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**NUMERICAL AND EXPERIMENTAL MODELLING OF
CONTAMINANT TRANSPORT IN GROUND WATER AND OF
SOUR GAS REMOVAL FROM NATURAL GAS STREAMS**

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ABSTRACT

This thesis addresses the environmental issues relating to natural gas and ground water contamination. The entire research work in the present study has been divided into four parts, and presented as chapters with different objectives and a summary in each chapter. Chapter one describes the removal of the carbon dioxide from the natural gas stream.

A numerical model was developed which explains the facilitated transport of CO_2 across immobilized liquid membranes. The model is based on homogeneous chemical-diffusion. The governing equations were solved using the finite difference Barakat-Clark scheme. Results were used to determine the facilitation factor, a dimensionless measure of the solute flux through the membrane. The facilitation factor was evaluated with respect to the effect of the inverse Damkohler number, the mobility ratio, and the dimensionless reaction equilibrium constant.

A series of experiments was conducted using potassium nitrate as the contaminant to study the phenomenon of contaminant transport in carbonate formations in the presence of fractures. Dynamic adsorption and desorption tests were carried out using both homogeneous and fractured formation models. Initial modeling and experiments were carried out for a range of initial concentration values. The concentration at the outlet was measured with the Flame Ionization technique. A numerical model was developed using the surface excess theory, combined with a non-Fickian dispersion coefficient. Numerical results agreed favorably with experimental results. It was found that the non-Fickian model was necessary for modeling fracture flow results and with this version, there was no need to use the dual porosity/dual permeability formulation. Strong dependence of adsorption on initial concentration was observed and was justified with the numerical model.

The characteristics of limestone substance naturally occurring were evaluated for its sulfur removal capability from natural gas streams. Nitrogen gas, containing sulfur dioxide was passed through limestone packed column and a change in concentration was noticed by bubbling it through a water beaker. The pH of water was monitored throughout the experiment.

A numerical model developed for the simulation of sulfur adsorption in limestone is reported in chapter four. The model is based on surface excess theory and governing equation was solved using the finite difference Barakat and Clark scheme. The breakthrough time for adsorption was evaluated with respect to different values of parameters used in the governing equation.

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LIST OF SYMBOLES AND ABBREVIATIONS

A	Permeating gas or solute
B	Carrier or solvent
AB	Carrier complex.
C _{A0}	Initial concentration of solute gas.
C _i	Concentration of component i.
C _T	Total amine concentration.
CO ₂	Carbon dioxide.
DEA	Diethanolamine.
D _i	Diffusivity of component i..
F	Facilitation factor.
i	Variable representing location in the discretized membrane.
k ₁ ,k ₂	Forward and reverse reaction rate constants for equations (1.1), (1.4) and (1.7).
k _a , k _b , k _c	Forward and reverse reaction rate constants for Equations (1.2), (1.3), (1.5), and (1.6).
L	Membrane thickness.
MDEA	Methyldiethanolamine.
MEA	Monoethanolamine.
n	Variable representing time in Fortran model.
N	Represents the last location in the discretized membrane (x=L).
R	Functional group for MEA = -CH ₂ CH ₂ OH
r _i	Reaction rate for species i.

t	Time
TEA	Triethanolamine.
x	Distance in x-direction.
x1	Variable for location at discretized membrane inlet.
A	= cross sectional area of the core, cm ²
C	= concentration of the chemical, %wt
C ₀	= concentration of the chemical, %wt
k _i	= kinetic constant of adsorption (i=1) or desorption (i=2), 1/hr
k	= absolute permeability of the porous medium, mD
L	= length of the porous bed, cm
m _i	= monolayer coverage of component i per unit of adsorbent, mg/g
n ⁰	= amount of liquid per unit mass of adsorbent, mg/g
n'	= amount adsorbed per unit mass of adsorbent, mg/g
n' _i	= amount of component i adsorbed per unit mass of adsorbent, mg/g
n' _i	= equilibrium surface excess of component i per unit mass of adsorbent, mg/g
n _i ^{ea}	= Actual surface excess of component i per unit mass of adsorbent, mg/g
PV	= pore volume, AφL, cm ³
q	= flow rate, ml/hr
S	= selectivity, dimensionless
t	= time, s
u	= local speed, cm/s
x _i	= bulk phase mass fraction of component i
x' _i	= adsorbed phase mass fraction of component i
z	= distance along porous bed, cm
α	= entrainment rate constant, 1/cm
λ	= Dispersion parameter, cm
φ	= Porosity of the rock
ρ	= liquid density, mg/ml
ρ _r	= rock density, g/ml
ρ _g	= Gas density, mg/ml

Dimensionless Variables

$$\Delta = \frac{D_C}{D_A} \frac{k_1 C_T}{k_2} \quad \text{Mobility Ratio}$$

$$\varepsilon = \frac{D_C}{k_2 L^2 C^T} \quad \text{Inverse Damkohler number.}$$

$$K = \frac{k_1 C_{A0}}{k_2} \quad \text{Reaction equilibrium constant}$$

$$X = \frac{x}{L} \quad \text{Dimensionless Distance}$$

$$\tau = \frac{tD_A}{L^2} \quad \text{Dimensionless Time}$$

$$C_A^* = \frac{C_A}{C_{A0}} \quad \text{Dimensionless concentration of the solute gas.}$$

$$C_B^* = \frac{C_B}{C_T} \quad \text{Dimensionless concentration of the carrier or solvent.}$$

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Alkanolamines are used to absorb carbon dioxide (CO_2) in a variety of industrial processes. In the case of immobilized liquid membrane systems, alkanolamines can be used to promote facilitated transport. Facilitated transport occurs when the mass transport rate of a species across a membrane is increased or enhanced by the permeation of a carrier complex across the membrane. In CO_2 -amine systems, the carrier complex is the product of the reaction between CO_2 and the amine, or the carbamate.

