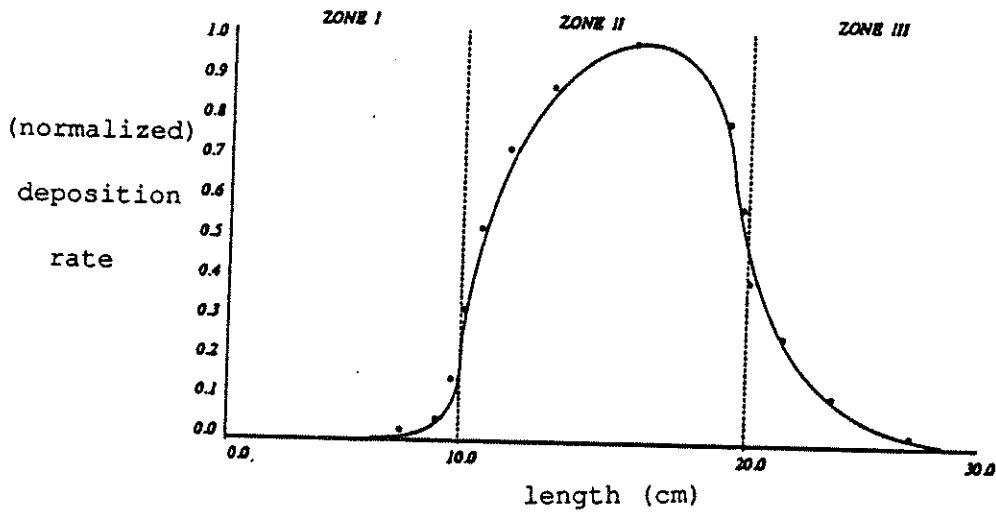
In the first zone the concept of ambipolar diffusion was utilized



(collective behavior of charges). The assumptions are : concentration of electrons and ions are equal, constant electron temperature, and no significant potential drop. An analytical solution was obtained in zone one (bulk plasma). In the second zone we have to use the full set of equations. Electron and ion continuity equations, consisting of diffusion and migration terms, the Poisson's equation, and the electron energy equation. A numerical solution (collocation on finite elements) was utilized to get an approximate solution. More work is needed to get a better solution for this zone. The third zone is very close to the cathode. The assumptions here are : constant ion flux, constant electron flux, the dominant term in the flux equations is the migration term, and no generation due to high energy (small collision cross section). An analytical solution was obtained for zone three.

#### D. Further Research plan

Add the electric field to the plasma-activated chemical vapor deposition model and study the effect of the field strength on the deposition profile. Complete the solution of the DC discharge model, and test the model with available experimental data, and explore the possibility of some additional critical experiments to verify the models.



Zones I and III - generation of active species

Zone II - active plasma zone.

Figure 2. Deposition profiles predicted by simple mass transfer model. Circles represent experimental results of Turban and Catherine (J. thin solid films, 48, 57, 1978) for deposition of silicon nitride.

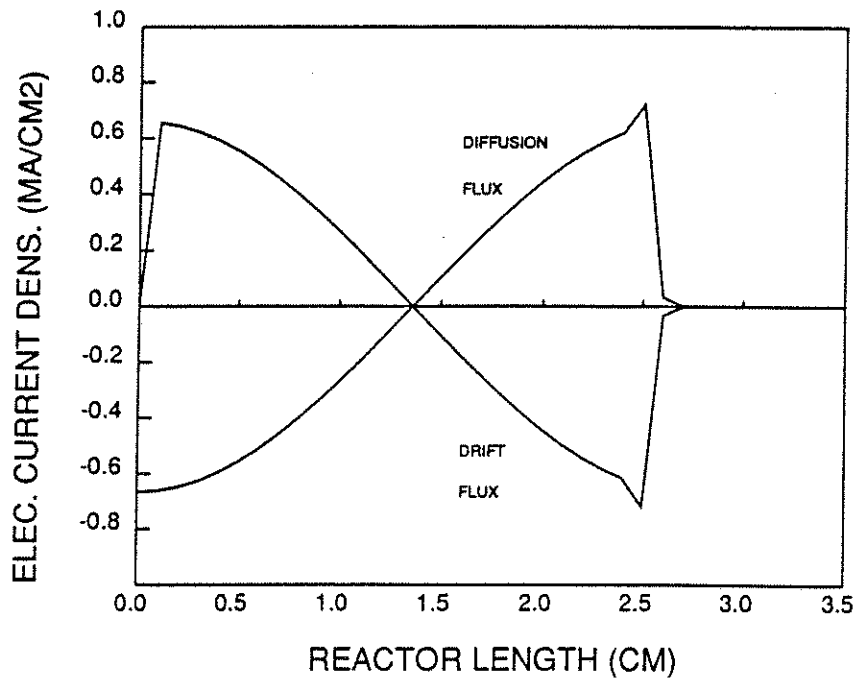


Figure 3. Relative contributions of electron drift and diffusion to total electron flux.

