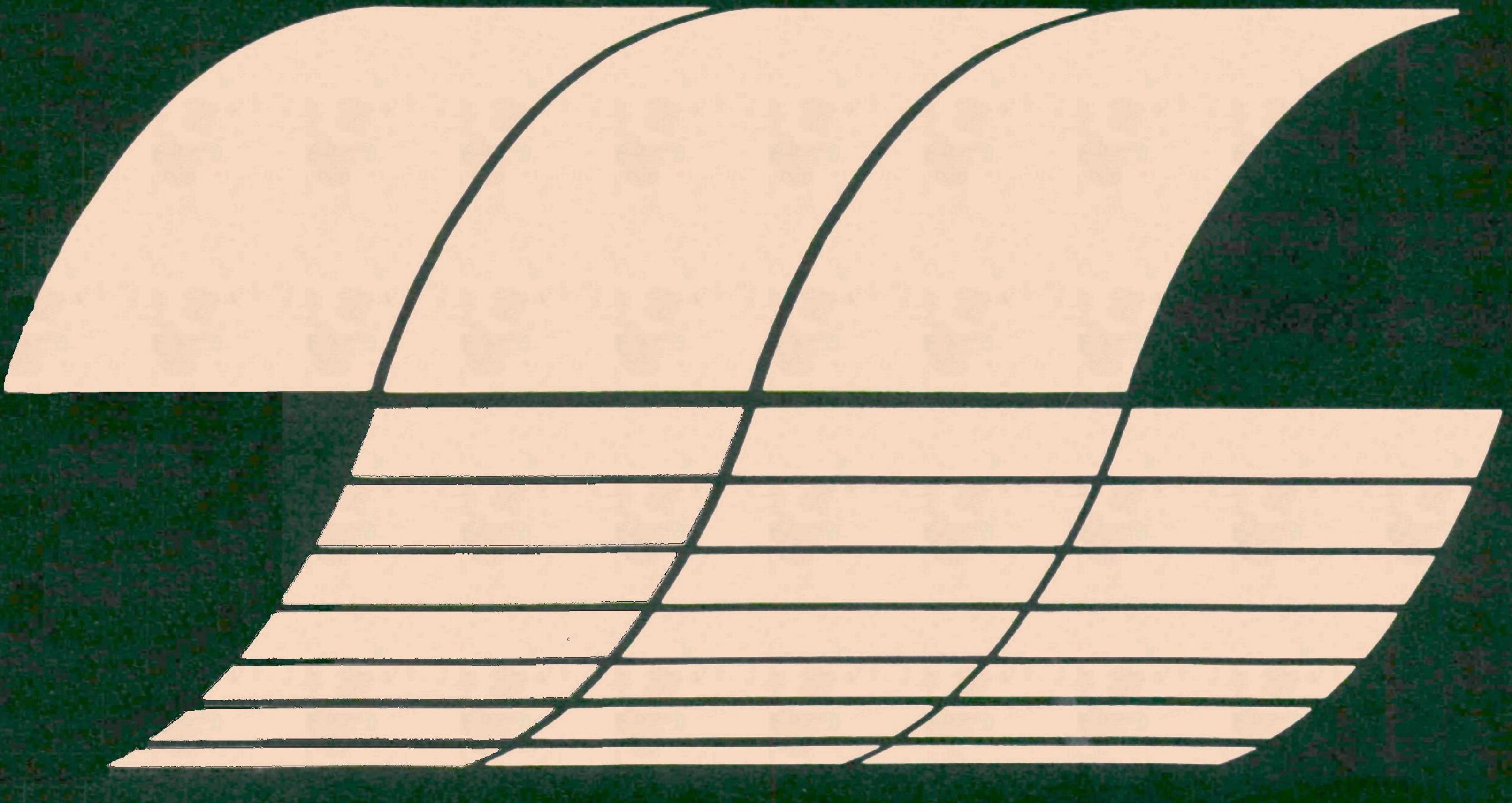
EPA U.S. Environmental Protection Agency
Office of Research and Development

Industrial Environmental Research
Laboratory
Research Triangle Park, North Carolina 27711

EPA-600/7-77-026
March 1977

ANALYSIS AND SIMULATION OF RECYCLE SO_2-LIME SLURRY IN TCA SCRUBBER SYSTEM

Interagency
Energy-Environment
Research and Development
Program Report



RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into seven series. These seven broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The seven series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development

This report has been assigned to the INTERAGENCY ENERGY-ENVIRONMENT RESEARCH AND DEVELOPMENT series. Reports in this series result from the effort funded under the 17-agency Federal Energy/Environment Research and Development Program. These studies relate to EPA's mission to protect the public health and welfare from adverse effects of pollutants associated with energy systems. The goal of the Program is to assure the rapid development of domestic energy supplies in an environmentally--compatible manner by providing the necessary environmental data and control technology. Investigations include analyses of the transport of energy-related pollutants and their health and ecological effects; assessments of, and development of, control technologies for energy systems; and integrated assessments of a wide range of energy-related environmental issues.

EPA-600/7-77-026
March 1977

ANALYSIS AND SIMULATION OF RECYCLE SO_2-LIME SLURRY IN TCA SCRUBBER SYSTEM

by

C.Y. Wen and Fred K. Fong

West Virginia University
Department of Chemical Engineering
Morgantown, West Virginia 26506

Grant No. R800781-03-0
Program Element No. EHE624A

EPA Project Officer: R.H. Borgwardt

Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
Research Triangle Park, N.C. 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, D.C. 20460

CONTENTS

Appendix

List of Figures

List of Figures (Con't)

List of Tables

List of Abbreviations and Symbols

A	Cross sectional area of the TCA, m.
a	Interfacial area per unit volume of bed, m^2/m^3.
A_p, A_s	Pre-exponential factor in the expression for the ratio of the gas to liquid film mass transfer resistance for the packed and spray sections, dimensionless.
C	Concentration of the total carbon dioxide in the slurry, gmole/liter.
C_{abs}	CO_2 absorbed per unit volume of scrubbing slurry, gmole/liter.
C°	Concentration of H_2CO_3 in the bulk liquor phase, gmole/liter.
C_i°	Concentration of H_2CO_3 in the slurry at the interface of gas-liquid film, gmole/liter.
C_{af}	Lime fed rate, gmole/sec.
C_x	Concentration of magnesium or chloride in the liquor phase, gmole/liter.
C_Z	Concentration of total carbon dioxide at a height of Z, gmole/liter.
D	Equivalent diameter for free sectional area, meter.
d	Diameter of each hole in the grid, m.
dp	Diameter of the packing sphere, meter.
F	Feed rate of magnesium or chloride into the system, gmole/sec.
F_{C_aO}	Lime feed rate, gmole/sec.
f	Fraction opening of the grid, dimensionless.
G	Gas flow rate based on the cross-sectional area of the scrubber at 0°C, m/sec.
$\hat{G}$	Gas flow rate based on the cross-sectional area of the scrubber, $Kg/m^2sec.$ (=1.2946 G)

g	Gravitational acceleration, m/sec.
H^+	Concentration of free hydrogen ion, gmole/liter.
$\overline{H}$	Average concentration of free hydrogen ion in the scrubber, gmole/liter.
K	Equilibrium constant for H_2CO_3, liter/gmole.
K'	Proportional constant, Kg/mole.
K''	Proportional constant defined as the product of K' and M, liter/gmole.
K_Ga	Overall gas side mass transfer coefficient for CO_2 absorption, gmole/m^3atm sec.
k_g^Pa	Gas side mass transfer coefficient for the packed section, gmole/m^3atm sec.
k_g^Sa	Gas side mass transfer coefficient for the spray section, gmole/m^3atm sec.
L'	Liquid flow rate, liter/sec.
M	Liquor content in the purge, based on the dry solid, liter of liquid/Kg of solid.
M_{CO_2}	Absorption rate of CO_2 in the scrubber, gmol/sec.
M_{SO_2}	Absorption rate of SO_2 in the scrubber, gmol/sec.
N_{CO_2}	Molar flux of CO_2 across the gas-liquid interface, gmole/m^2sec.
Ng	Number of grids.
P	Purge rate, liter/sec.
Pa	Pascal, N m^{-2}.
P_T	Total pressure, atm.
ΔP_b	Pressure drop in the packing section, Pa.
ΔP_f	Friction loss in the packing, Pa.
ΔP_g	Pressure drop across the grids, Pa.
ΔP_h	Liquid holdup in the packing section, Pa.
ΔP_p	Static bed weight, Pa.

ΔP_N	Normal pressure drop across the scrubber, Pa.
ΔP_s	Pressure drop across the spray section, Pa.
ΔP_t	Total pressure drop, Pa.
$P_{CO_2}^{b}$	Partial pressure of CO_2 in the bulk gas phase, atm.
$P_{CO_2,i}$	Partial pressure of CO_2 at the gas-liquid interface, atm.
$P_{CO_2}^{*}$	Partial pressure of CO_2 in the gas phase that is in equilibrium with H_2CO_3 in the bulk liquid phase, atm.
$P_{SO_2}^{in}$	Inlet partial pressure of SO_2 in the bulk gas phase, atm.
$P_{SO_2}^{out}$	Outlet partial pressure of SO_2 in the bulk gas phase, atm.
R_h	Mean hydraulic radius defined as the ratio of cross-section of the flow and the wetted perimeter, meter.
S	Henry's law constant, atm/gmole-liter.
T	Liquid temperature, degree Kelvin.
V	Liquid flow rate, liter/m^2sec.
$\hat{V}$	Liquid mass velocity, Kg/m^2sec.
Z	Height of the scrubber, meter.
Zo	Total height of the scrubber, m.
Zp	Height of the packing section in the TCA, m.
Z_s	Height of the spray section in the TCA, m.
Z_p^{e}	Equivalent packing height, meter.
Z'_{PT}	Total equivalent packing height, meter.
Δ_{in}	$(S)_{in} + (C)_{in} - (Ca)_{in}$, gmole/liter.
Δ_{out}	$(S)_{out} + (C)_{out} - (Ca)_{out}$, gmole/liter.
Δ_{pg}	$(S)_{purge} + (C)_{purge} - (Ca)_{purge}$, gmole/liter.
Δ_p, Δ_s	Magnesium correction factor for A_p and A_s, dimensionless.

ρ_p	Density of the packing sphere, Kg/m^3.
ε	Voidage of the static packed bed (packings are randamly arranged), dimensionless.
ρ_L	Density of the slurry, Kg/m^3.
ρ_W	Density of the water, Kg/m^3.
α	Coefficient on the exponential term relating to the inlet partial pressure of SO_2, $\exp(\alpha P_{SO_2,in})$, atm^{-1}.

CHAPTER 1

INTRODUCTION

The combustion of coal is accompanied by the two major sources of environmental pollution, sulfur dioxide and ash. Considerable research and development efforts have been spent to make use of the vast resources of coal available in the states and to meet the enviromental limitations.

Two alternatives being considered for protecting the environment from the consequence of an extensive use of coal are:

(A) Reduction in sulfur dioxide and particulate emissions from new and existing power plants and other facilities.

(B) Conversion of coal into a pollutant-free and usable liquid or gas which is convenient to handle, transport, and utilize in the final energy consumption stage.

1.1 Processes for Desulfurizing the Flue Gas

Of more than 50 gas desulfurization control concepts (Nelson 1974) which have been proposed and studied, the major routes can be classified into three categories: amines, metal oxides,and alkaline solutions. Complete descriptions are given by Woodies et al. (1973), Shale et al. (1971), Strauss (1972), Berkowitz (1973), LaMantia et al. (1973), McIlrg et al. (1973), and Nannen et al. (1974).

The lime/limestone wet-scrubbing system is considered to be one of the viable ways to reduce stack gas emission, because it employs least expensive reactants, is less sensitive to operating conditions, and requires no complex control or regeneration equipment.

1.2 Description of the Wet Lime/Limestone Scrubbing Systems

The Environmental Protection Agency (EPA) through its Office of Research and Development and Control Systems Laboratory, sponsored a program to test the wet lime and limestone scrubbing system for removing sulfur dioxide and particulates from flue gases.

A pilot and a prototype wet scrubbing facility for removing sulfur dioxide are set at EPA Research Triangle Park (RTP) and the Tennessee Valley Authority (TVA) Shawnee Power Station respectively to test the reliability and performance of the systems. The schematics of these facilities are shown in Figure 1.1 and 1.2.

In these wet-scrubbing systems, the particulates (fly ash) are captured by liquid droplets while sulfur dioxide is absorbed by the scrubber into the lime/limestone slurry where it reacts with the dissolved lime/limestone, forming calcium sulfite and calcium sulfate (gypsum).

The holding tank which receives the scrubber effluent provides enough time for the precipitation of calcium sulfite and calcium sulfate. The precipitants are then purged out by the vacuum filter. For a limestone wet scrubbing system, fresh limestone slurry is fed into the holding tank as the reactant. For a lime wet scrubbing system, the unslaked residue of lime slurry is discarded and the slurry is fed into the scrubber-effluent holding tank (Borgwardt (1974b)).

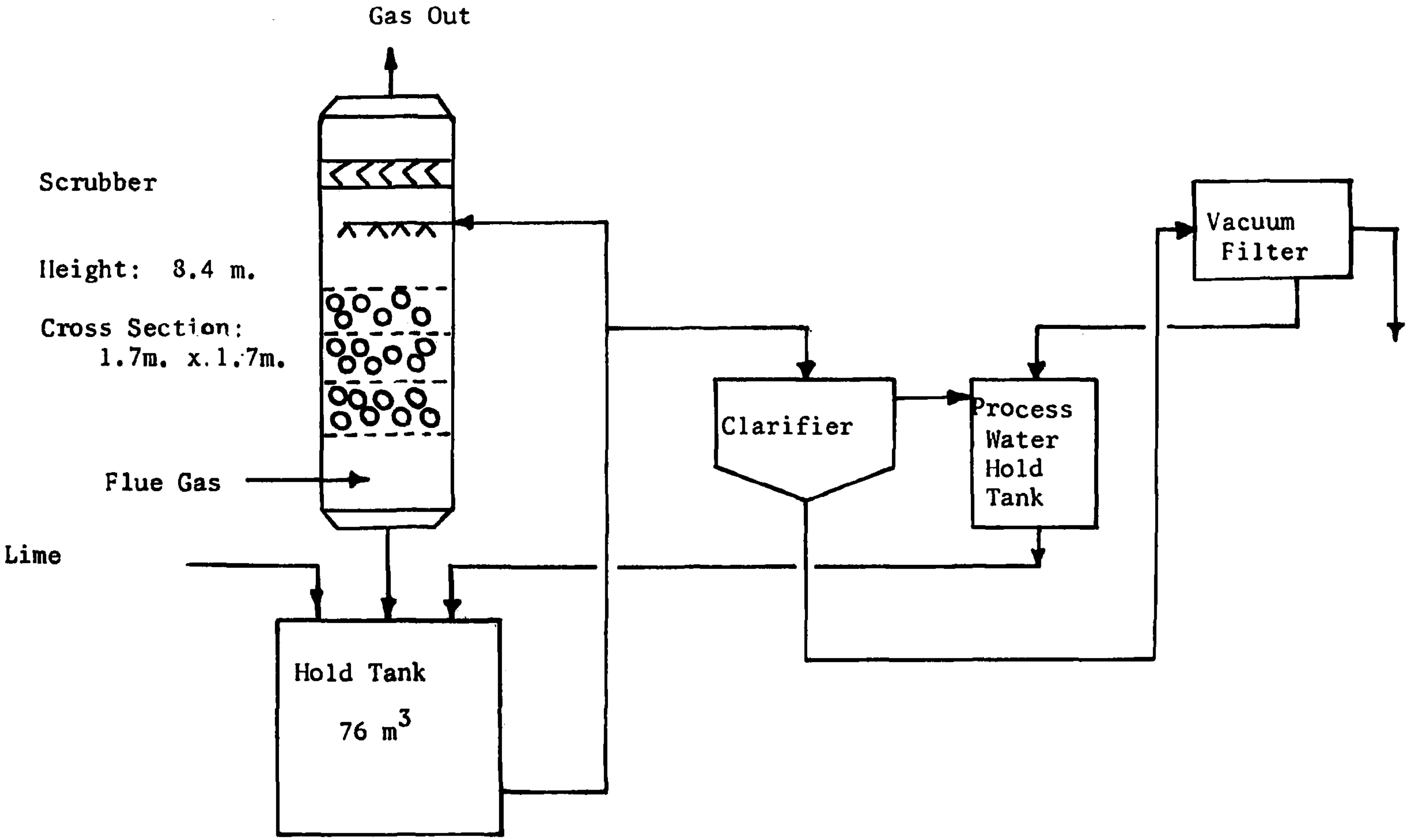


Figure 1.1: Schematic Arrangement of the TVA Scrubber System.

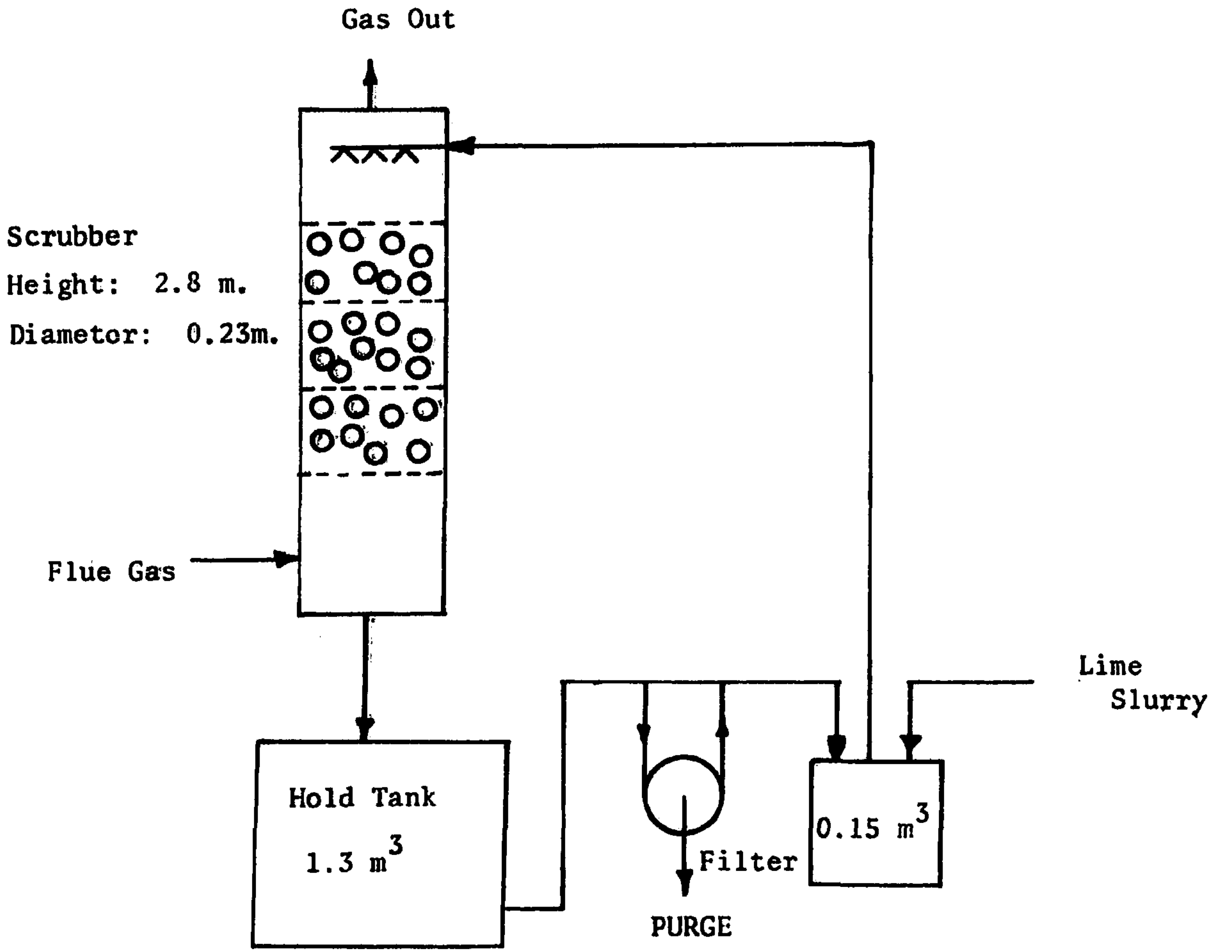


Figure 1.2: Schematic Arrangement of the EPA Pilot Scrubber System.

1.3 Objective of This Study

In order to analyze data on the scrubbing of flue gas using lime , a simulation model of the system is very useful. Such a model can be used to predict the SO_2 removal efficiency, lime utilization,and pH values at the inlet and outlet slurries of the scrubber. The known variables are the lime feed rate, the size of the scrubber, the recycling liquid flow rate, the composition and the feed rate of flue gas. The first objective therefore is to simulate the scrubber hold-tank flue gas desulfurization (FGD) process by formulating the mass balance equations across the scrubber and the whole system. Each term in these equations, namely, the absorption rates for SO_2 and CO_2, and the concentrations of total dissolved sulfur plus carbon minus calcium in the inlet and outlet recycling liquors of the scrubber must be determined separately.

The second objective is to determine the maximal rate of flue gas that can be treated, as a function of liquid flow rate for a specified lime feed and SO_2 removal efficiency, for a given size of scrubber. The achievement of this objective can contribute greatly to the effort which would be needed in the design of a scrubber unit for a specific application.

In this study, the wet scrubbing system with lime as the recycled medium is simulated. Data are taken from the EPA inhouse turbulent contacting absorber (TCA) at Research Triangle Park, North Carolina and the TCA scrubber located at the TVA Shawnee Power Station.

CHAPTER 2

LITERATURE REVIEW

The turbulent bed contact absorber (TCA) with movable packing, first described in 1959 for removing particulates from a dust laden gas (Douglas et al. (1963)), has been recently used in desulfurization of flue gas (Douglas et al 1964, Kielback et al. 1959). It consists of large diameter uniform spheres of low density placed between retaining grids sufficiently far apart to permit turbulent and random motion of the packings. Hollow polyethylene, foam polystyrene,and thermo-plastic rubber spheres have been found to be satisfactory for this purpose. Because of the low density and the counter-current flow of liquid and gas, TCA provides a state of vigorous contacting between liquid and gas.

This equipment has some advantages over a conventional gas-liquid contactor with fixed packings. The motion of the packing prevents plugging and by-passing which may occur when gases and liquids containing suspended solid particles are used. Rates of heat and mass transfer have also been reported to increase owing to the bed agitation (Douglas 1964). The use of TCA also permits much greater gas and liquid velocities than are possible in conventional scrubbers. Thus, a smaller TCA tower may be employed for a given operation compared to other conventional scrubber.

Result of the investigation by Gel'perin (1965) shows a strong dependence of liquid holdup,bed expansion and pressure drop on the liquid and gas flow rates. Blykher (1967) has also studied the pressure drop in TCA. However, these investigators did not report the pressure drop across a mobile bed, but the pressure drop data reported included the contribution of the bottom grid with the free cross-sectional area in one case as small as 19%.

Levsh (1968) studied the pressure drop of TCA with low density packings and found that pressure drop increases linearly with the gas flow rate. Tichy (1972) correlated the pressure drop data with the well-known Fanning equations. A substantial wall effect was observed by Tichy (1972) in his small scale scrubber (0.14-m. dia.).

Epstein (1975) has run a series of experiments by passing air and sodium carbonate solution through a large TCA scrubber (1.7 m. square) at TVA Shawnee power station to observe the pressure drop without the presence of scaling. When lime or limestone slurry is used, deposition of calcium sulfite and calcium sulfate on the wall and grids of the scrubber takes place. An empirical correlation of pressure drop was presented by Epstein (1975).

Liquid holdup was measured and correlated by Groeneveld (1967), Chen and Douglas (1968), Barile and Meyer (1971), and Kito et al(1975).

Groeneveld (1967) measured the liquid holdup in TCA. A slow increase of holdup with increasing gas velocity was observed below the flooding point. At the flooding point a rapid increase of liquid holdup was observed. Liquid holdup was found to be nearly proportional to the liquid flow rate below the flooding point. The effect of grids on the liquid holdup was not discussed.

In the investigation conducted by Chen and Douglas (1968), the effect of the packing density and the characteristics of the supporting grid on the liquid holdup were not considered.

The results of Barile and Meyer's (1971) study are applicable only at the minimum fluidization velocity. However, Kito et al (1975) studied the dependence of liquid holdup on the grid characteristics, packing density and diameter over a wide range of operating conditions. The liquid holdup was found to be independent of the gas flow rate.

Tichy and Douglas (1973), using the pressure drop as the criterion, classified the operation of TCA into three hydrodynamic regimes. They are static, semi-mobile and fully mobile regimes. The fully mobile regime can be divided into a constant liquid holdup region, an increasing liquid holdup region, and a flooding region.

Douglas et al. (1963) also investigated mass and heat transfer in TCA. From the absorption of CO_2 and SO_2 by alkaline solutions they found that the gas and liquid flow rates could be much greater than those possible in conventional packed towers, and could greatly increase the absorption capacity for a given tower size.

Recently, Borgwardt (1972b) and Epstein (1970) studied the absorption of SO_2 by alkaline solutions and limestone/lime slurries in TCA, venturi scrubbers, and marble bed scrubbers. Their data from the TCA scrubber demonstrated a significant improvement in SO_2 removal efficiency over the conventional packed tower. McMichael et al. (1975) presented a mathematical model to describe the absorption of SO_2 in TCA. Later, Fan (1975) successfully correlated the data for TCA and spray tower units by considering the combined effects of spray section and packing section which are affected by the hydrodynamics, the magnesium concentration and the pH value of the scrubber.

Kito et al. (1975) measured the gas-liquid interfacial area and gas mass transfer coefficient in a TCA operated with stagnant liquid. Further, the specific gas-liquid interfacial area in TCA was investigated by Groeneveld (1967). According to his study, the specified interfacial area was proportional to the liquid flow rate, and increased with increasing gas flow rate. A slow increase was observed below the flooding point and a rapid increase at the flooding point, where the interfacial area reached a value of 200 m^2/m^3.

CHAPTER 3

PRESSURE DROP IN THE TURBULENT CONTACTING ABSORBER

In this chapter, an analysis of pressure drop will be made on data reported by Epstein (1975). Since a large diameter scrubber was used, the correlation obtained could be used for the design of commercial sized scrubbers.

3.1 Model of Pressure Drop in TCA Scrubber

Typical TCA configurations to be considered in this study are shown schematically in Figure 3.1 and 3.2.

The pressure drop data of TVA Shawnee scrubber (1.7 m. square) for the air/water and sodium carbonate runs and four additional limestone runs with 0.76 m. static packing height are summarized in Figure 3.4 and 3.5. Data from the EPA small scale (0.23 m. dia.) TCA scrubber with lime slurry as the scrubbing liquor are also presented in Figure 3.4.

