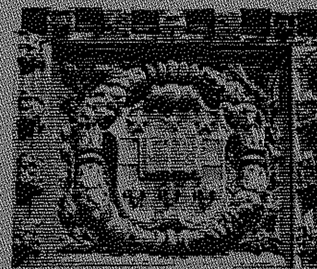

WASHINGTON UNIVERSITY

SCHOOL OF ENGINEERING AND APPLIED SCIENCE

CHEMICAL REACTION ENGINEERING LABORATORY

ANNUAL REPORT

1976

WASHINGTON UNIVERSITY / ST. LOUIS / MISSOURI 63130

Annual Report

1976

CHEMICAL REACTION ENGINEERING LABORATORY

Department of Chemical Engineering

Washington University

St. Louis, Missouri 63130

Prepared by:

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INTRODUCTION

This report covers the major developments in the Chemical Reaction Engineering Laboratory (CREL) for the period September 1, 1975 through September 30, 1976.

During the last year a viable operation of the Laboratory was maintained. Two NSF grants were received as well as continued financial support from Alcoa, Amoco, and Monsanto. This continued industrial interest is especially gratifying and much appreciated. The affiliate faculty members: Drs. R. Calcaterra and K. Robinson (Amoco), C. Hagberg (Monsanto), A. Pearson (Alcoa) and other industrial consultants provided invaluable assistance in discussing various research projects. In addition C. Hagberg offered a one semester course in polymerization engineering thus providing some "industrial" flavor to a reaction engineering course.

One doctoral student (P. Medellin) completed his dissertation during the past year in the Laboratory, two doctoral thesis proposals were presented (H. Lamba, Y. Hsu). Currently three D.Sc. candidates are working in the Laboratory and two M.S. students. In addition a number of undergraduates (freshmen through seniors) participated in the research activities. Four of these students were sponsored by the NSF undergraduate research participation fund.

The Laboratory staff was active in the reaction engineering area also outside Washington University. Dr. E. Weger presented a paper on trickle beds in Heidelberg at the 4th International Symposium on Chemical Reaction Engineering. Dr. M. Duduković presented 1 (one) paper at the Boston and Kansas City National AIChE Meetings and

. 4 (four) papers at the Los Angeles Annual AIChE Meeting. He also gave invited seminars at IIT and University of Illinois, Circle Campus, in Chicago and at Rensselaer Polytechnic Institute in New York. Four papers were published, several are in preparation for publication.

Some changes in communications between CREL and participating industries are planned. In the future the participating companies will be receiving brief reports on the work in progress every six months i.e. each November and May. These reports will summarize the work on all active projects. Progress on every individual project will be described in more detail in an appendix. Each participating company will receive the appendices for the projects which they are supporting. Other appendices will be available upon request. Additional reports at irregular time intervals will be issued as work gets completed on a particular project.

Finally it should be mentioned that industrial sponsors sometimes expressed views that experimental work in CREL should proceed at a faster pace. The research pace in an University environment is limited by three major factors: a) the student is not employed full time to work on his project but rather during the school year spends most of his time on course work, b) the student has hardly any technical help in ordering, designing and constructing his equipment and does most of it singlehanded, c) delays in delivery of some equipment items often are longer than several months. For the above reasons one cannot compare CREL with an industrial laboratory and it should be remembered that the primary function at the University is training of students. This process by its nature is always slow.

Those of industrial participants who employed undergraduate or graduate students for the summer and asked them to perform experiments on an already existing apparatus know very well the rate of their progress. In comparison to this students in CREL who in addition built their own apparatus are progressing at a satisfactory pace.

TABLE I

Active Projects in the Chemical Reaction Engineering Laboratory Jan. 75 - present

Project	Funding	Investigators	Major Results, Publications and Presentations
1. The Efficiency Liquid-Solid Contacting in Trickle-Bed Reactors <u>Relevance</u>: Desulfurization of petroleum and coal derived oils and other trickle-bed applications. Trickle-bed scale-up and design.	NSF and Amoco	Prof. E. Weger Prof. M.P. Duduković P.L. Mills A.A. El-Hisnawi	Development of a new tracer method for evaluation of contacting efficiency in trickle-bed reactors. Construction of a stirred Carberry take reactor for evaluation of catalyst effectiveness factors. 1. J.G. Schwartz, M.P. Duduković, and E. Weger "The Efficiency of Liquid-Solid Contacting in Trickle-Bed Reactors", 4th ISCRE, Heidelberg, April 1976. 2. J.G. Schwartz, E. Weger and M.P. Duduković "A New Tracer Method for Determination of Liquid-Solid Contacting Efficiency in Trickle-Bed Reactors", AIChE J., 22(5), 894-904 (1976). 3. J.G. Schwartz, E. Weger and M.P. Duduković "Liquid Holdup and Dispersion in Trickle Bed Reactors", AIChE J., 22(5), 953-957 (1976).
2. Gas-Lift Recirculation Reactor <u>Relevance</u>: Catalytic hydrogenations and oxidations in chemical industry	Monsanto and departmental	Prof. M.P. Duduković Prof. E. Weger Y. Hsu	Reactor prototype constructed in plexiglass. Effect of liquid recirculation rates and solids concentration on gas holdup, residence time distributions and mass transfer is to be studied. Project just initiated.

TABLE I (Cont.)

Project	Funding	Investigators	Major Results, Publications and Presentations
3. Gas and Liquid Residence Time Distributions in Bubble Columns Relevance: Identification of the extent of gas and liquid back-mixing	Monsanto and departmental	Prof. M.P. Duduković Prof. E. Weger J. Faber	Investigation of gas and liquid backmixing in bubble columns in the presence and absence of solids, baffles, and at different L/D ratios. Significant gas backmixing detected even in columns of 6" diameter.
4. A Two Dimensional Model for a Packed Bed Reactor Relevance: Improved packed bed design for highly non-isothermal reactions	departmental	Prof. M.P. Duduković J. Bogdan	A computer program for design of packed bed reactors. The program is based on the two dimensional model and can handle any number of chemical species, adiabatic and general nonisothermal operation.