While a number of researchers have worked on developing facilitated transport models, few have been developed that properly address CO_2 separation systems. This work re-examines the facilitated transport of CO_2 across immobilized liquid membranes using a homogeneous chemical-diffusion model. The governing equations were solved using the finite difference Barakat-Clark scheme. Results were used to determine the facilitation factor, a dimensionless measure of the solute flux through the membrane. The facilitation factor was evaluated with respect to the effect of the inverse Damkohler number, the mobility ratio, and the dimensionless reaction equilibrium constant.

In the past three decades, fractured rock domains have received increasing attention by the researchers from a number of disciplines, including hydrogeology, petroleum engineering, and environmental engineering. The importance of fractures is particularly enhanced when one deals with carbonate formations, both in water flow and petroleum production, because most of these formations are known to be fractured. The subject has been investigated by petroleum engineers in connection with multiphase flow because many important petroleum reservoirs are in fractured rock formations. Of special interest are reservoirs composed of fractured porous rocks in which the matrix blocks, surrounded by the network of fractures, are porous. The permeability of such blocks is often rather low, but the porosity and the storage capacity for fluids are very high. Environmental engineers have been investigating the problem in connection with geological isolation of radioactive waste and remediation of ground water. Hydrologists deal with fractured

formations because numerous deep aquifers are fractured. Chemical engineers mainly deal with chemical transport in limestone, but not necessarily in its fractured form (Arsic et al., 1991; Couturier et al., 1993).

In Canada, Switzerland, and Sweden large national research programs are underway to study radionuclide transport in crystalline rocks. Finland also intends to situate their repository in similar rocks and has a research program directed toward this end. Other countries, including Japan, France, Spain, the United Kingdom, and the USA have or have had research programs oriented towards crystalline rocks. In addition, an international field of research program is in progress in the Stripa mine in Sweden. The research is aimed at understanding the processes that determine the flow paths and the flow rates of water in the fractured rock masses.

Solutes that are dissolved in water will be carried by moving water, but various other mechanisms are involved in the process of solute transportation. Small molecules or ions diffuse in a concentration gradient and can move from one 'stream tube' to another. Different water volumes move with different velocities and may mix at more or less regular intervals. The dissolved species may also experience kinetic effects caused by physical processes. One such process that may have a large impact for solute transport in fractured rock is the diffusion in and out of zones in which the water is moving so slowly that it can, for all practical purposes, be assumed to be stagnant. Such stagnant zones can be expected in fractures with uneven surfaces and with fracture-filling materials. In rocks with a connected matrix they can be very much larger than the mobile water volume in the fracture. Because the stagnant zones are reached by diffusion, the volume of stagnant water accessed depends on the residence time of the flowing water.

Different approaches to solute transport in fractured media have been attempted. These include the analysis of a single fracture (e.g. Grisak and Pickens, 1981; Tang et al., 1981; Sudicky and Frind, 1984). While some researchers considered the porous medium as comprised of equally spaced fractures (Sudicky and Frind, 1984), others have used deterministic study of flow in an irregular network of fractures contained in an

impermeable rock. Yet others (Schwartz and Smith, 1988) considered the same problem with a stochastic model. Recently, Choi et al. (1997) used a dual-permeability, dual-porosity approach to model fluid flow through a fractured formation. They built their model using non-Darcian flow through the fracture while allowing Darcian flow through the matrix. Even though this work was devoted to advancing the hydrodynamic aspect of fluid flow, no species transport was considered.

Adsorption and desorption are important phenomena in chemical transport. A Langmuir isotherm has been used most commonly to model adsorption at the solid/liquid interface. The widespread use of the Langmuir model arises from its ability to represent the general shape of many adsorption isotherms. However, more recently, the surface excess theory has been proven to be more theoretically sound and better apt in modelling adsorption (Islam and Chakma, 1991). Recently, Sarwar and Islam (1997) demonstrated that the surface excess theory is also capable of representing chemical transport through fractured formations. However, non-Fickian dispersion had to be introduced, along with non-equilibrium adsorption and desorption rates. They considered the transportation of several chemicals in silica sand formation and observed very good agreement between experimental and numerical results, even for the regime with non-uniform adsorption and desorption profiles.

This research comprises of laboratory flow experiments and numerical modeling of KNO_2 transport in carbonate formations. Such flow is of relevance to agricultural applications for which run-offs from fertilizers constitute major contamination problems for groundwater. Also, in petroleum engineering applications, mathematical models of chemical transport are of importance, especially for the case of fractured carbonate formations.