For the TCA operating with packing spheres, the column can be divided into spray, packed, and grid sections as shown in Figure 3.3. The following equation is proposed for determining the pressure drop across the TCA scrubber:

$$\Delta P_t = \Delta P_g + \Delta P_s + \Delta P_b \tag{3.1}$$

where ΔP_t is the total pressure drop in Pascals, Pa,

ΔP_g is the pressure drop across the grids, Pa,

ΔP_s is the pressure drop in the spray section, Pa, and

ΔP_b is the pressure drop in the packing section, Pa,

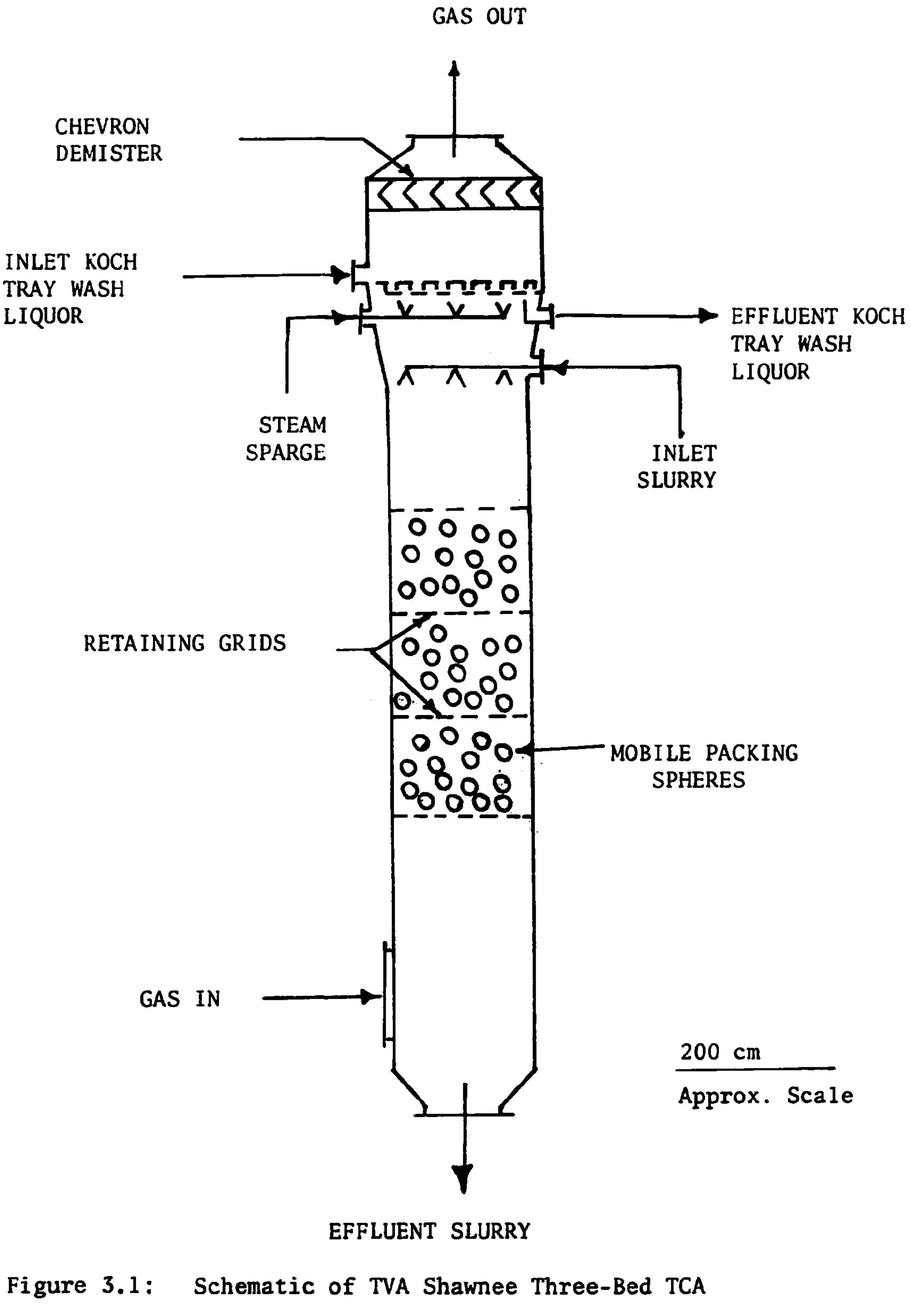


Figure 3.1: Schematic of TVA Shawnee Three-Bed TCA

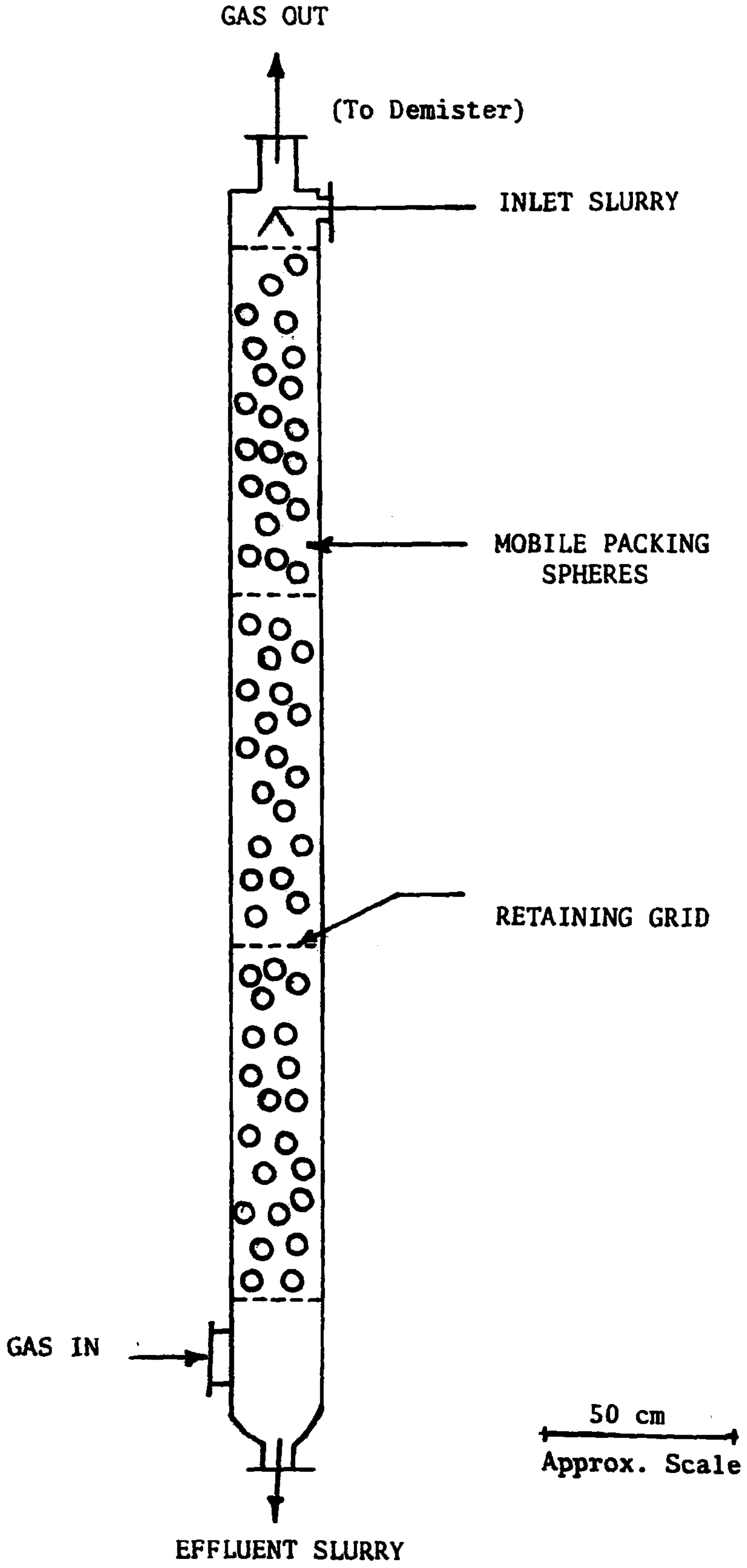


Figure 3.2: Schematic of the EPA/RTP Research TCA Scrubber

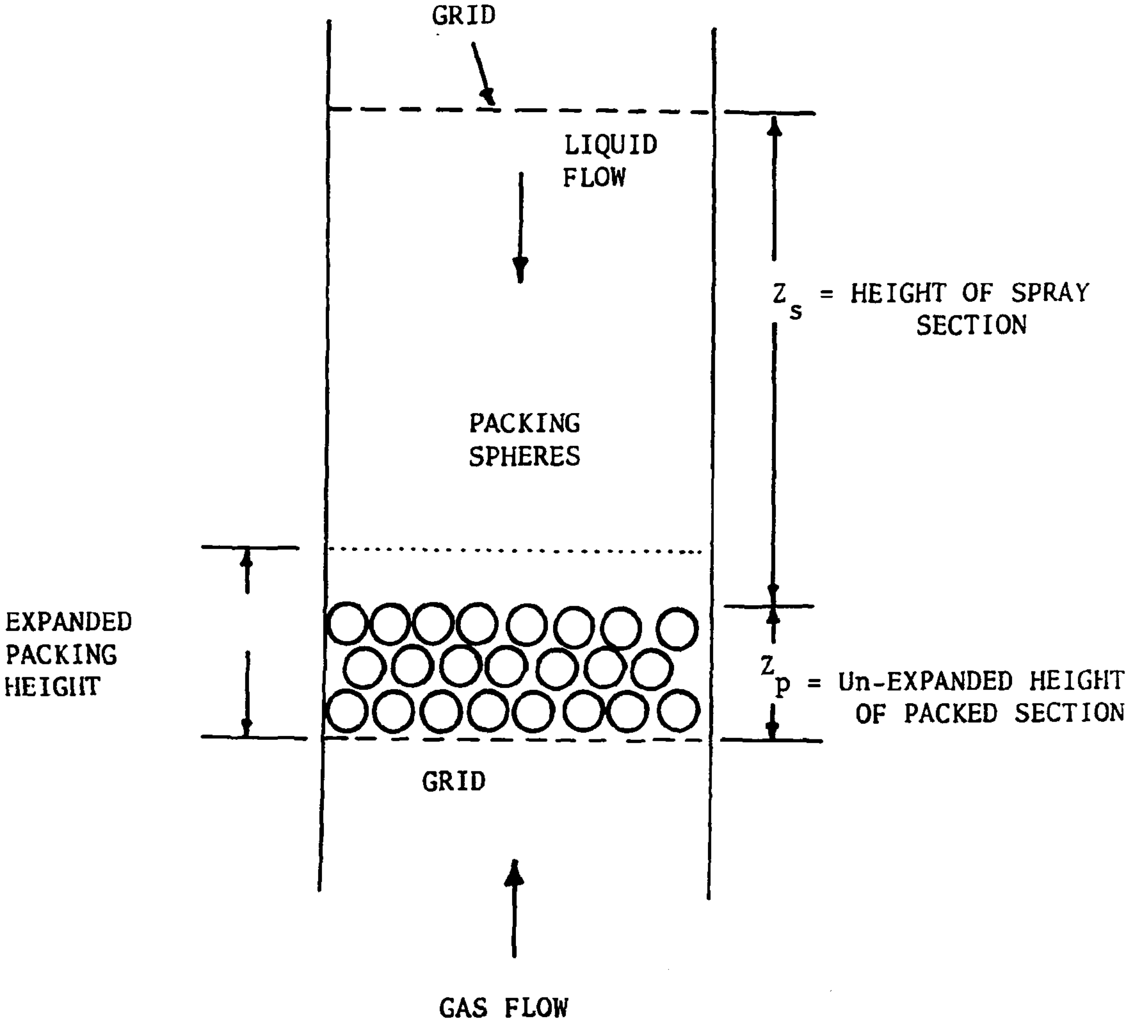


Figure 3.3: An Idealized Stage of a Turbulent Contacting Absorber.

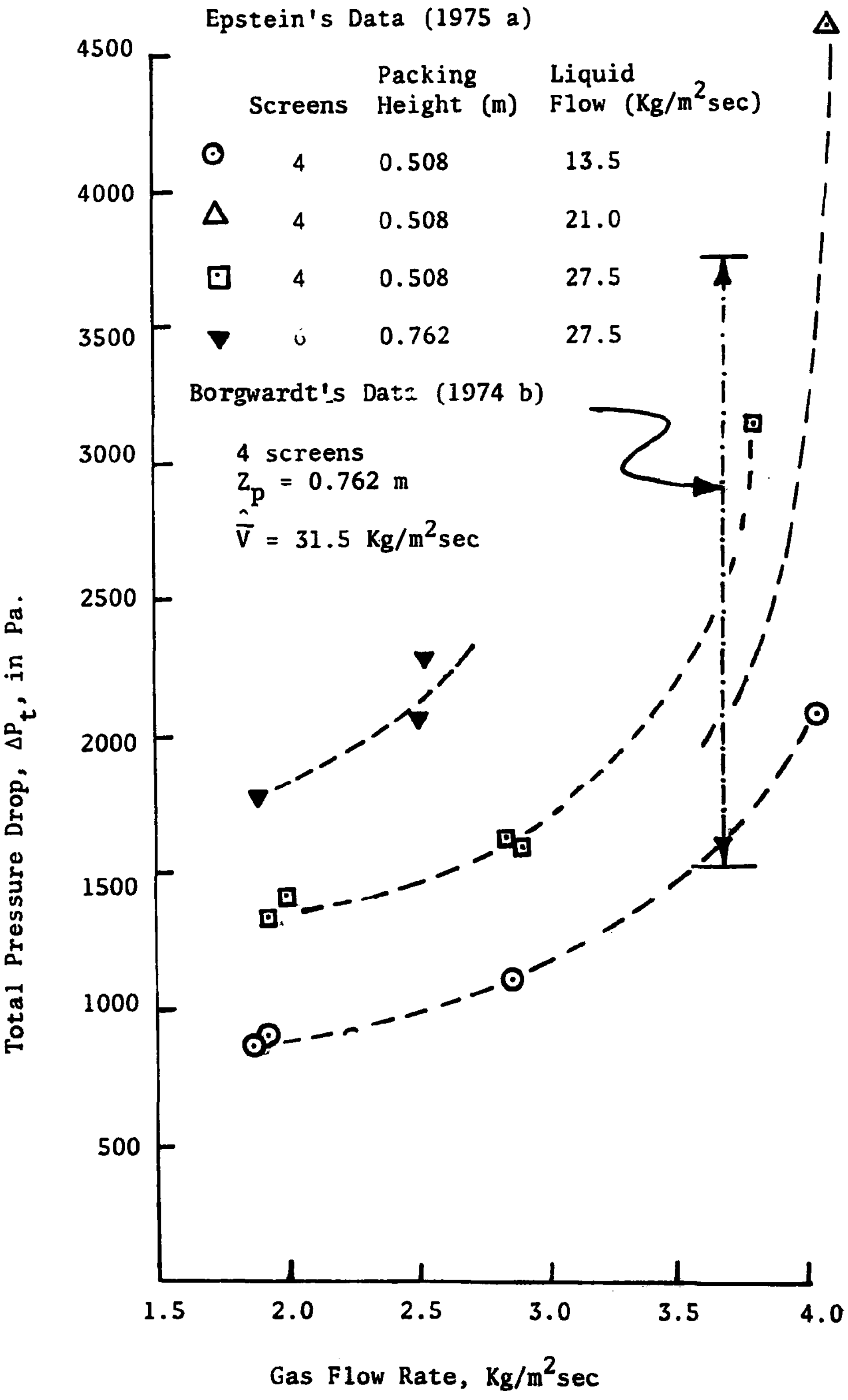


Figure 3.4: Effect of Gas Velocity and Liquid Velocity on Pressure Drop for TCA.

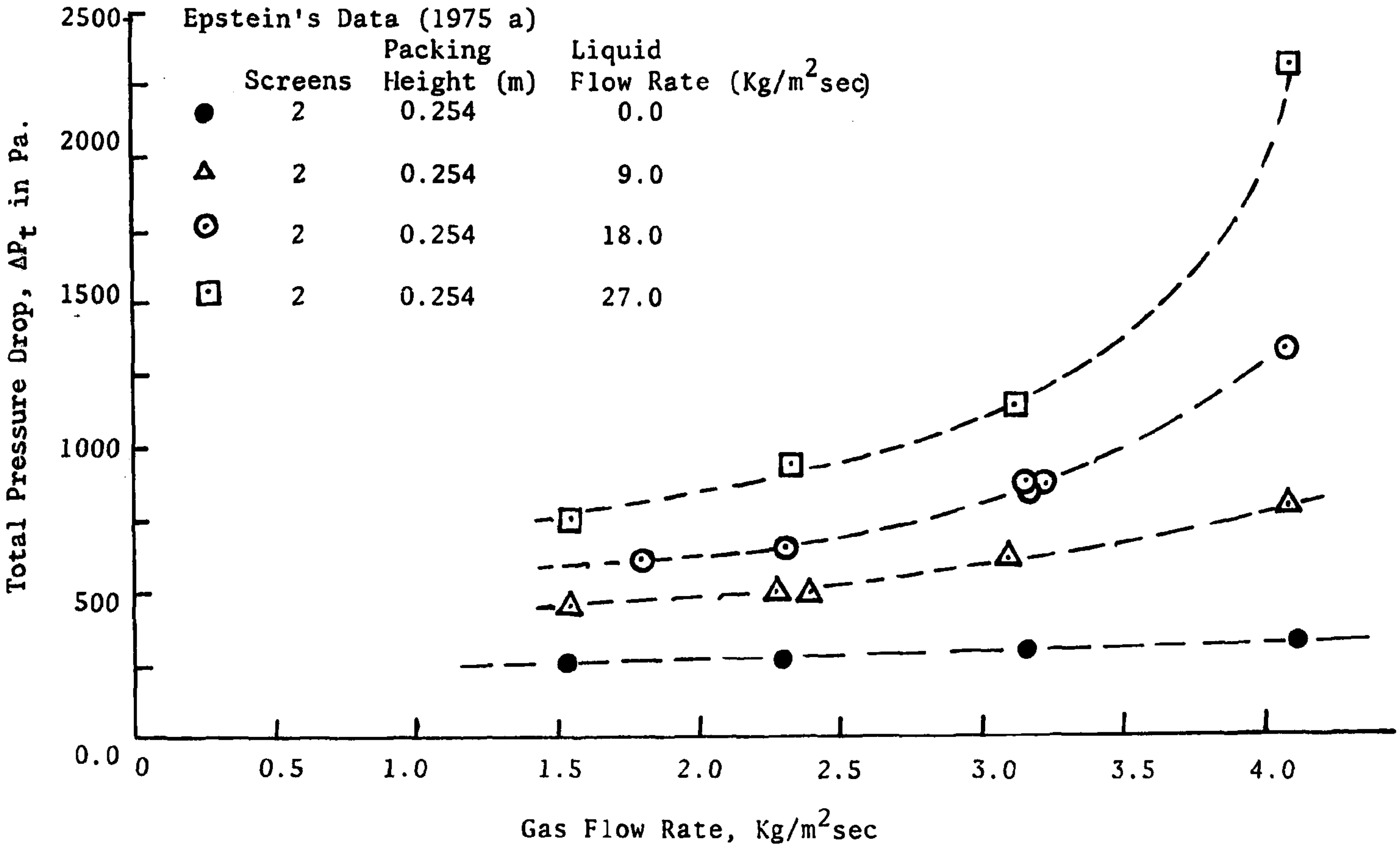


Figure 3.5: Effect of Gas Velocity and Liquid Velocity on Pressure Drop for TCA.

Effect of the Grid:

The pressure drop across the grid, ΔP_g, as a function of liquid and gas flow rates is shown in Figure 3.6. The following empirical equation is obtained when a first-order dependence on each of the variables is assumed so as to approximate ΔP_g which is a small part of the total pressure drop.

$$\Delta P_g = 0.579\ \hat{G}\ \hat{V}\ N_g \tag{3.2}$$

where $\hat{G}$ is the superficial gas mass velocity, Kg/m^{2}sec,

$\hat{V}$ is the superficial liquid mass velocity, Kg/m^{2}sec,

and Ng is the number of grids.

Effect of the Spray Section:

The pressure drop of the spray section of the Shawnee TCA has been correlated by Wen (1973) in terms of the gas and liquid flow rates as

$$\Delta P_s = 1.79\ \hat{G}^{1.17}\ \hat{V}^{0.6}\ Z_s \tag{3.3}$$

where $\hat{G}$ is the gas mass velocity, Kg/m^{2}sec,

and Z_s is the height of spray section, m.

Equation (3.3) will be used in this study.

Effect of the Packing Section:

A TCA scrubber utilizes very low density packings. The gas flow rate is increased in a TCA scrubber at a constant liquid flow rate until the upward force of the gas flow balances the weight of the packings plus the liquid holdup, which are both equal to the total pressure drop.

The pressure drop of the bed sections, ΔP_b, is thus assumed to have the following form:

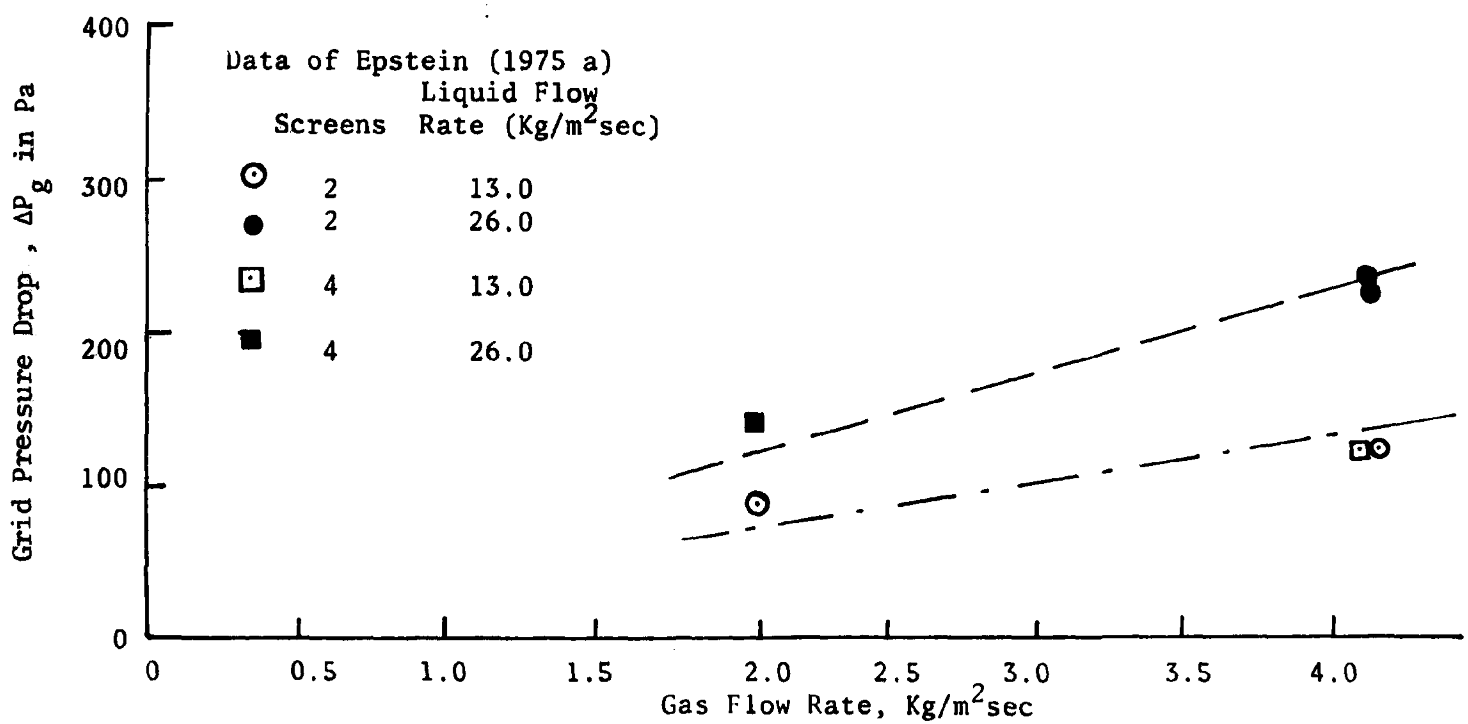


Figure 3.6: Pressure Drop Across the Grids as a Function of Gas and Liquid Mass Velocity in the Shawnee TCA Operated Without Packing Spheres.

$$\Delta P_b = \Delta P_h + \Delta P_p + \Delta P_f \qquad (3.4)$$

where ΔP_h is the pressure drop due to the liquid holdup in the packing section, Pa,

ΔP_p is the pressure drop due to the static bed weight, Pa,

and ΔP_f represents the pressure drop due to the friction loss as the operating conditions are close to the flooding point, Pa.

A few investigators, such as Barile et al. (1971), Chen et al. (1968) and Kito et al. (1975), have correlated the results of the liquid and gas holdups of a TCA scrubber. Their investigations have shown that there is a strong dependence of liquid holdup on liquid velocities,on the characteristics of the supporting grid, and on the properties of the packing spheres.

Although Chen and Douglas (1968) presented a correlation for the pressure drop in a TCA scrubber, the effects of the packing properties and the characteristics of the supporting grid on the liquid holdup were not considered. The correlation of Barile and Meyer (1971) on the other hand is applicable only at the minimum fluidization velocity.

Kito et al. (1975) studied the liquid holdup by considering the effects of liquid velocity, diameter and density of the packing spheres, and the static height of the bed. Since their correlation includes the effects of packing properties and characteristics of the supporting grid, it will be used in this study. Their correlation has the following form:

$$\Delta P_h = 0.024 \left(f \frac{d}{D}\right)^{-.84} (d_p)^{-.84} (\rho_p)^{.18} Z_p^{.6} \hat{V} \rho_L/\rho_W$$

$$+ 147.1 Z_p \rho_L/\rho_W \qquad (3.5)$$

where Z_p is the static height of the packing bed, m,

f is the percent opening of the grid, dimensionless,

d is the diameter of each hole in the grid, m,

D is the equivalent diameter for free sectional area, m,

dp is the diameter of the packing sphere, m,

ρ_L is the density of the slurry, Kg/m^3,

ρ_p is the density of the packing sphere, Kg/m^3,

and ρ_W is the density of water, Kg/m^3.

The static bed weight can be expressed as

$$\Delta P_p = (1 - \varepsilon)\rho_p g Z_p \qquad (3.6)$$

where ε is the voidage of the static packed bed (packings are randomly arranged), dimensionless; and g is the gravitational accelaration, m/sec^2.

If ε is assumed as a constant, Equation (3.6) can be simplified as

$$\Delta P_p = 5.06 Z_p \rho_p \qquad (3.7)$$

The value of ΔP_f in Equation (3.4) can be obtained from experimental data.

Substitution of Equation (3.4) into Equation (3.1) gives

$$\Delta P_t = \Delta P_g + \Delta P_s + \Delta P_h + \Delta P_p + \Delta P_f \qquad (3.8)$$

or

$$\Delta P_f = \Delta P_t - \Delta P_g - \Delta P_s - \Delta P_h - \Delta P_p \qquad (3.9)$$

where ΔP_t is obtained from Epstein's data while ΔP_g, ΔP_s, ΔP_h, and ΔP_p are calculated from Equations (3.2), (3.3), (3.4), and (3.7) respectively.

The values of ΔP_f obtained from Equation (3.9) are shown in Figure 3.7 as a function of the liquid and gas mass velocities. The result shows that ΔP_f is negligible for all the gas mass velocities tested in the experiments if the liquid mass velocity is less than 8.0 kg/m^2 sec.

3.2 Simulation of the Pressure Drop across TCA Scrubber

Table 3.1 summarizes the correlations which can be used to simulate the pressure drop across a TCA.Based on the model presented in this study the pressure drop across the TVA Shawnee TCA can be computed fairly accurately, in most cases within 10% accuracy. A comparison of the calculated and observed pressure drop is shown in Figure 3.8 for TCA units. Data for EPA's small scale TCA scrubber are excluded since they varied over a large range at the same gas and liquid velocity as shown in Figure 3.4.

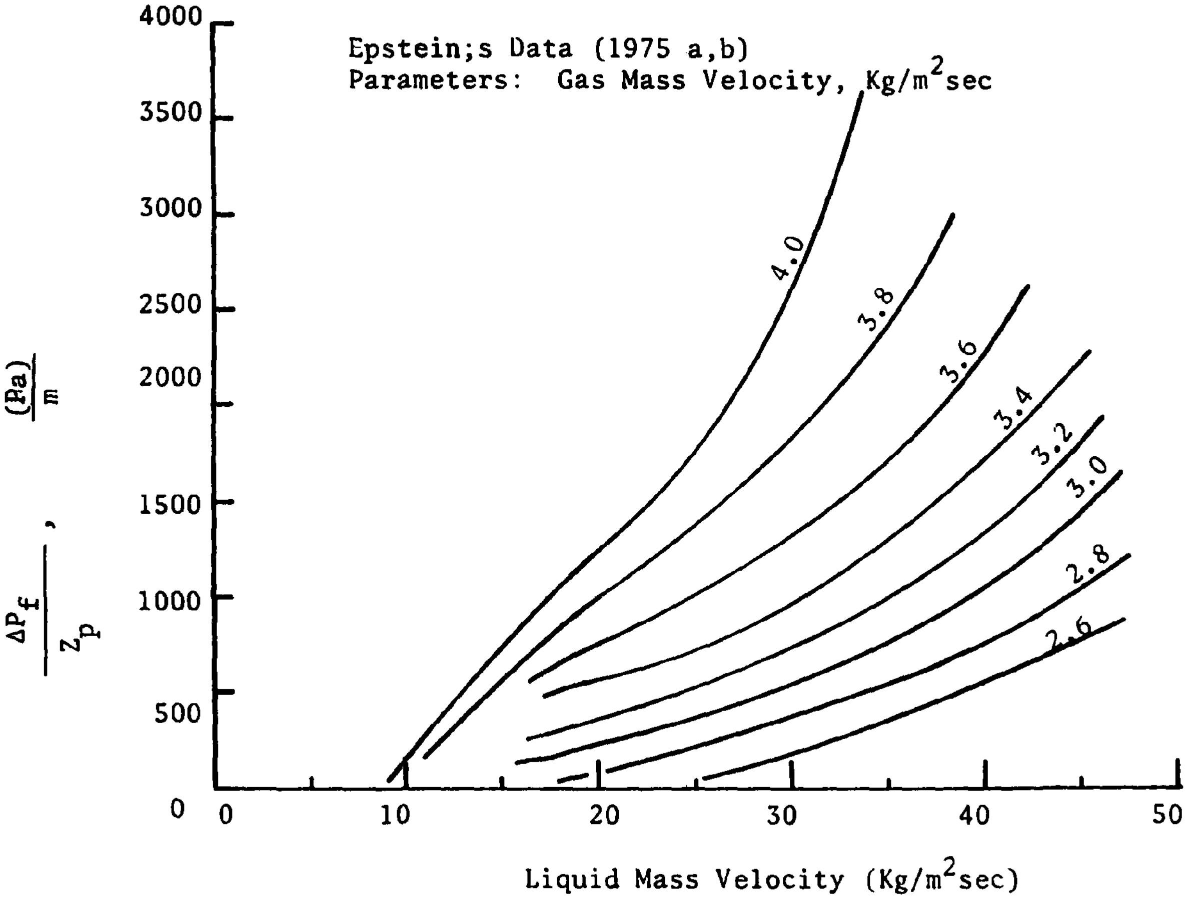


Figure 3.7: Pressure Drop for the Packed Section as a function of Gas and Liquid Flow Rates

Table 3.1

Summary of Equations Necessary for Simulating The Pressure

Drop Across a TCA:

$$\Delta P_t = \Delta P_g + \Delta P_s + \Delta P_h + \Delta P_p + \Delta P_f \qquad (3.8)$$

$$\Delta P_g = 0.579\ \hat{G}\ \hat{V}\ N_G \qquad (3.2)$$

$$\Delta P_s = 1.79\ \hat{G}^{1.17}\ \hat{V}^{0.6}\ Z_s \qquad (3.3)$$

$$\Delta P_h = 0.024\ (f\ \frac{d}{D})^{-0.84}\ (d_p)^{-0.84}\ \rho_p{}^{0.18}\ Z_p{}^{0.6}\ \hat{V}\ \rho_L/\rho_W$$

$$+\ 147.1\ Z_p\ \rho_L/\rho_w \qquad (3.5)$$

$$\Delta P_p = 5.06\ Z_p\ \rho_p \qquad (3.7)$$

ΔP_f is given in Figure 3.7

Table 3.2

Range of Data Used in Testing the Validity of the Pressure Drop Correlation

Data are for TVA Shawnee TCA Using Water-Soda Ash and Limestone as Scrubbing Media (Epstein (1975 a,b))