TABLE I (Cont.)

Project	Funding	Investigators	Major Results, Publications and Presentations
8. Fluorine Recovery From the Waste Products of the Phosphate Fertilizer Industry Relevance: Recovery of fluorine and use in making fluorinated chemicals	NSF and Alcoa	Prof. M.P. Duduković H. Lamba	Use of waste products to fluorinate halogenated hydrocarbons. Experimental work just started. Complete equipment for analysis of single pellet reactions has been assembled.
9. Simultaneous Removal of SO_2 and NO_x by Adsorption Relevance: Removal of SO_2 and NO_x from flue gases in power plants	industrial	Prof. E. Weger Prof. M.P. Duduković P. Medellin	Characterization of the breakthrough curves, adsorbent capacity and rate parameters. 1. P. Medellin. D.Sc. 1976 2. Two papers in preparation for publication.
10. Sulfur Dioxide Adsorption on Metal Oxides Supported on Alumina Relevance: Removal of SO_2 from flue gases	departmental and NSF URP	Prof. M.P. Duduković and undergraduate students	Characterization of rate limiting steps 1. T. Kobbala and M.P. Duduković, "Sulfur Dioxide Adsorption on Metal Oxides Supported on Alumina" 68th AIChE Ann. Meeting, Los Angeles, Nov. 1975 (on microfiche No. 10) - to appear in the Symp. Proceedings.

REVIEW OF RESEARCH PROJECTS

Research efforts within CREL have been concentrated in two major areas:

I. Analysis and Scale-up of Multiphase Reactors,

II. Parameter Identification in Reactions of Solid Particles (Fluid-Solid Noncatalytic Reactions).

The overall objectives in these two areas are:

i) to develop more fundamental information about multiphase reactors (trickle beds, gas lift slurry reactor) that will be useful in scale-up, design and process synthesis.

ii) to develop a better understanding of complex phenomena occurring in fluid-solid noncatlytic reactions and to provide guidelines and rational experiment designs for determination of important rate parameters which are necessary for proper reactor design.

All active research projects in CREL are listed in Table I. A brief summary of major research accomplishments and further planned work on continuing projects follows.

I. The Efficiency of Liquid Solid Contacting in Trickle-Bed Reactors

A. Description of the problem

A trickle-bed reactor consists of a fixed bed of catalyst particles with liquid, containing one or more of the reactants, trickling through the bed. A gas, containing the other reactant(s) is simultaneously passed through the bed in concurrent or countercurrent flow. When the reactants in the liquid phase are nonvolatile at the operating conditions used the reaction between the dissolved gas and liquid occurs only at the liquid-solid interface where it is catalyzed by the solid catalyst. In the case of volatile reactants the reaction may also occur at the vapor-solid interface. In any case one of the most important parameters for scale-up and design of trickle-beds is the catalyst area that is effectively wetted by liquid (contacting efficiency). It can be shown that catalyst effectiveness factor and mass transfer characteristics of the bed depend on contacting efficiency.

B. Research accomplishments

Extracting contacting efficiency data by running a reaction in the trickle bed and by comparing conversions to the one found in a slurry or basket reactor packed with the same catalyst is subject to many errors due to the possible effects of mass transfer limitations. Data of this nature taken in industrial laboratories has never been conclusive. A new independent tracer method of evaluating contacting efficiency directly has been developed in CREL (see Appendix A). This led to the surprising result that liquid holdup increases slightly with liquid mass velocity but that contacting efficiency stays the same at about 0.65 ($0.3 < L_m < 5$ kg/m^{2}s). This constant contacting was attributed to reactor scale incomplete contacting due in part to a large L/D ratio causing preferential wall flow of liquid. In obtaining the data two main problems were encountered: 1. unstable base line of the refractometer which was used to measure tracer concentrations in a moving liquid stream, 2. reactor scale incomplete contacting.

During the last year the equipment has been completely redesigned including the redesign of the Waters refractometer in our shop. Stable operation of the refractometer is now achieved by improved heat exchange of the sampled fluid and refractometer block and by addition of a more sensitive (within 0.01°C) temperature bath controller for the circulating thermostating fluid. The schematic of the streams exiting from the trickle-bed is presented in Figure 1.1. The added temperature bath (3) and the heat exchanging coil (4) and the pressure differential controller (7) assure stable on line operation of the refractometer. It is important to point out that in spite of the addition of the coil the dead time (transportation lag) between the trickle bed and the optical detector of the refractometer has been reduced by a factor of five by using smaller diameter tubing. This considerably improves the resolution of the response.

Several glass columns of different L/D ratios have been constructed with a central liquid distributor consisting of a fritted disc. These columns will be used to find the L/D ratio which minimizes reactor scale incomplete contacting.

In addition a stirred tank reactor for reactions in three phase systems has been designed and constructed as presented in Figures 1.2 - 1.4. This reactor can be used as a slurry reactor for evaluation of intrinsic kinetics and as a basket reactor for evaluation of the catalyst effectiveness factor. Its additional use may be found in determining adsorption isotherms for the tracers of interest.

All the trickle-bed equipment and basket reactor equipment is now available and is being mounted with the exception of a gas chromatograph which is on order.

C. <u>Further research plans</u>

1. Repeat J. G. Schwartz's data using the same packing but different columns L/D ratios in the same range of liquid mass velocities.

2. Select a reaction to run. This is a very critical point and neither H_2O_2 decomposition or hydrogenation of α-methyl styrene satisfy all the desired criteria. One wants preferably a liquid phase catalytic (affected by solid catalyst) decomposition at normal T, P such that the gas will be a nonreacting phase. This will eliminate the possible mass transfer effects. Our search for such a reaction is continuing. If unsuccessful by November, the two above mentioned reactions with all their drawbacks will be studied.
3. Run the reaction in a slurry (using pulverized catalyst pellets) and basket reactor using diluted liquid reactant so that reaction is 1st order. Determine kinetics and catalyst effectiveness.
4. Determine contacting efficiency in the trickle bed at a set of operating conditions.
5. Run the reaction in trickle bed at the same set of conditions. Compare the predicted conversion based on known kinetics and contacting with actual conversions.
6. Proceed to determine contacting in various systems of different physical properties and establish a correlation.