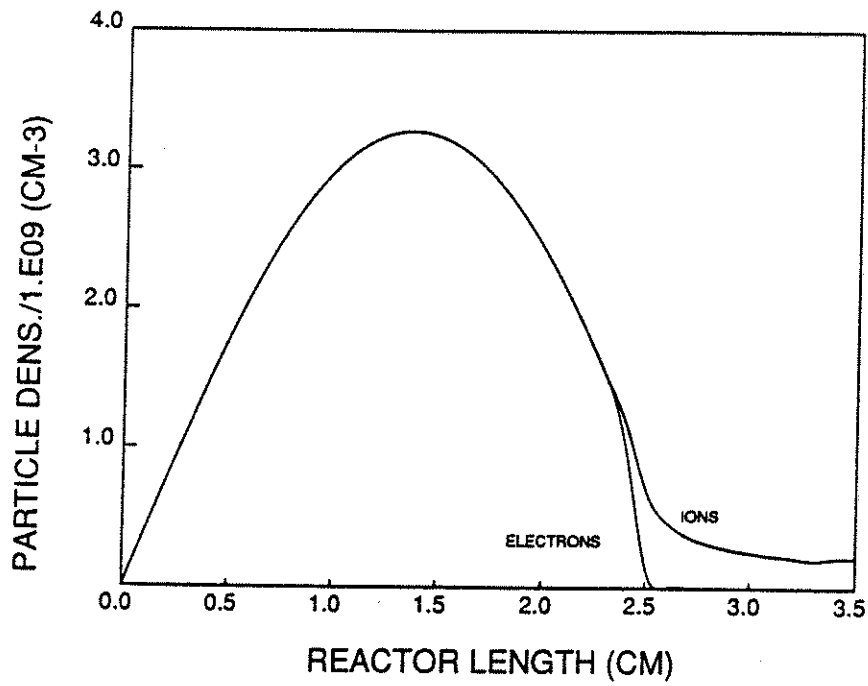


Figure 4. Electron and positive ion number densities, DC solution.

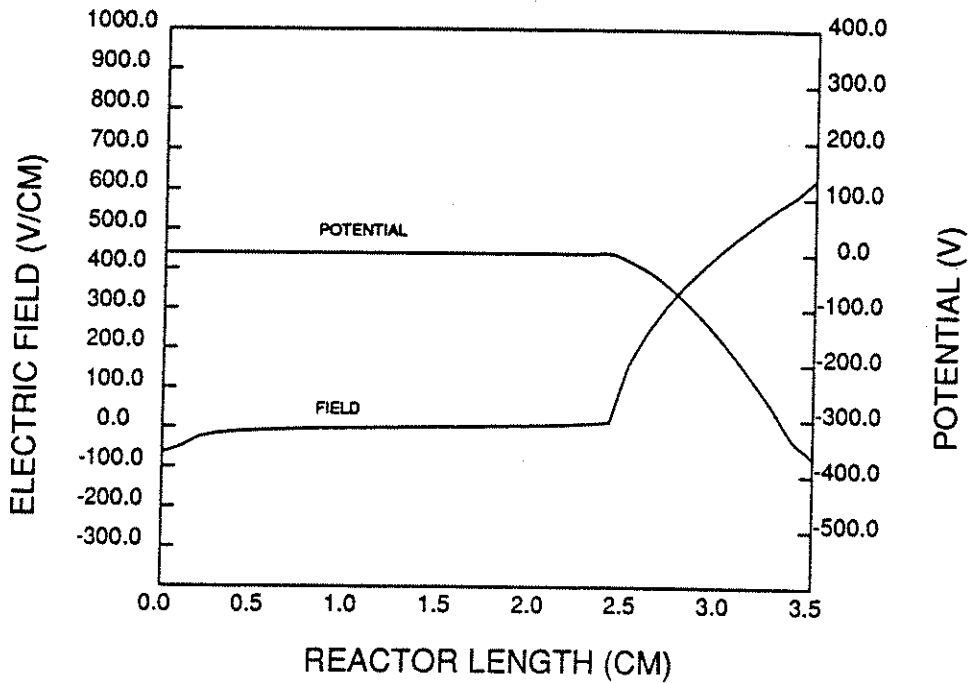


Figure 5. Voltage and electric field profiles, DC solution.

## ANTICIPATED NEW PROJECTS AND AREAS

### Project N1. Applications of Artificial Intelligence and Expert System Technology to Safety and Diagnostics in Process Plants

#### A. Problem Definition

Recent advances in the Artificial Intelligence Area of Computer Science has opened up some new avenues for improving plant safety through the development of computer-aids for operators to detect, diagnose and repair process malfunctions. One area that has received a lot of attention recently is the use of expert system technology. This technology has introduced some powerful new tools in computing that allows us to capture and manipulate knowledge represented in symbolic form as opposed to the traditional algorithmic representation of knowledge. As a result, it becomes possible to develop computer aids in a number of areas that were difficult to handle previously. The area of process plant safety and malfunction diagnosis is one of them.