Gas Flow Rate (kg/m^{2}sec)	1.5 to 4.2
Liquid Flow Rate (kg/m^{2}sec)	0 to 34
Packing Height (m)	0 to 0.76
Number of Grids (-)	0 to 6
Equivalent Diameter of the scrubber (m)	0.084 to 0.0925
Packing diameter (m)	0.0097 to 0.029
Diameter of the Hole in the Grid (m)	0.002 to 0.012
Packing Density (kg/m^3)	170 to 1250
Fraction Free Opening of the Grid (-)	0.5 to 0.84

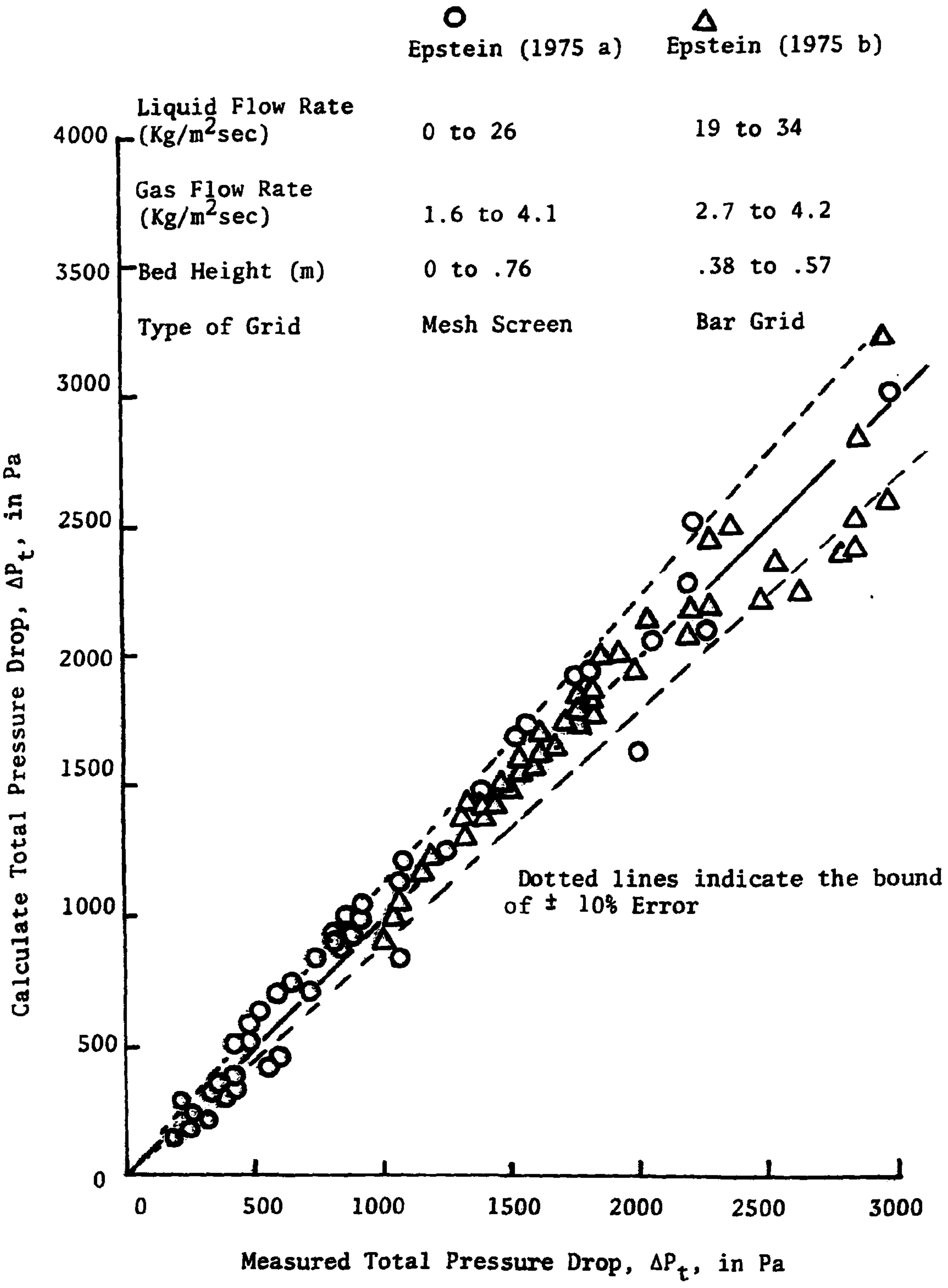


Figure 3.8: Comparison of the Predicted and Observed Pressure Drop Across TCA Scrubber.

CHAPTER 4

ABSORPTION OF SO_2 AND CO_2 IN TCA

Flue gas containing SO_2 and CO_2 passes through the EPA scrubber. Upon absorption of SO_2 and CO_2 from the flue gas, sulfite, sulfate and carbonate salts of calcium begin to form and the pH of the scrubbing lime slurry drops rapidly greatly reducing the amount of CO_2 absorbed.

In this chapter, the effect of pressure drop on SO_2 scrubbing efficiency and the effect of CO_2 absorption in flue gas scrubbing are studied.

4.1 SO_2 Absorption--Effect of Pressure Drop on the SO_2 Absorption Efficiency

McMichael et al. (1976) reported a procedure by which the sulfur dioxide removal efficiency of a TCA scrubber can be calculated from the specification of the scrubber characteristics and inlet slurry composition. This procedure is based on the following equation:

$$\frac{G}{P_T} \ln \frac{p_{SO_2}^{in}}{p_{SO_2}^{out}} = \frac{k_g^s a\, Z_s}{1+\dfrac{\Delta_s\, e^{330P_{SO_2}^{in}}}{A_s}} + \frac{k_g^p a\, Z_p}{1+\dfrac{\Delta_p\, e^{330P_{SO_2}^{in}}}{A_p}} \qquad (4\text{-}1)$$

Correlations for the parameters appearing in this equation are given in Table 4.1.

Equation (4.1) can be simplified by converting the height of spray section into an equivalent height of packing. The equivalent packing height, Z_p^e, is defined as the height of packing which gives the same amount of absorption of SO_2 as the absorption in the spray

Table 4.1

Summary of Equations Nessary for Simulating the SO_2 Absorption of the TVA Shawnee TCA and Spray Column and the EPA In-House TCA (McMichael et al. 1976)

$k_g^s a = 0.1586\ G^{0.8}\ V^{0.4}$	$k_g^p a = 1.188\ G^{0.47}\ V^{0.51}$
$A_s^{-1} = \exp(-1.35\ \mathrm{pH} + 7.82) - 0.15$	$A_p^{-1} = -0.417\ \mathrm{pH} + 3.41$; for $\mathrm{pH} \geq 6.0$
	$A_p^{-1} = 0.308$; for $\mathrm{pH} < 6.0$
$\Delta_s = 50.1\ \mathrm{Mg}^{-0.6682}$; for $\mathrm{Mg} \geq 350$ ppm	$\Delta_p = 2.2 \times 10^7\ \mathrm{Mg}^{-2.065}$; for $\mathrm{Mg} \geq 3600$ ppm
$\Delta_s = 1.0$; for $\mathrm{Mg} < 350$ ppm	$\Delta_p = 1.0$; for $\mathrm{Mg} < 3600$ ppm

where the pH refers to the log mean hydrogen ion concentration across the scrubber.

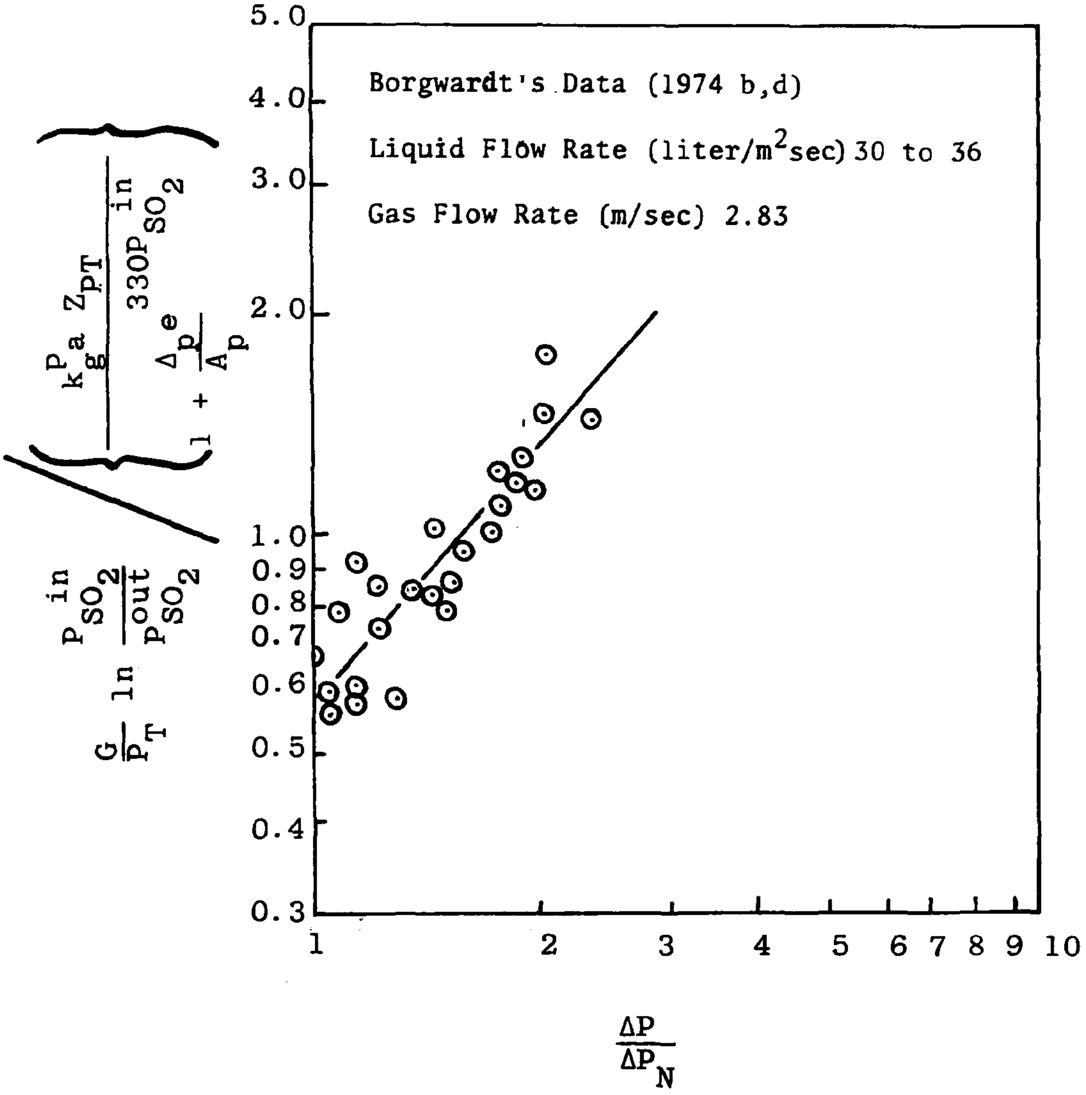


Figure 4.1: Effect of Pressure Drop on the SO_2 Removal Efficiency for TCA Lime Slurry Scrubber.

section at a height of Z_s. Thus,

$$Z_P^{\,e} = Z_S \left(\frac{k_g^S a}{k_g^P a}\right) \frac{1 + \frac{\Delta_p}{A_p} e^{330 P_{SO_2}^{in}}}{1 + \frac{\Delta_s}{A_s} e^{330 P_{SO_2}^{in}}} \tag{4.2}$$

Equation (4.1) can then be written as

$$\frac{G}{P_T} \ln \frac{P_{SO_2}^{in}}{P_{SO_2}^{out}} = \frac{k_g^P a \; Z_{PT}}{1 + \frac{\Delta_p}{A_p} e^{330 P_{SO_2}^{in}}} \tag{4.3}$$

where $Z_{PT} = Z_P + Z_P^{\,e}$

Equation (4.1) was derived from the data of flue gas desulfurization (FGD) in TCA and spray columns (see McMichael (1976)) without regard to the effect of the pressure drop across the columns. It is known that as the scale is formed the pressure drop across the column increases and the sulfur dioxide removal efficiency increases. Presumably, this is due to the increase in the interfacial area available for mass transfer as a result of an increase in the liquid hold-up. Equation (4.3) can be corrected to take into account the effect of pressure drop across the scrubber on the sulfur dioxide absorption efficiency. Figure 4.1 shows this effect based on Borgwardt's data (1974b,d). From Figure 4.1 the scrubber equation (Equation (4.3)) can be revised to include the pressure drop effect as follows:

$$\frac{G}{P_T} \ln \frac{P_{SO_2}^{in}}{P_{SO_2}^{out}} = 0.6 \left[\frac{\Delta P}{\Delta P_N}\right]^{1.1} \cdot \frac{k_g^P a \, Z_{PT}}{1 + \frac{\Delta_p}{A_p} e^{330 P_{SO_2}^{in}}} \qquad (4.4)$$

The normal pressure drop without scale formation, ΔP_N, (Equation (4.4)) is difficult to calculate as discussed in Chapter 3. The values of ΔP_N used in calculation of the data points in Figure 4.1 and in formulation of Equation (4.4) were based on the lowest pressure drops reported by Borgwardt (1974 b,d) at a given set of flow conditions.

4.2 CO_2 Absorption

In TCA, carbon dioxide is absorbed from flue gas into the scrubbing medium, lime slurry, and in turn is precipitated in the holding tank as $CaCO_3$ according to the following reaction:

$$CO_2 + CaO = CaCO_3$$

Calcium carbonate is then purged out from this wet-scrubbing system with solid calcium sulfite and calcium sulfate as a waste. As a result of the recarbonation of lime and precipitation of calcium carbonate, the utilization of lime, is reduced.

The lime utilization is defined as follows:

$$\text{Utilization of lime} = \frac{\text{moles } SO_2 \text{ absorbed}}{\text{moles CaO fed}}$$

$$= \frac{\text{moles } SO_2 \text{ absorbed}}{SO_2 \text{ absorbed} + CO_2 \text{ absorbed} + \text{slaking loss}}$$

In the desulfurization scrubbing system, the absorption of carbon dioxide into the scrubbing medium is undesirable since the precipitation of calcium carbonate lowers the usage of lime. For the purpose of designing a scrubber, the utilization of lime must be predicted. This in turn requires that a model for the absorption of carbon dioxide from flue gas be developed.

4.2.1 CO_2 Absorption in the absence of SO_2

The absorption of carbon dioxide into an aqueous alkaline solution, such as KOH and NaOH, is a process which has been studied by a number of investigators.

When carbon dioxide is absorbed in the absence of SO_2 in an alkaline solution, it reacts according to the following reactions as proposed by Payne and Dodge (1932).

$$CO_2(g) = CO_2(1) \tag{a}$$

$$CO_2(1) + H_2O = H_2CO_3 \tag{b}$$

$$H_2CO_3 = H^+ + HCO_3^- \tag{c}$$

$$HCO_3^- = H^+ + CO_3^= \tag{d}$$

$$H^+ + OH^- = H_2O \tag{e}$$

$$CO_2 + OH^- = HCO_3^- \tag{f}$$

$$HCO_3^- + OH^- = CO_3^{--} + H_2O \tag{g}$$

$$CO_2 + 2OH^- = CO_3^= + H_2O \tag{h}$$

Although the ionic reactions are known to be very rapid, the rates of the other reactions are not well known.

Various assumptions as to which of these reactions may be controlling lead to different mechanism of the absorption process. Hatta (1928) assumed that the reaction (a), (f), and (g) are controlling and that (g) is much more rapid than (f).

Eucken and Grutzner (1927) concluded that the following reaction:

$$CO_2 + 2OH^- = CO_3^{--} + H_2O \qquad (h)$$

was the major reaction.

Tepe and Dodge (1943) have reported their experimental study of the absorption of carbon dioxide by sodium hydroxide solutions in a 0.15 m.-diameter column filled to a height of 0.91 m. with 0.0127 m.(0.5 in.) carbon Rashig rings. The overall mass transfer coefficient K_Ga was found to be a function of concentration of sodium hydroxide. Changes in the gas flow rate was found to have a negligible effect on K_Ga. The value of K_Ga increased in proportion to the liquid temperature.

A comprehensive investigation of CO_2 in an alkali solution has been carried out by Nijsing (1969). He used two different absorbers, a laminar jet and a wetted-wall column, to study its mechanism. The gas phase was pure CO_2 at pressure from 20 KPa (0.2 atm) to 101 kPa (1 atm) and the liquid phase consisted of concentrated hydroxide solutions (0.5 to 2.0 gmole/liter).

From the studies cited above, Astarita (1967) has drawn the following conclusions:

(1) The absorption of CO_2 into an alkaline solution is a process of chemical absorption.

(2) The overall absorption coefficient is rather insensitive to the gas flow rate, which clearly indicates liquid-side mass transfer control.

(3) The overall gas absorption coefficient increases with liquid flow rate.

(4) The overall gas absorption coefficient increases with increase in the bulk-liquid concentration of the reacting solute, namely of OH^- ion.

However, the absorption of CO_2 in the liquid medium accompanied with the absorption of SO_2 has not been investigated to date.

4.2.2 CO_2 Absorption in the presence of SO_2

The absorption of CO_2 into recycled lime slurries in TCA scrubbers is a complex problem for several reasons. Firstly, the liquid film mass transfer coefficients for TCA scrubbers have not been reported. This fact makes the analysis of CO_2 absorption difficult in that mass transfer and chemical effects cannot be isolated from each other. Secondly, upon absorption, CO_2 hydrates can participate in several reactions. Absorption of CO_2 into recycled lime slurries, which contain various sulfur, magnesium, chlorine and carbon compounds, is not simple, even though the studies on absorption of CO_2 into water or sodium hydroxide solutions have been well documented in the literature. And finally, detailed data on the absorption of CO_2 into recycled lime slurries in TCA scrubbers have not been reported. Only qualitative information on the inlet and outlet streams of the scrubber and the scrubber-hold tank system is available.

In this section experimental data reported by Borgwardt (1974b,d), on a TCA scrubber at the Research Triangle Park, are analyzed. A mathematical model describing the absorption of CO_2

from flue gas in the presence of SO_2 into lime slurry in a TCA scrubber is developed.

Model of CO_2 Absorption in TCA:

Both SO_2 and CO_2 are absorbed in a flue gas scrubber by the recycling lime slurry. It is a competing reaction for a common liquid phase reactant, OH^-. The pH values along the TCA scrubber may decrease more drastically compared to the case of CO_2 absorption in the absence of SO_2. Based on the experimental observation reported by Borgwardt (1974b,d), the reduction in the value of pH is usually from about 10 at the top to about 5.0 at the bottom of a TCA. The significant drop in pH value as a result of the presence of SO_2 in flue gas greatly reduces the rate of absorption of CO_2 or the value of its mass transfer coefficient. In addition, the following assumptions are made in developing this model:

(1) Negligible precipitation of calcium carbonate in the scrubber.

(2) Negligible slaking loss which was experimentally shown to be only about 5% of the total lime feed.

(3) In the bulk liquid phase, the following reaction is at equilibrium:

$H_2CO_3 = H^+ + HCO_3^-$

The concentration of carbonate ion is appreciable only when pH is greater than 10.

(4) The change in the partial pressure of CO_2 (approximately 30 Pa (or 0.0003 atm)) in the bulk gas phase can be ignored since the amount of CO_2 absorbed by the scrubbing liquid is very small compared to the CO_2 content in the bulk gas phase. Even though

the change in the partial pressure of CO_2 in the bulk gas phase is small, the CO_2 absorption can not be ignored since it is critical in determining the calcium utilization.

A schematic drawing of the scrubber and a depiction of the driving forces for carbon dioxide transfer across the gas liquid interface are shown in Figure 4.2. For this sketch, the following nomenclature are employed.

V = liquid flow rate, liter/m sec

Z = height of the scrubber, m

dZ = differential tower height, m

C = concentration of the total carbon dioxide in the slurry, gmol/liter,

C_{in} = concentration, C, at the inlet slurry of the scrubber, gmol/liter,

C_{out} = concentration, C, at the outlet slurry of the scrubber, gmol/liter,

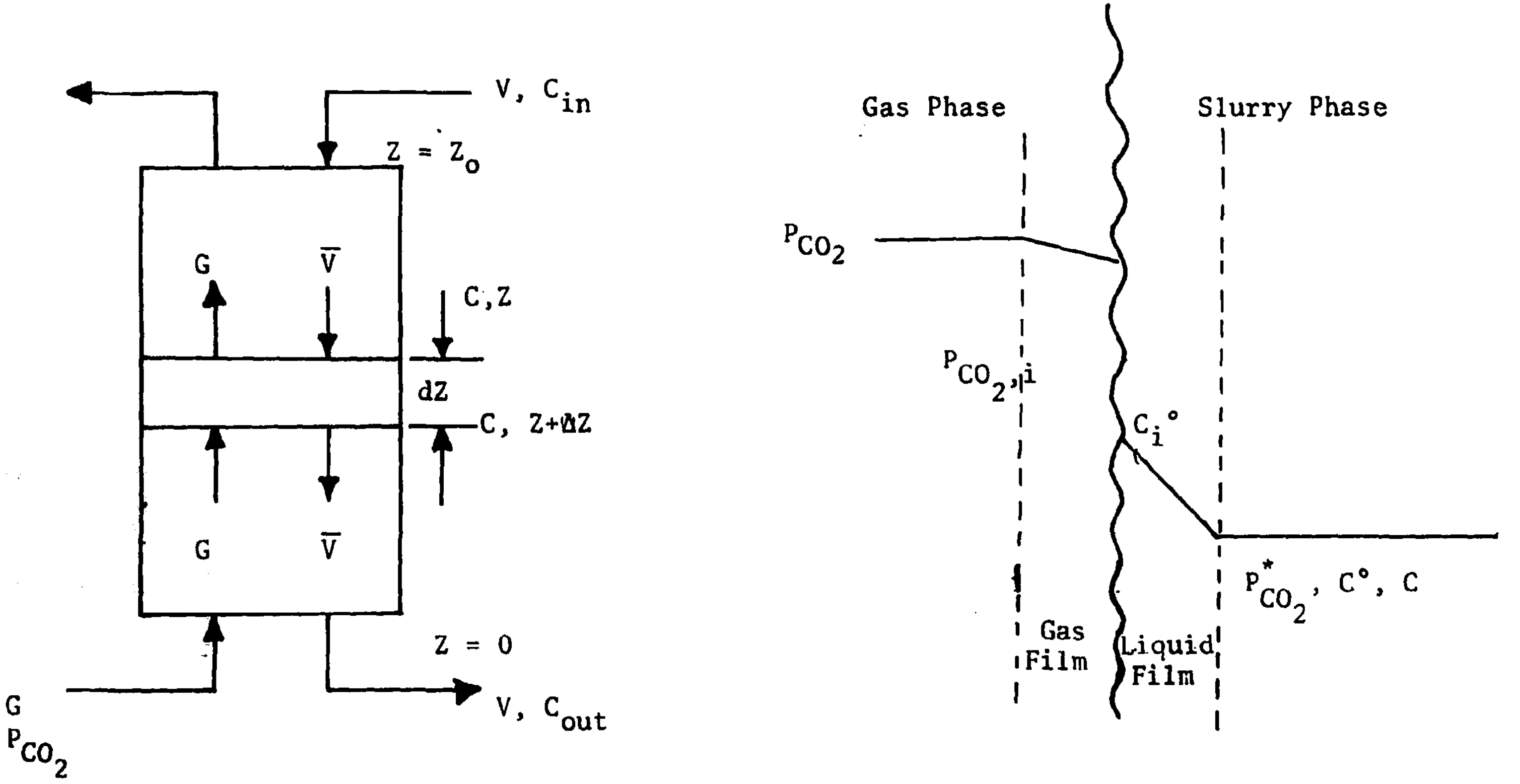
$P^{b}_{CO_2}$ = partial pressure of carbon dioxide in the bulk gas phase, atm,

$P_{CO_2,i}$ = partial pressure of carbon dioxide at the gas-liquid interface, atm .

The molar flux of carbon dioxide across the gas-liquid interface of the scrubber can be written in terms of the overall gas phase resistance.

$$N_{CO_2} = K_G a \, (P^{b}_{CO_2} - P^{*}_{CO_2}) \qquad (4.5)$$

where N_{CO_2} is the molar flux of carbon dioxide across the gas-liquid interface, $gmol/m^2 sec$,



(a) Flow Diagram of Scrubber

(b) Concentration profile

Figure 4.2: Scrubber and Idealization of the Concentration Profile of Carbon Dioxide.

K_Ga is the overall gas phase resistance, gmole/atm.sec.m^3

$P^b_{CO_2}$ is the partial pressure of carbon dioxide in the bulk gas phase, atm,

and $P^*_{CO_2}$ is the partial pressure of carbon dioxide in the gas phase that is in equilibrium with H_2CO_3 in the bulk liquid phase, atm;

For a dilute system $P^*_{CO_2}$ can be defined by the Henry's Law as

$$P^*_{CO_2} = S\ C^\circ \tag{4.6}$$

where S is the Henry's Law constant, atm/gmole/ liter

C° is the concentration of H_2CO_3 in the bulk liquor phase, gmole/liter.

Astarita (1967) concluded in his work that the absorption of CO_2 into alkali solution is a liquid phase controlled reaction. Thus, $P^b_{CO_2}$ may be related to the interfacial concentration of H_2CO_3 by the expression

$$P^b_{CO_2} = S\ C_i^\circ \tag{4.7}$$

where C_i° is the interfacial concentration of H_2CO_3 in gmole/liter;

The Henry's Law constant, S, as a function of temperature has been given by Lowell (1970) as

$$S = EXP\ (11.215 - \frac{2337.5}{T}) \tag{4.8}$$

where T is the liquid temperature in degrees Kelvin.

The molar flow of carbon dioxide through the gas-liquid interface can be obtained in terms of liquid phase concentration by substituting Equations (4.6) and (4.7) into Equation (4.5).

$$N_{CO_2} = K_Ga\ S\ (C_i^\circ - C^\circ) \tag{4.9}$$

By applying the mass balance on carbon dioxide across a differential height of the scrubber, dZ, the rate of CO_2 absorption can be written as:

$$V \frac{dC}{dZ} + K_G a \; S \; (C_i^{\circ} - C^{\circ}) = 0 \qquad (4.10)$$

where a is the interfacial area per unit volume of bed, m^2/m^3.

Since equilibrium between carbon dioxide and the bulk liquor phase is assumed and since the concentration of the carbonate ion is negligible, the following reaction is the key reaction that takes place in the bulk solution:

$$H_2CO_3 = H^+ + HCO_3^-$$

Hence, the concentration of bicarbonic acid is given by

$$HCO_3^- = \frac{K \; (H_2CO_3)}{(H^+)} \qquad (4.11)$$

where K is the equilibrium constant in liter/gmol.

This equilibrium constant, K, has been given by Lowell (1970) as a function of temperature as follows:

$$K = EXP \left(- \frac{7841}{T} - 0.075506 \; T + 34.183\right) \qquad (4.12)$$

Thus, the total carbon concentration, C, in the liquor can be obtained in terms of H_2CO_3 and H^+ by employing Equation (4.11)

$$C = H_2CO_3 + HCO_3^-$$

$$= H_2CO_3 + \frac{K \; (H_2CO_3)}{(H^+)}$$

After rearranging,

$$H_2CO_3 = \frac{(C)(H^+)}{K + (H^+)} \tag{4.13}$$

In terms of the nomenclature defined in Equation (4.6), Equation (4.13) is rewritten as

$$C^\circ = \frac{(C)(H^+)}{K + H^+} \tag{4.14}$$

Substitution of Equation (4.14) into Equation (4.10) gives

$$\frac{dC}{dZ} - \frac{K_G a\ S}{V(\frac{K}{H^+}) + 1} C + \frac{K_G a\ S}{V} C_i{}^\circ = 0 \tag{4.15}$$

The overall mass transfer coefficient, $K_G a$, in this equation is a function of pH value, liquid flow rate, and partial pressure of CO_2. When integrating Equation (4.15), $K_G a$ and H^+ are taken as constant and are designated as $\overline{K_G a}$ and $\overline{H}$ respectively.

$$\frac{dC}{dZ} - \frac{\overline{K_G a}\ S}{V(\frac{K}{\overline{H}} + 1)} C + \frac{\overline{K_G a}\ S}{V} C_i{}^\circ = 0 \tag{4.16}$$

The boundary conditions associated with Equation (4.16) are

$$\begin{aligned} &1.\quad Z = 0 \qquad C = C_{out} \\ &2.\quad Z = Z_0 \qquad C = C_{in} \end{aligned} \tag{4.17}$$

Since the magnitude of the change in the partial pressure of carbon dioxide along the tower is in an order of 0.0003 atm, $P^b_{CO_2}$ can be treated as a constant. This, in turn, assures the constancy of $C_i{}^\circ$ in Equation (4.16). The integration, from Z_0 to Z, of

Equation (4.16) satisfying Equation (4.17) is

$$C_Z = (C,^{\circ}in - C_i^{\circ} (\frac{K}{H} + 1)) \, EXP(\frac{\overline{K_G a} \, S}{V(\frac{K}{H} + 1)} (Z - Z_o))$$

$$+ C_i^{\circ} (\frac{K}{H} + 1) \qquad (4.18)$$

where C_Z is the concentration of total carbon dioxide at a height of Z, gmol/liter.