II. Gas-Lift Slurry Recirculation Reactor

A. Problem definition

Gas-Lift-Slurry Reactors represent another alternative to trickle-beds for gas-liquid contacting in the presence of the solid catalyst. This reactor configuration is very useful for operation at terminal conditions as it can be operated at large recycle ratios as a stirred tank without moving parts.

Although bubble columns with suspended slurries have been extensively investigated almost no experimental information is available on gas-lift reactors where liquid velocity in the up-leg can be orders of magnitude greater than in bubble columns. Therefore it is of interest to determine how liquid holdup and liquid-gas mass transfer depend on liquid recirculation and solids concentration.

B. Research accomplishments

A thorough literature survey of the work done on bubble columns and gas lift systems has been performed. This is summarized in a useful review appended as Appendix B.

A reactor prototype has been constructed and is presented in Figure 2.1. Details of planned experiments are given in Appendix B.

C. Further research plans

1. Prediction of liquid recirculation rates as a function of design parameters and physical properties.

2. Gas holdup correlations at different slurry concentrations and its variation with column height.

3. Gas, liquid and solid backmixing correlations as function of design and physical parameters.

4. Evaluation and prediction of gas-liquid mass transfer rates.

Air-water-glass beads (sand) system will be used initially for holdup measurements. Air with CO_2-water-sand system will initially be employed for backmixing and mass transfer determinations.

III. Backmixing in Bubble Columns

A. Problem definition

Gas-sparged reactors are used extensively in the chemical industry. Reactor performance can only be predicted if gas holdup and gas and liquid backmixing are known. Our literature survey shows considerable disagreement in the available correlations for prediction of liquid and especially gas Peclet numbers. In part these discrepancies are due to improper application of tracer techniques. Our goal was to determine liquid and gas backmixing in a medium size column and check it against available correlations.

B. Research accomplishments

Tracer experiments were performed in a glass column 6" in diameter. Liquid levels were maintained at 3, 5, 6, 8, 10 feet in order to obtain data at different L/D ratios. Gas superficial velocities from 0.01 to 1 ft/s (0.003 to 0.3 m/s) and liquid velocities from 0 to 1 ft/min (0 to 0.005 m/s) were used. Substantial backmixing in the gas phase (Pe_g from 2 to 20) has been found even in this small diameter column. Details are presented in Appendix C.

C. Further research plans

Examination of the effect of internals on liquid and gas backmixing.

IV. A Two Dimensional Model For a Packed Bed Reactor

A. Problem definition

One dimensional models (based on the plug flow assumption) are often inadequate in predicting accurate conversions, yields and temperature profiles in nonisothermal catalytic fixed bed reactors when one deals with a large number of species. They are particularly inept in predicting a hot spot formation. While axial dispersion effects in a vast majority of industrial applications can be neglected radial effects cannot. It is particularly important to account for the radial temperature distribution.

Our goal is as follows: given the composition and physical properties of S-chemical species, the stoichiometry of reactions presumed to occur, the kinetic forms and constants and catalyst form and intrinsic activity calculate either the reactor size required for a desired process or evaluate the concentration and temperature profiles in the reactor as function of operating conditions such as heat removal, catalyst size, activity etc. The model assumes plug flow in the axial direction and radial dispersion of mass and heat. The important aspects of the program to be developed are:

a) Important physical properties are calculated at a number of positions in the bed,

b) Effectiveness factors are calculated at a number of locations in the bed,

c) Any number of species can be handled,

d) Hot spot detection is more accurate

Industrial support for this project is being sought.

B. <u>Research accomplishments</u>

An algorithm has been developed to accomplish the proposed modeling.

C. <u>Further research plans</u>

Testing the computer program. Development of subroutines. Card punching.

V. Fluid-Solid Noncatalytic Reactions

A. Problem definition

Reactions of solid particles play an important role in ore roasting and leaching, in coal conversion, and in a number of chemical processes. Modeling reactions of solid particles is necessary for evaluation of rate parameters from experimental data and in proper reactor design. Experimental evidence points to important effects that the changing structure of solid particles with reaction has on the transport parameters and overall reaction rates. Reactions in which overall size of solid pellets stays practically constant with reaction but the internal porosity and structure changes dramatically due to vastly different molar densities of solid reactant and product are common in chemical and metallurgical engineering. Roasting of pyrite, fluorination of uranium dioxide, sulphur dioxide uptake by dolomite, reduction of hematite etc. fall into this category. Our goal is to develop a comprehensive mathematical model for reaction of solid particles which relies on experimental evidence of physical phenomena. The incorporation of structural changes with reaction into the model is of major importance. Other previous attempts in this area were not successful due to a lack of efficient computational techniques.

B. Research accomplishments

During the last year the following major accomplishments were achieved:

- comprehensive critical literature survey of fluid-solid noncatalytic reactors (will be prepared as a monograph);

- critical comparison of simple models (shrinking core) and more complex models (diffusion with simultaneous reaction, structrual, etc.) and evaluation of the range of parameters where simple models can be used;
- development of a new integral transformation for calculation of diffusion with simultaneous reaction models which reduces computing costs by two orders of magnitude;
- development of a new computational method using the novel integral transformation and collocation to evaluate new comprehensive structural models which account for changes in structure with the progress of reactions;
- construction of a single pellet reactor for vapor-solid noncatalytic reactions. Details are provided in Appendix D.

C. <u>Further research plans</u>

- use of the model in evaluation of rate parameters in SO_2 + CaO reaction and others
- development of approximate semi-analytical model solutions to be used in reactor design.