#### B. Research Objectives

The objective of this research is to develop strategies for fault detection, malfunction diagnostics, and operator aids for process plants using artificial intelligence and expert system technology. The concept will be extended to develop intelligent control systems capable of monitoring and controlling the plant with levels of intelligence approaching that of an experienced operator. We are not proposing to replace the human in the control and operation loop, but we are interested in bringing as much of the power of computer to aid the operator in any way possible to optimize the operation and to prevent catastrophic events.

#### C. Research Accomplishments

We have just initiated this research and we hope to have initial results by the end of Summer of 1987.

Project N2. Investigation of Heterogeneous Catalyzed  
Systems and Gas-Solid Interactions  
Using the TAP Reactor.

A. Problem Definition

A complete fundamental description of the physical processes and chemical transformations that occur on the surfaces of a bulk catalyst is currently impossible using available analytical methods and experimental techniques. If this were feasible, catalyst scientists could then begin to understand how to design and optimize heterogeneous catalyst performance for a particular application through manipulation of key variables that are used during catalyst preparation and through the selection of reaction conditions. The concept of developing a molecular level understanding for gas-solid systems represents a key opportunity that, if successful, would have a significant impact on future catalytic science and industrial processes for the 1990's.

Scientists at Monsanto have designed and patented a new instrument for investigation of gas-solid interactions called TAP for Temporal Analysis of Products. One of the primary motivations for inventing the TAP reactor was to provide catalyst scientists with an experimental device that would incorporate some useful features of previous devices, such as molecular beam reactors, along with some new concepts so that certain new fundamental aspects of catalyst behavior could be examined. Key features of TAP include the following: (i) the reactor configuration is a micro-scale fixed-bed that accepts a bulk form of the catalyst, (ii) the reactants are introduced to the reactor using a pulse input

so that the transient response of the catalyst is observed, (iii) the time-scale of the experiment is minimally 10 microseconds so that the potential for observing reaction intermediates is significantly increased when compared to other types of transient catalytic methods, (iv) the reaction products are sensed by mass spectroscopy for positive identification, (v) the catalyst bed temperature can be either isothermal or programmed for adsorption or desorption studies, (vi) the number of molecules that are introduced to the catalyst bed can be carefully controlled over a wide range, and (vii) two separate gas pulses can be introduced to the reactor through independently controlled pulse valves for periodic, transient experiments.

Monsanto Chemical Company has donated one of the prototype TAP reactors to CREL for use in both fundamental and applied aspects of catalysis and materials science research. Since TAP is a new experimental technique, its full capabilities and possible limitations have not yet been exploited or identified. Up until now, the primary use of TAP at Monsanto has been to investigate the qualitative features of mixed metal oxide catalysts. Example of reaction systems that have been studied include propylene oxidation to acrolein, methanol oxidation to formaldehyde, butane oxidation to maleic anhydride, and the ammoxidation of methanol to hydrogen cyanide. The principle goal of this project is to use the TAP reactor to study various fundamental aspects of specific catalytic reactions that have commercial potential. Of equal importance in this work is to develop quantitative methods for interpretation of the TAP transient response data and to compare the reaction parameters to those obtained from other independent experiments.

#### B. Research Objectives

The TAP project is currently viewed as a long-term one that will lead to broad contributions in catalysis and materials research. While the above

emphasis has been in the area of vapor-phase heterogeneous catalysis, it is conceivable that the fixed-bed reactor could be replaced with any surface or target where a knowledge of the gas-solid interactions might be of interest as in materials or electronics processes. The current emphasis will be upon using TAP to gain novel insight into specific heterogeneous catalyzed systems with the following objectives:

1. Investigate the kinetics and mechanism of selected oxidation reactions, such as butane oxidation to maleic anhydride, and to compare the results to those deduced from either interpretation of steady-state differential reactor experiments or other transient response methods.

2. Development of models for interpretation of TAP transient response data that can be applied to the molecular flow region and to the continuum region (two cases) that are supported by experimental data.

3. Investigation of other heterogeneous catalyzed reactions of interest, such as selective methanol conversion to chemicals using zeolites, Fischer-Tropsch synthesis over iron or cobalt catalysts, or amination of olefins to selected amines.

#### C. Research Accomplishments

The TAP reactor is currently being re-assembled at Washington University following its donation from Monsanto and is expected to be operational by mid-1987. Considering the complexity of the device and that several useful modifications are being performed during the re-assembly, this represents a significant accomplishment.

The principle components of TAP are the fast pulse gas delivery system, the catalytic microreactor, the real-time detection system (quadrupole mass spectrometer), and a high throughput vacuum system. A schematic diagram that illustrates these key components and the flight of a single gas pulse is given

in Figure 1. Referring to Figure 1, it can be seen that TAP is divided into three pumped vacuum chambers. These are the reactor chamber, which includes the pulse input system, the differential chamber, and the detector chamber. An important feature here is the ability to isolate the reactor chamber from the remaining chambers. This allows the catalyst to be removed and replaced within a matter of minutes without losing the vacuum throughout the entire system. In this fashion, many different types of catalyst samples can be examined in a relatively short time.