Based on the assumption (1) carbon dioxide absorbed per unit volume of scrubbing medium can be obtained

$$\begin{aligned} C_{abs} &= C_{out} \quad C_{in} \\ &= C,Z=0 - C,Z=Z_0 \end{aligned} \qquad (4.19)$$

where C_{abs} is CO_2 absorbed per unit volume of scrubbing medium, gmole/liter;

Substituting Equation (4.18) into Equation (4.19) gives

$$C_{abs} = (1 - EXP(- \frac{\overline{K_G a} \, S}{V(\frac{K}{H} + 1)} Z_o)) \, (C_i^{\circ} (\frac{K}{H} + 1)$$

$$- C_{in}) \qquad (4.20)$$

In this equation, C_{in} is the concentration of total carbon dioxide in the effluent of the holding tank and is very small compared to the other term, $C_i^{\circ} (\frac{K}{H} + 1)$. Equation (4.20) can be rewritten in a simpler form:

$$C_{abs} = (1 - EXP(- \frac{\overline{K_G a} \, S}{V(\frac{K}{H} + 1)} Z_o))(\frac{K}{H} + 1) \, C_i^{\circ} \qquad (4.21)$$

The interfacial concentration of H_2CO_3, C_i°, can be obtained by use of Equation (4.7)

$$C_i^\circ = P_{CO_2}^{\,b}/S \qquad (4.22)$$

Substituting Equation (4.22) into (4.21) leads to

$$C_{abs} = (1 - EXP(- \frac{\overline{K_G a}\, S}{V(\frac{K}{\bar{H}} + 1)} Z_o))(\frac{K}{\bar{H}} + 1)\, P_{CO_2}^{\,b}/S \qquad (4.23)$$

This equation is used to obtain the amount of carbon dioxide absorbed from the flue gas. $\overline{K_G a}$ and $\bar{H}$ can be estimated by the method described in the following section.

Mass Transfer Coefficients:

Equation (4.23) can be arranged to give

$$\overline{K_G a} = - \frac{V(\frac{K}{\bar{H}} + 1)}{SZ_o} \ln(1 - \frac{C_{abs}\,.S}{P_{CO_2}^{\,b}(\frac{K}{\bar{H}} + 1)}) \qquad (4.24)$$

In the case of lime slurries the pH variation across the scrubber is substantial, ranging from 8.0 at the inlet to 4.8 at the outlet. With this large change in pH it is not reasonable to assume that the inlet slurry pH characterizes the behavior of the scrubber as usually done by previous investigators. As shown in Appendix B, it has been found that the overall mass transfer coefficient of the lime scrubbing system can be correlated fairly accurately by the model developed in this chapter when the mean hydrogen ion concentration is calculated based on the following arithmetic mean pH value:

$$pH_m = (pH_{in} + pH_{out})/2$$
$$\overline{H} = EXP\ (-2.3\ pH_m) \tag{4.25}$$

The results are shown in Figure 4.3. The data were correlated by the following equation

$$\overline{K_G a} = V^{6.73}\ EXP(22.3 + 11.11\ pH_m) \tag{4.26}$$

The power of V is apparently much higher than the usual 0.7 power for a packing tower. This may be explained as follows:

Since Borgwardt's data (1974 b,d) available for the investigation of CO_2 absorption were obtained from a rather small scale scrubber (0.229 m.-dia), a study of its pressure drop is conducted in Chapter 3. Figure 3.4 in Chapter 3 displays the pressure drop reported by Borgwardt (1974 b,d) along with Epstein's data from a large TCA scrubber. As seen in Figure 3.4, the data were possibly in a regime near the loading point due to the steep slopes observed.

Groeneveld (1967) observed a rapid increase in the specific point, and from the observation of Groeneveld (1967), it is not surprising that the value of $K_G a$ increased in proportion to the 6.7 power of the liquid rate under the experimental conditions corresponding to Figure 4.3.

Although Equation (4.26) shows that the overall mass transfer coefficient is extremely sensitive to the liquid flow rate, the magnitude of the CO_2 absorption compared to SO_2 absorption does not vary greatly because of the extremely low solubility of CO_2 in the scrubbing slurries.

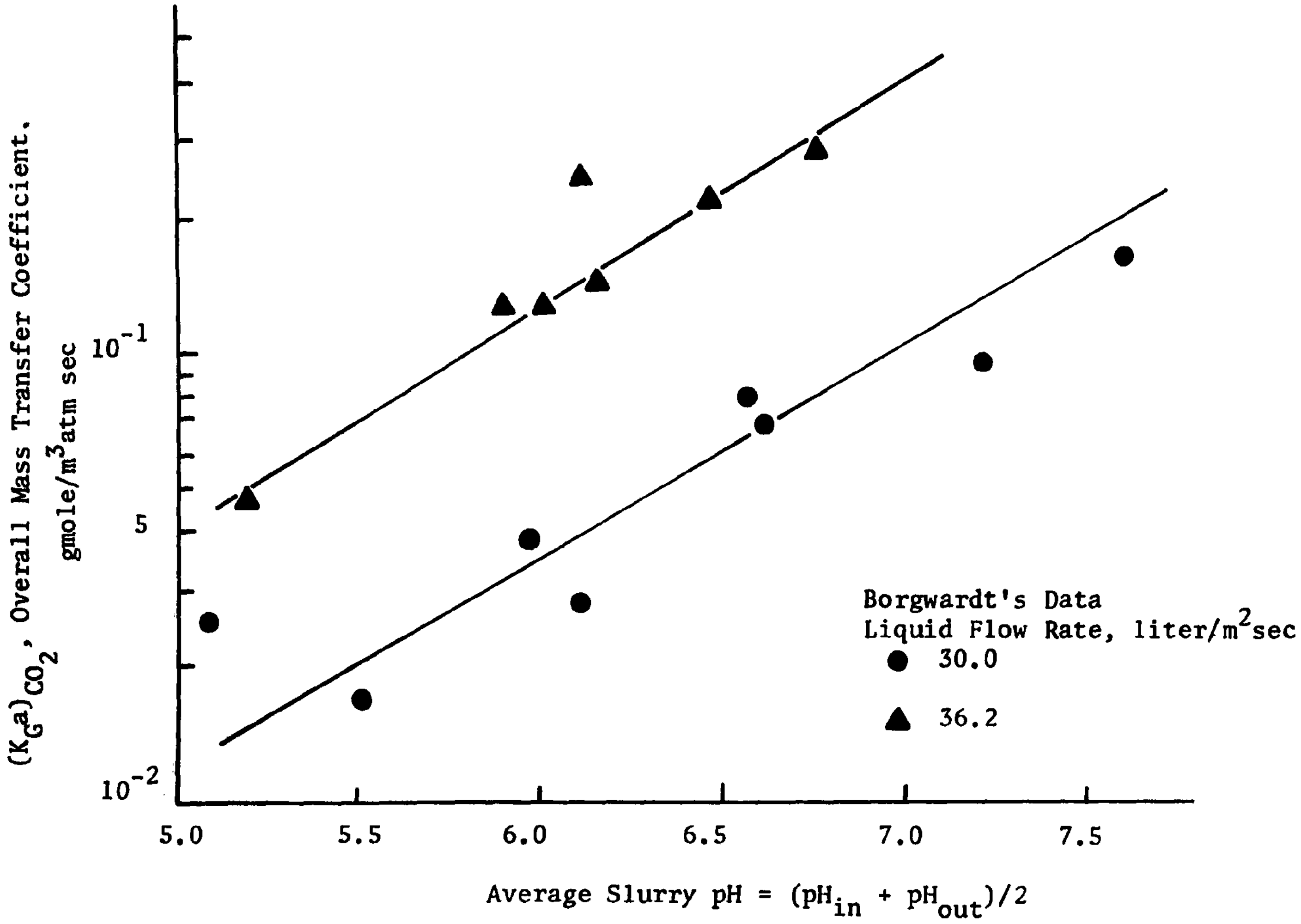


Figure 4.3: Effect of Slurry pH and Flow Rate on the Overall Mass Transfer Coefficient for CO_2 Absorption into Recycled Lime Slurries in a TCA Scrubber.

CHAPTER 5

SIMULATION AND DESIGN OF RECYCLED LIME SCRUBBING SYSTEM

A simplified schematic of a scrubber-hold tank system is shown in Figure 5.1. Flue gas loaded with SO_2 passes counter-currently to recycled lime slurry flowing downward in a TCA scrubber. At the top of the scrubber the slurry has a pH value in the range of 6.0 to 10.0. The slurry effluent from the scrubber passes to the hold tank where lime and make up water are added, and the high pH of the scrubbing slurry is recovered. The solid loading in the scrubbing slurry is approximately 10%. A portion of this slurry is fed to the solid separation system from which a waste sludge is discharged. The clear liquor produced in this step is recycled to the system.

In essence, the SO_2 absorbed from the flue gas is converted to calcium sulfite and sulfate which are extremely insoluble in the slurry. The precipitation of calcium sulfate is one of the problem areas in lime scrubbing in that calcium sulfate forms a hard, stubborn coating on the process equipment. Methods of preventing sulfate precipitation include reducing oxidation of sulfite to sulfate and operating the system in the sulfate unsaturated mode. In this mode calcium sulfate is incorporated into the crystal structure of calcium sulfite. Borgwardt (1974 b) has discussed the sulfate unsaturated mode of operation in lime scrubbing systems.

5.1 Material Balances

Given the inlet conditions of the slurry and flue gas, setting the operating parameters for the scrubber and neglecting the small

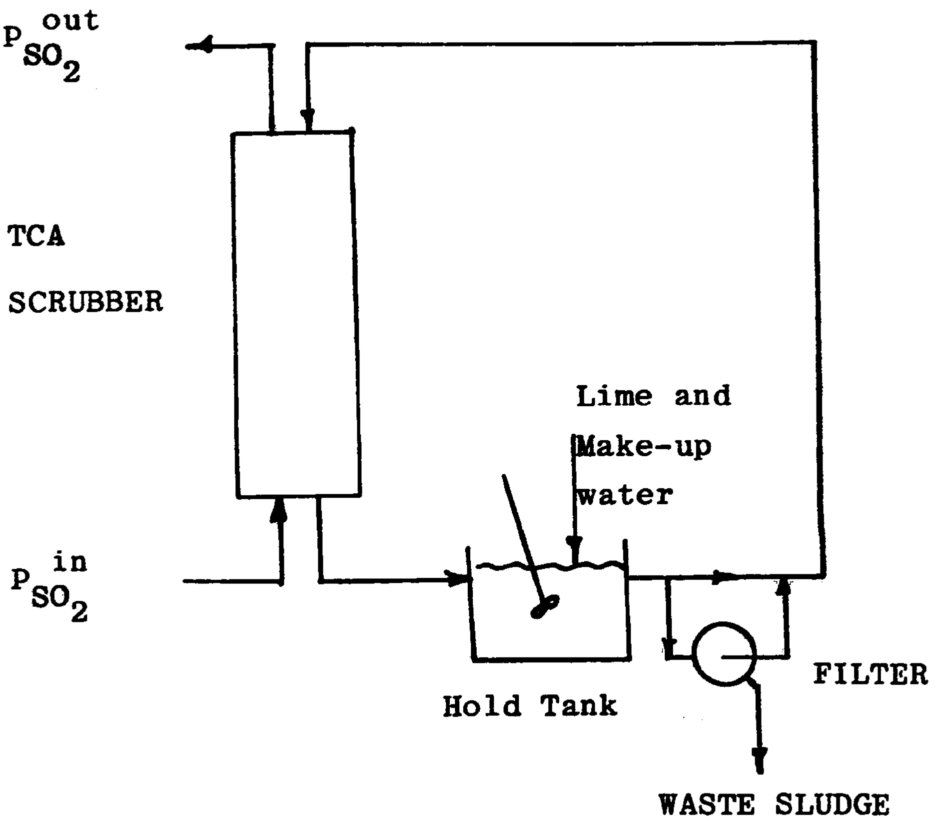


Figure 5.1:A Simplified Lime-TCA Flue Gas Desulfurization System.

change in the magnesium concentration across the scrubber, Equation (4.1) (or equivalently Equation (4.4) represents a relationship between two unknowns: 1) SO_2 removal efficiency and 2) outlet slurry pH. To provide a second relationship between these variables, McMichael et al. (1975) proposed that sulfur and carbon balances around the scrubber could be subtracted from the calcium balance to give

$$M_{SO_2} + M_{CO_2} = L' \, (\Delta_{out} - \Delta_{in}) \tag{5.1}$$

where Δ_{in} and Δ_{out} are the concentration of total dissolved sulfur plus carbon minus the concentration of total dissolved calcium in the inlet and outlet slurry of the scrubber, respectively,in gmole/liter. It is observed that the CO_2 absorption and the "Δ" concentration can be related to the pH in lime systems through equilibrium calculations (Nelson (1974)). Equation (5.1) becomes

$$M_{SO_2}/L' = (\Delta_{out} - \Delta_{in}) \tag{5.2}$$

By solving Equations (4.4) and (5.2) simultaneously the SO_2 absorption efficiency and outlet pH of the scrubbing slurry can be predicted with reasonable accuracy.

Taking material balances around the entire scrubber-hold tank system and subtracting the calcium balance from the sum of the carbon and sulfur balances gives

$$M_{SO_2} + M_{CO_2} = F_{CaO} + P\Delta pg \tag{5.3}$$

The second term on the right hand side of this equation is usually extremely small compared to the lime feed rate, F_{CaO}. Thus, Equation (5.3) can be reduced to

$$M_{CO_2} + M_{SO_2} = F_{CaO} \tag{5.4}$$

Equation (5.4) ignores the losses which experimentally have been found to be only about 5% of the total lime feed.

A comment is needed at this point to explain why the rate of CO_2 absorption can be ignored in the development of Equation (5.2) but not in Equation (5.4). Equation (5.2) was developed to provide estimates of the SO_2 removal efficiency. Since the rate of absorption of SO_2 is much larger than that of CO_2, we may neglect the CO_2 contribution in Equation (5.2) for convenience and still obtain reasonable estimates. However, in Equation (5.4), the CO_2 absorption cannot be ignored because it is critical in determination of the calcium utilization.

The equilibrium calculations used in Equations (5.1) and (5.2) are those of Nelson (1974). In this calculation several variables must be specified. These include pH, CO_2 partial pressure and the total concentration of dissolved magnesium and chloride. The total sulfate concentration must also be specified. The procedure for the specification of the total concentrations of magnesium and chloride in the slurry are discussed in the following section.

5.2 Prediction of the Concentrations of Magnesium and Chloride in the Scrubbing Slurry

The flue gas may contain chlorine compounds which are absorbed in slurry of the TCA scrubbers. Magnesium is fed to the system in the form of magnesium oxide along with lime. The concentration of chloride and magnesium will build up and will not reach a steady state until the losses from the purge can be balanced.

Since chloride and magnesium have high solubilities in the slurry, it may be assumed that their concentrations in the solid phase of purge from the system are very low. Based on this assumption, the following mass balance is formulated

$$P\ M\ C_x = F \tag{5.5}$$

where P is the solid purge rate, Kg/sec,

M is the liquor content in the purge, based on the dry solid, liter of liquid/Kg. of solid,

C_x is the concentration of magnesium or chloride in the liquor phase, gmole/liter,

and F is the feed rate of magnesium or chloride into this system, gmole/sec;

If we make an assumption that the solid purge rate is proportional to the lime fed (F_{CAO} (gmol/sec)] and since more than 95% of calcium in the feed will be purged out as solid, Equation (5.5) can be written in the following form

$$F = K'M\ F_{CaO}\ C_x \tag{5.6}$$

$$= K''\ F_{CaO}\ C_x \tag{5.7}$$

where K' is the proportionality constant defined by Equation (5.6), Kg/gmol,

K" is defined as the product of K and M, liter/gmol.

Rearranging Equation (5.7),

$$\frac{F}{F_{CaO}} = K''\ C_x \tag{5.8}$$

A plot of C_x vs. $\frac{F}{F_{CaO}}$ is shown in Figure 5.2. The line can be correlated by the least square fit of data.

$$C_{Cl\ \text{or}\ Mg} = 2.6\ F_{CaO} \tag{5.9}$$

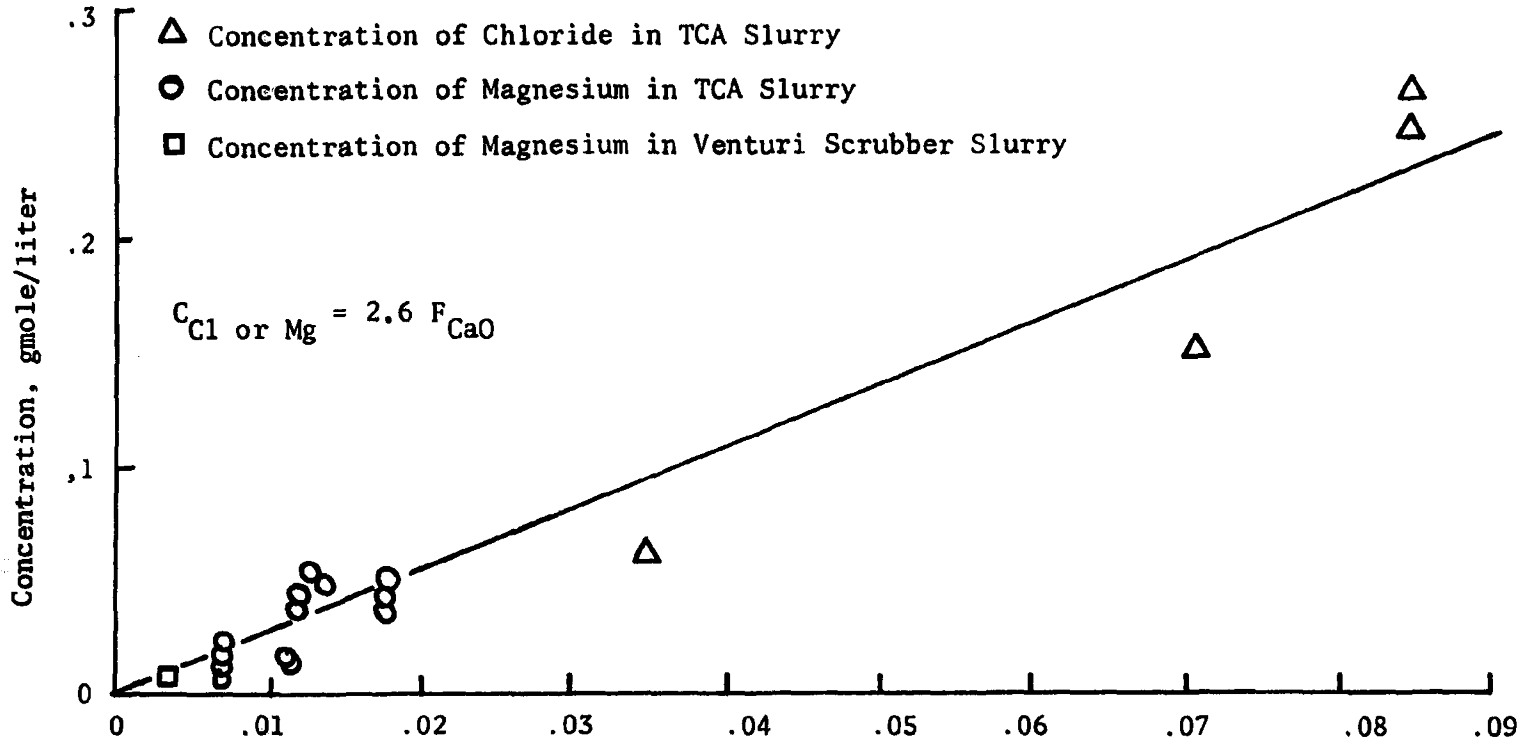


Figure 5.2: $\frac{\text{(Magnesium content in the lime fed + MgO fed rate) or (Cl fed rate), gmole/sec}}{\text{Lime feed rate, gmole/sec}}$

Concentrations of Magnesium and Chloride in the Recycle Slurry

Equation (5.9) can be used to predict the concentration of magnesium in the slurry of a TCA and the venturi scrubber as shown in Figure 5.2.

5.3 Simulation

Using the procedures outlined above,the operation of a scrubber-hold tank FGD system using lime slurry can be simulated according to the following sequence of steps:

1) Specify values of the independent variables,such as P_{SO_2}, P_{CO_2}, gas and slurry flow rates, lime feed rate, size of the scrubber, etc.

2) Assume the inlet pH to the scrubber.

3) Calculate SO_2 removal efficiency and the outlet pH of the scrubber by solving Equations (4.4) and (5.2) simultaneously.

4) Use Equation (4.23) to calculate the CO_2 absorption.

5) Determine whether Equation (5.4) is satisfied. If it is not, assume another inlet pH to the scrubber and proceed from Step 3. If Equation (5.4) is satisfied, then the simulation is complete.

The flow diagram for this simulation is given in Figure 5.3. This simulation procedure has been applied to the Borgwardt's data (1974 b,d),which were obtained from the TCA scrubber hold-tank system utilizing lime slurry to desulfurize flue gas. The results of simulating Borgwardt's data are given in Figures 5.4 and 5.5. It can be seen from the Figure 5.4 that the SO_2 removal efficiency can be predicted within 5% of the observed value. As shown in Figure 5.5 the inlet and outlet pH of the scrubbing slurry cannot be predicted as

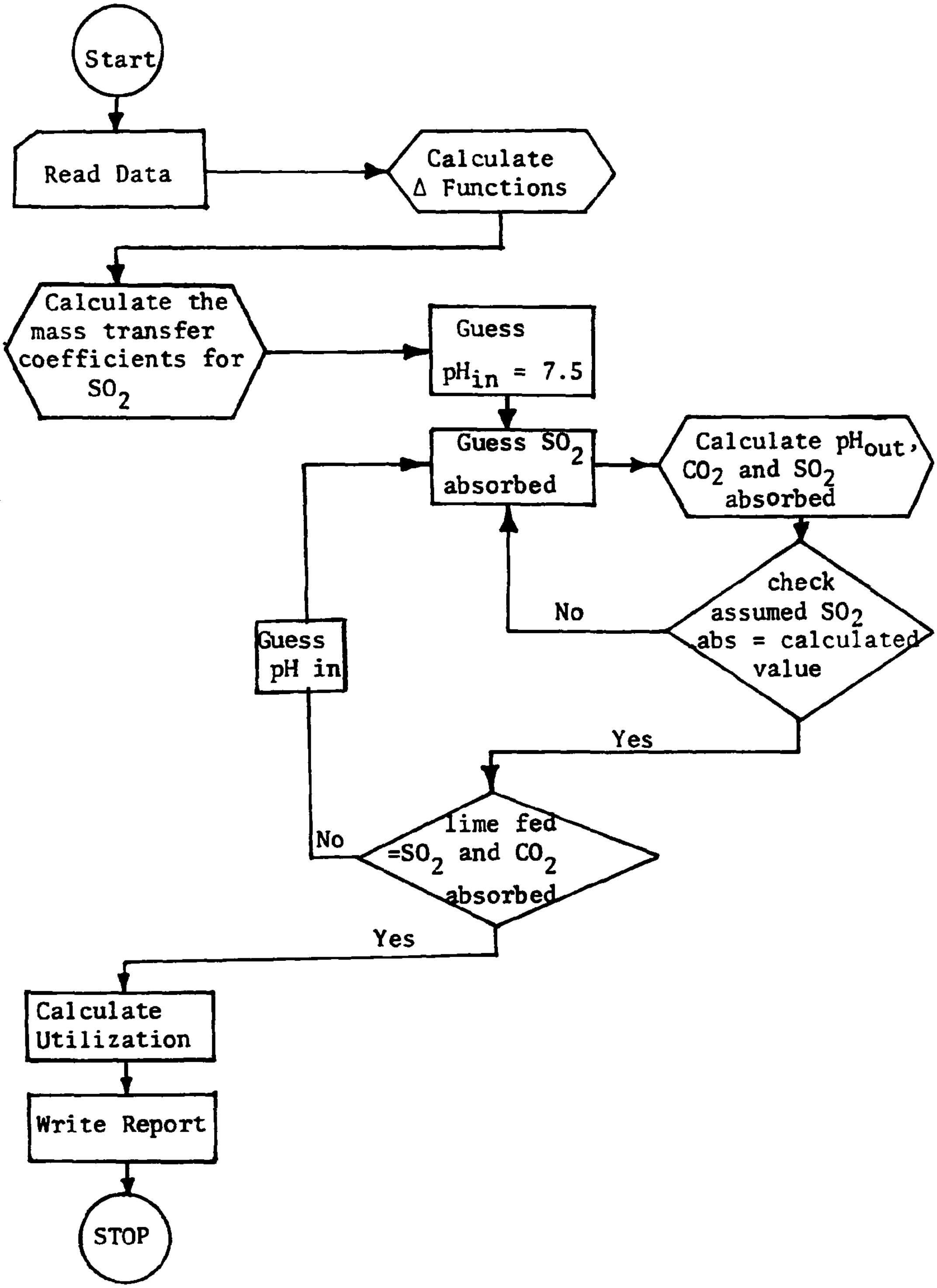


Figure 5.3: Flow Diagram for the Simulation of Wet Lime Scrubbing Process.

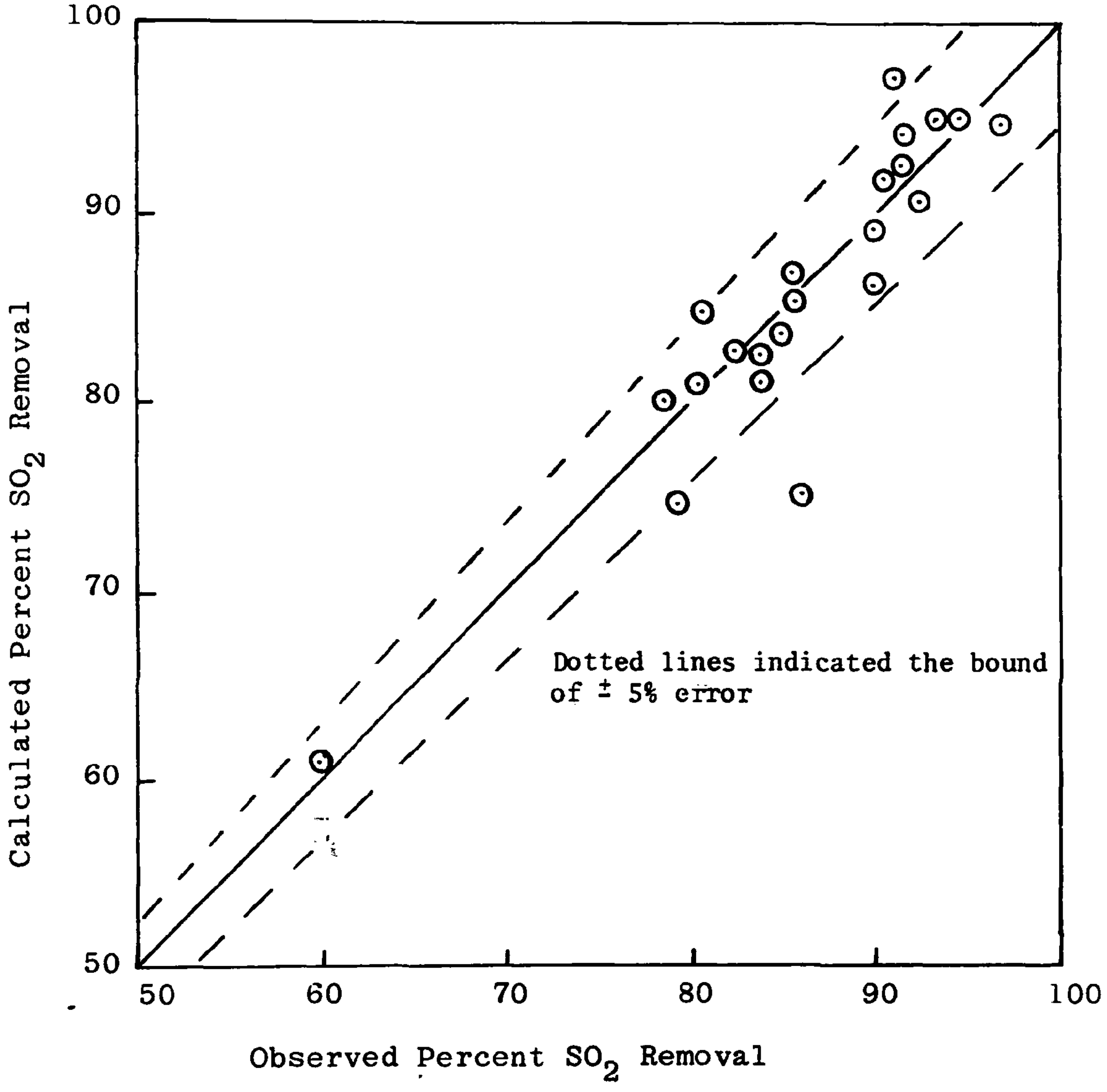


Figure 5.4: Comparison Between the Observed and Calculated SO_2 Removal Efficiencies in TCA Lime Slurry Scrubber.