VI. Fluorine Recovery From the Waste Products of the Phosphate Fertilizer Industry

A. Problem definition

The limited world wide proven reserves of cryolite and fluorspar, which are the only two naturally occurring minerals containing industrially significant amounts of fluorine are decreasing and cannot sustain the exponentially increasing production of fluorinated chemicals for an extended period. However, many man made materials and byproducts of several industries contain considerable amounts of fluorine. Among them, silicofluorides, the waste products of the phosphate fertilizer industry contain more fluorine than any naturally occurring mineral. Our goal is to investigate the possibilities of using silicofluorides directly as fluorinating agents.

B. Research accomplishments

All available properties of silicofluorides have been tabulated. Reactions between barium silicofluoride and carbon tetrachloride on chloroform are selected for further study. Solid pellets were made in sizes 1/8 - 5/8" (0.3 to 1.5 cm) under pressures of 4000 - 8000 psi (272 to 544 atm). Equipment for the vapor-solid reaction of sample pellets has been assembled as shown in Figure 6.1. Additional details are given in Appendix D.

C. Further research plans

Evaluation of diffusional and kinetic parameters by analyzing the sample pellet reaction data in terms of developed models for fluid-solid reaction. Analysis of structural changes with reaction via scanning electron microscopy and porosity measurements and their incorporation in the model.

CURRENT STAFF

The staff of the Laboratory consists of the following members of the Chemical Engineering Department:

A. Faculty

1. Dr. Eric Weger, Professor and Department Chairman,
2. Dr. Milorad (Mike) P. Duduković, Associate Professor and Director of the Chemical Reaction Engineering Laboratory.

B. Graduate students

1. J. E. Bogdan, M. S. student
2. T. C. Chen, M. S. student
3. J. R. Faber, M. S. student
4. A. A. El-Hisnawi, M. S. student
5. Y. C. Hsu, D. Sc. candidate
6. H. S. Lamba, D. Sc. candidate
7. P. M. Medellin, D. Sc. (graduated 1976)
8. P. L. Mills, D. Sc. student

CURRENT FUNDING

The support for the Laboratory is derived from NSF grants and industrial contributions and it consists of:

1. NSF Grant ENG 57406A "Trickle Bed Reactors: Contacting Efficiency and Reactor Performance"

   $55,000 for the period 7/1/76 - 7/1/78

2. NSF Grant ENG 76-0700 "Fluorine Recovery form the Waste Products of the Superphosphate Industry"

   $60,900 for the period 9/1/75 - 9/1/77

3. Industrial contributions: Alcoa, Amoco, Monsanto

Total $10,000 for fiscal 1976.

PAPERS

1. "The Efficiency of Liquid-Solid Contacting in Trickle-Bed Reactors", J. G. Schwartz, M. P. Duduković and E. Weger, Proceedings 4th Intern. Symp. Chem. Reaction Engineering (ISCRE) Heidelberg, Germany, April 1976.
2. "A New Tracer Method for Determination of Liquid-Solid Contacting Efficiency in Trickle-Bed Reactors", J. G. Schwartz, E. Weger and M. P. Duduković, AIChE J., 22(5), 894 (1976).
3. "Liquid Holdup and Dispersion in Trickle-Bed Reactors", J. G. Schwartz, E. Weger and M. P. Duduković, AIChE J., 22(5), 953 (1976).
4. "A Note on Gas Solid Noncatalytic Reactions", M. P. Duduković, AIChE J., 22(5), 945 (1976).
5. "Sulfur Dioxide Adsorption on Metal Oxides Supported on Alumina", T. E. Koballa and M. P. Duduković, AIChE Symp. Series on Air Pollution (1976) (in print).

PRESENTATIONS AT NATIONAL AND INTERNATIONAL MEETINGS

1. "Analysis of the Radical Flow Fixed Bed Reactors", M. P. Duduković and H. Lamba, AIChE 80th National Meeting, Boston, September 1975 (microfiche No. 3).
2. "Sulfur Dioxide Dry Deposition and Uptake by Aerosols in Urban Plumes", R. B. Hursar, N. V. Gillani, and M. P. Duduković, AIChE 68th Annual Meeting, Los Angeles, November 1975.

3. "Analysis of Gas-Solid Noncatlytic on Catalyst Deactivation Reactions", M. P. Duduković, AIChE 68th Annual Meeting, Los Angeles, Nov. 1975 (microfiche No. 20).
4. "Effects of Substrate Inhibition and Micromixing on Multiplicity of Steady States", M. P. Duduković and H. Lamba, AIChE 68th Annual Meeting, Los Angeles, Nov. 1975 (microfiche No. 35).
5. "Sulfur Dioxide Adsorption on Metal Oxides Supported on Alumina", T. E. Koballa and M. P. Duduković, AIChE 68th Annual Meeting, Los Angeles, Nov. 1975 (microfiche No. 10).
6. "The Efficiency of Liquid-Solid Contacting in Trickle-Bed Reactors", J. G. Schwartz, M. P. Duduković and E. Weger, 4th ISCRE, Heidelberg, April 1976.
7. "Using a Calvin Cycle for Glucose Production--A Simulation", B. Han, N. Dinos and M. P. Duduković, AIChE 81st National Meeting, Kansas City, April 1976.

PRESENTATIONS AT LOCAL MEETINGS AND SEMINARS

1. "Contacting Efficiency and Liquid Holdup in Trickle Bed Reactors", M. P. Duduković, AIChE One Day Symposium, St. Louis, March 1976.
2. "An Experimental and Theoretical Investigation of Fluorine Recovery from Silicofluorides", H. Lamba, Washington University, St. Louis, June 1976.
3. "Gas Holdup and Gas Liquid Mass Transfer in Gas Lift Slurry Recirculation Reactors", Y. Hsu, Washington University, St. Louis, August 1976.