The H_2S present in natural gas stream is highly poisonous and toxic even if its concentration is below 5%. Moreover the deposition of the elemental sulfur in tubular and flow lines can lead to decreased production, increased corrosion rate and higher filtration costs. So it is necessary to remove the sulfur gas in order to keep the gas at

acceptable specifications. The conventional employed treatment techniques are chemical based and are expansive along with serious environmental concerns. Environmentally friendly, naturally occurring substance limestone was investigated for its sulfur adsorption capability in down-hole applications. It was found satisfactory for sulfur adsorption capability. The gas containing SO_2 was passed through limestone packed column and a change in concentration at the outlet was noticed by bubbling the exit stream through a water beaker. The pH of water was monitored throughout the experiment. A numerical model was developed to simulate the sulfur adsorption on limestone.

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CHAPTER 1

FACILITATED TRANSPORT: A NUMERICAL MODEL FOR PREDICTING FACILITATION FACTORS

1.1 Summary

Alkanolamines are used to absorb carbon dioxide (CO_2) in a variety of industrial processes. In the case of immobilized liquid membrane systems, alkanolamines can be used to promote facilitated transport. Facilitated transport occurs when the mass transport rate of a species across a membrane is increased or enhanced by the permeation of a carrier complex across the membrane. In CO_2 -amine systems, the carrier complex is the product of the reaction between CO_2 and the amine, or the carbamate.

While a number of researchers have worked on developing facilitated transport models, few have been developed that properly address CO_2 separation systems. This work re-examines the facilitated transport of CO_2 across immobilized liquid membranes using a homogeneous chemical-diffusion model. The governing equations were solved using the finite difference Barakat-Clark scheme. Results were used to determine the facilitation factor, a dimensionless measure of the solute flux through the membrane. The facilitation factor was evaluated with respect to the effect of the inverse Damkohler number, the mobility ratio, and the dimensionless reaction equilibrium constant.

1.2 INTRODUCTION

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There are a number of methods available for effectively capturing CO₂ and depending on the nature of the problem one process will be favored over another. With a number of mature technologies available, economics often serves as the determining factor for process selection. Common separation methods include absorption, low temperature distillation, adsorption, and membrane systems (Geankopolis et al., 1993).

1.2.1 Membrane Systems

In general, a membrane can be defined as a semi-permeable barrier that allows the passage of select components. The success of its application depends highly on the membrane's permeability and selectivity. A good membrane system will have a high permeability to promote high fluxes. It will also have a high degree of selectivity to ensure that only a mass transfer of the correct component occurs. Unfortunately the permeability and selectivity of common membranes are inversely related (Kulkarni et al., 1983). The development of liquid membranes has lead to systems that have both a high permeability and high selectivity. Traditional membranes are essentially solid micro porous filters. Liquid membranes operate by immobilizing a liquid solvent in a micro porous filter or between polymer layers.

A high degree of solute removal can be obtained when using chemical solvents. When the gas, or solute, reacts with the liquid solvent in the membrane, the effect is increased liquid phase diffusivity. As a result, the over all flux of the solute is increased. Furthermore, solvents can be chosen to selectively remove a single solute from a gas stream (Astrita et al., 1983), thus improving selectivity.

The schematic diagram shown in figure 1 illustrates mass transfer across a regular membrane and a liquid membrane. In the regular membrane the solute A passes through the membrane under a pure solution diffusion mechanism, leaving the other gas behind. In the liquid membrane, the enhanced effect of having the liquid solvent, B, can be seen by the additional flux of species AB. This system, with the additional flux is known as facilitated transport. Without the effects of the liquid, mass transfer would be reduced to that of the regular diffusion membrane system whereby the total flux only consists of the flux of species A.