As mentioned earlier, the current TAP design employs a dual valve assembly for the introduction of gas pulses to the fixed-bed microreactor. Importantly, through variations in the time between the reactant pulses, it is possible to examine the effect of surface lifetimes of adsorbed species or product formation. Each valve has its own separate gas supply and driver so that the user can introduce gas pulses of different composition to the reactor. With this design, the elapsed time interval between the pulse valve activation for each valve can be independently controlled. Figure 2 illustrates a typical concentration versus time behavior for both valves for the case where the valves are actuated at unequal time intervals. The time intervals between the pulse valve activation for each valve are  $\Delta t_1$ , and  $\Delta t_2$ , respectively. The pulse rate of each valve can be varied from a single shot to about 50 pulses per second with a reproducibility of 2%.

TAP can be operated in one of two possible modes which are referred to as the SCAN mode and the TAP mode. In the SCAN mode, the gas pulse valves are actuated and the mass fragmentation patterns produced at the quadrupole mass spectrometer are scanned over a predefined mass range. In this fashion, one can identify the reaction intermediates by comparison to known mass fragmentation



patterns. Also, this allows the user to select a unique set of mass fragments for use in the TAP mode. In this latter mode, the quadrupole mass spectrometer is set to sense the intensity of a particular mass fragment in the gas pulse. Once the gas pulse is introduced and the intensity versus time data are collected, the mass spectrometer is set to monitor the intensity of the next fragment, and the gas pulse is introduced. By repeating this procedure, the transient response of each reaction intermediate can be obtained to produce a set of TAP curves. Figure 3 shows typical normalized intensity versus time curves when a 4:1 mixture of butane and oxygen is pulsed into a reactor that contains a PVO catalyst at 420°C. Besides the reaction products shown here, carbon dioxide, carbon monoxide, and water were also observed. These are not shown since the resulting intensity versus time curves are either very broad for the indicated time scale, or required the use of isotopically labelled oxygen to be positively identified from the remaining mass fragmentation patterns.

The results given in Figure 3 show that butene and butadiene are present as reaction intermediates. These are typically not observed in fixed-bed steady-state reactor experiments which provides insight into the reaction pathway and relative lifetimes of the reactants, intermediates, and products. From the identified product distribution, the reaction network given in Figure 4 for butane oxidation to maleic anhydride can be constructed. By calibration of the mass intensity with concentration, it should be possible to integrate the TAP response curves for the individual species and perform a mass balance. From this data and the known composition of the input pulse, the selectivity-conversion relationship for each species can be obtained. By analysis of the transient response curves with an appropriate model, it should be possible to extract kinetic parameter estimates and other related parameters. This will be one of the key research accomplishments that we hope to demonstrate during the next year.