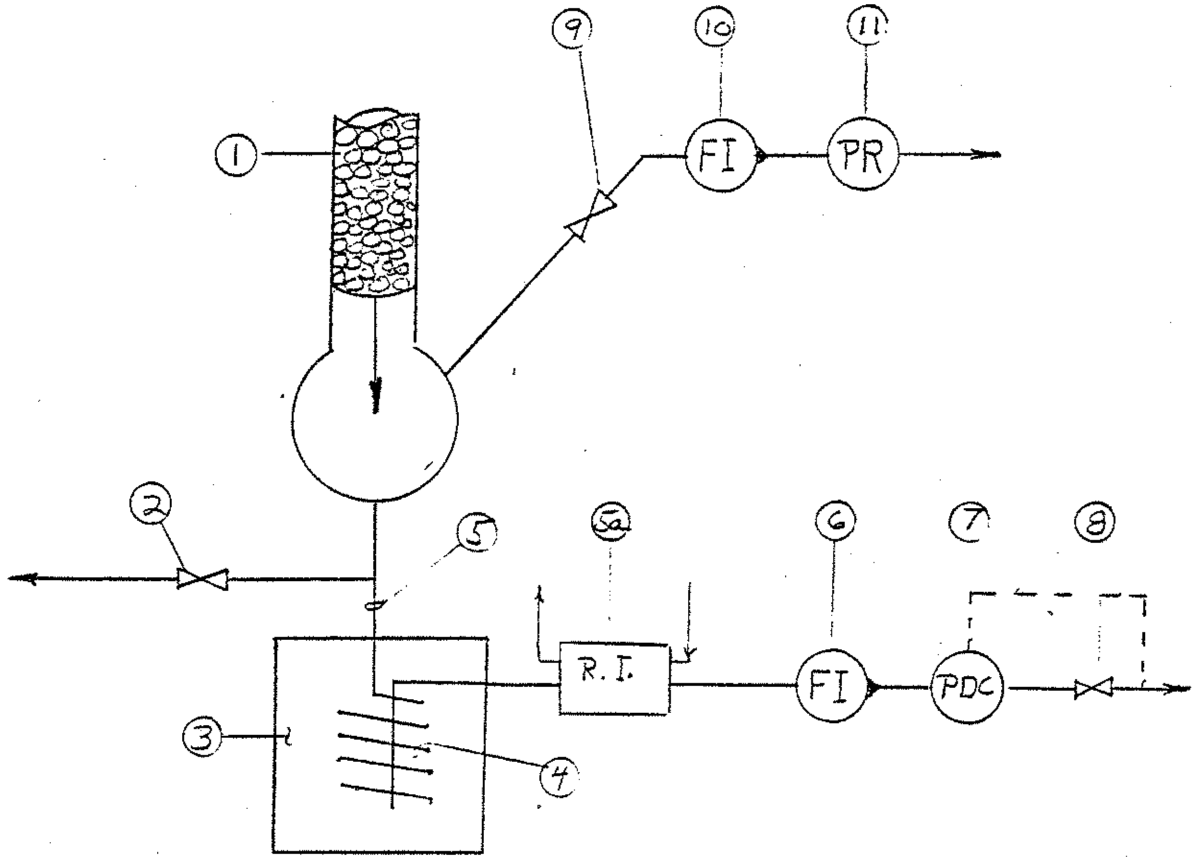
APPENDICES - DETAILED PROGRESS REPORTS ON VARIOUS PROJECTS (available upon request)

Appendix A: Two papers summarizing our previous work on contacting efficiency.

Appendix B: Gas lift recirculation reactor literature survey and proposed research.

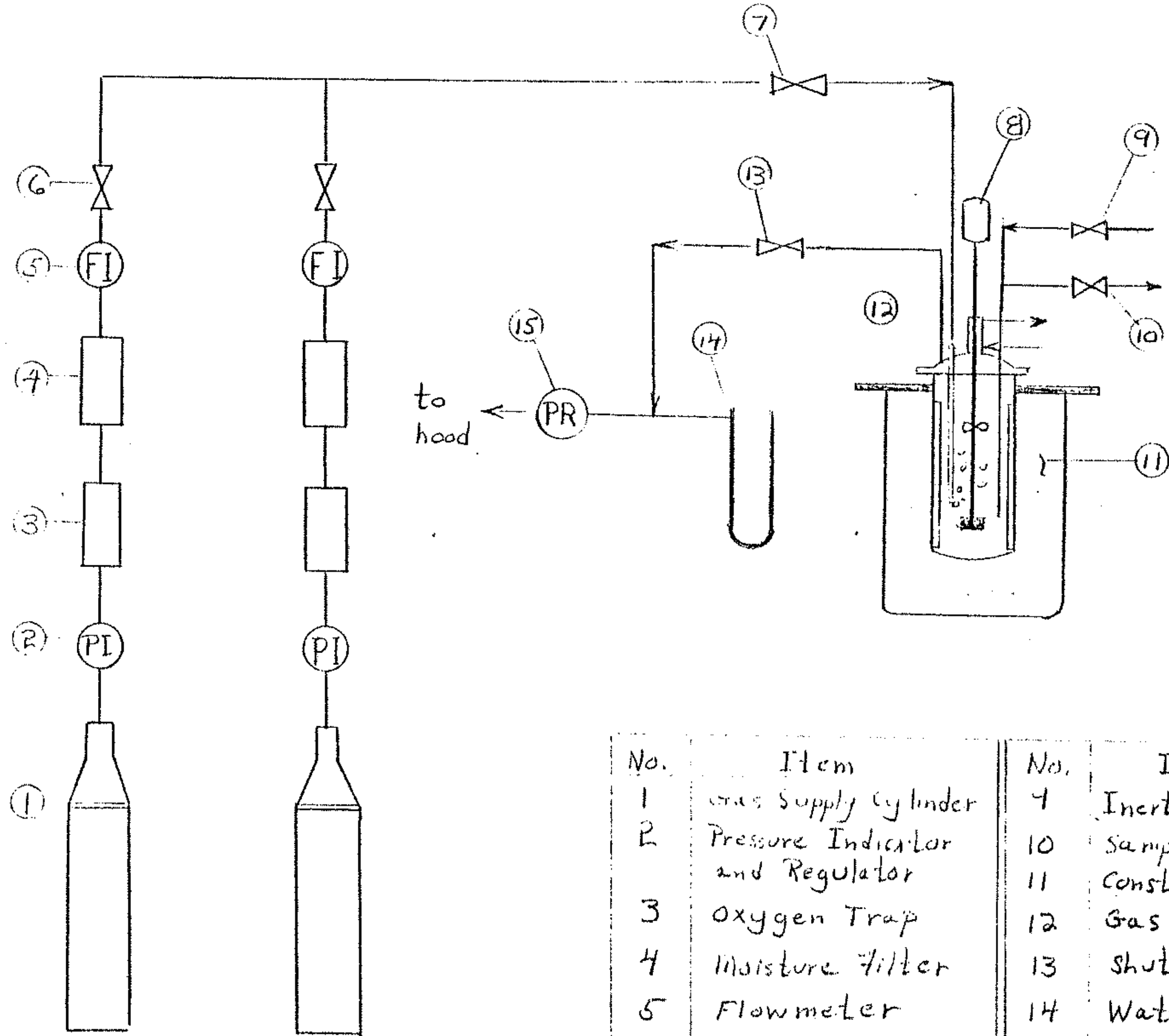
Appendix C: Axial dispersion and holdup in a bubble column - experimental setup and first series of results.