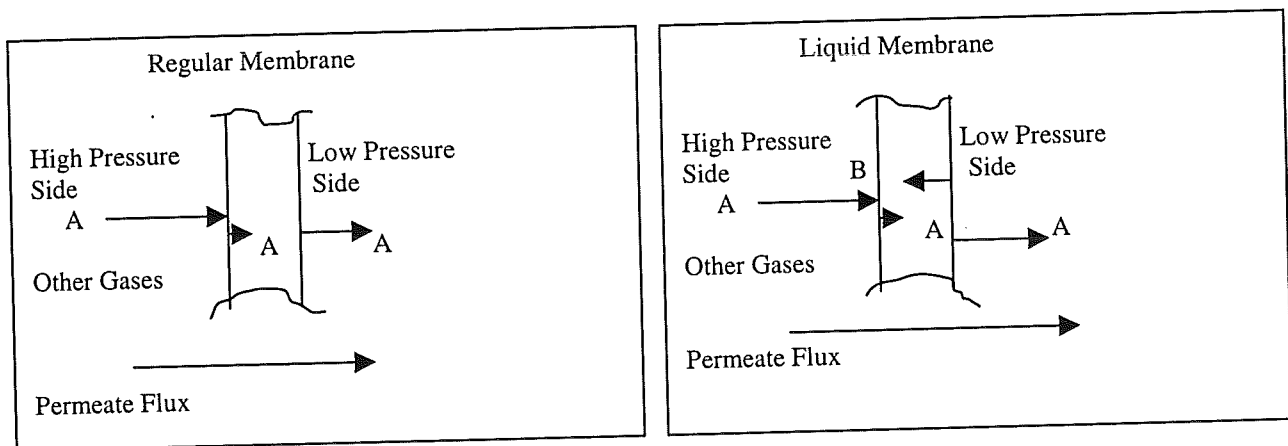


Figure 1.1 Facilitated Transport in a Membrane

1.3 Literature Review

The first work demonstrating a general quantitative understanding of facilitated transport was done by Ward (1970). The work itself carried out a detailed mathematical and experimental investigation of facilitated transport. The basic facilitated transport reaction scheme was modeled for a nitrous oxide / ferrous ion system. The system was modeled under steady state conditions with the goal of developing a model, which predicts the flux of permeate across a membrane. The method of solution was explained very clearly. Since this was some of the first work completed in the area of facilitated transport, a lot of potential was left for future researchers. Namely, the system should be modeled under transient conditions.

Donaldson and Quinn (1975) also studied facilitated transport in liquid membranes, but they applied the theory to a carbon dioxide system. The model was developed as a means of determining diffusional and kinetic parameters for the reaction system. The derivation and solution of equations for the model was not explained clearly. The reaction system was a CO₂ hydration system for the formation of bicarbonate. This left the door wide open for future works in studying CO₂- amine systems, which have evolved into a much more common system for CO₂ capture.

Smith (1977) wrote one of the first reviews on facilitated transport. They provided a comprehensive summary of the research into facilitated membranes at that time. They discussed facilitated oxygen transport, facilitated CO₂ transport and nitric oxide-ferrous chloride facilitated transport system. They provided a very good write up on the governing equations and the formulation of facilitation factor. One drawback of this paper is that the section of CO₂ systems was not for an amine system. At that time CO₂- amine systems were becoming common and therefore one would expect to see researchers exploring that area more aggressively.

Smith and Quinn (1979) developed a model for predicting the facilitation factors in facilitated transport systems. Using the standard reaction mechanism for facilitated transport, they solved one-dimensional, steady state equations, considering both the physical diffusion and chemical reaction terms. They introduce the assumption of equal carrier and carrier complex diffusivities, such as $D_B = D_{AB}$ in order to simplify the analysis. The equations were solved using analytical techniques. Initially they solved the system for nitric oxide / ferrous ion facilitated transport, obtaining comparable results to other studies. Then they studied a CO_2 -MEA system that had more complex chemistry. They did not clearly explain how the governing equations were incorporated into the model. Since the reaction kinetics of CO_2 -amine systems are not fully understood, researchers should be very clear in describing which reaction equations they are using and what assumptions they are employing when simplifying their work. Although they have calculated facilitation factors that compare with the literature, they have not presented any figures that show the facilitation factor trends. Data analysis, be it experimental or mathematical, should include the presentation of charts that illustrate any trends in the data.

Folkner and Noble (1983) studied facilitated transport in membranes under transient conditions. Models were developed in one dimension for the standard facilitated transport reaction mechanism under flat plate, cylindrical, and spherical geometries. The effects of the inverse Damkohler number, the equilibrium constant, the carrier concentration and geometry on the facilitation factor were determined. The assumption that $D_B = D_{AB}$ was used. No real discussion was presented concerning how the equations were solved except to say a computer package was used. Very few authors seem to provide useful, easy-to-understand, information in their articles about their specific modeling procedure. Researchers should be more willing to share such information in the hopes of aiding future projects.

Meldon (1985) modelled the standard reaction mechanism for facilitated transport under transient conditions. In this work the permeation across the membrane was studied with emphasis on the permeation time lag. In this work they state that previous researchers

$$K = \frac{k_1 C_{A0}}{k_2} \quad \text{Reaction equilibrium constant}$$

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1.2 INTRODUCTION

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There are a number of methods available for effectively capturing CO₂ and depending on the nature of the problem one process will be favored over another. With a number of mature technologies available, economics often serves as the determining factor for process selection. Common separation methods include absorption, low temperature distillation, adsorption, and membrane systems (Geankopolis et al., 1993).

1.2.1 Membrane Systems

In general, a membrane can be defined as a semi-permeable barrier that allows the passage of select components. The success of its application depends highly on the membrane's permeability and selectivity. A good membrane system will have a high permeability to promote high fluxes. It will also have a high degree of selectivity to ensure that only a mass transfer of the correct component occurs. Unfortunately the permeability and selectivity of common membranes are inversely related (Kulkarni et al., 1983). The development of **liquid membranes** has lead to systems that have both a high permeability and high selectivity. Traditional membranes are essentially solid micro porous filters. Liquid membranes operate by immobilizing a liquid solvent in a micro porous filter or between polymer layers.

A high degree of solute removal can be obtained when using chemical solvents. When the gas, or solute, reacts with the liquid solvent in the membrane, the effect is increased liquid phase diffusivity. As a result, the over all flux of the solute is increased. Furthermore, solvents can be chosen to selectively remove a single solute from a gas stream (Astrita et al., 1983), thus improving selectivity.