# TAP (Temporal Analysis of Products) REACTOR

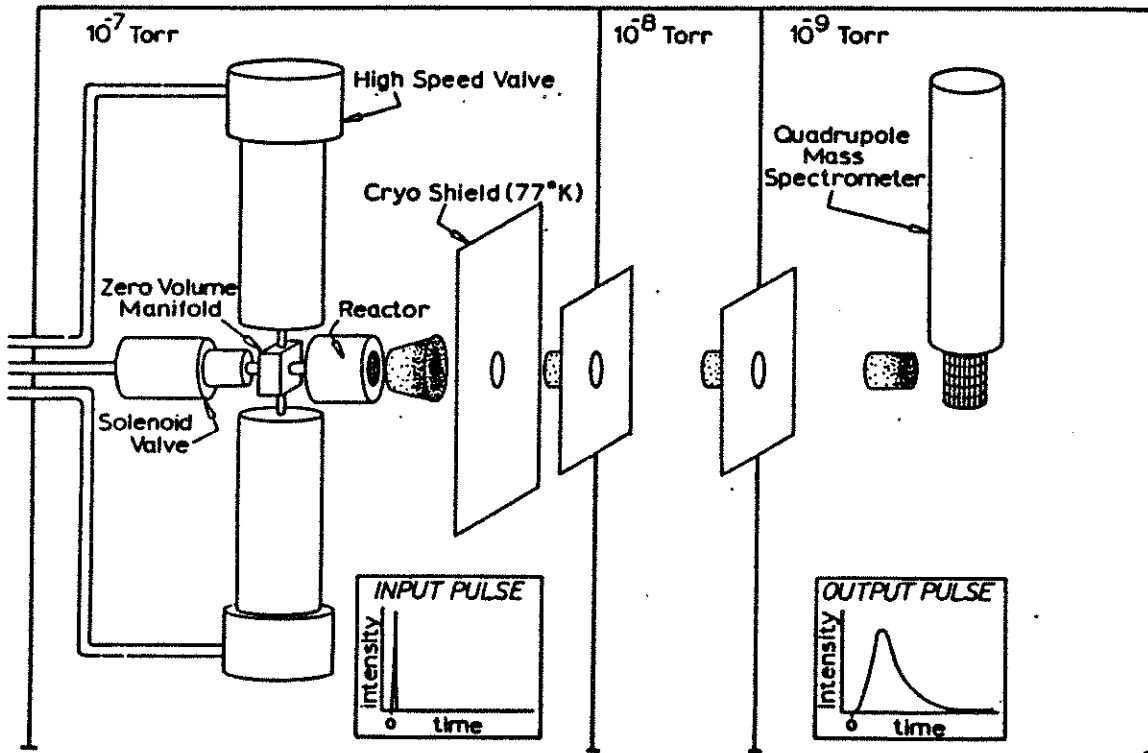


Figure 1. Schematic Diagram of the TAP Reactor System.

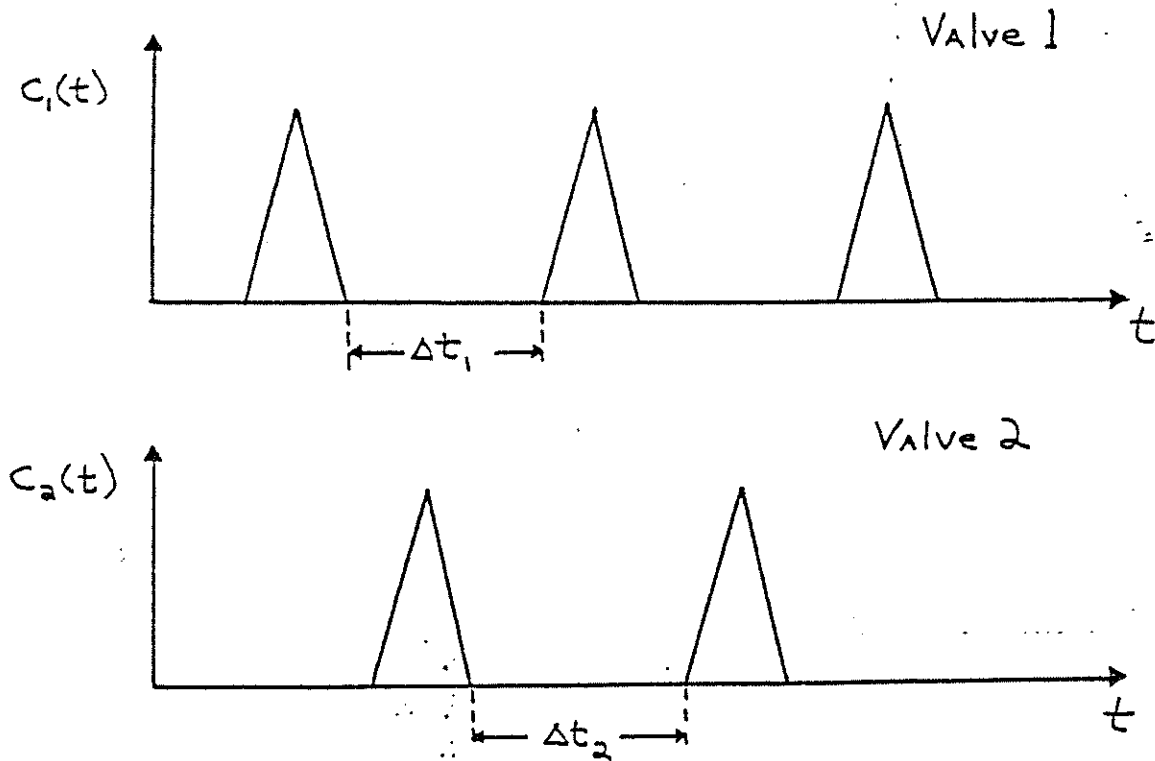


Figure 2. Illustration of the Pulse Concentration versus Time Behavior for Double Pulse Valve Assembly for the General Case where Each Pulse is Introduced at an Unequal Time Increment.