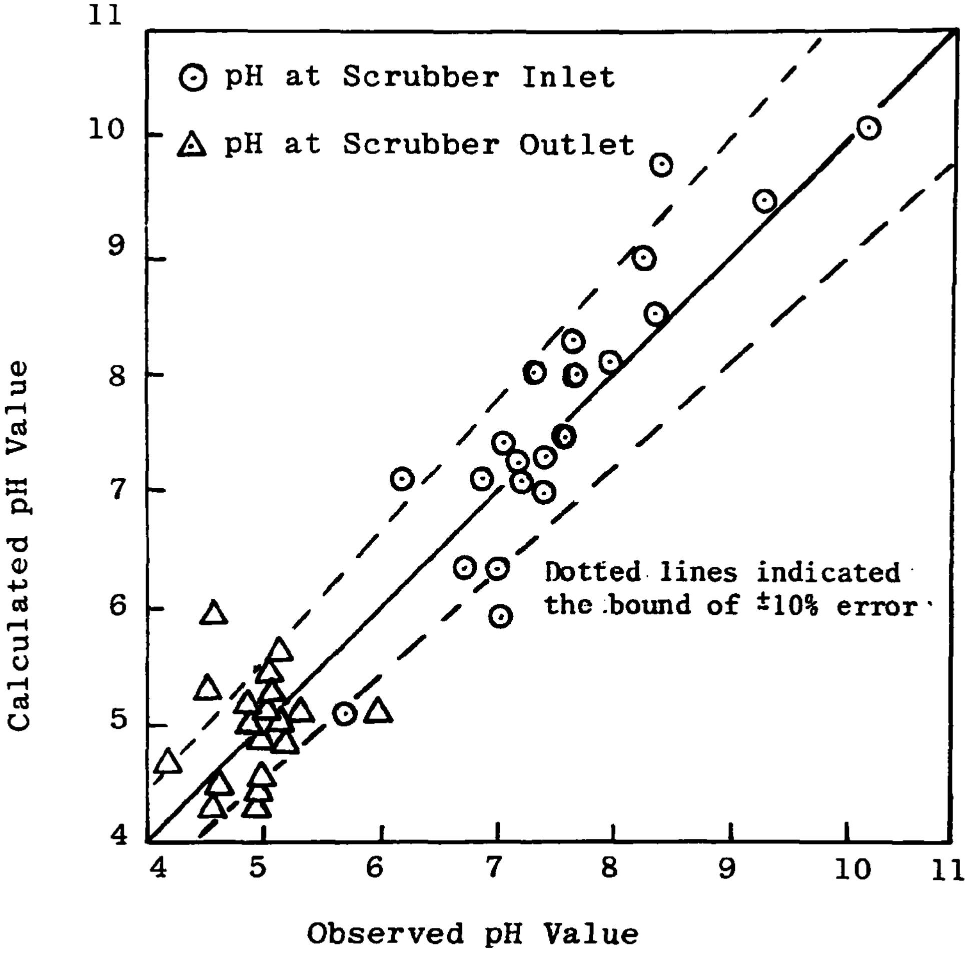


Figure 5.5: Comparison of the Observed and Calculated pH at the Entrance and Exit of the TCA Lime Scrubber.

accurately as the removal efficiency.

In preparing Figures (5.4) and (5.5) the calculated concentrations of chloride and magnesium were used in the equilibrium calculations. The concentration of the components are calculated by employing Equation (5.9) assuming that the precipitation of the magnesium and chlorine can be ignored. It is also assumed that at the steady state, all chlorine in the flue gas is eventually absorbed in the scrubber and can be balanced by the losses from the purge. The sulfate concentration in the slurry is assumed as the saturated value. Since the degree of saturation of the observed sulfate concentration varies on average around its saturated value to within 20%, the assumption of saturated sulfate is quite acceptable.

5.4 Design of Lime Slurry FGD Systems Using TCA Scrubbers

Using the simulation procedure discussed in the previous section charts can be prepared with which lime slurry FGD system utilizing spray or TCA scrubbers can be designed. In the remainder of this study it will be assumed that there is no chlorine or magnesium in the slurry to keep complications at a minimum. However, the methods discussed here can easily be applied to cases where the scrubbing slurry contains chlorine or magnesium compounds. The sulfate concentrations in the slurry are determined by assuming sulfate saturation. In a commercial application the sulfate levels will probably be maintained only slightly below saturation because of the expense of adding magnesium to the system to reduce the saturation. Therefore, the saturated concentration of sulfate should be a reasonable approximation to the sulfate concentration in an actual system.

The procedure, by which design charts can be constructed, is given below:

1) Specify SO_2 removal efficiency, slurry flow rate, lime feed rate, equivalent packing height, inlet SO_2 partial pressure and pressure drop above the normal pressure drop.

2) Assume a gas flow rate.

3) Compute the SO_2 removal efficiency by the five step simulation procedure given in the previous section.

4) If the SO_2 removal efficiency calculated in Step (3) does not agree with the SO_2 removal efficiency specified in Step (1), go to Step (2). If the calculated and specified SO_2 removal efficiencies agree reasonably well, then the simulation is complete. The result of carrying out this procedure is shown in Figure 5.6. It can be seen from this figure that for a given lime feed rate there exists a maximum in the amount of gas that can be treated. The locus of these maximum points is presented in Figure 5.7 as solid lines. Thus for a given slurry flow rate and equivalent packing height the maximum amount of gas that can be treated (at 90% efficiency) and the lime stoichiometry can be read directly from Figure 5.7.

A significant observation concerning the operation of a lime scrubbing FGD system, which can be drawn from Figure 5.7 is that for a given gas treatment rate a decrease in the specific flow rate

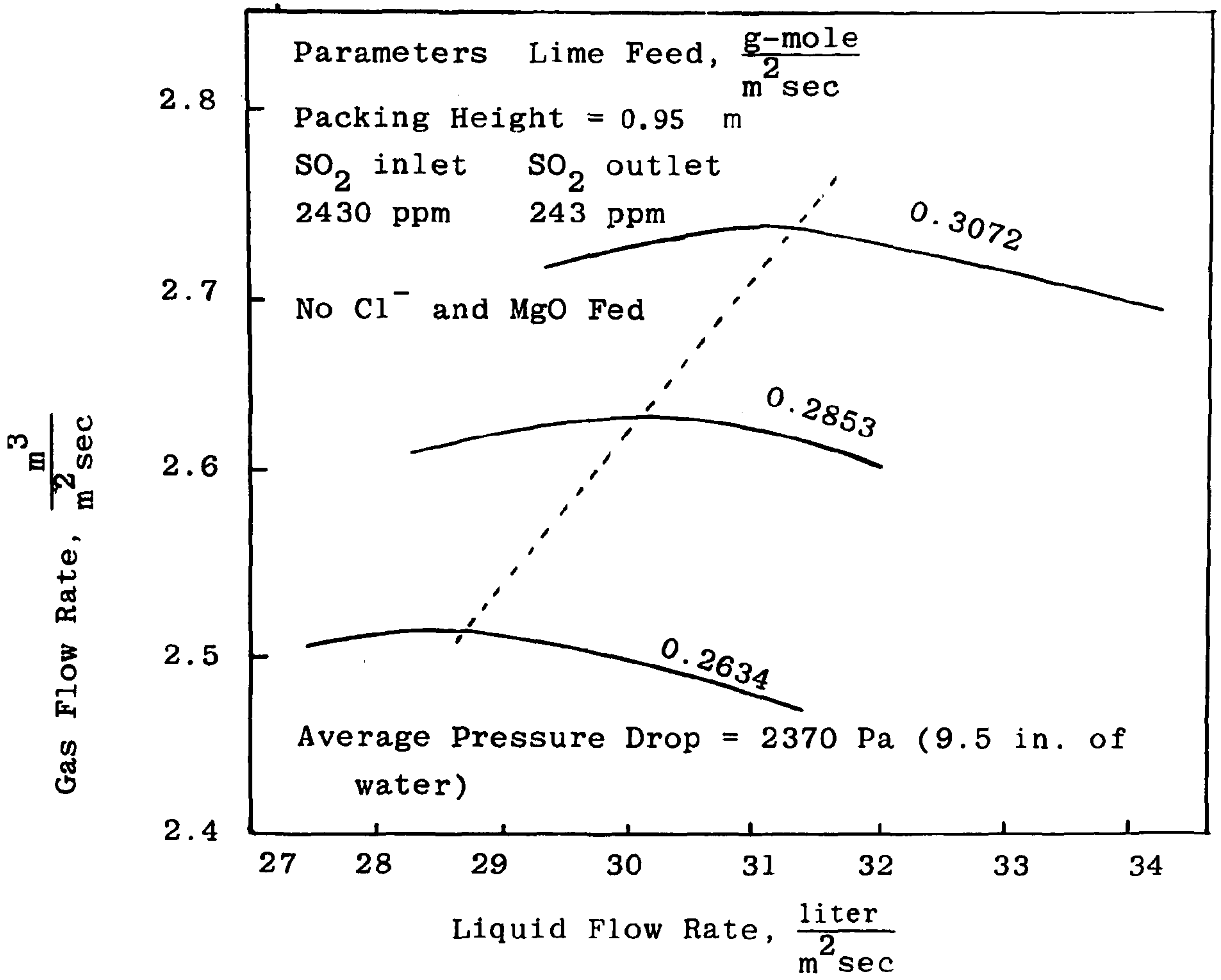


Figure 5.6: Simulation of Lime Slurry TCA Scrubber Indicating Maximum Flue Gas Flow Rates.

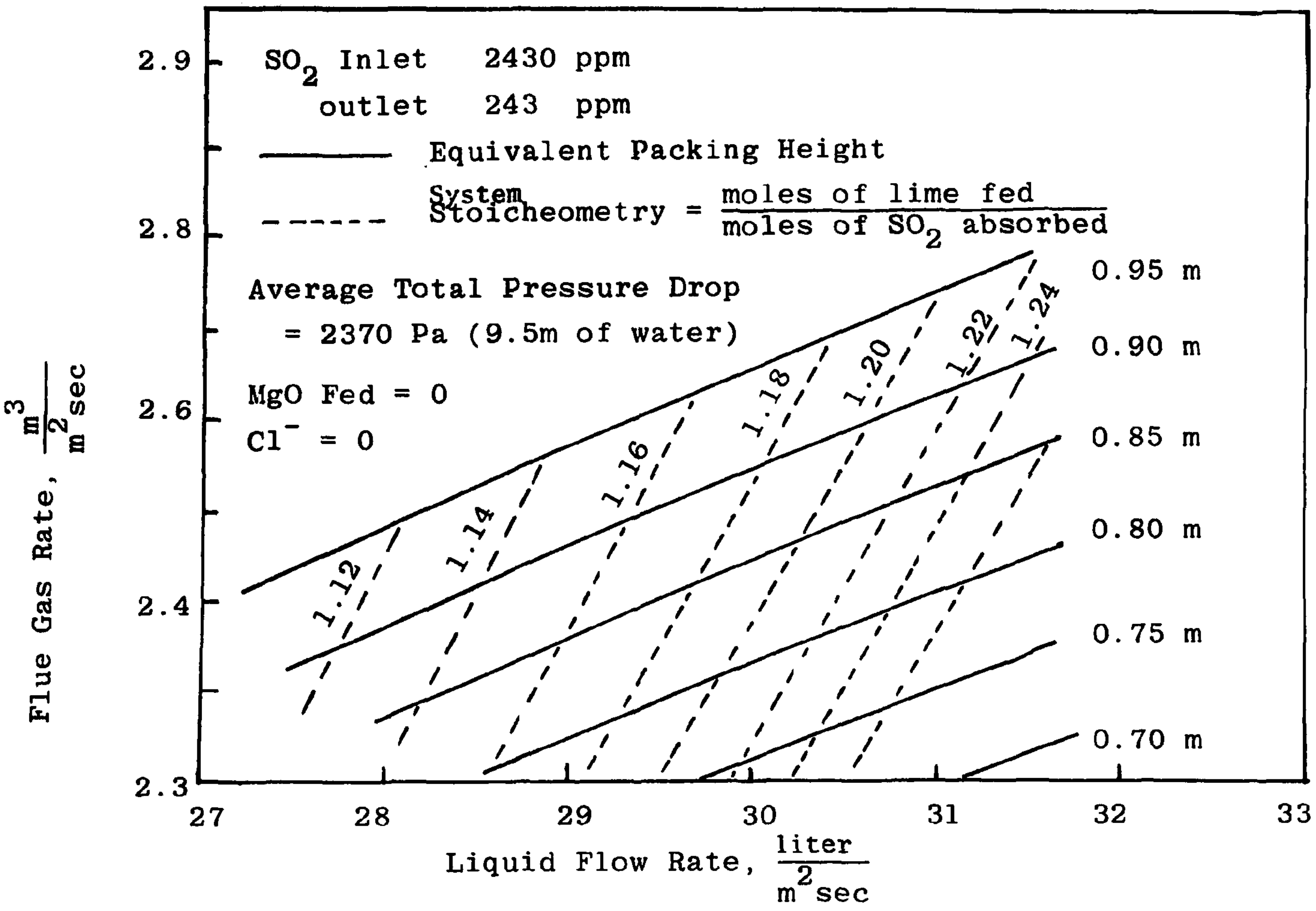


Figure 5.7: Operating Lines for Lime TCA Scrubber at Various Equivalent Packing Heights.

of the lime slurry in the TCA scrubber decreases the "system stoichiometry"(i.e.,increases lime utilization) but increases the equivalent packing height necessary to achieve the prescribed SO_2 removal efficiency (e.g., 90% in Figure 5.7. Thus decreasing the lime slurry circulation rate decreases operating costs (increases lime utilization) but increases capital costs (i.e., larger scrubber volume). It can be seen from this observation that the possibility of having an optimal slurry circulation rate exists. This optimal rate will be also dependent upon the effect of gas and liquid flow rates on the pressure drop across the TCA (or the power requirements). The power requirements will be minimized at low values of the slurry and gas flow rates.

In the design of TCA FGD systems,operating costs will likely be more important than the capital cost requirements of the TCA scrubber. Hence, the preferred region of operation of a lime scrubbing FGD system, which uses a TCA scrubber, will be at the lower left hand corner of Figure 5.7.

For purposes of illustration, suppose that the economic evaluation is carried out on the lime-TCA FGD system and that the optimal liquid flow rate and stoichiometry are found to be 27.8 liter/m^2sec and 1.12,respectively. Thus,from Figure 5.7,the gas rate should be 2.4 m/sec and the equivalent packing height should be 0.88 m. For a scrubber treating the flue gas of a 50 MW train of a power station (89,000 SCF/min or 42.01 m^3sec.) a scrubber diameter of 4.72 meters would be necessary. The actual height of the scrubber would have to be determined by mechanical considerations; however,the equivalent height of packing represented by the spray sections plus the height of the unexpanded packing pieces in the TCA would have to total to 0.88 meters.

5.5 Effect of Variations in the Parameters of the Models for SO_2 and CO_2 Absorptions on the Outcome of the Simulation

In the simulation procedure, the parameters, such as the mass transfer coefficients for the CO_2 and SO_2 absorptions, were correlated from experimental data (Borgwardt 1974b,d) by the least square method as a function of flow characteristics, pH values and the concentration of magnesium in the recycling slurries. Thus, it is expected that the result of the simulation may deviate from the actual performance of the scrubber due to the uncertainty of the parameters. In this section, the variations in the results of the simulation due to the changes in the model parameters are studied. The parameters investigated include:

1) the mass transfer coefficient, $k_g^p a$, for SO_2 absorption in the packing section.
2) the mass transfer coefficient, $k_g^s a$, for SO_2 absorption in the spray section.
3) the overall mass transfer coefficient, $(K_G a)_{CO_2}$, for CO_2 absorption.
4) the magnesium effect factor, Δ_p, in the packing section.
5) the magnesium effect factor, Δ_s, in the spray section.
6) the pH effect factor, A_p, in the packing section.
7) the pH effect factor, A_s. in the spray section.
8) the coefficient, α, on the exponential term relating to the inlet partial pressure of SO_2, $\exp(\alpha P_{SO_2,in})$.

Perturbation of a given parameter at ±10% of the estimated value was made to test the sensitivity of the model performance. The ±10% perturbation of each parameter is chosen because it is the approximate average error of the correlation value of each of the parameters. The remaining parameters were kept constant at the best estimated values. The result of the perturbation test at the equivalent packing heights of 0.75m. and 0.95m. are shown in Figures 5.7 through 5.15. From these figures, it is clear that all the parameters tested are not sensitive with respect to the liquid and gas flow rates required for 90% absorption of SO_2 in flue gas.

The effect of variations in these parameters on the SO_2 removal efficiency is also tested. The results are listed in Table 5.1. The operating conditions selected are similar to those used by Borgwardt (1974b). From this table, it is seen that the most sensitive parameter is the overall mass transfer coefficient for CO_2 absorption, $(K_G a)_{CO_2}$. A perturbation of ±10% of this value results in approximately ±3.8% variation in the SO_2 removal efficiency while the same amount of perturbation in other parameter changes the removal efficiency by less than ±2%.

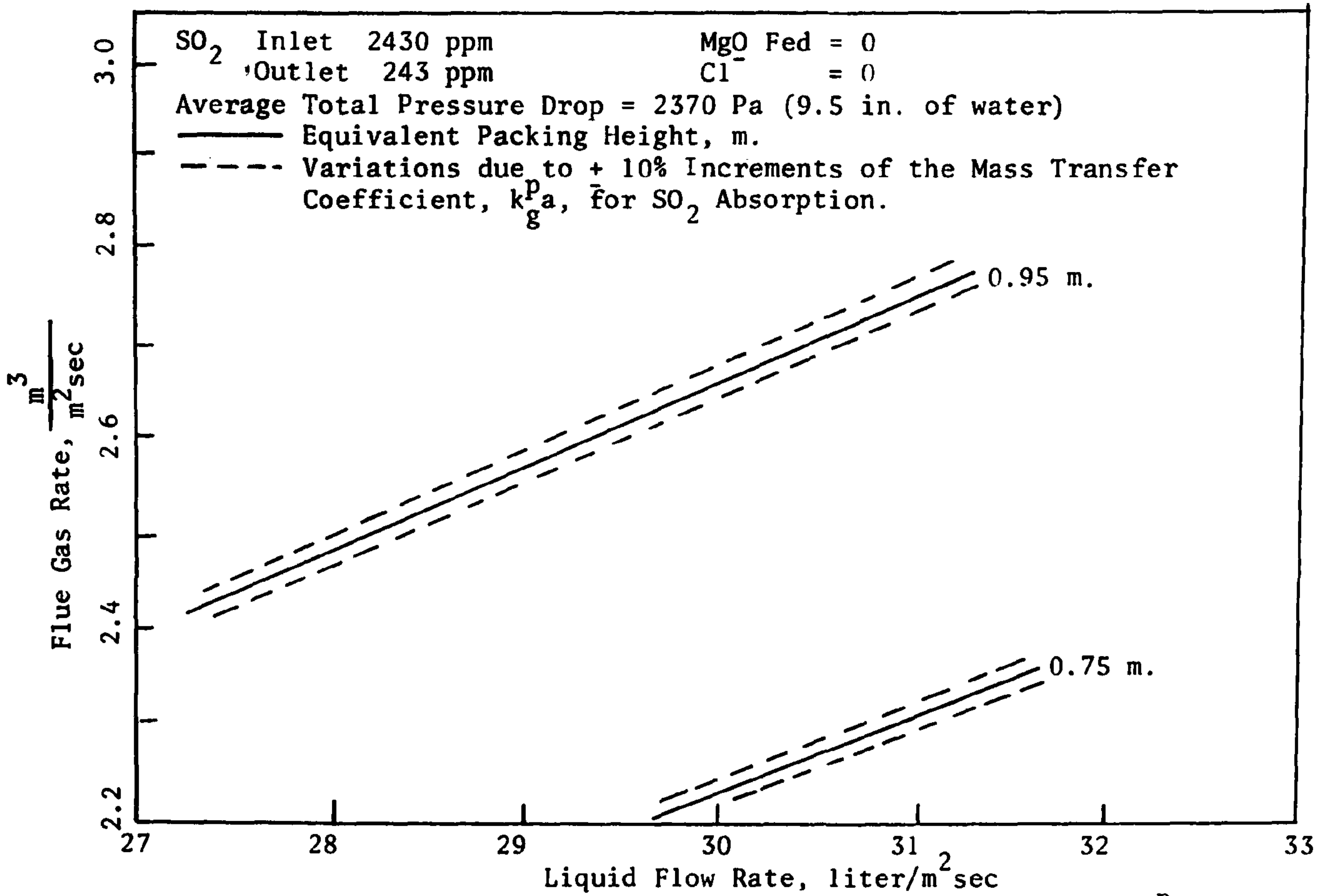
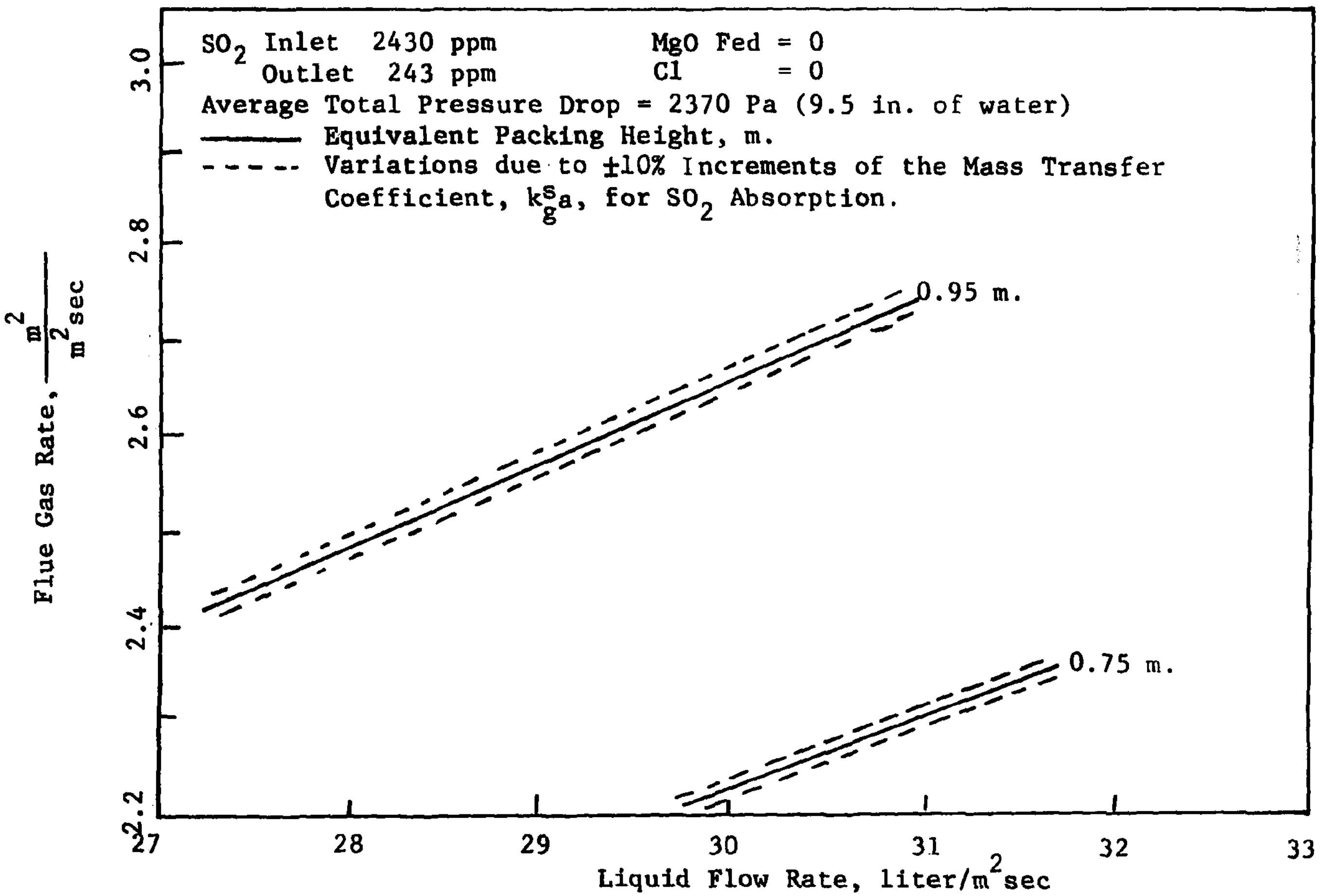


Figure 5.8 Effect of the Variations of the Mass Transfer Coefficient, $k_g^p a$, for SO_2 Absorption on the System Operating Lines.



Firure 5.9 Effect of Variations of the Mass Transfer Coefficient, $k_g^s a$, for SO_2 Absorption on the System Operating Lines.

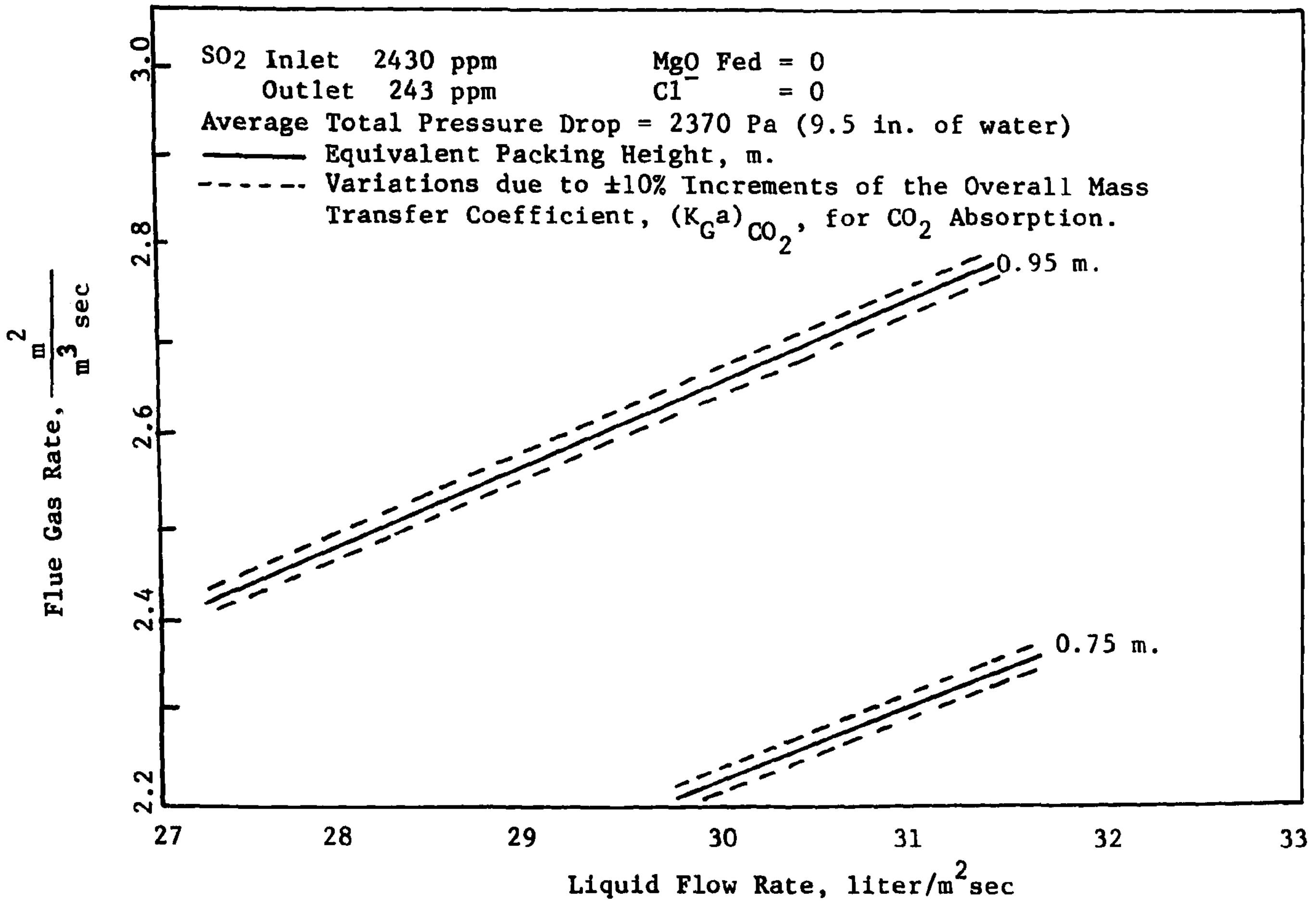


Figure 5.10 Effect of Variations of the Overall Mass Transfer Coefficient, $(K_Ga)_{CO_2}$, for CO_2 Absorption on the System Operating Lines.