The schematic diagram shown in figure 1 illustrates mass transfer across a regular membrane and a liquid membrane. In the regular membrane the solute A passes through the membrane under a pure solution diffusion mechanism, leaving the other gas behind. In the liquid membrane, the enhanced effect of having the liquid solvent, B, can be seen by the additional flux of species AB. This system, with the additional flux is known as facilitated transport. Without the effects of the liquid, mass transfer would be reduced to that of the regular diffusion membrane system whereby the total flux only consists of the flux of species A.

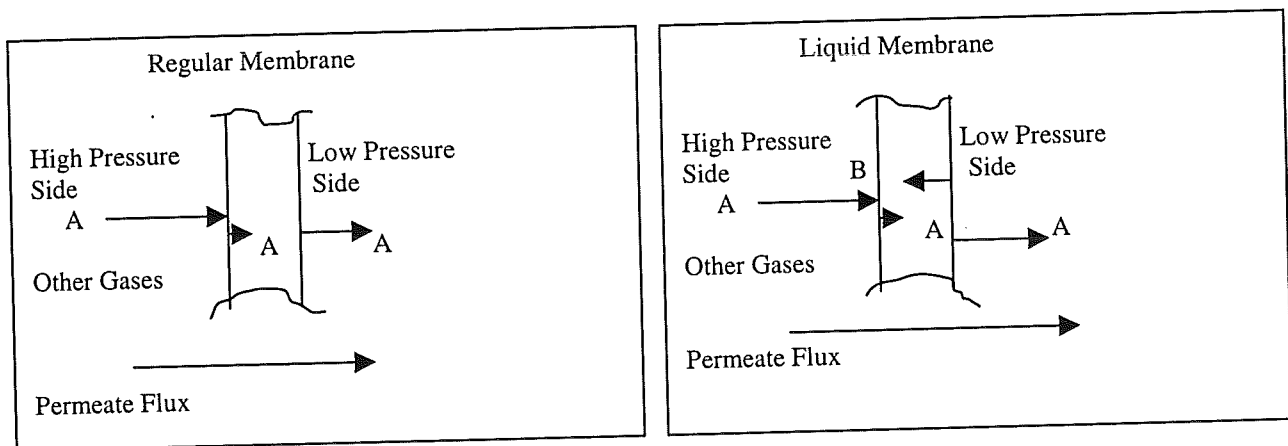


Figure 1.1 Facilitated Transport in a Membrane

1.3 Literature Review

The first work demonstrating a general quantitative understanding of facilitated transport was done by Ward (1970). The work itself carried out a detailed mathematical and experimental investigation of facilitated transport. The basic facilitated transport reaction scheme was modeled for a nitrous oxide / ferrous ion system. The system was modeled under steady state conditions with the goal of developing a model, which predicts the flux of permeate across a membrane. The method of solution was explained very clearly. Since this was some of the first work completed in the area of facilitated transport, a lot of potential was left for future researchers. Namely, the system should be modeled under transient conditions.

Donaldson and Quinn (1975) also studied facilitated transport in liquid membranes, but they applied the theory to a carbon dioxide system. The model was developed as a means of determining diffusional and kinetic parameters for the reaction system. The derivation and solution of equations for the model was not explained clearly. The reaction system was a CO₂ hydration system for the formation of bicarbonate. This left the door wide open for future works in studying CO₂- amine systems, which have evolved into a much more common system for CO₂ capture.

Smith (1977) wrote one of the first reviews on facilitated transport. They provided a comprehensive summary of the research into facilitated membranes at that time. They discussed facilitated oxygen transport, facilitated CO₂ transport and nitric oxide-ferrous chloride facilitated transport system. They provided a very good write up on the governing equations and the formulation of facilitation factor. One drawback of this paper is that the section of CO₂ systems was not for an amine system. At that time CO₂- amine systems were becoming common and therefore one would expect to see researchers exploring that area more aggressively.

Smith and Quinn (1979) developed a model for predicting the facilitation factors in facilitated transport systems. Using the standard reaction mechanism for facilitated transport, they solved one-dimensional, steady state equations, considering both the physical diffusion and chemical reaction terms. They introduce the assumption of equal carrier and carrier complex diffusivities, such as $D_B = D_{AB}$ in order to simplify the analysis. The equations were solved using analytical techniques. Initially they solved the system for nitric oxide / ferrous ion facilitated transport, obtaining comparable results to other studies. Then they studied a CO_2 -MEA system that had more complex chemistry. They did not clearly explain how the governing equations were incorporated into the model. Since the reaction kinetics of CO_2 -amine systems are not fully understood, researchers should be very clear in describing which reaction equations they are using and what assumptions they are employing when simplifying their work. Although they have calculated facilitation factors that compare with the literature, they have not presented any figures that show the facilitation factor trends. Data analysis, be it experimental or mathematical, should include the presentation of charts that illustrate any trends in the data.