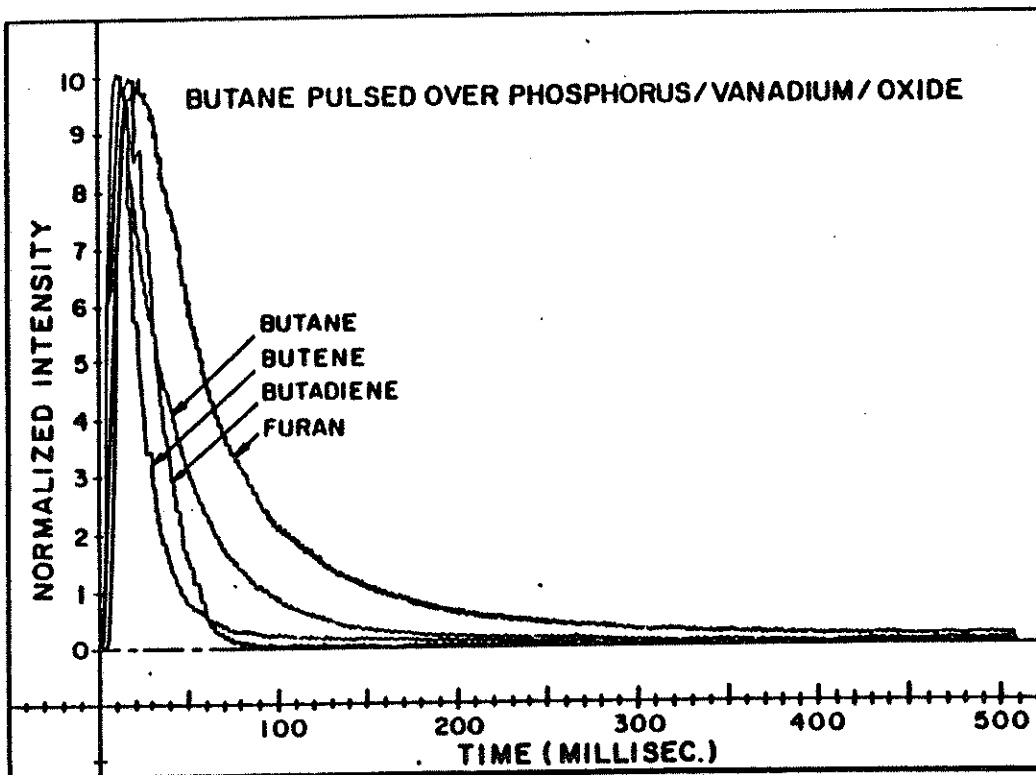


Figure 3. TAP Response Curves Obtained When a Mixture of Butane and Oxygen are Pulsed Over a Vanadium Phosphorous Catalyst Used for Maleic Anhydride Production.

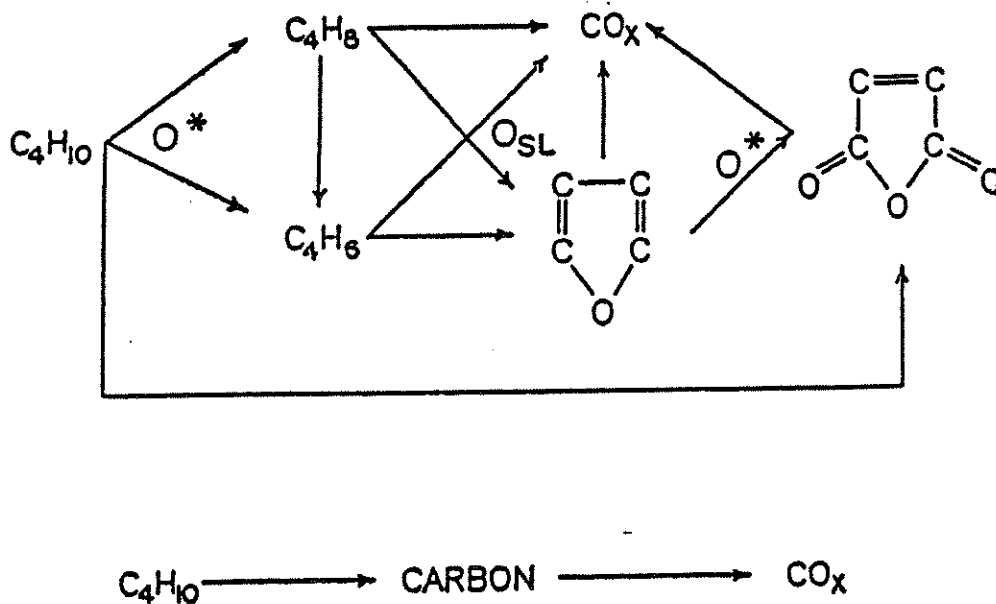


Figure 4. Reaction Network for Butane Oxidation.

### Project N3. New Materials

We plan to initiate a number of new projects to study reaction engineering aspects in production of new materials such as:

- high performance ceramics
- silicon carbide - silicon composites
- glass fibers.

Final selection will depend on the availability of funding.

### Project N4. Other Initiatives

Among other initiatives we are exploring the possibilities of studying Fischer-Tropsch reactions in the context of reactor models. In addition, oxidation of hazardous wastes in trickle-beds is a potential future topic.

### CURRENT FUNDING

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

Industrial participation fees supported the research in all areas and amounted to \$122,500.

Modeling of Czochralski growth was supported by the 2nd year of a three year EPRI contract at \$70,000 per year.

Funding for trickle-bed research and rotating packed beds will be forthcoming from NSF in 1987/88.

CURRENT STAFF (1986/87)

During the period covered by this report (June 1, 1986 through May 31, 1987) the following individuals have been associated with the various projects in the laboratory.