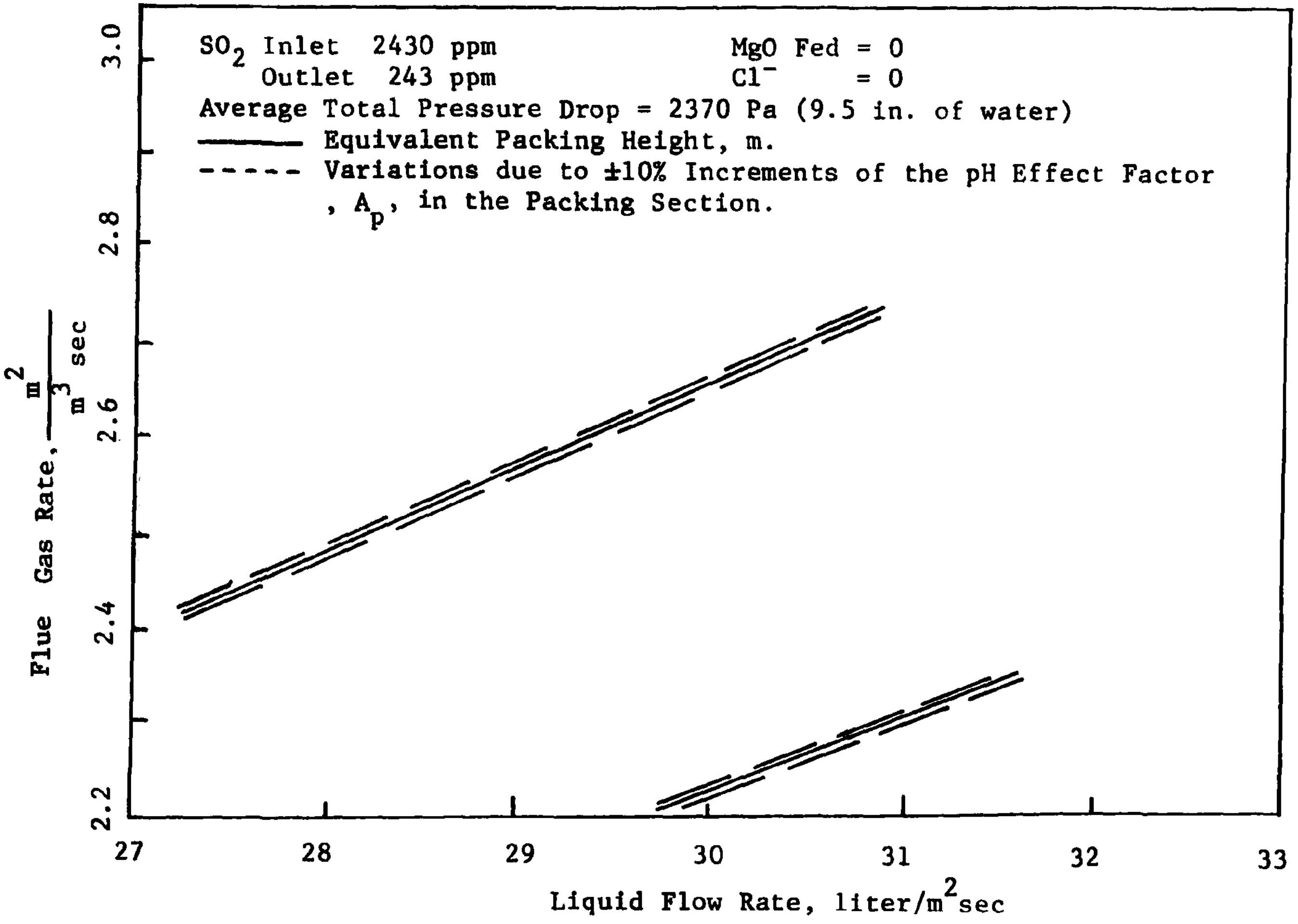


Figure 5.11 Effect of Variations of the pH Effect Factor, A_p, in the Packing Scetion for SO_2 Absorption on the System Operating Lines.

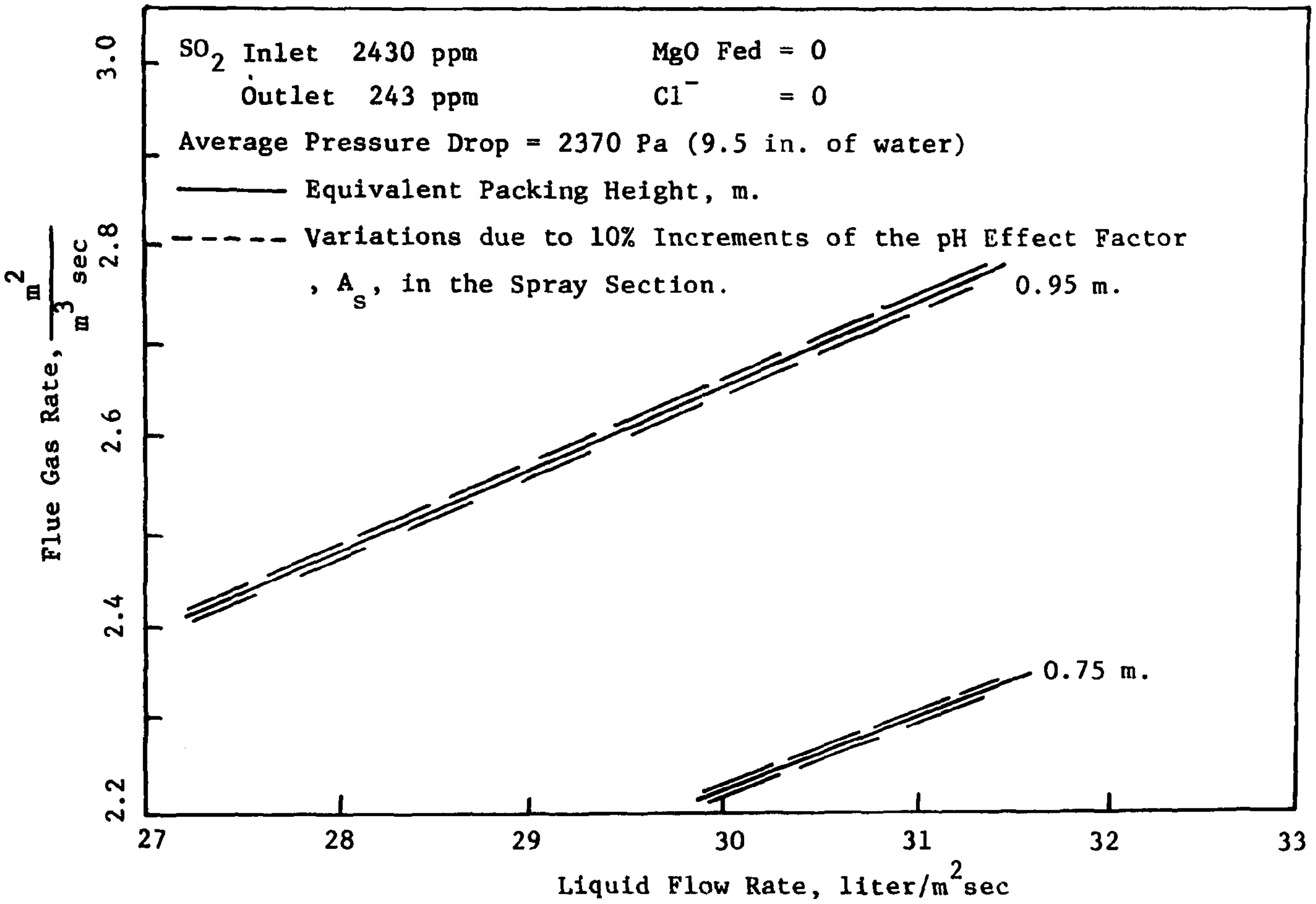


Figure 5.12 Effect of Variations of the pH Effect Factor, A_s, in the Spray Section for SO_2 Absorption on the System Operating Lines.

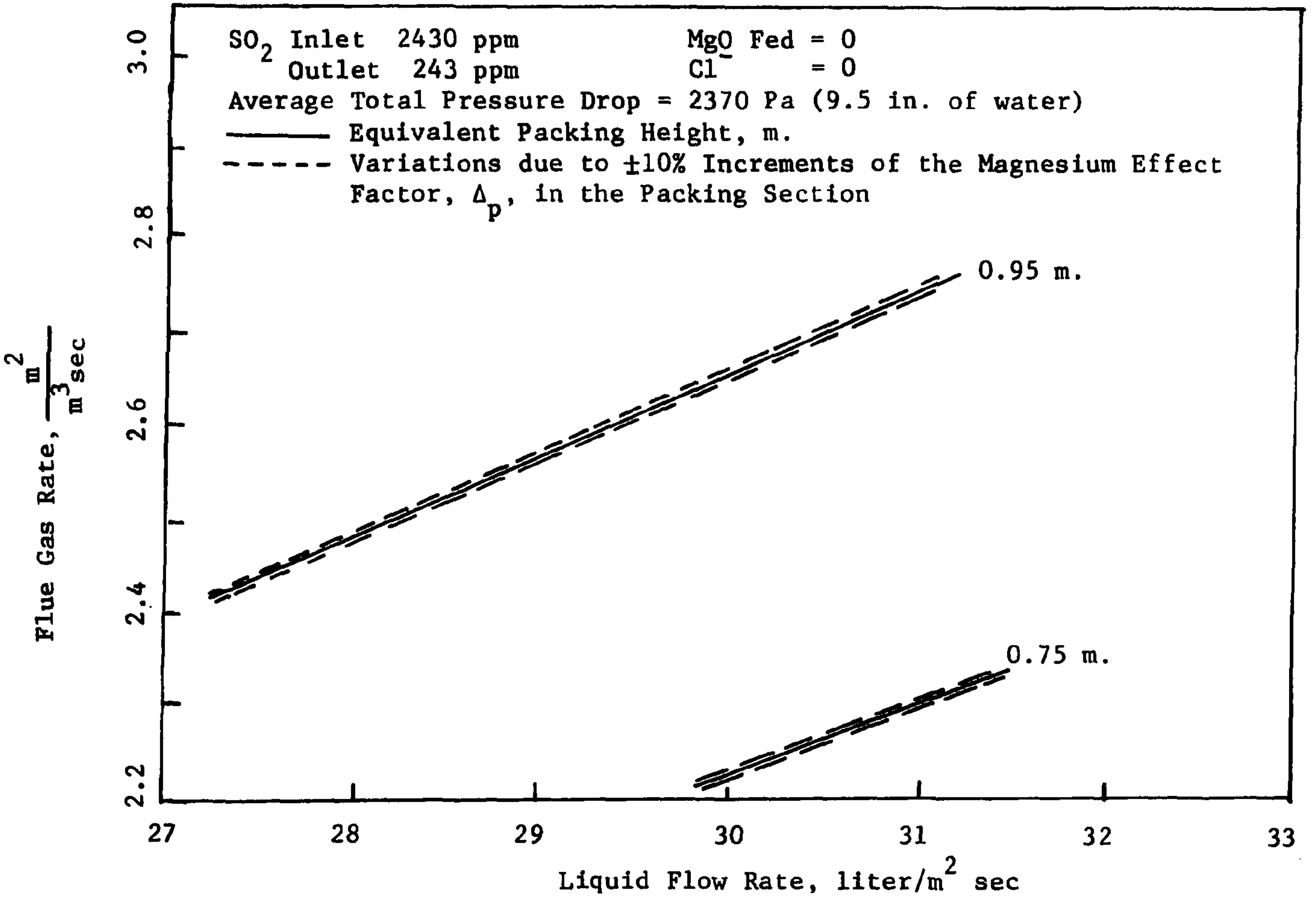


Figure 5.13 Effect of Variations of the Magnesium Effect Factor, Δ_p, in the Packing Section on the System Operating Lines.

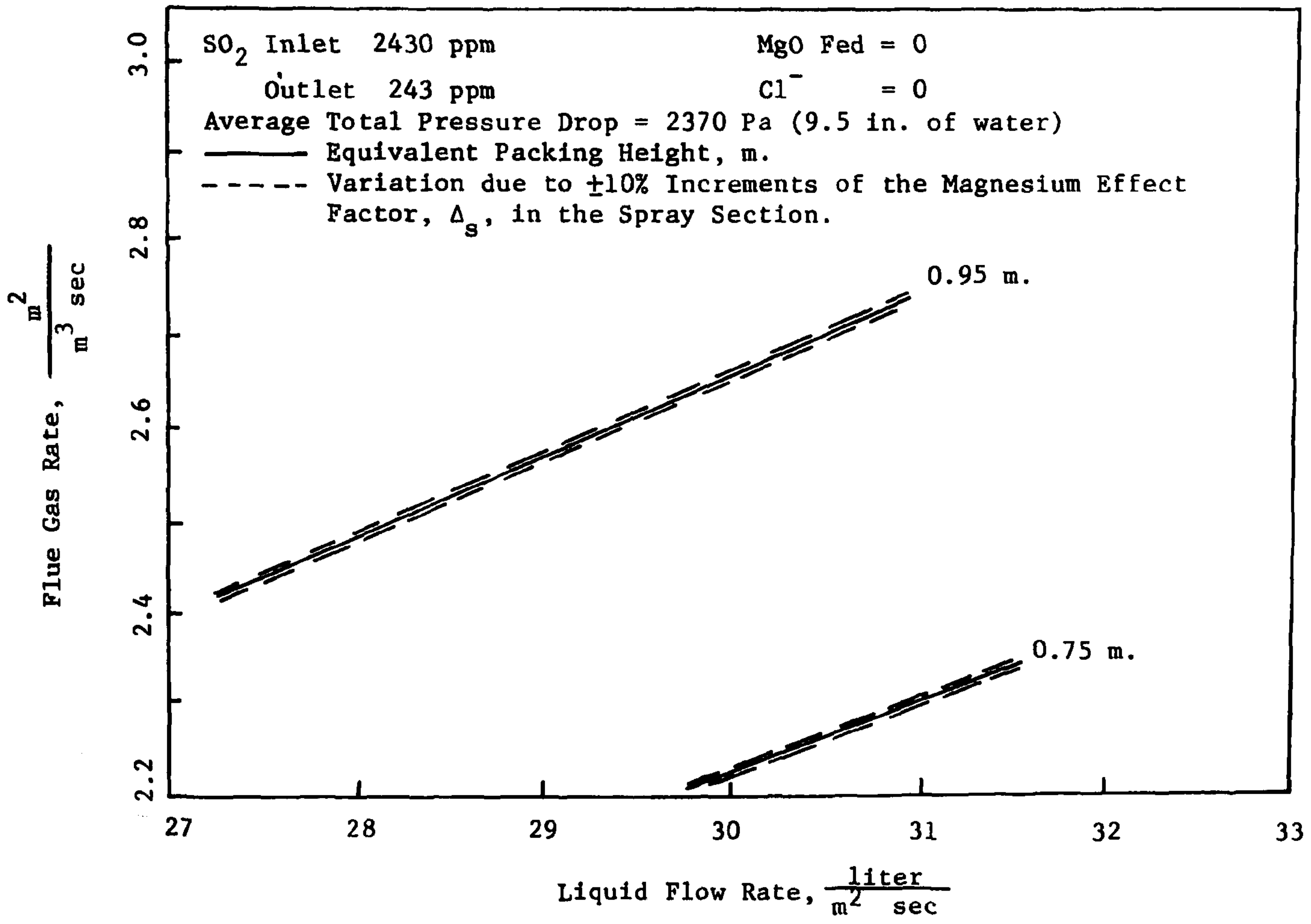


Figure 5.14 Effect of Variations of the Magnesium Effect Factor, Δ_s, in the Spray Section on the System Operating Lines

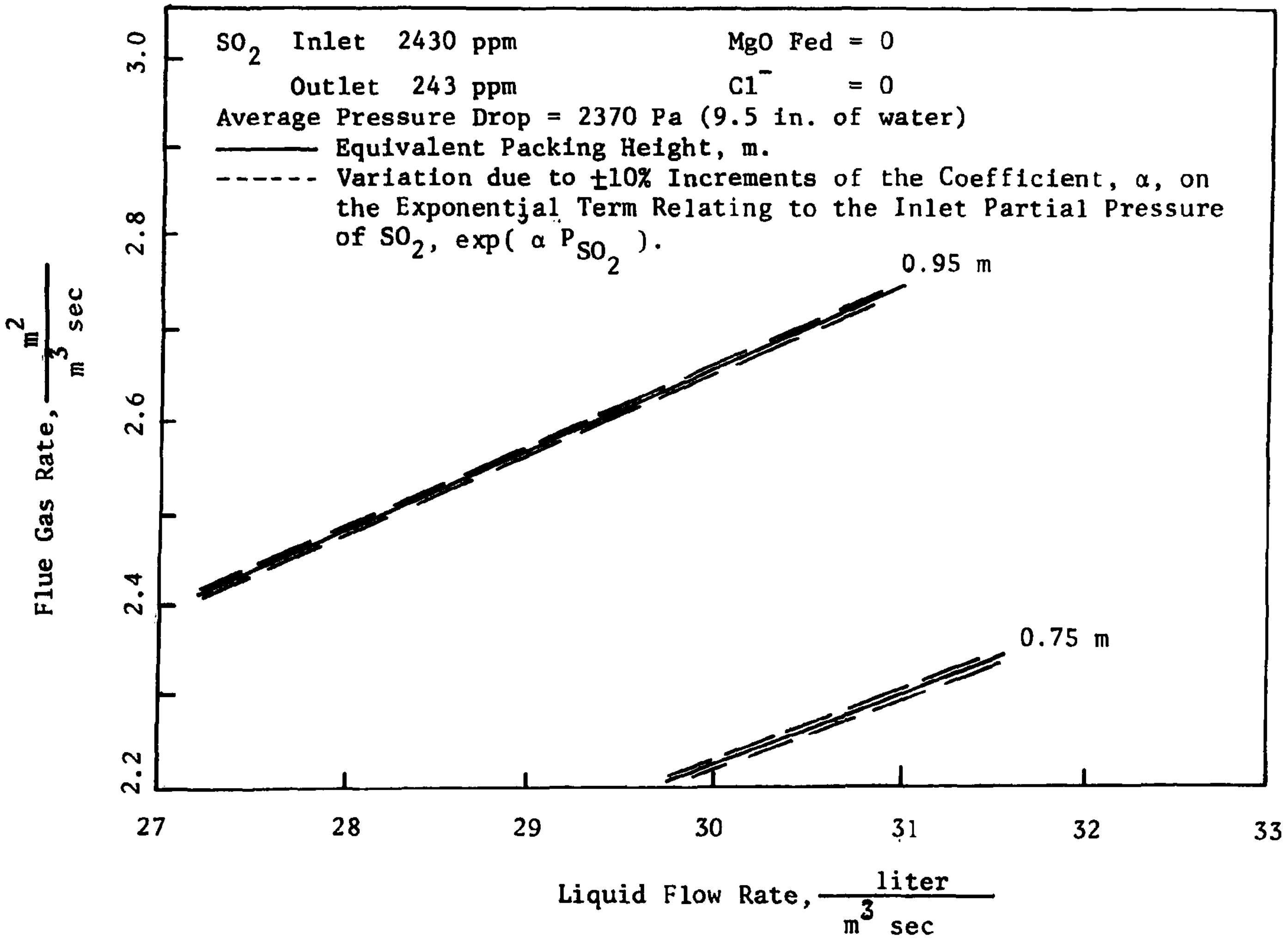


Figure 5.15 Effect of Variations of the Coefficient, α, on the Exponential Term Relating to the Inlet Partial Pressure of SO_2, $\exp(\alpha P_{SO_2})$.

Table 5.1

Sensitivity of Parameter Accuracy on the SO_2 Removal Efficiency

Perturbation of the Parameter from the Estimated Value = ±10%

SO_2 Removal Efficiency Based on the Estimated Values of the Parameters = 90%

Gas Flow Rate = 2.8 m/sec

Liquid Flow Rate = 30 liter/m^2sec

Equivalent Packing Height = 0.95 m.

Negligible M_g and Cl in the Slurry

		SO_2 Removal Efficiency(%)	
Parameter	Estimated Value of the Parameter	+10% Perturbation of the Parameter	-10% Perturbation of the Parameter
$k_g^p a$	10.922 (gmole/m^3atm sec)	91.7	88.1
$k_g^s a$	1.409 (gmole/m^3atm sec)	91.0	88.9
$(K_G a)_{CO_2}$	0.127 (gmole/m^3atm sec)	93.6	86.1
A_p	1.954 (Dimensionless)	90.6	89.3
A_s	16.78 (Dimensionless)	90.1	89.9
Δ_p	1.0 (Dimensionless)	89.2	90.5
Δ_s	1.0 (Dimensionless)	89.5	90.4
α	330 (atm^{-1})	89.3	90.6

CHAPTER 6

CONCLUSION AND DISCUSSION

In this study, a mathematical model which can simulate the pressure drop across a large scale TCA used for the scrubbing of SO_2 from flue gas has been proposed. It includes the effects of spray, packing, and grid sections. The pressure drop across a grid with more than 50% opening is very small compared to the pressure drop across the spray and packing sections. It accounts for about 5% of the total pressure drop across the TCA scrubber. A correlation for the pressure drop of a large TCA has been developed and is compared with experimental data covering wide ranges of packing heights, types of grids, and flow conditions up to the loading zone. The calculated pressure drops were in agreement with experimental data for a large TCA within 10%. However, the correlation can not be used to calculate the normal pressure drop in a small scale TCA scrubber with lime slurry. Due to the lack of the experimental pressure drop data taken under no scaling in the small scale TCA, further development of a better correlation could not be undertaken. The scale formation in the small TCA scrubber may be a possible reason for the inadequacy of the pressure drop correlation developed to provide better agreement with the experimental data.

CO_2 absorption from flue gas in the presence of SO_2 was also studied. The CO_2 absorption rate was reduced drastically due to the presence of SO_2 in flue gas. The extremely sensitive nature of its mass transfer coefficient to the liquid flow rate revealed that the operation of the EPA/RTP scrubber was near the loading zone. Thus it is evident that the CO_2 absorption has been examined only in a narrow range of gas and liquid flow rates. A more reliable mass transfer correlation could have been obtained if data in other operating conditions were available. The temperature dependence of the mass transfer coefficient has not been determined since the experimental data were available only in a narrow range of temperature. However, the variation in the temperature of the recycled slurry was very small, ±2°C; thus, the temperature effect on the CO_2 mass transfer coefficient can be neglected.

A procedure by which a complete scrubber-hold tank system for FGD using lime slurries can be designed has been presented. The procedure relies on equilibrium calculations to determine the state of the inlet and outlet conditions of the TCA slurry streams, and semi-empirical methods for determining the extent of SO_2 and CO_2 absorption into the lime slurry in the TCA.

It is found that the simulation procedure could estimate the SO_2 removal efficiency within 5% of the observed efficiency and that the calculated inlet and outlet pH of the scrubber are within 10% of the observed values. The procedure is believed to be good enough for engineering estimations.

Using the simulation procedure developed in this paper, an optimal operating regime can be identified where a maximum amount of gas can be treated for a given lime feed rate. However, this optimal regime is calculated based on the limited experimental values of the mass transfer coefficient for CO_2 absorption. The mass transfer coefficients for CO_2 absorption in the regime other than for that of the experimental conditions are obtained by extrapolation. More experimental values are needed within the operating regime to estimate the optimal operating conditions more accurately.

An optimal scrubber size which minimizes SO_2 removal costs can be estimated. However, these costs are intimately tied to the power requirements associated with pressure drop across the TCA scrubber. Based on the simulation procedures given in this study, it should be possible to design an optimal TCA scrubber-hold tank FGD system.

BIBLIOGRAPHY

Astarita, G.: Mass Transfer with Chemical Reaction. Elseview publishing Co., 1967.

Balabekov, O. S., P. G. Romankov, E. Ya. Tarat and M. F. Mikhlev: J. of Appl. Chem. of U.S.S.R., Vol. 42, 1454 (1969).

Barile, R. G. and D. W. Meyer: Chem. Eng. Progr. Symp. Ser., Vol. 67, No. 119, 134 (1971).

Barile, R. G., Dengler, J. L. and Hertwig, T. A., A.I.Ch.E. Symposium Series, Vol. 70, 154 (1974).

Bergelin, Kegel, Carpenter, and Gazley, Proc. Heat Transfer and Fluid Mech. Inst., A.S.M.E., June 22-24, 19 (1949).

Berkowitz, J., EPA-R2-73-214, Environmental Protection Agency, Washington, DC, April, 1973, "Evaluation of Problems Related to Scaling in Limestone Wet Scrubbing".

Blyakher, L. G., L. Ya. Zhivaikin, and N. A. Yurovskaya: Int. Chem. Eng., Vol. 7, 485 (1967).

Borgwardt, R., Limestone Scrubbing of Sulfur Dioxide at EPA Pilot Plant, Report No. 1 (Aug. 1972 a).

Borgwardt, R., ibid, reports prepared for the EPA Since 1972 b.

Borgwardt, R., ibid, Report No. 6 (Jan. 1973).

Borgwardt, R., ibid, Report No. 14 (Jan, 1974 a).

Borgwardt, R., ibid, Report No. 15 (Feb, 1974 b).

Borgwardt, R., ibid, Report No. 16 (June, 1974 c).

Borgwardt, R., ibid, Report No. 17 (July, 1974 d).

Borgwardt, R., ibid, Report No. 21 (June, 1975 a).

Borgwardt, R., Sulfur Dioxide Scrubber Studies Related to Improving Limestone Utilization, March 1975 b.

Chen, B. H., and W. J. M. Douglas: Can. J. Chem. Eng., Vol. 46, 245 (1968).

Douglas, H. R., Snider, I. W. A., Tomlinson, G. H., Chem. Eng. Progr., Vol. 59, 85 (1963).

Douglas, W. J. M., Chem. Eng. Progr., Vol. 60, 66 (1964).

Epstein, M., EPA Alkali Scrubbing Test Facility at TVA Shawnee Power Plant, Bechtel Progress Report Prepared for the EPA, 1970 to 1976.

Epstein, M., ibid, July 1, 1973 to Aug. 1, 1973 (Aug. 31, 1973).

Epstein, M., EPA Alkali Scrubbing Test Facility: Summary of Testing Through October 1974. Prepared for EPA in June, 1975 a.

Epstein, M., EPA Alkali Scrubbing Test Facility: Advanced Program. First Progress Report Prepared for EPA in Sep. 1975 b.

Fan, L. S., 1975, Dissertation, West Virginia University, Morgantown.

Gel'perin, N. I., Savchenko, V. I., Ksenzenko, B. I., V. Z., Grishko, and Dianov, E. A., Khimicheskoe Promyshlennost, 11 (1965).

Gel'perin, N. I., V. Z. Grishko, V. I. Savchenko, V. M. Shchedrov, Khim. Neft. Masninostroenie, No. 1, 22 (1966).

Gel'perin, N. I., Yu. M. Latyshev and L. I. Blyakham: Intl. Chem. Eng., Vol. 8, 691 (1968).

Groeneveld, K. J. W. (1967), Dissertation, Technische Hogeschool, Delft.

Hatta, S., Technol. Repts. Tohoku Imp. Univ., Vol. 8, 1 (1928).

Khanria, R. T., Ph.D. Thesis, McGill Univ., Canada, 1971.

Kielback, A. W., Chem. Eng., Vol. 66, 106 (Dec. 14, 1959).

Kito, M., Shimada, M., Sakai, T. Sugiyama, S., and Wen, C. Y., paper presented at Engineering Foundation Conferences, California (June, 1975).

Kito, M., Sawada, M. Shimada, T. Takata, T. Sakai and S. Sugiyama: Submitted to KagakuKogaku, to be published.

Krainev, N. I., M. I. Niyazov, I. P. Levsh and S. U. Umarov J. of Appl. Chem. of U.S.S.R., Vol. 41, 1961 (1968).

Kulbach, A. W., Chem. Eng. Progr. Symp. Ser., Vol. 57, No. 35 (1961).

LaMantia, C. R., Hunt, R. R., and Shah, I. S., Paper 25c, presented at the 66th AIChE Meeting, New York, NY, Nov. 1973, "Dual Alkali Process for Sulfur Dioxide Control".

Levsh, L. P., Krainev, N. I., Niyasov, M. I., Intl. Chem. Eng., Vol. 8, 311 (1968).

Lowell, Philip S., A Theoretical Description of the Limestone Injection Wet Scrubbing Process, Radian Report for EPA in June 9, 1970.

McIlroy, R. A., Atwood, G. A., and Major, C. J., Environ. Sci. and Technol., Vol. 7, 1022 (1973), "Absorption of Sulfur Dioxide by Molten Carbonates".

McMichael, W. J., Fan, L. S. and Wen, C. Y., paper presented at AIChE Meeting, Houston, Texas (March 16-20, 1975).

McMichael, W. J., Fan, L. S. and Wen, C. Y., I and EC Process Design and Development, Vol. 15, 459 (1976).

Nelson, R. D., M. S. Thesis, West Virginia University, Morgantown, W.Va. (1974).

Nannen, L. W., West, R. E., and Kreith, F., J. Air Poll. Control Assoc. Vol. 24, 29 (1974).

Nijsing, R. A. T. O., 1975, 1969, cited by Astarita, G. (ref. 1.)

O'nell, B. K., Nicklin, D. J., Morgan, N. J., and Leung, L. S., Canadian J. Chem. Eng., Vol. 50, 595 (1972).

Payne, J. W., and Dodge, B. F., Ind. Eng. Chem., Vol. 24, 630 (1932).

Shale, C. C., Simpson, D. G., and Lewis, P. S., Chem. Eng. Progress, Vol. 67, 52 (1971).

Slack, A. V., Intl. J. Sulfur Chem. Vol. 7B, 67 (1972).

Strauss, W., Industrial Gas Cleaning, Pergamon Press,

Oxford, 1966, Section 3.7.1. and Section 3.4.

Tepe, J. B., and Dodge, B. F., Trans. Am. Inst. Chem. Engrs., Vol. 39, 255 (1943).

Tichy, J., Wong A. and Douglas, W. J. M., Can. J. Chem. Eng., Vol. 39, 255 (1943).

Tichy, J., and Douglas, W. J. M., Can. J. Chem. Eng., Vol. 51, 618, (1973).

Wen, C. Y., Wet Scrubber Study, Report prepared by West Virginia University for the EPA, Report No. 35 (Dec. 1973).

Woodies, T. C., Cummings, J. M., Jr., and Hunter, G. B., Environ. Sci. and Technol. Vol. 7, 827 (1973).

APPENDIX A.