Folkner and Noble (1983) studied facilitated transport in membranes under transient conditions. Models were developed in one dimension for the standard facilitated transport reaction mechanism under flat plate, cylindrical, and spherical geometries. The effects of the inverse Damkohler number, the equilibrium constant, the carrier concentration and geometry on the facilitation factor were determined. The assumption that $D_B = D_{AB}$ was used. No real discussion was presented concerning how the equations were solved except to say a computer package was used. Very few authors seem to provide useful, easy-to-understand, information in their articles about their specific modeling procedure. Researchers should be more willing to share such information in the hopes of aiding future projects.

Meldon (1985) modelled the standard reaction mechanism for facilitated transport under transient conditions. In this work the permeation across the membrane was studied with emphasis on the permeation time lag. In this work they state that previous researchers

may have made mistakes when analysing transient systems with fast chemical reactions. In their work they explain the error but the overall paper is confusing. The system was modelled using finite difference techniques, but no other details are given.

Basaran (1989) studied facilitated transport using unequal carrier and complex diffusivities, such that $D_B \neq D_{AB}$. The standard reaction mechanism for facilitated transport was modeled, but for the first time the simplifying assumption that $D_B = D_{AB}$ was not used. The equations were solved by asymptotic analysis and numerically by the Galerkin finite element method. Many of these methods are very confusing and few authors explain their procedures clearly. The model was solved for facilitation factors. The system seemed to be for a very generic case. A discussion that supported the reasons for modeling with unequal carrier and carrier complex diffusivities would add weight to their work. Mentioning situations where the assumption $D_B = D_{AB}$ was a poor modeling choice would have been beneficial.

Guha (1990) studied the steady state facilitated transport of CO_2 through an immobilized liquid membrane containing diethanolamine (DEA) solution. The effects of membrane thickness and downstream CO_2 partial pressure were investigated. The system was represented by a set of coupled diffusion reaction equations that were solved semi-analytically using matched asymptotic expansions and the regular perturbation method. The system was also solved numerically, using a finite difference technique with non-uniform mesh size, and using orthogonal collocation on finite elements. There was little explanation for this procedure. The reaction mechanism for CO_2 DEA was presented, including the intermediate steps and overall reaction term. A good description of the development of the governing equations is given. Their work would have been more beneficial if the model was expanded to be valid for other amines such as MEA, triethanolamine (TEA), and methyldiethanolamine (MDEA).

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LIST OF SYMPBOLS AND ABBREVIATIONS

A	Permeating gas or solute
B	Carrier or solvent
AB	Carrier complex.
C _{A0}	Initial concentration of solute gas.
C _i	Concentration of component i.
C _T	Total amine concentration.
CO ₂	Carbon dioxide.
DEA	Diethanolamine.
D _i	Diffusivity of component i..
F	Facilitation factor.
i	Variable representing location in the discretized membrane.
k ₁ ,k ₂	Forward and reverse reaction rate constants for equations (1.1), (1.4) and (1.7).
k _a , k _b , k _c	Forward and reverse reaction rate constants for Equations (1.2), (1.3), (1.5), and (1.6).
L	Membrane thickness.
MDEA	Methyldiethanolamine.
MEA	Monoethanolamine.
n	Variable representing time in Fortran model.
N	Represents the last location in the discretized membrane (x=L).
R	Functional group for MEA = -CH ₂ CH ₂ OH
r _i	Reaction rate for species i.

t	Time
TEA	Triethanolamine.
x	Distance in x-direction.
x ₁	Variable for location at discretized membrane inlet.
A	= cross sectional area of the core, cm ²
C	= concentration of the chemical, %wt
C ₀	= concentration of the chemical, %wt
k _i	= kinetic constant of adsorption (i=1) or desorption (i=2), 1/hr
k	= absolute permeability of the porous medium, mD
L	= length of the porous bed, cm
m _i	= monolayer coverage of component i per unit of adsorbent, mg/g
n ⁰	= amount of liquid per unit mass of adsorbent, mg/g
n'	= amount adsorbed per unit mass of adsorbent, mg/g
n' _i	= amount of component i adsorbed per unit mass of adsorbent, mg/g
n' _i	= equilibrium surface excess of component i per unit mass of adsorbent, mg/g
n _i ^{ea}	= Actual surface excess of component i per unit mass of adsorbent, mg/g
PV	= pore volume, AφL, cm ³
q	= flow rate, ml/hr
S	= selectivity, dimensionless
t	= time, s
u	= local speed, cm/s
x _i	= bulk phase mass fraction of component i
x' _i	= adsorbed phase mass fraction of component i
z	= distance along porous bed, cm
α	= entrainment rate constant, 1/cm
λ	= Dispersion parameter, cm
φ	= Porosity of the rock
ρ	= liquid density, mg/ml
ρ _r	= rock density, g/ml
ρ _g	= Gas density, mg/ml