A. Faculty

Dr. Milorad (Mike) Duduković, Professor and Director

Dr. Babu Joseph, Associate Professor

Dr. P. A. Ramachandran, Associate Professor

Dr. R. Srivastava, Research Associate

B. Graduate Students

A. Basic

E. Beaudry

S. J. Choi

R. Dave

N. Devanathan

D. Dorsey

P. Hanratty

R. Holub - Amoco Fellowship Recipient

S. Lai

S. Munjal

D. O'Connor - Shell Fellowship Recipient

S. Pirooz

B. Thomas - Monsanto Electrochemical Fellowship Recipient

Y. Yang

I. S. Yoon

INDUSTRIAL ADVISORY BOARD (1986/87)

L. P. Bosanquet	Monsanto
L. Clomburg	Shell Development
J. Cropley	Union Carbide
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R. E. W. Jansson	Monsanto
F. Krambeck	Mobil
P. R. H. Martin	3M
F. X. Mayer	Exxon
P. L. Mills	Monsanto
G. Robertson	Hughes Research
B. L. Tarmy	Exxon
P. Wanser	Sohio

## CREL PUBLICATIONS AND PRESENTATIONS IN 1986

### A. PAPERS AND CHAPTERS

1. "Tracer Methods in Chemical Reactors. Techniques and Applications", M. P. Duduković, in Chemical Reactor Design and Technology, edited by H. DeLasa. NATO ASI Series E: Applied Sciences No. 110. Dordrecht, Holland: Martinus Nijhoff Publ. Co., 1986, pp. 107-189.
2. "A New Model for Assessment of External Liquid-Solid Contacting in Trickle-Bed Reactors from Tracer Response Measurements". P. A. Ramachandran, M. P. Duduković and P. L. Mills, Chem. Eng. Science, 41(4), 855-860 (1986).
3. "Experimental and Modeling Studies in Fixed-Bed Char Gasification", A. Bhattacharya, L. Salam, M. P. Duduković and b. Joseph, I&EC Process Des. Develop., 25 (4), 988-996 (1986).
4. "Chemical Vapor Deposition and Homogeneous Nucleation in Fluidized Bed Reactors: Silicon from Silane", S. Lai, M. P. Duduković and P. A. Ramachandran, Chem. Eng. Science 41(4), 633-642 (1986).
5. "Aerosol Reactor Design: Effect of Reactor Type and Process Parameters on Product Aerosol Characterization", S. E. Pratsinis, T. T. Kodas, M. P. Duduković and S. K. Friedlander, I&EC Process Design & Develop., 25, 634-642 (1986).
6. "Aerosol Reactor Design: The Effect of Reactor Geometry", S. E. Pratsinis, T. T. Kodas, M. P. Duduković and S. K. Friedlander, Powder Technology, 47, 17-23 (1986).
7. "The Effect of Aerosol Reactor Residence Time Distribution on Product Aerosol Characteristics", S. E. Pratsinis, T. T. Kodas, M. P. Duduković and S. K. Friedlander, Chem. Eng. Science 41(4), 693-702 (1986).
8. "Gas-Solid Reactions: A Method of Direct Solution for Solid Conversion Profiles", P. C. Prasanna, P. A. Ramachandran, and L. K. Doraiswamy, Chem. Eng. J., 1986, 33, 19.
9. "Design and Performance Evaluation of Heat Regenerators". P. A. Ramachandran, and M. P. Duduković, in Encyclopedia of Chemical Processing, J. J. McKetta, Ed., Marcel Dekker Publishing Co., 1986.
10. "Radiation View Factors in Czochralski Crystal Growth Apparatus for Short Crystals", R. K. Srivastava, P. A. Ramachandran and M. P. Duduković, J. Crystal Growth, 79, 281-291 (1986).
11. "Czochralski Growth of Crystals: Simple Models for Growth Rate and Interface Shape", R. K. Srivastava, P. A. Ramachandran and M. P. Duduković, J. Electrochem. Soc.: Solid-State and Technology, 133 (5), 1009-1015 (1986).



12. "Simulation of Jet Cooling Effects on Czochralski Crystal Growth", R. K. Srivastava, P. A. Ramachandran and M. P. Duduković, J. Crystal Growth, 76, 395-407 (1986).
13. "Void Growth and Resin Transport During Processing of Thermosetting-Matrix Composites", J. L. Kardos, M. P. Duduković and R. Dave, Advances in Polymer Science (K. Dusek, ed.) 80, 101-123 (1986).
14. "A Model for Resin Flow During Processing of High Performance Composites", R. Dave, J. L. Kardos and M. P. Duduković, Polym. Mater. Sci., 55, 334-338 (1986).
15. "A Model for Resin Flow During Composite Processing: Part 1 - General Mathematical Development", R. Dave, J. L. Kardos and M. P. Duduković, Polymer Composites, 8, 29-38 (1986).
16. "Process Modeling of Thermosetting Matrix Composites: A Guide for Autoclave Cure Cycle Selection", R. Dave, J. L. Kardos and M. P. Duduković, Proc. Amer. Soc. Composites, Technomic Publ. Co., Lancaster, PA (1986). pp. 137-145.
17. "On-line Optimization of Constrained MULTivariable Processes", B. Joseph, S. S. Jang and H. Mukai. AIChE Journal, 33, (1987). pp. 26-31.
18. "A Comparison of Two Approaches to On-Line Parameter Estimation and State Estimation of Nonlinear Systems", B. Joseph, S. S. Jang and H. Mukai. Ind. Eng. Chem., Proc. Des. Dev., 25, (1986). pp. 809-813.