SIMULATION COMPUTER PROGRAM

The following program and subroutines were used to simulate the lime scrubber-hold tank system. Flow diagram for the computations have been given earlier in the thesis (Figure 5.3).

```
C       SIMULATION COMPUTER PROGRAM.
        COMMON/ALIN2/PH2(12),DLT(12),NDTPH
        COMMON/REEF/PMG,SKGA,PKGA,PSO2,ZS,ZP,G,P
        COMMON/ALIN1/DLT4,DLT9,PH4
        COMMON/ENEL/AMG,CL,SO3,ANK
        COMMON/CCO2/SOF,CAF,VV,AK,COO,S,Z,V,CO2,ABS3,MMM
        COMMON/SOLU/MM,GPM,CAO,EFFSP
        COMMON/PRINM/TITLE(18),COBS(7),PHOBS,IT5,PCSR,PPCC,STOI
        COMMON/SYPLX/ SO2,UTI,PHIN,PHOT,EFFCY
C       ##################################################
C.....A......CROSS SECTION AREA,CM**2
C.....V......L/SEC.CM**2,LIQ FLOW
C.....AMG....MMOL/L
C.....PMG....PPM,USED IN THE CALCULATION OF SO2 REM EFF
C.....CAO....FEED,#/HR
C.....CAF....LIME FED,MMOLE/L
C.....GPM....LIQ FLOW RATE,GPM
C.....SO2....FEED,#/HR
C.....SOF....SO2 FED,MMOLE/L
C.....PHIN...PH AT INLET OF TOWER
C.....PHOT...PH AT OUT LET OF TOWER
C.....EFFCY..SO2 REM EFF
C.....DLTI...DLT AT PH IN FROM EQLM PROGRM
C.....DLTO...DLT AT PH OUT FROM EQLM PROGRM
C.....ABS1...SO2 ABSORBED,MMOL/L
C       ************************************************
        MM=0
        MM=MM+1
C       IF(MM.GT.1) GO TO 120
        MMM=2
C       ************************************************
        A=410.
        Z=285.
        ZP=60.
```

```
      PSO2=.00243
      SO2=0.
      P=9.5
C     ******************************************************
      MN=5
      NN=6
      NDTPH=12
      NDDP=12
    1 CONTINUE
      AMG=15.
      SL=0.
      CL=0.
      SO3=27.6
      PPCC=.12
      T=51.6
      READ (MN,700) TITLE
      READ(MN,701)PPCC,T,AMG,CL,ANK,SL
      IF (T.EQ.0.) STOP
      READ(MN,702)G,V,Z,ZP,P,PSO2,CAF,SOF
      GPM=A*V/.06308
      SO2=SOF*GPM/31.2365
      CAO=CAF*GPM/35.699
      AL=1050.*V
      CALL SUFAT(SO3,CL,AMG)
      WRITE (NN,815) TITLE
C     *******************************************
      IF(MMM.LE.1) GO TO 150
      WRITE(6,72)
      WRITE(6,8)
      WRITE(6,5) AMG,CL,SO3
      WRITE(6,10)P,PSO2,PPCC
      WRITE(6,6) CAF,SOF,T,SL
      WRITE (6,11)G,V,Z,ZP
```

```
   72 FORMAT(//,' TEST   EPA   SCRUBBER SIZE.')
    8 FORMAT(//, 4X,'MG',16X,'CL',11X,'SO3')
    5 FORMAT(1X,F10.4,5X,F10.4,5X,F10.4)
   10 FORMAT(/,6X,'P',14X,'PSO2',10X,'PCO2',/, 3X,F5.2,10X,F10.6, 6X,
     C F4.2)
    6 FORMAT(/,6X,'CAF',12X,'SOF',11X,'T',15X,'SL',/,1X,F10.3, 5X,F10.3,
     /  5X,F10.3,10X,F10.3)
   11 FORMAT(/,6X,'G',14X,'V',13X,'Z',15X,'ZP',/,2X,F7.5,10X,F7.4, 6X,
     / F7.1,10X,F10.3)
  700 FORMAT(18A4)
  701 FORMAT(6F10.4)
  702 FORMAT(8F10.6)
  815 FORMAT (///,10X,18A4)
C     ********************************************
      CALL ENELS(T)
      WRITE(6,7)
    7 FORMAT (//,'      PH           DLT')
      DO 2 I=1,NDDD
      WRITE (6,4)PH2(I),DLT(I)
    4 FORMAT(1X,2F10.4)
    2 CONTINUE
  150 CONTINUE
C     #######################################################
      DO 3 I=1,NDDD
      IF(PH2(I).GT.4.0) GO TO 41
      DLT4=DLT(I)
      PH4=PH2(I)
   41 IF (PH2(I).GE.9.) DLT9=DLT(I)
    3 CONTINUE
C     #######################################################
      AK=.0005125
      COO=2.1676
      S=.05536
```

```
      VV=V**(-.4157)
      ZS=Z-ZP
      PMG=AMG*24.3
C     ***************************************************
  120 CONTINUE
      SO2=452.35*A*G*PSO2
      SOF=31.2365*SO2/GPM
      SKGA=0.00134*(G**0.8)*(AL**0.4)
      PKGA=.00132*(G**.47)*(AL**.51)*((P/6.1)**1.1)
   21 CALL PHEFF (CAF,SOF,PHIN,PHOT,EFFCY)
      UTI =SOF*EFFCY/CAF
      STOI=1./UTI
C     ***************************************************
      WRITE(6,71)V,GPM  ,CAF,CAO,SOF,SO2
      WRITE(6,73)Z,ZP
      WRITE(6,500) UTI,STOI
      WRITE(6,20) ABS3,CO2,G
      WRITE(6,9) PHIN,PHOT,EFFCY
  500 FORMAT(/,5X,'UTI =',F5.2,5X,'STOI=',F6.3)
   20 FORMAT(  5X,'ABS =',F5.2,5X,'CO2 =',F5.2,5X,'G  =',F7.5)
    9 FORMAT(   5X,'PHIN=',F5.2,5X,'PHOT=',F5.2,5X,'EFF=',F6.4)
   73 FORMAT(5X,'Z  =',F6.2,5X,'ZP =',F7.2)
   71 FORMAT(/,5X,'V  =',F9.6,2X,'GPM=',F7.1,/,5X,'CAF=',F6.2,
     C 5X,'CAO=',F7.2,/,5X,'SOF=',F6.2,5X,'SO2=',F7.2)
      STOP
      END
      SUBROUTINE PHEFF (CAF,SOF,PHIN,PHOT,EFFCY)
      COMMON/ALIN2/PH2(12),DLT(12),NDTPH
C.....INPUT:CAF,SOF. OUTPUT:PHIN,PHOT,EFFCY.
C     ##################################################
      NTT=0
      PHI1=7.5
      ABS1=.9*CAF
```

```
C     ######################################################
      CALL PRDIT(PHI1,ABS1,CAF1,CAFD1,EFF1,PHO1)
      IF(ABS(CAFD1/CAF).LE..0005) GO TO 63
      IF(CAFD1.GT.0.) GO TO 62
      PHI2=5.5
   60 CALL PRDIT(PHI2,CAF1,CAF2,CAFD2,EFF2,PHO2)
      IF(ABS(CAFD2/CAF).LE..0005) GO TO 64
   61 CONTINUE
      IF(ABS(CAFD2-CAFD1).GT..00001) GO TO 50
      PHI3=(PHI2+PHI1)*.5
      NTT=NTT+1
      WRITE(6,53) PHI1,PHI2,CAFD1,CAFD2
   53 FORMAT(//,4F10.6,/,5X,'IN SUB PHEFF ')
      GO TO 51
   50 PHI3=PHI1-CAFD1*(PHI2-PHI1)/(CAFD2-CAFD1)
   51 A=PHI3
      B=CAF2
      CALL PRDIT(A,B,C,D,E,F)
      CAF3=C
      CAFD3=D
      EFF3=E
      PHO3=F
      IF(NTT.GT.0) GO TO 65
      IF(ABS(CAFD3/CAF).LE..0005) GO TO 65
      PHI1=PHI2
      CAFD1=CAFD2
      CAF1=CAF2
      PHI2=PHI3
      CAFD2=CAFD3
      CAF2=CAF3
      GO TO 61
C     ######################################################
   62 PHI2=10.2
```

```
      GO TO 60
   63 PHIN=PHI1
      PHOT=PHO1
      EFFCY=EFF1
      RETURN
   64 PHIN=PHI2
      PHOT=PHO2
      EFFCY=EFF2
      RETURN
   65 PHIN=PHI3
      PHOT=PHO3
      EFFCY=EFF3
   70 RETURN
      END
      SUBROUTINE PRDIT (PHI,ABS1,ABS2,CAFD,EFF,PHO)
      COMMON/ALIN2/PH2(12),DLT(12),NDTPH
      COMMON/ALIN1/DLT4,DLT9,PH4
      COMMON/CCO2/SOF,CAF,VV,AK,COO,S,Z,V,CO2,ABS3,N
C.....ABS1...GUESS SO2,ABS , MMOL/L
C.....ABS2...SO2,ABS CALC'D
C.....CAFD...DIFFERENCE BETWEEN CAF DATA & PREDICTED VALUE.
C.....PHI PHO...PH AT IN & OUT.
      SF=0.
      I=0
C     ######################################################
      IF(N.LE.4) GO TO 90
      IF(PHI.LE.10.2) GO TO 90
      WRITE(6,62)
      WRITE(6,81)SOF,EFF,PHI,PHO,ABS1,CO2,DLTI,DLTO
   62 FORMAT(//,' PHIN>10.2,IN SUB PRDIT')
      STOP
   90 IF(PHI.GE.9.) GO TO 56
      IF(PHI.GT.PH4) GO TO 63
```

```
      WRITE(6,61)
      WRITE(6,81)SOF,EFF,PHI,PHO,ABS1,CO2,DLTI,DLTO
   61 FORMAT(' PHIN IS TOO LOW.IN SUB PRDIT')
      STOP
C     *******************************************************
   63 CALL ALINE(NDTPH,PH2,DLT,PHI,DLTI)
      GO TO 51
C     #######################################################
   56 DLTI=DLTO
   51 DLTO=DLTI+ABS1
      I=I+1
      IF (I.GT.30) GO TO 50
      IF(DLTO.GT.DLT4 ) GO TO 58
      CALL ALINE (NDTPH,DLT,PH2,DLTO,PHO)
      GO TO 54
C     #######################################################
   58 WRITE(6,80)
      WRITE(6,81)SOF,EFF,PHI,PHO,ABS1,CO2,DLTI,DLTO
   80 FORMAT(//,' CALCULATED DLT OUT IS TOO HIGH.',/,' PROBABLY 1.DLT IS
     / NEARLY CONSTANT. 2.DLTOUT IS HEIGHER THAN THE DLT AT THE LOWEST P
     /H2.')
   81 FORMAT(//,' SOF      EFF     PHIN    PHOT     ',/,4F7.3,//,' ABS1
     /CO2   DLTI     DLTO ',/,4F7.3)
      STOP
C     #######################################################
   54 PHLM=.362+ALOG10((PHI-PHO)/(10.**(-PHO)-10.**(-PHI)))
C     #######################################################
      CALL REMEF (PHLM,EFF)
      ABS2=EFF*SOF
      SPER=ABS1-ABS2
      IF(ABS(SPER)     .LE..001) GO TO 50
      ABS1=SF*SPER+ABS2
C.....SF.....SCALE FACTOR
```

```
      GO TO 51
C     ##################################################
C.....CO2 PORTION
   50 PHM=(PHI+PHO)/2.
      H=10.**(3.-PHM)
      CKGA=EXP(1.108*PHM-1.504*VV)
      AKH=1.+AK/H
      CO2=COO*AKH*(1.-EXP(-CKGA*S*Z/AKH/V))
C     **************************************************
      ABS3=ABS2
      CAFD=CAF-CO2-ABS2
      IF(N.LE.2) RETURN
      WRITE(6,81)SOF,EFF,PHI,PHO,ABS1,CO2,DITI,DLTO
   60 RETURN
      END
      SUBROUTINE REMEF(PHLM,EFF)
      COMMON/REEF/PMG,SKGA,PKGA,PSO2,ZS,ZP,G,P
      COMMON/RRR/AS,RS,RP,AP,SPRAY,PACK
C.....AL.....GM/SEC.CM**2
C.....G......GMOLE/SEC.CM**2
C.....P......IN OF WATER
C.....PMG....PPM
C.....PSO2...ATM
C.....ZS ZP..CM
      IF(PMG.GT.350.)GO TO 3
      SDELT=1.
      PDELT=1.
      GO TO 6
    3 SDELT=50.1/(PMG**0.6682)
      IF(PMG.GT.3600.)GO TO 5
      PDELT=1.
      GO TO 6
    5 PDELT=22./(0.0012429*PMG)**2.065
```

```
    6 CONTINUE
      PHS=PHLM
      IF(PHLM.GE.7.19)PHS=7.19
      AS=1./(EXP(-1.35*PHS+7.82)-0.15)
      IF(PHLM.GT.6.) GO TO 1
      AP=1./0.308
      GO TO 2
    1 CONTINUE
C.....IF PH VALUE IS GREATER THAN 6.59 , AP VALUE WILL BE NEGATIVE
      PHP=PHLM
      IF(PHLM.GE.6.59)PHP=6.59
      AP=1./(-.517*PHP+3.41)
    2 E=EXP(-330.*PSO2)
      RS=(AS/SDELT)*E
      RP=(AP/PDELT)*E
      PACK=PKGA*ZP*RP/G/(1.+RP)
      SPRAY=SKGA*ZS*RS/G/(1.+RS)
      EFF  =1.-1./EXP(SPRAY+PACK)
      RETURN
      END
      SUBROUTINE ALINE (N,X,Y,XX,YY)
      DIMENSION Y(12),X(12)
C     ######################################################
      M=N-1
      DO 4 I=1,M
      X1=X(I)-XX
      X2=X(I+1)-XX
      X3=X1*X2
      IF(ABS(X1).LE..0002) GO TO 5
      IF(ABS(X2).LE..0002) GO TO 6
      IF(X3.LT.0.) GO TO 7
    4 CONTINUE
    5 YY=Y(I)
```

```
      GO TO 8
    6 YY=Y(I+1)
      GO TO 8
    7 SLOP=(Y(I)-Y(I+1))/(X(I)-X(I+1))
      YY=SLOP*(XX-X(I))+Y(I)
    8 RETURN
      END
      SUBROUTINE ENELS (T)
      DIMENSION C(35),EK(25),CONS(10)
      COMMON/ALIN2/PH2(12),DLT(12),NDTPH
      COMMON/PPINM/TITLE(18),COBS(7),PHOBS,IT5,PCSP,PPCC,STOI
      COMMON/DEFU/DELTB
       COMMON/ENEL/AMG,CL,SO3,ANK
      COMMON/TESTS/TEST,TEST2,TEST3,TEST4
      MN=5
      NN=6
      COBS(1)=0.
      COBS(4)=0.
      COBS(6)=0.
      COBS(2)= AMG
      COBS(3)= ANK
      COBS(5)= SO3
      COBS(7)= CL
      TT = T + 273.16
      CALL EOCON(EK,TT)
C     ##################################################
      K=0
  302 CONTINUE
      K=K+1
      PH=PH2(K)
C     ##################################################
      CONS(1) = 0.6 * COBS(5) / 1000.
      CONS(2) = 0.9 * COBS(2) / 1000.
```

```
      CONS(3) = COBS(7) / 1000.
      CONS(4) = COBS(3) / 1000.
      CONS(5) = PPCC
      CONS(6) = 10.**(-PH)
      CONS(7) = 0.0
      CONS(8) = CONS(1)
      CONS(9) = CONS(2)
      CONS(10) = CONS(5)
C     ##################################################
      CALL EQUIC(C,EK,CONS,TT,PH)
      QSMG = CONS(1) + CONS(2)
      IF(QSMG .LT. 0.001) GO TO 415
C     CHECK FOR SPECIFIED SULFATE BEYOND SATURATION
      IF (CONS(1) .LT. 0.001) GO TO 413
      IF (TEST .EQ. 0.) GO TO 201
      IF (CONS(1) .GT. C(33)) GO TO 413
  201 CONS(1) = 0.001 * COBS(5) * C(14) / C(33)
C     CHECK FOR SPECIFIED MAGNESIUM ABOVE SATURATION
  413 IF (CONS(2) .LT. 0.001) GO TO 414
      IF (TEST2 .EQ. 0.)GO TO 203
      IF (CONS(2) .GT. C(35)) GO TO 414
  203 CONS(2) = 0.001 * COBS(2) * C(19) / C(35)
C     ##################################################
  414 CALL EQUIC(C,EK,CONS,TT,PH)
  415 CONTINUE
C     ##################################################
      DLT(K)=(C(32)+C(33)+C(34)-C(31))*1000.
      IF(K.LT.12)GO TO 302
      RETURN
      END
      SUBROUTINE SUFAT(SO3,CL,AMG)
C.....INPUT:CL,AMG . OUTPUT:SO3
C     SO3 CONC PREDICTION AT CL AND MG
```

```
C      MG...AMG ,MMOL/L
C      CL...CL,MMOL/L
C      SO3..AMG+X,MMOL/L
C      CA...CL/2+X , MMOL/L
C       FIND X BY ITERATION....ASSUME SAT'D SO3 SOLUTION
C      **************************************************************************
       SFT=-.2
    43 X=10.
C      INITIAL GUESS
C      SFT...SCALE FACTOR
       I=0
C.....I......NO. OF ITERATION
    42 I=I+1
       IF(I.GT.100) GO TO 45
       U=(3.*CL+8.*AMG+8.*X)/2000.
C      U...IONIC STRENGTH
       SQUA=SQRT(U)
       AL=EXP(-4.651*SQUA/(1.+.7*SQUA))
C      AL..ALFA
       IF(U.LE..18) GO TO 40
       C=EXP(-1.091-.49*ALOG(U))
       GO TO 41
    40 C=EXP(-.6253-.2257*ALOG(U))
    41 CLMG=CL/2.+AMG
       XX=.5*(-CLMG+SQRT(CLMG*CLMG-2.*CL*AMG+128.8*C/AL/AL))
       XXX=X-XX
       X=SFT*XXX+XX
C      NEW GUESS VALUE
       IF(ABS(XXX ).GE..001) GO TO 42
       GO TO 46
    45 WRITE(6,1)
     1 FORMAT(//,1X,'ITERATION IN SUBROUTINE SUFAT IS OVER 100.')
    46 SO3=AMG+XX
```

```
C     SO3..MMOLE/L
C     ***************************************************************************
  100 RETURN
      END
      SUBROUTINE EQCON (EK,TT)
      DIMENSION EK(25)
C     GIVEN THE TEMPERATURE, THIS RETURNS THE EQUILIBRIUM CONSTANTS
      R = 1.9872
C     EK(2), EK(14), AND EK(17) ARE FILLED IN BY THE EQUIC SUBROUTINE
C        DEPENDING ON SATURATION IN CACO3, CASO4, AND MGSO3
      EK(2)  = 0.
      EK(14) = 0.
      EK(17) = 0.
C     FIRST GROUP IN STANDARD FORM FOR ENTHALPY AND ENTROPY
C     KSP FOR CASO3
      EK(1)  = EXP((4933.5/TT-46.27)/R)
C     KB FOR H2SO3
      EK(3)  = EXP((2900.8/TT-42.71)/R)
C     KA FOR H2SO3
      EK(5)  = EXP((3861.1/TT-21.54)/R)
C     KDISS FOR ION PAIR CASO3
      EK(7)  = EXP((2310.2/TT-23.30)/R)
C     KDISS FOR ION PAIR CACO3
      EK(8)  = EXP((2176.1/TT-21.94)/R)
C     KDISS FOR ION PAIR CAHCO3+
      EK(9)  = EXP((1381.2/TT-10.40)/R)
C     KDISS FOR ION PAIR CAOH+
      EK(10) = EXP((1250.4/TT-10.45)/R)
C     1/H FOR SO2 (H=P/C)
      EK(12) = EXP((6269.8/TT-20.64)/R)
C     1/H FOR CO2 (H=P/C)
      EK(13) = EXP((4645.2/TT-22.29)/R)
C     KDISS FOR ION PAIR MGOH+
```

```
      EK(16) = EXP((2370.6/TT-19.78)/R)
C     KSP FOR MGSO3
      EK(25) = EXP((-3671.3/TT-7.24)/R)
C     KDISS FOR ION PAIR MGHCO3+
      EK(18) = EXP((1075.9/TT- 8.00)/R)
C     KDISS FOR ION PAIR MGSO3
      EK(19) = EXP((1979.3/TT-20.00)/R)
C     KDISS FOR ION PAIR MGSO4
      EK(20) = EXP((4841.5/TT-26.52)/R)
C     KDISS FOR ION PAIR CASO4
      EK(21) = EXP((1940.6/TT-17.08)/R)
C     KDISS FOR ION PAIR MGCO3
      EK(22) = EXP((2310.2/TT-23.30)/R)
C     KSP FOR CACO3
      EK(23) = EXP((7597.0/TT-63.52)/R)
C     SECOND GROUP NOT IN STANDARD FORM, TEMPERATURE DEPENDENCE
C        OF ENTHALPY AND ENTROPY HAVE BEEN MERGED
C     KB FOR H2CO3
      EK(4)  = EXP((-13282.9/TT-0.10888*TT+29.74)/R)
C     KA FOR H2CO3
      EK(6)  = EXP((-15581.7/TT-0.15005*TT+67.93)/R)
C     KW
      EK(11) = EXP((-20461.6/TT-0.07808*TT+27.86)/R)
C     KB FOR H2SO4
      EK(15) = EXP((- 2174.5/TT-0.08339*TT+23.08)/R)
C     KSP FOR CASO4.2H2O
      EK(24) = EXP((-22626.3/TT-75.007*ALOG(TT)+482.18)/R)
C     KSP FOR ANHYDROUS CASO4, THE STABLE FORM ABOVE 42 DEG-C
      IF (TT .GE. 315.) EK(24) = EXP((-5495.9/TT+13.213*ALOG(TT)
     1 -0.14877*TT-32.42)/R)
      RETURN
      END
      SUBROUTINE EQUIC(C,EK,CONS,TT,PH)
```

```
      COMMON/PRINT/A(22),XF(22),L,PCC,PCS,PCH2
      COMMON/TESTS/TEST,TEST2,TEST3,TEST4
      DIMENSION F(70,22),ZI(22)
      DIMENSION C(35),EK(25),CONS(10)
      DATA ZI/.4,.4,.8,.8,1., 1.,1.,1.,.8,.8, .8,.8,.4,.4,.8,
     * .8,1.,.8,.4,1., 1.,1./
C     THIS SUBROUTINE CONTROLS THE ADL SET OF EQUILIBRIUM SUBROUTINES
C     INITIALIZE VALUES FOR THIS CALCULATION
      DO 501 J=1,22
      A(J)=0.0
  501 F(1,J)=ZI(J)
      DO 504 J=1,35
  504 C(J)=0.0
      TEST = 0.0
      TEST2 = 0.0
      TEST4=1.0
      I5 = 0
      I6 = 0
      I7 = 0
      CONS(6) = 10.**(-PH)
      CONS(8) = CONS(1)
      CONS(9) = CONS(2)
      C(23) = CONS(3)
      C(24) = CONS(4)
      CONS(10) = CONS (5)
      A(11) = CONS(6)
C     SET SATURATION SITUATION
  326 EK(2)=EK(23)
      IF(TEST4 .LT. 1.)EK(2)=EK(8)
      EK(14)=EK(24)
      IF (TEST .LT. 1.)EK(14)=EK(21)
      EK(17)=EK(25)
      IF (TEST2 .LT. 1.)EK(17)=EK(19)
```

```
      I7 = I7+1
      IF (I7 .LE. 10) GO TO 401
      WRITE (6,805)
  805 FORMAT (10X,'TOO MANY CHANGES IN SOLIDS PRESENT')
      STOP
C     REPEAT THE CALCULATION UNTIL ALL TESTS ARE MET OR >70 LOOPS
  401 DO 510 L = 1,70
C     FIRST LOOP PASS USES ESTIMATED ACTIVITY COEFFICIENTS
      IF (L .EQ. 1) GO TO 412
C     AFTER 15 LOOPS, USE ALTERNATE FORM OF CORRECTING ACTIVITY COEFFS
      IF (L .LE. 15) GO TO 402
      DO 513 JN = 1,22
      DELTA = (F(L,JN)-F(L-1,JN))/2.
      F(L,JN) = F(L-1,JN)+DELTA
  513 XF(JN) = F(L,JN)
      GO TO 412
C     ####################################################
  402 CALL CFUG4(C,XF,TT,I6)
      DO 503 I = 1,22
  503 F(L,I) = XF(I)
  412 TEST3=0.
C     ####################################################
      CALL CABAL(F,EK,CONS,L,I5,I6)
      A(13) = CONS(7)
      IF(TEST3 .GT. 0.) GO TO 326
C     ####################################################
      FL14 = F(L,14)
      FL19 = F(L,19)
      CALL CONCE(EK,A,CONS,L,FL14,FL19)
      DO 507 J=1,22
  507 C(J) = A(J) / F(L,J)
      IF (L .EQ. 1) GO TO 510
      DO 505 JN =1,22
```

```
      IF (ABS((F(L-1,JM)-F(L,JM))/F(L,JM)) .GT. 0.001) GO TO 510
  505 CONTINUE
      TEST3=0.
C     ##################################################
      CALL TTEST(C,EK,A,CONS,PCC,PCS,PCM2)
      IF (TEST3 .NE. 0.) GO TO 326
C     FOLLOWING ARE ION SUMS, IONIC IMBALANCE, IONIC STRENGTH
      C(25) = C(9) + C(10) + C(11) + C(16) + C(18) + C(24)
      C(26) = C(3) + C(4) + C(12) +C(15) + C(23)
      C(27) = C(13) + C(19)
      C(28) = C(1) + C(2) + C(14)
      C(29) = C(25)-C(26) + 2. * (C(27)-C(28))
      C(30) = (C(25)+C(26))/2. + 2. * (C(27)+C(28))
C     FOLLOWING ARE TOTAL CA, SULFITE, SULFATE, CARBONATE, MG
      C(31) = C(7) + C(8) + C(9) + C(10) + C(13) + C(21)
      C(32) = C(1) + C(3) + C(5) + C(7) + C(17)
      C(33) = C(14) + C(15) + C(20) + C(21)
      C(34) = C(2) + C(4) + C(6) + C(8) + C(9)  + C(18) + C(22)
      C(35) = C(16) + C(17) + C(18) + C(19) + C(22) + C(20)
      RETURN
  510 CONTINUE
      WRITE (6,806)
  806 FORMAT (10X,'MORE THAN 70 ITERATIONS IN EQUIC')
      STOP
      END
      SUBROUTINE CFUG4(C,EF,TT,IG)
      DIMENSION C(35),EF(22)
      DIMENSION        CA(22),CB(22),U(22)
      REAL IZ(22)
      DATA IZ/4.,4.,1.,1.,0., 0.,0.,0.,1.,1., 1.,1.,4.,4.,1.,
     11.,0.,1.,4.,0., 0.,0./
      DATA U/0.,0.,0.,0.,.076,.076,.076,.076,0.,0.,0.,0.,0.,0.,0.,
     10.,.076,0.,0.,.076,.076,.076/
```

```
      DATA CA/4.5,4.5,4.5,4.5,3.,3.,3.,3.,3.,3.,6.,3.,4.5,3.,3.,        00364000
     13.,3.,3.,3.,3.,3.,3./                                             00365000
      DATA CB/0.,0.,0.,0.,.3,.3,.3,.3,.3,.3,.4,.3,.1,0.,.3,             00366000
     1.3,.3,.3,.3,.3,.3,.3/                                             00367000
      TC = TT-273.16                                                    00369000
      DS = 87.74 - .40008*TC + 9.38E-4*(TC**2.) - 1.41E-6*(TC**3.)      00370000
      DA = (1.8248E6)/((DS*TT)**1.5)                                    00371000
      DB = 50.292/((DS*TT)**.5)                                         00372000
C     SI IS THE IONIC STRENGTH TIMES TWO                                00373000
      SI = C(23) + C(24)                                                00374000
      DO 501 I = 1,22                                                   00375000
      SI = SI + IZ(I) * C(I)                                            00376000
  501 EF(I) = 0.0001                                                    00377000
      DO 503 I = 1,22                                                   00378000
      IF (C(I) .LE. 0.) GO TO 503                                       00379000
      EF(I) = EXP(2.303*(U(I)*SI + DA*IZ(I)*(-(SI**.5)/(1. + DB*CA(I)*  00380000
     1(SI**.5)) + CB(I)*SI)))                                           00381000
      IF (EF(I) .LT. 0.001) GO TO 401                                   00382000
      IF (EF(I) .LE. 10.) GO TO 503                                     00383000
  401 EF(I) = -1.                                                       00384000
      WRITE (6,801) I,SI,C(I)                                           00385000
  801 FORMAT (10X,'POSSIBLE ERROR IN SPECIES ',I2,' I S= ',F12.6,       00386000
     1' CONC = ',F12.6)                                                 00387000
      I6 =I6 + 1                                                        00388000
      IF (I6 .GE. 8) STOP                                               00389000
  503 CONTINUE                                                          00390000
      RETURN
      END
      SUBROUTINE CABAL(F,EK,CONS,L,I5,I6)
      DIMENSION E(35,3),A(13)                                           00394000
      DIMENSION F(70,22),EK(25),CONS(10)                                00395000
      COMMON/TESTS/TEST,TEST2,TEST3,TEST4                               00396000
      MN=6                                                              00399000
```

```
      A(11) = CONS(6)
      S = CONS(8)
      TM = CONS(9)
      D = CONS(10)
      DO 220 I=1,35
      DO 220 J=1,3
  220 E(I,J)=0.0
      E(1,1) = 1./F(L,13)
      E(2,1) = EK(11)/(2.*A(11)*F(L,10)*EK(10))
      E(3,1) = EK(19)*EK(11)/(2.*EK(2)*EK(16)*F(L,16)*A(11))
      E(4,1) = EK(19)/(EK(2)*F(L,19))
      E(5,1) = E(1,1)+E(2,1)
      E(6,1) = E(3,1)+E(4,1)+E(5,1)
      E(7,1) = D*EK(6)*EK(13)/(2.*EK(9)*F(L,9)*A(11))
      E(8,1) = E(5,1)+E(7,1)
      E(9,1) = EK(17)/(F(L,19)*EK(1))
      E(10,1) = EK(17)*EK(11)/(A(11)*F(L,16)*EK(1)*EK(16)*2.)
      E(11,1) = EK(17)*EK(6)*EK(13)*EK(4)*D/(EK(1)*EK(18)*
     1F(L,18)*EK(4)*A(11)*2.)
      E(12,1) = E(8,1)+E(9,1)+E(10,1)+E(11,1)
      E(13,1) = E(5,1)+E(9,1)+E(10,1)
      E(1,2) = EK(11)/(2.*A(11)*F(L,12))
      E(2,2) = A(11)/(2.*F(L,11))
C     ADD IN ANY OTHER NONCOMPLEXING SINGLY CHARGED - SPECIES CONC
      E(1,2) = E(1,2) + CONS(3)/2.
C     ADD IN ANY OTHER NONCOMPLEXING SINGLY CHARGED + SPECIES CONC
      E(2,2) = E(2,2) + CONS(4)/2.
      E(3,2) = EK(2)*A(11)/(2.*EK(4)*EK(9)*F(L,9))
      E(4,2) = S
      E(5,2) = A(11)*S*F(L,14)/(2.*EK(15)*F(L,15))
      E(6,2) = TM*F(L,19)*EK(11)/(2.*EK(16)*F(L,16)*A(11))
      E(7,2) = TM
      E(8,2) = E(1,2)-E(2,2)
```

```
      E(9,2) = E(8,2)-E(3,2)                                            00436000
      E(10,2) = E(9,2)+E(4,2)+E(5,2)                                    00437000
      E(11,2) = E(10,2)-E(6,2)-E(7,2)                                   00438000
      E(12,2) = E(9,2)-E(6,2)-E(7,2)                                    00439000
      E(13,2) = EK(19)*A(11)/(2.*EK(18)*F(L,18)*EK(4))                  00440000
      E(14,2) = E(10,2)-E(13,2)                                         00441000
      E(15,2) = E(9,2)-E(13,2)                                          00442000
      E(16,2) = D*EK(6)*EK(13)*EK(4)/(A(11)**2.*F(L,2))                 00443000
      E(17,2) = D*EK(6)*EK(13)/(2.*A(11)*F(L,4))                        00444000
      E(18,2) = E(8,2)+E(16,2)+E(17,2)                                  00445000
      E(19,2)=EK(19)*A(11)**2.0/(D*EK(6)*EK(13)*EK(4)*F(L,19))          00446000
      E(20,2)=EK(11)*EK(19)*A(11)/(2.0*D*F(L,16)*EK(16)*EK(6)*EK(13)    00447000
     1*EK(4))                                                           00448000
      E(21,2) = E(18,2)-E(19,2)-E(20,2)-E(13,2)                         00449000
      E(22,2) = E(21,2)+E(4,2)+E(5,2)                                   00450000
      E(23,2)= E(18,2)+E(4,2)+E(5,2)-E(6,2)-E(7,2)                      00451000
      E(24,2) = E(18,2)-E(6,2)-E(7,2)                                   00452000
      E(25,2) = TM*F(L,19)*EK(6)*EK(13)*D/(EK(18)*F(L,18)*A(11)*2.)     00453000
      E(26,2) = E(23,2) - E(25,2)                                       00454000
      E(27,2) = E(24,2) - E(25,2)                                       00455000
      E(28,2) = EK(17)*EK(2)*A(11)/(F(L,18)*EK(1)*EK(18)*EK(4)*2.)      00456000
      E(29,2) = E(18,2)+E(4,2)+E(5,2)                                   00457000
      E(30,2)= E(10,2)-E(28,2)                                          00458000
      E(31,2) = E(9,2)-E(28,2)                                          00459000
C    CR TERMS IN CONCENTRATION TIMES ACTIVITY OF CALCIUM                00460000
      E(1,3) = EK(1)/F(L,1)                                             00461000
      E(2,3) = A(11)*EK(1)/(2.*F(L,3)*EK(3))                            00462000
      E(3,3) = EK(2)/F(L,2)                                             00463000
      E(4,3) = EK(2)*A(11)/(2.*EK(4)*F(L,4))                            00464000
      E(5,3) = EK(14)/F(L,14)                                           00465000
      E(6,3) = A(11)*EK(14)/(2.*EK(15)*F(L,15))                         00466000
      E(7,3) = TM*F(L,19)*A(11)*EK(2)/(2.*F(L,18)*EK(18)*EK(4))         00467000
      E(8,3) = E(1,3)+E(2,3)                                            00468000
```

```
      E(9,3) = E(8,3)+E(3,3)+E(4,3)                                     00469000
      E(10,3) = E(9,3)+E(5,3)+E(6,3)                                    00470000
      E(11,3) = E(9,3)-E(7,3)                                           00471000
      E(12,3) = E(11,3)+E(5,3)+E(6,3)                                   00472000
      E(13,3) = E(8,3)+E(5,3)+E(6,3)                                    00473000
      E(14,3) = E(8,3)-E(7,3)                                           00474000
      E(15,3) = E(13,3)-E(7,3)                                          00475000
C     ##################################################                00476000
      IT = TEST + 2.*TEST2 + 4.*TEST4 + 1.                              00478000
      GO TO (201,202,203,204,205,206,207,208),IT                        00479000
  201 AR = E(8,1)                                                       00480000
      BR = E(26,2)                                                      00481000
      CR = E(8,3)                                                       00482000
      GO TO 128                                                         00483000
  202 AR = E(8,1)                                                       00484000
      BR = E(27,2)                                                      00485000
      CR = E(13,3)                                                      00486000
      GO TO 128                                                         00487000
  203 AR = E(12,1)                                                      00488000
      BR = E(29,2)                                                      00489000
      CR = E(8,3)                                                       00490000
      GO TO 128                                                         00491000
  204 AR = E(12,1)                                                      00492000
      BR = E(18,2)                                                      00493000
      CR = E(13,3)                                                      00494000
      GO TO 128                                                         00495000
  205 AR = E(5,1)                                                       00496000
      BR = E(11,2)                                                      00497000
      CR = E(11,3)                                                      00498000
      GO TO 128                                                         00499000
  206 AR = E(5,1)                                                       00500000
      BR = E(12,2)                                                      00501000
      CR = E(12,3)                                                      00502000
```

```
      GO TO 128
  207 AR = E(13,1)
      BR = E(30,2)
      CR = E(9,3)
      GO TO 128
  208 AR = E(13,1)
      BR = E(31,2)
      CR = E(10,3)
  128 CR = -CR
      BR = -BR
      ARG = BR**2  - 4.*AR*CR
      IF (ARG .LT. 0.) GO TO 422
      A(13) = (-BR + ARG**.5)/(2.*AR)
      CONS(7) = A(13)
  451 IF (A(13) .GT. 0.) RETURN
      IF (A(13) .EQ. 0.) GO TO 421
      WRITE(NN,198)
  198 FORMAT(10X,'THE ROOT IS NEGATIVE',/)
      I5 = I5+1
      IF (I5 .GT. 3) GO TO 76
      A(13) = (-BR-ARG**.5)/(2.*AR)
      CONS(7) = A(13)
      GO TO 451
  421 WRITE (NN,197)
  197 FORMAT(10X,'THE ROOT IS ZERO',/)
      GO TO 76
  422 WRITE(NN,199)
  199 FORMAT(10X,'THERE IS NO REAL ROOT',/)
C     RDN DOESN'T UNDERSTAND WHY ADL SETS TEST2 = 1. HERE
   76 TEST2 = 1.
      WRITE (NN,701)
  701 FORMAT (' PROBLEM WITH ROOT IN CABAL')
      I6 = I6+1
```

```
      TEST3 = 1.                                                        00536000
      IF (I6 .LT. 8.)  RETURN                                           00537000
      STOP
      END
      SUBROUTINE CONCE(EK,A,CONS,L,FL14,FL19)
      DIMENSION EK(25),A(22),CONS(10)                                   00541000
      COMMON/TESTS/TEST,TEST2,TEST3,TEST4                               00542000
      A(11) = CONS(6)                                                   00545000
      A(13) = CONS(7)                                                   00546000
      S = CONS(8)                                                       00547000
      TM = CONS(9)                                                      00548000
      D = CONS(10)                                                      00549000
      A(1) = EK(1)/A(13)                                                00550000
      A(2) = EK(6)*EK(13)*EK(4)*D/A(11)**2.                             00551000
      IF (TEST4 .EQ. 1.) A(2) = EK(2)/A(13)                             00552000
      A(3) = A(11)*A(1)/EK(3)                                           00553000
      A(4) = A(11)*A(2)/EK(4)                                           00554000
      A(5) = A(11)*A(3)/EK(5)                                           00555000
      A(6) = A(11)*A(4)/EK(6)                                           00556000
      A(7) = A(13)*A(1)/EK(7)                                           00557000
      A(8) = A(13)*A(2)/EK(8)                                           00558000
      A(9) = A(13)*A(4)/EK(9)                                           00559000
      A(12) = EK(11)/A(11)                                              00560000
      A(10) = A(13)*A(12)/EK(10)                                        00561000
      A(14) = FL14 * S                                                  00562000
      IF (TEST .EQ. 1.) A(14) = EK(14)/A(13)                            00563000
      A(15) = A(11)*A(14)/EK(15)                                        00564000
      A(19) = TM * FL19                                                 00565000
      IF (TEST2 .EQ. 1.) A(19) = EK(17)/A(1)                            00566000
      A(16) = A(19)*A(12)/EK(16)                                        00567000
      A(18) = A(19)*A(4)/EK(18)                                         00568000
      A(17) = A(19)*A(1)/EK(19)                                         00569000
      A(20) = A(19)*A(14)/EK(20)                                        00570000
```

```
      A(21) = A(13)*A(14)/EK(21)                                        00571000
      A(22) = A(19)*A(2)/EK(22)                                         00572000
      RETURN
      END
      SUBROUTINE TTEST(C,EK,A,CONS,PCC,PCS,PCM2)
      DIMENSION C(35),EK(25),A(22),CONS(10)                             00576000
      COMMON/TESTS/TEST,TEST2,TEST3,TEST4                               00577000
      T1 = TEST                                                         00579000
      T2 = TEST2                                                        00580000
      T4 = TEST4                                                        00581000
      ES = CONS(1)                                                      00582000
      TMG = CONS(2)                                                     00583000
      CO3 = CONS(5)                                                     00584000
      S = CONS(8)                                                       00585000
      TM = CONS(9)                                                      00586000
      D = CONS(10)                                                      00587000
      PCC = 100.*A(13)*A(2)/EK(23)                                      00589000
      IF (TEST4 .EQ. 1.) GO TO 401                                      00590000
      IF (PCC .GT. 100.) TEST4 = 1.                                     00591000
      GO TO 402                                                         00592000
  401 D   =A(11)**2.*EK(2)/(EK(4)*EK(6)*EK(13)*A(13))                   00593000
      IF (D .GT. CO3) TEST4 = 0.                                        00594000
  402 IF (TEST4 .EQ. 0.) D = CO3                                        00595000
      PCS=100.*A(13)*A(14)/EK(24)                                       00597000
      IF(TEST .EQ. 1.) GO TO 403                                        00598000
      IF (PCS .GT. 100.) TEST = 1.                                      00599000
      GO TO 404                                                         00600000
  403 S = C(14)                                                         00601000
      IF (C(14) .GT. ES) TEST = 0.                                      00602000
  404 IF (TEST .EQ. 0.) S = ES                                          00603000
      PCM2=100.*A(19)*A(1)/EK(25)                                       00605000
      IF (TEST2 .EQ. 1.) GO TO 405                                      00606000
      IF (PCM2 .GT. 100.) TEST2 = 1.                                    00607000
```

```
      GO TO 406
  405 TM = C(19)
      IF (TM .GT. TMG) TEST2 = 0.
  406 IF (TEST2 .EQ. 0.) TM = TMG
      IF (T1 .NE. TEST) TEST3 = 1.
      IF (T2 .NE. TEST2) TEST3 = 1.
      IF (T4 .NE. TEST4) TEST3 = 1.
      CONS(8) = S
      CONS(9) = TM
      CONS(10) = D
      RETURN
      END
```