Dimensionless Variables

$$\Delta = \frac{D_C}{D_A} \frac{k_1 C_T}{k_2} \quad \text{Mobility Ratio}$$

$$\varepsilon = \frac{D_C}{k_2 L^2 C^T} \quad \text{Inverse Damkohler number.}$$

$$K = \frac{k_1 C_{A0}}{k_2} \quad \text{Reaction equilibrium constant}$$

$$X = \frac{x}{L} \quad \text{Dimensionless Distance}$$

$$\tau = \frac{t D_A}{L^2} \quad \text{Dimensionless Time}$$

$$C_A^* = \frac{C_A}{C_{A0}} \quad \text{Dimensionless concentration of the solute gas.}$$

$$C_B^* = \frac{C_B}{C_T} \quad \text{Dimensionless concentration of the carrier or solvent.}$$

$$C_{AB}^* = \frac{C_{AB}}{C_T} \quad \text{Dimensionless concentration of the carrier or complex.}$$

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Carbon dioxide plays a significant role industrially, economically, and environmentally in our world. Whether it is a component in urea manufacture, a contaminant in natural gas stream, or used for beverage carbonation, the presence of CO₂ in modern existence is unmistakable. There are many uses for CO₂ in both small and large-scale applications. These uses are quite diverse, ranging from chemical feedstock to recreation. The majority of the CO₂ market, however, involves the production of urea (Astraita et al., 1983), the food and beverage industry (Rushing et al., 1994), and enhanced oil recovery (Cacoana et al., 1992).

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process selection. Common separation methods include absorption, low temperature distillation, adsorption, and membrane systems (Geankopolis et al., 1993). In the present study membrane system has been focused.

Alkanolamines are used to absorb carbon dioxide (CO_2) in a variety of industrial processes. In the case of immobilized liquid membrane systems, alkanolamines can be used to promote facilitated transport. Facilitated transport occurs when the mass transport rate of a species across a membrane is increased or enhanced by the permeation of a carrier complex across the membrane. In CO_2 -amine systems, the carrier complex is the product of the reaction between CO_2 and the amine, or the carbamate.

While a number of researchers have worked on developing facilitated transport models, few have been developed that properly address CO_2 separation systems. This work re-examines the facilitated transport of CO_2 across immobilized liquid membranes using a homogeneous chemical-diffusion model. The governing equations were solved using the finite difference Barakat-Clark scheme. Results were used to determine the facilitation factor, a dimensionless measure of the solute flux through the membrane. The facilitation factor was evaluated with respect to the effect of the inverse Damkohler number, the mobility ratio, and the dimensionless reaction equilibrium constant.

In the past three decades, fractured rock domains have received increasing attention by the researchers from a number of disciplines, including hydrogeology, petroleum engineering, and environmental engineering. The importance of fractures is particularly enhanced when one deals with carbonate formations, both in water flow and petroleum production, because most of these formations are known to be fractured. The subject has been investigated by petroleum engineers in connection with multiphase flow because many important petroleum reservoirs are in fractured rock formations. Of special interest are reservoirs composed of fractured porous rocks in which the matrix blocks, surrounded by the network of fractures, are porous. The permeability of such blocks is often rather low, but the porosity and the storage capacity for fluids are very high. Environmental engineers have been investigating the problem in connection with geological isolation of radioactive waste and remediation of ground water. Hydrologists deal with fractured

formations because numerous deep aquifers are fractured. Chemical engineers mainly deal with chemical transport in limestone, but not necessarily in its fractured form (Arsic et al., 1991; Couturier et al., 1993).

In Canada, Switzerland, and Sweden large national research programs are underway to study radionuclide transport in crystalline rocks. Finland also intends to situate their repository in similar rocks and has a research program directed toward this end. Other countries, including Japan, France, Spain, the United Kingdom, and the USA have or have had research programs oriented towards crystalline rocks. In addition, an international field of research program is in progress in the Stripa mine in Sweden. The research is aimed at understanding the processes that determine the flow paths and the flow rates of water in the fractured rock masses.

Solutes that are dissolved in water will be carried by moving water, but various other mechanisms are involved in the process of solute transportation. Small molecules or ions diffuse in a concentration gradient and can move from one 'stream tube' to another. Different water volumes move with different velocities and may mix at more or less regular intervals. The dissolved species may also experience kinetic effects caused by physical processes. One such process that may have a large impact for solute transport in fractured rock is the diffusion in and out of zones in which the water is moving so slowly that it can, for all practical purposes, be assumed to be stagnant. Such stagnant zones can be expected in fractures with uneven surfaces and with fracture-filling materials. In rocks with a connected matrix they can be very much larger than the mobile water volume in the fracture. Because the stagnant zones are reached by diffusion, the volume of stagnant water accessed depends on the residence time of the flowing water.

Different approaches to solute transport in fractured media have been attempted. These include the analysis of a single fracture (e.g. Grisak and Pickens, 1981; Tang et al., 1981; Sudicky and Frind, 1984). While some researchers considered the porous medium as comprised of equally spaced fractures (Sudicky and Frind, 1984), others have used deterministic study of flow in an irregular network of fractures contained in an

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acceptable specifications. The conventional employed treatment techniques are chemical based and are expansive along with serious environmental concerns. Environmentally friendly, naturally occurring substance limestone was investigated for its sulfur adsorption capability in down-hole applications. It was found satisfactory for sulfur adsorption capability. The gas containing SO_2 was passed through limestone packed column and a change in concentration at the outlet was noticed by bubbling the exit stream through a water beaker. The pH of water was monitored throughout the experiment. A numerical model was developed to simulate the sulfur adsorption on limestone.