B. PRESENTATIONS

a) Meetings and Workshops

1. "Simulation of the Temperature Distribution in Crystals Grown by Czochralski Method", P. A. Ramachandran, M. P. Duduković and R. K. Srivastava, World Congress III Chem. Eng., Keio Plaza Hotel, Tokyo, Japan, Sept. 21-25, 1986; Vol. I, 335-338; paper 5a-254.
2. "Gas-Liquid Downflow, Upflow and Countercurrent Flow in Packed-Beds: Reactor Performance for a Gas-Limiting Reaction", World Congress III Chem. Eng., Keio Plaza Hotel, Tokyo, Japan, Sept. 21-25, 1986; Vol. IV, 173-176; paper 9b-152.
3. "Fluidized Bed Reactor Modeling for Production of Silicon by Silane Pyrolysis", M. P. Duduković, S. Lai and P. A. Ramachandran, World Congress III Chem. Eng., Keio Plaza Hotel, Tokyo, Japan, Sept. 21-25, 1986; Vol. IV, 295-298, paper 9b-354.
4. "Resin Flow and Voids Formation During Curing of Reinforced Graphite Composites", J. L. Kardos, M. P. Duduković and R. Dave, World Congress III Chem. Eng., Keio Plaza Hotel, Sept. 21-25, 1986; Vol. VI, 499-502, paper 11a-354.
5. "A Model for Resin Flow During Processing of High Performance Composites", R. Dave, J. L. Kardos and M. P. Duduković, Proc. Polym. Mat. Sci. Eng. Div., ACS NATO Meeting, Anaheim, CA, Sept. 1986.
6. "Autoclave vs Non-Autoclave Composite Processing", R. Dave, J. L. Kardos, S. J. Choi and M. P. Duduković, Proc. 32nd Nat. Symp. SAMPE, Anaheim, CA., April 1987.
7. "Autoclave Processing of Thermosetting Matrix Composites: Models for Automation and Cure Cycle Selection", R. Dave, J. L. Kardos and M. P. Duduković, Proc. 1987 Annual Technical Meeting Soc. Plastic Engineers, Los Angeles, CA., May, 1987.
8. "An Elevator-Mixing Cell Model for Churn Turbulent Bubble Columns", K. Myers, M. P. Duduković and P. A. Ramachandran, AICHE Annual Meeting, Miami Beach, November, 1986; paper 49c.
9. "Modeling of Fluidized Beds for Manufacture of Silicon by Silane Pyrolysis", M. P. Duduković, S. Lai and P. A. Ramachandran, AICHE Annual Meeting, Miami Beach, November, 1986; paper 66f.
10. "Convolution and Deconvolution of Nonideal Tracer Response Data with Application to Three-Phase Packed Beds", P. L. Mills and M. P. Duduković, Miami Beach, November, 1986; paper 84a.
11. "Tracer Studies and Parameter Characterization in Trickle-Beds", F. X. Mayer, E. Beaudry, M. P. Duduković and P. A. Ramachandran, Miami Beach, November, 1986, paper 84f.
12. "Jet Cooling Effects on Czochralski Crystal Growth of Silicon", M. P. Duduković, P. A. Ramachandran and R. K. Srivastava, Miami Beach, November, 1986; paper 120c.

13. "Control of Constrained Multivariable Nonlinear Processes", B. Joseph, S. S. Jang and H. Mukai, AIChE Annual Meeting, Miami, Nov., 1986.
14. "Expert Systems: Myth and Reality", B. Joseph, AIChE One-Day Symposium, St. Louis, April, 1987.

b) Seminars

M. P. Duduković

University of New York at Buffalo  
Amoco Oil Research Center, Naperville  
Sohio Research Center, Cleveland  
Wright Patterson Air Force Base  
University of Delaware  
Duke University

B. Joseph

Case Western Reserve University  
Indian Institute of Technology - Bombay

P. A. Ramachandran

Hofmann La Roche

c) Theses

1. R. Dave, "Computer Aided Processing of Composites", D.Sc. Thesis, Washington University, St. Louis, MO, December, 1986. (J. L. Kardos and M. P. Duduković, advisors).
2. S. S. Jang, "Control and Optimization of Constrained Multivariable Processes", D.Sc. Thesis, Washington University, St. Louis, MO, December, 1986. (B. Joseph and H. Mukai, advisors).
3. S. Munjal, "Fluid Flow and Mass Transfer in Rotating Packed Beds with Countercurrent Gas-Liquid Flow", D.Sc. Thesis, Washington University, St. Louis, MO, December, 1986. (M. P. Duduković, advisor).