Appendix D: Modeling reactions of solid particles and fluorine recovery from silicofluorides. Literature review. New computational techniques. Experimental set-up.



No.	Item	No.	Item
1	Trickle Bed Column Lower Section	6	Flow meter
2	Needle Valve	7	Flow (pressure differential) Controller
3	Constant Temp. Bath		
4	Immersed Coil	8	metering Valve
5	Split Flow to Refractometer	9	Shut-Off Valve
		10	Flow meter
5a	Refractometer optical module	11	Back-Pressure Regulator

Figure 1.1 Schematic of Refractometer Control Scheme



No.	Item	No.	Item
1	Gas Supply Cylinder	9	Inert Gas Inlet Valve
2	Pressure Indicator and Regulator	10	Sample Outlet Valve
3	Oxygen Trap	11	Constant Temperature Bath
4	Moisture Filter	12	Gas Outlet
5	Flowmeter	13	Shut-off Valve
6	Metering Valve	14	Water Manometer
7	Shut-off Valve	15	Back Pressure Regulator
8	Stirrer Motor		

Figure 1.2 Experimental Stationary Basket Reactor Apparatus

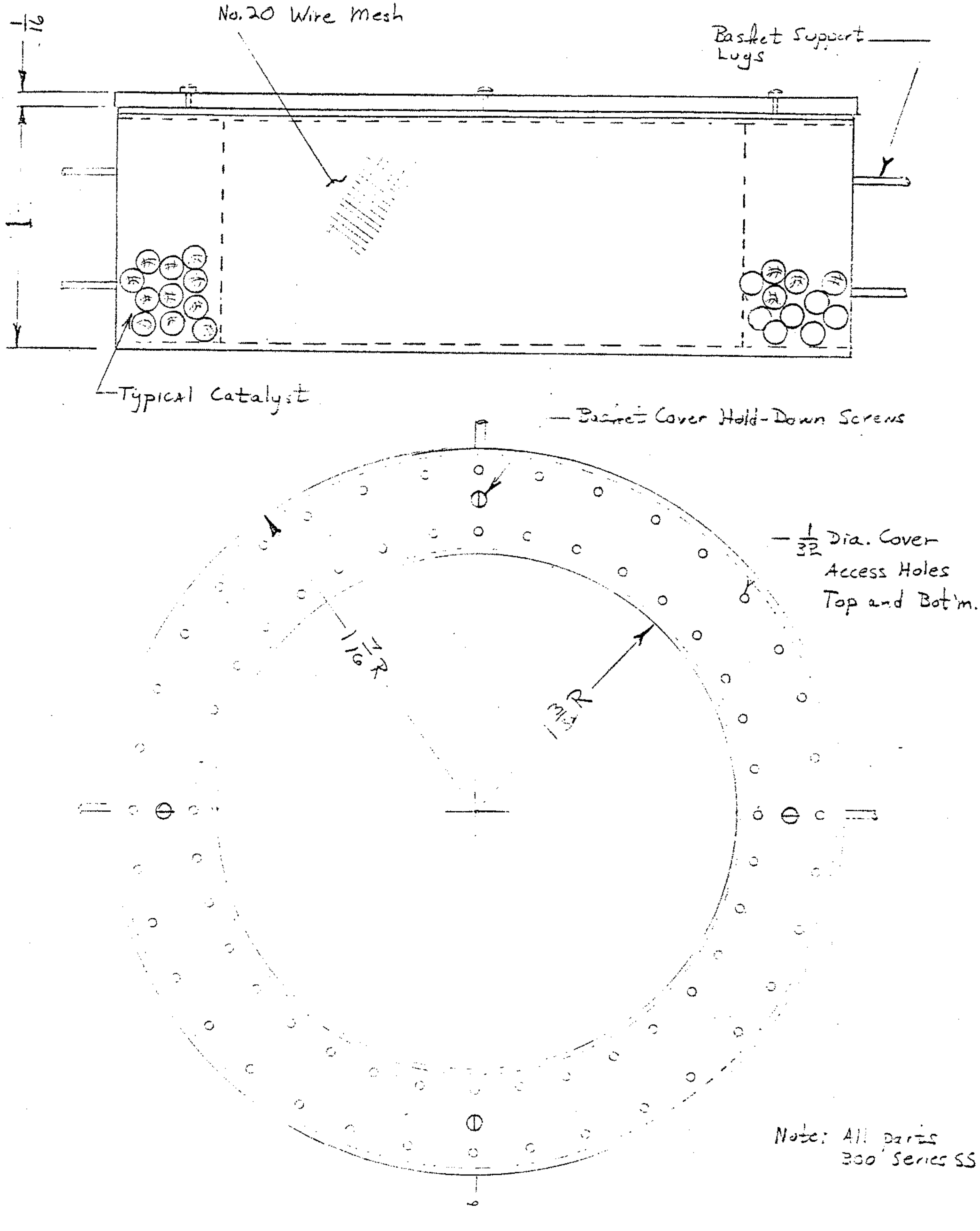


Figure 1.3 Stationary Basket Details

TLm 9/7/76

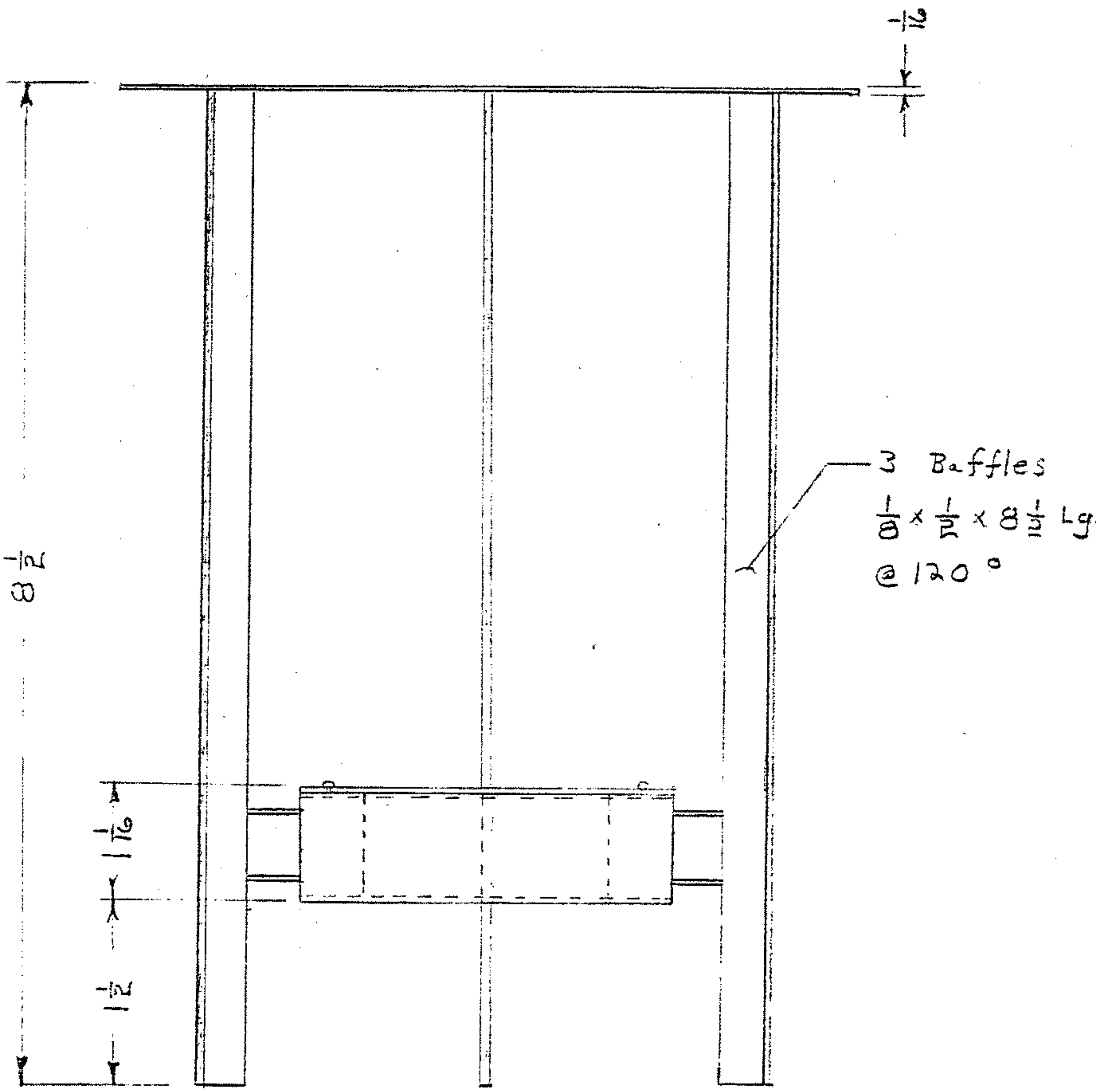


Figure 1.4 Basket - Baffle Assembly

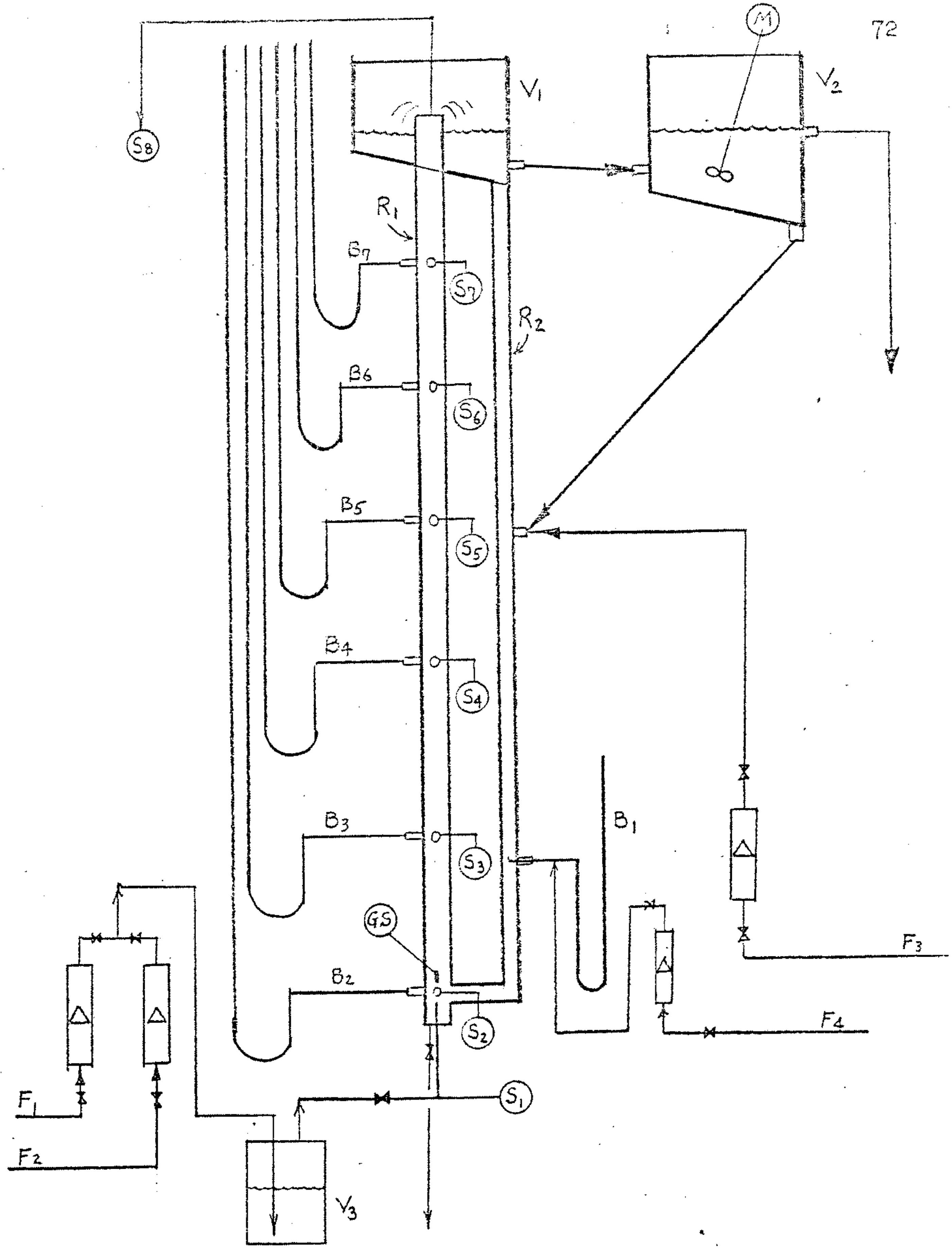


Figure 2.1 Proposed Research Equipment

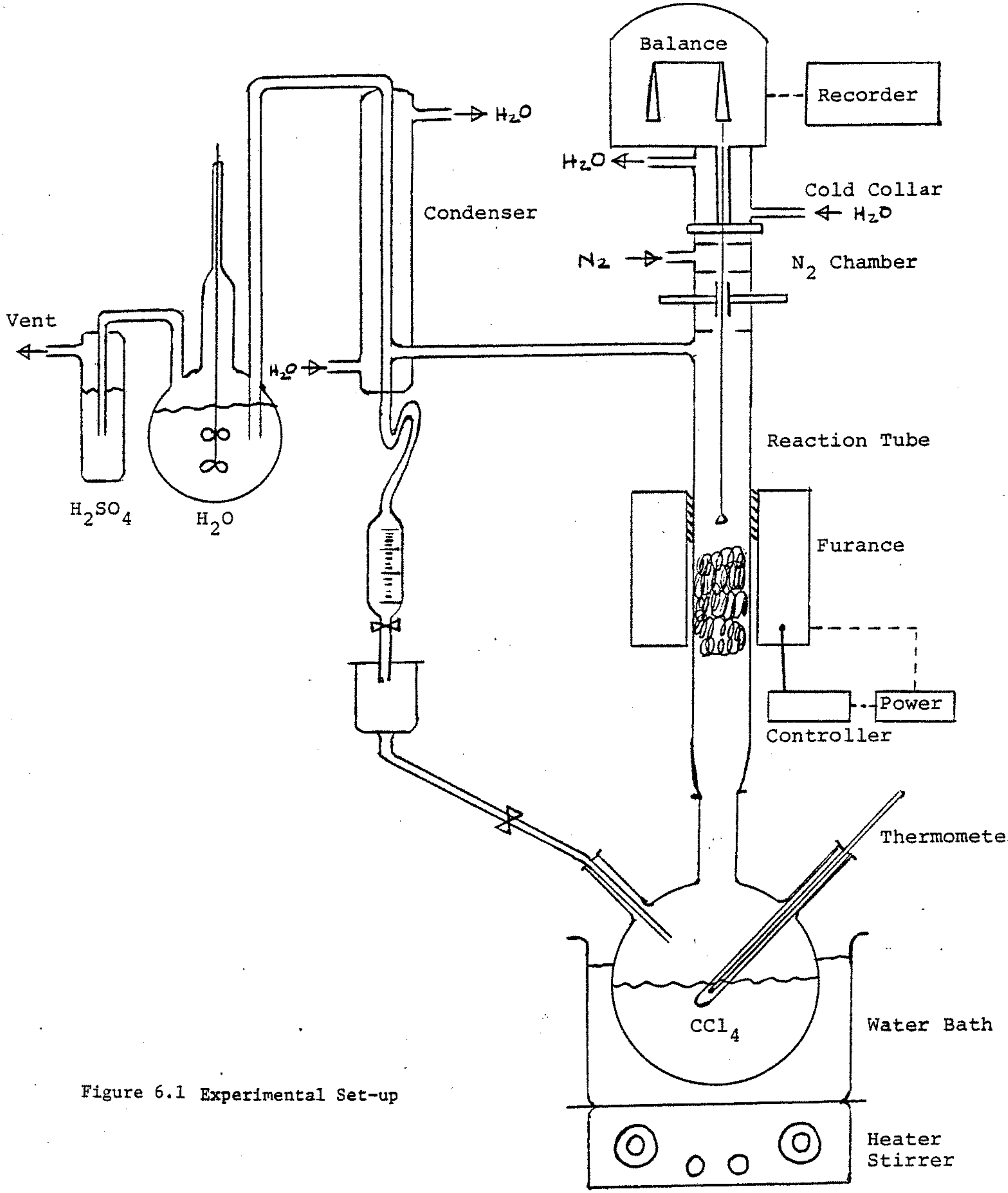


Figure 6.1 Experimental Set-up