APPENDIX B.

Plots of the Mass Transfer Coefficient for CO_2 Absorption vs. Various Average pH Values.

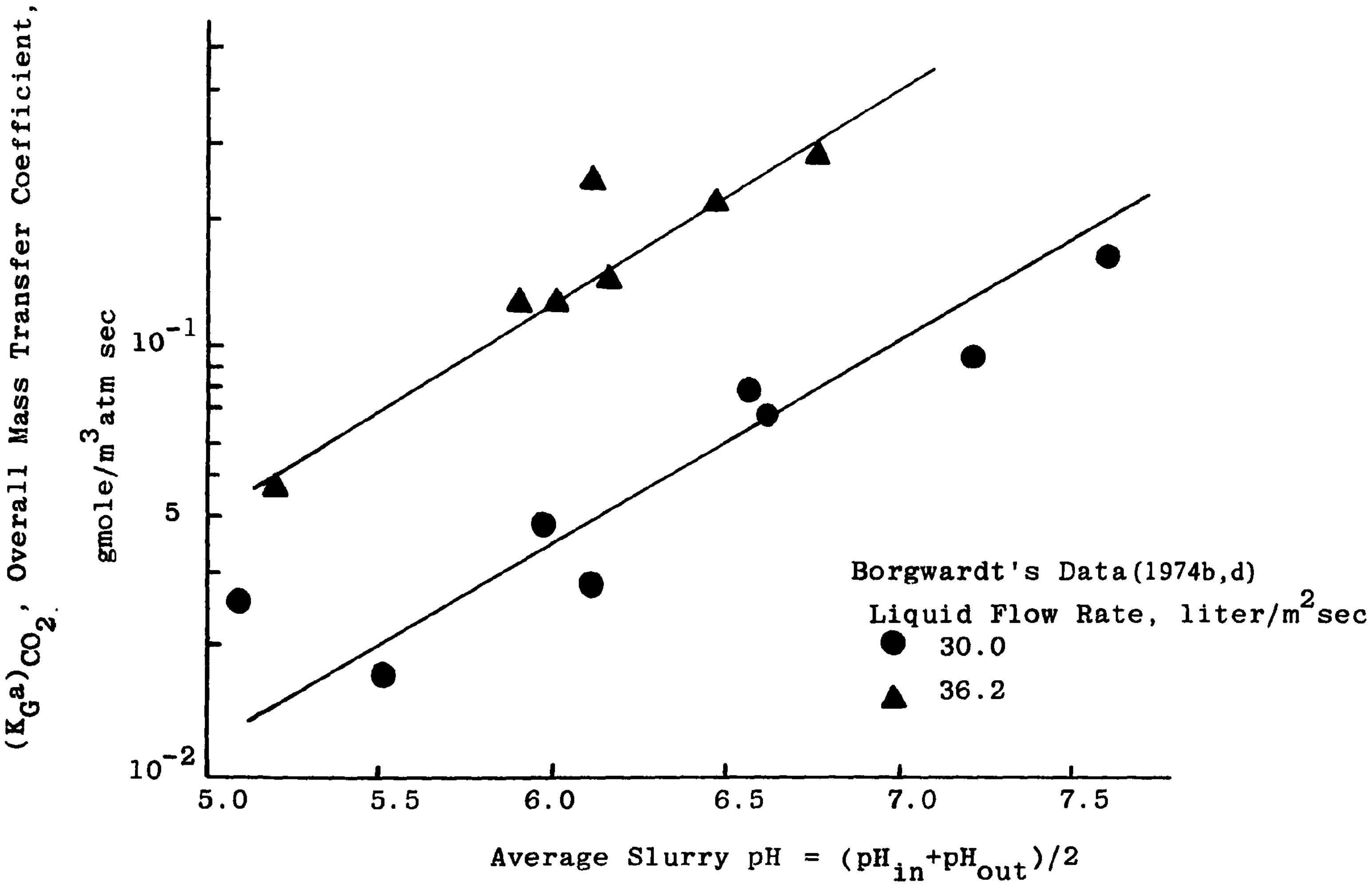


Figure B : Effect of Slurry pH and Flow Rate on the Overall Mass Transfer Coefficient for CO_2 Absorption into Recycled Lime Slurries in a TCA Scrubber.

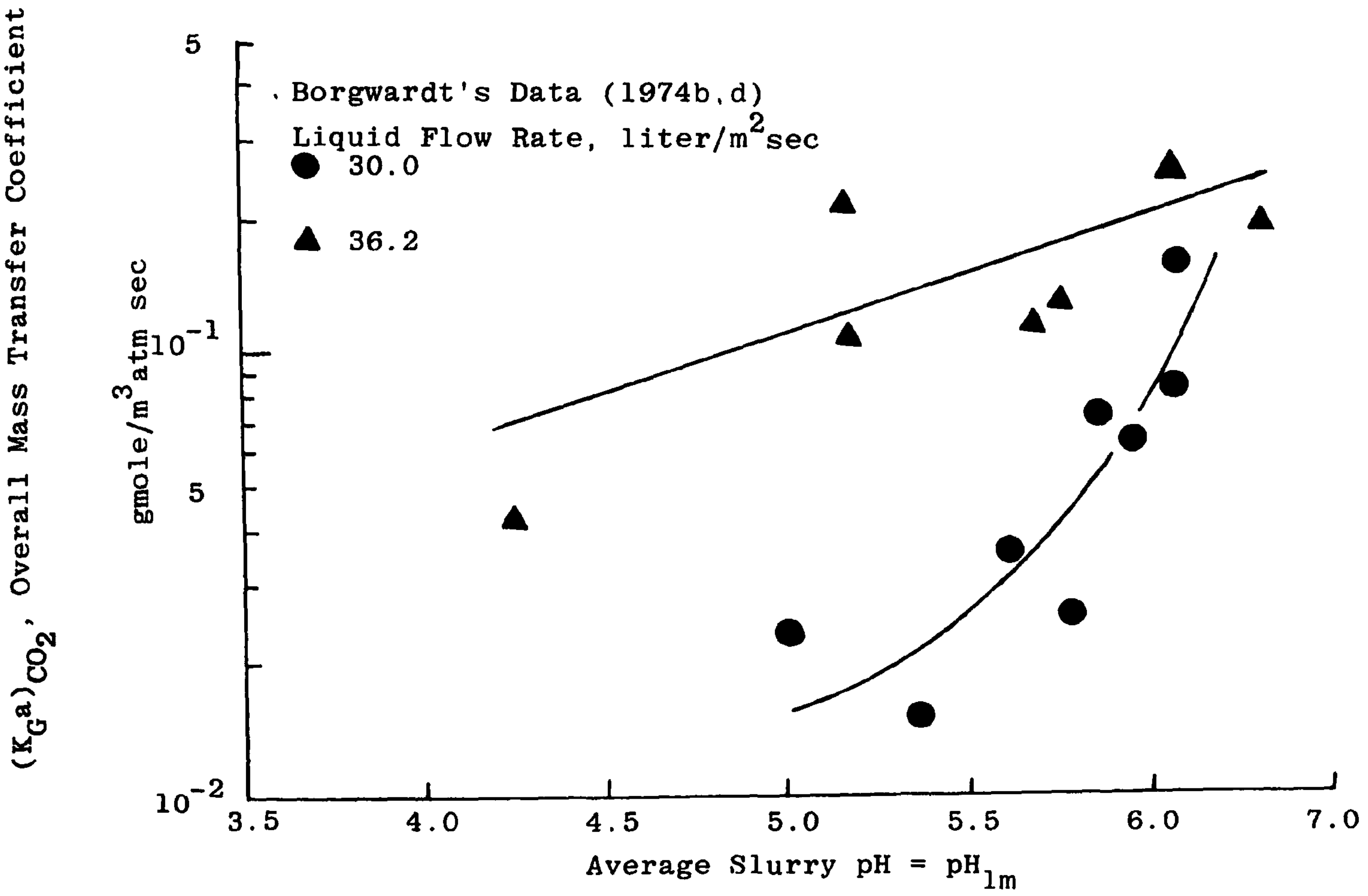


Figure B (Con't): Effect of Slurry pH and Flow Rate on the Overall Mass Transfer Coefficient for CO_2 Absorption into Recycled Lime Slurries in a TCA Scrubber.

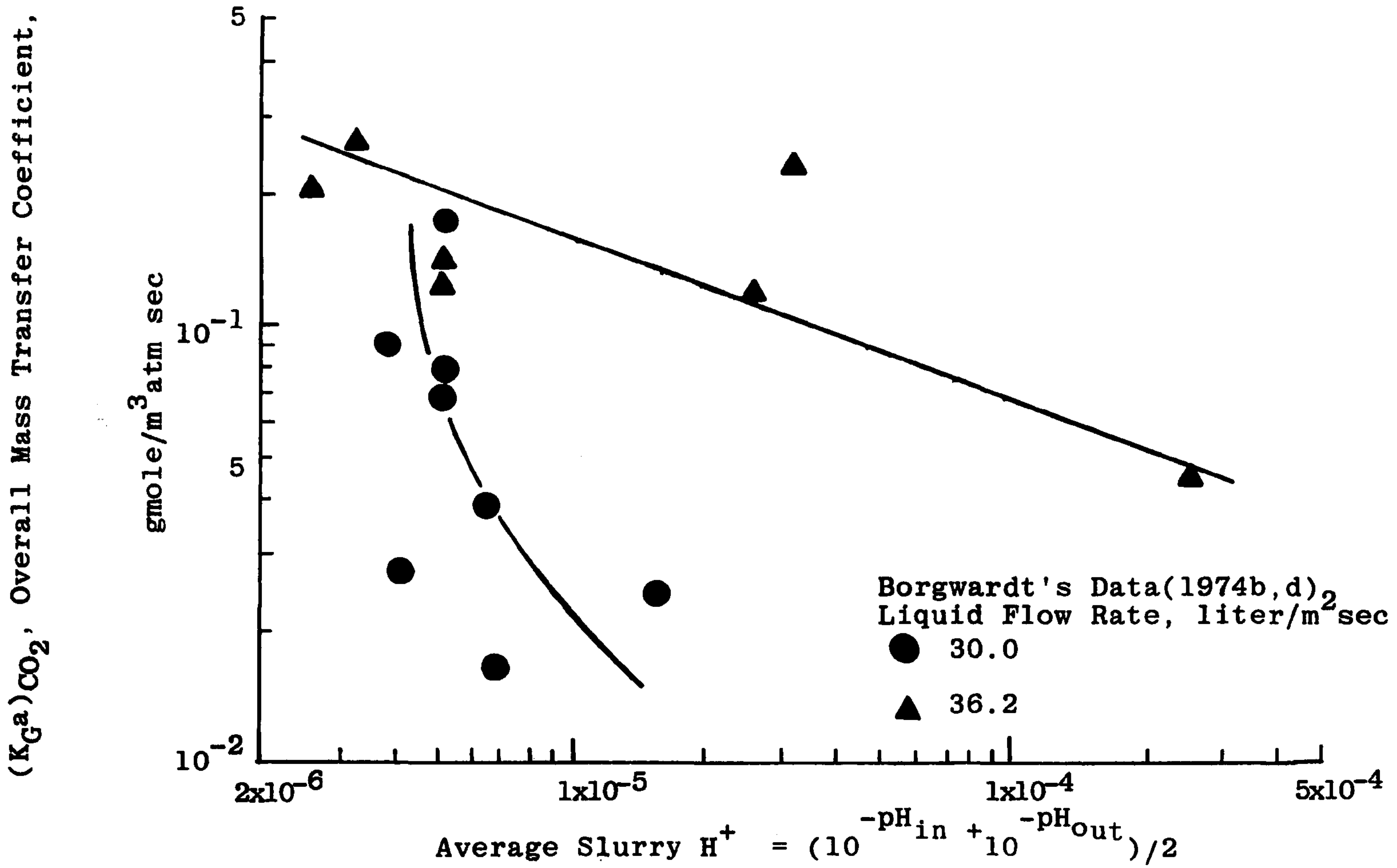


Figure B (Con't): Effect of Slurry pH and Flow Rate on the Overall Mass Transfer Coefficient for CO_2 Absorption into Recycled Lime Slurries in a TCA Scrubber.

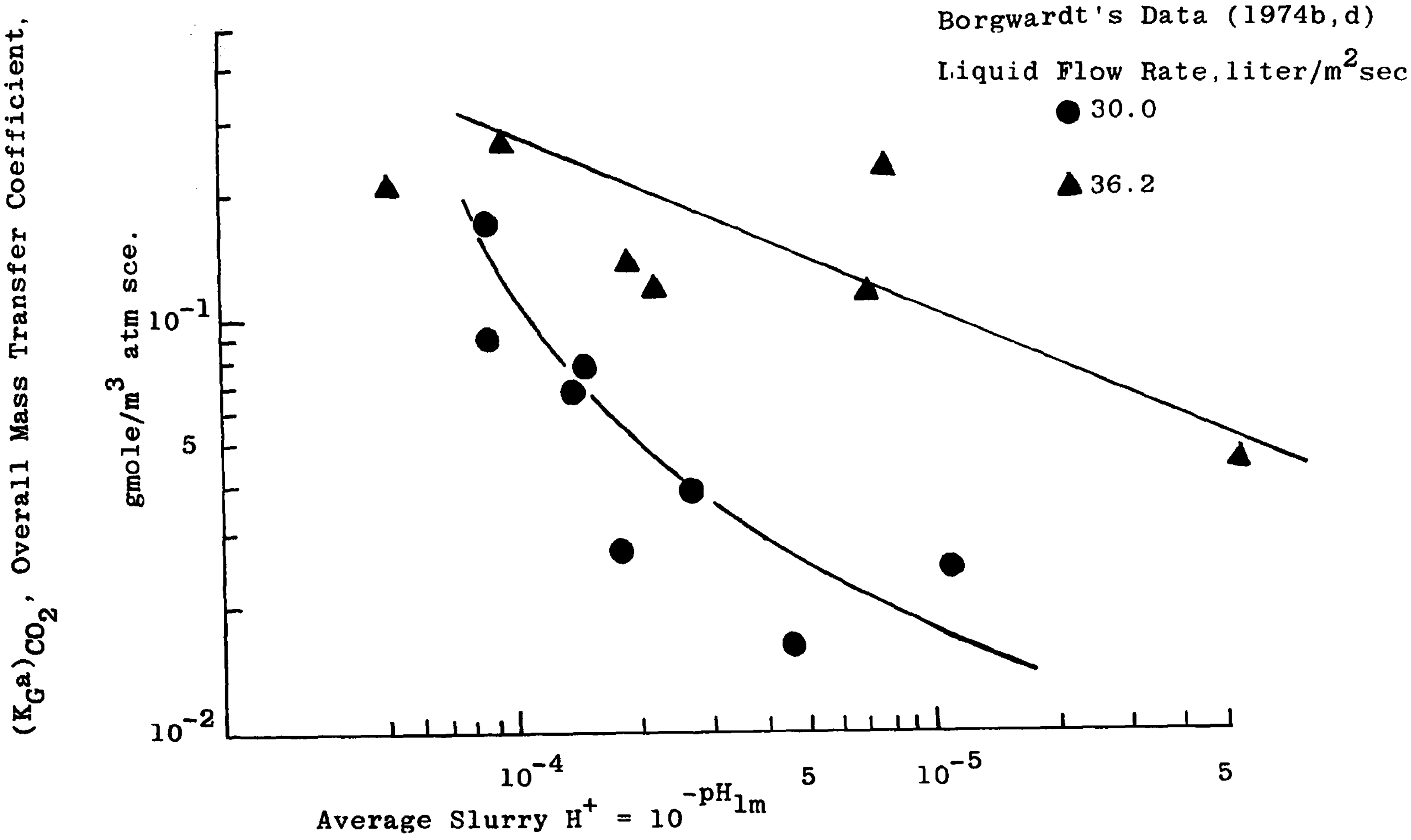


Figure B (Con't): Effect of Slurry pH and Flow Rate on the Overall Mass Transfer Coefficient for CO_2 Absorption into Recycled Lime Slurries in a TCA Scrubber .

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-77-026	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Analysis and Simulation of Recycle SO2-Lime Slurry in TCA Scrubber System		5. REPORT DATE March 1977 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) C.Y. Wen and Fred K. Fong		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS West Virginia University Department of Chemical Engineering Morgantown, West Virginia 26506		10. PROGRAM ELEMENT NO. EHE624A 11. CONTRACT/GRANT NO. Grant R800781-03-0
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Final; 6/74-8/76 14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES EPA project officer for this report is R.H. Borgwardt, Mail Drop 65, 919/549-8411 Ext 2234.

16. ABSTRACT The report gives results of an analysis of flue gas desulfurization by a turbulent contact absorber (TCA) employing lime slurry, including the development of performance equations for the scrubber-hold tank recycle system. Performance characteristics investigated include pressure drop of the scrubber, CO2 and SO2 absorptions, and lime utilization. Experimental data obtained from EPA/Research Triangle Park and TVA/Shawnee Power Station are used for the analysis and correlation. The analysis of CO2 absorption indicates that the overall mass transfer coefficient is a function of the pH of inlet and outlet scrubber liquor and is very sensitive to the liquor flow rate. (The rate of SO2 absorption in a TCA has been developed previously by McMichael et al., 1976.) The correlations developed are used to formulate a simulation procedure for predicting SO2 scrubbing efficiency as a function of pH of slurry and gas and liquor flow rates. The result of simulation indicates that, for a given lime feed rate and a fixed inlet and outlet SO2 concentration, a maximum flue gas flow rate exists which the scrubber can treat by the recycling slurry. An example is shown for the design of a TCA capable of desulfurizing flue gas from a 50-MW power station.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Air Pollution	Absorption	Air Pollution Control	13B	
Flue Gases	Scrubbers	Stationary Sources	21B	
Desulfurization	Circulation	TCA	07A,07D	
Calcium Oxides	Analyzing	Turbulent Contact Absorber	07B	14B
Slurries	Simulation		11G	
Sulfur Dioxide	Carbon Dioxide	Lime Slurry		

18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 118
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)