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At the very outset, heartfelt thanks go to my Supervisor Dr. M. R. Islam for his valuable guidance, encouragement, generous support and supervision throughout this work. His patience and his confidence in me throughout this work are gratefully acknowledged.

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CHAPTER 1

FACILITATED TRANSPORT: A NUMERICAL MODEL FOR PREDICTING FACILITATION FACTORS

1.1 Summary

Alkanolamines are used to absorb carbon dioxide (CO_2) in a variety of industrial processes. In the case of immobilized liquid membrane systems, alkanolamines can be used to promote facilitated transport. Facilitated transport occurs when the mass transport rate of a species across a membrane is increased or enhanced by the permeation of a carrier complex across the membrane. In CO_2 -amine systems, the carrier complex is the product of the reaction between CO_2 and the amine, or the carbamate.

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effect of various parameters including concentration, facilitation factor, upstream partial pressure, distance across the membrane and time were considered. Davis suggested that his work could be improved by studying the effects of convection and by considering multidimensional diffusion.

Fan (1992) studied the diffusion of gas through a membrane. In his work he looked at estimating diffusion coefficients and solubilities. The governing equation was Fick's second law of diffusion. Since their work operated solely on physical mass transfer, without chemical reaction, their system was quite simple mathematically. The methods of Laplace transformation and separation of variables were used to solve their equations. Results were compared to a three-point finite difference technique. Analytical solutions coincide with the numerical solutions. Although the paper is one of the more recent works being reviewed, they have taken a step backwards by simplifying the work involved and not considering systems operating under chemical reactions. Working models should offer the option of including a chemical reaction in the system.

Dindi (1992) modeled a two-step reaction mechanism for facilitated transport. The so-called "parasitic binding" mechanism was solved for a one-dimensional steady state flat plate geometry problem. The steady state equations were solved for the facilitation factor, investigating the effect of total carrier concentration, reaction equilibrium values, and membrane thickness. In this work the previously used assumption of equal carrier and carrier complex diffusivities ($D_{AB} = D_B$) has been extended to $D_B = D_{AB} = D_{AB2}$. Even the first assumption is not always valid; therefore care must be taken when extending such an assumption. Equations were solved using analytical techniques.

Jemaa and Noble (1992) improved an earlier analytical solution for predicting facilitation factors in facilitated transport systems. They still used the standard reaction mechanism. The improvement is accomplished by assuming a small non-zero solute concentration of the exit of the membrane. This is likely more realistic since not all separation systems will be entirely efficient. Researchers need to begin investigating more complex reaction mechanisms for facilitated transport.

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Teramoto (1996) studied the facilitated transport of CO₂ through supported liquid membranes that were based on the amines MEA and DEA. He conducted some very good experimental work and found that the DEA system performed slightly well than the MEA system. The model he developed was for a steady-state system, and it was not explained very clearly. He presented a set of algebraic equations that can be solved simultaneously to solve the facilitation factor. He simulated results compared with their experimental results.

1.4 Reaction Chemistry And Governing Equations

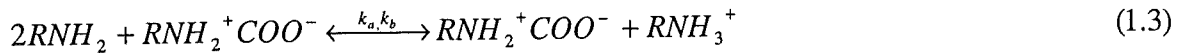
The standard reaction mechanism for facilitated transport systems was presented by Ward (1970) when he studied the nitrous oxide reaction with ferrous ions. The general mechanism is:



In this formulation the solute gas, A, reacts with a non-volatile molecular or ionic species, B, to form the carrier complex AB. The reversible reaction moves forward and backwards according to rate constants k_1 and k_2 respectively. This reaction mechanism has been the most commonly studied facilitated transport system (Smith and Quinn, 1989, Jemaa and Noble, 1992). Only a few researchers, such as Guha (1990) and Dindi (1992) have looked at variations of this reaction mechanism.

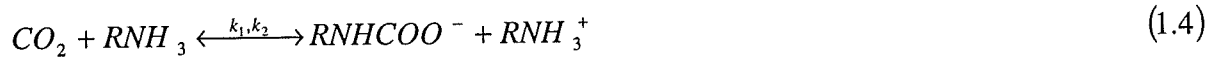
Industrially, monoethanolamine (MEA) has been proven as a feasible solvent for CO₂ separation and it is no surprise that there are numerous CO₂ separation plants operating throughout the world. Therefore this work focused on CO₂ separation in a liquid membrane system using MEA. Despite all of the research conducted on CO₂-MEA systems, the reaction mechanism for the process, or any amine system for that matter, is generally not well understood. The commonly accepted reaction mechanism, presented by Laddha and Dankwerts (1981) is:

Formation of Carbonate:



The addition of these two reactions leads to the overall reaction:

Overall Reaction:



The molecular interaction for the overall reaction during facilitated transport is shown in figure 1.2. On the high-pressure side the mass transfer is enhanced by the forward reaction of CO_2 with MEA. In this initial step the carrier is consumed. Similarly on the low-pressure side of the membrane the carrier is released due to the reversibility of the reaction. The transport of CO_2 through such a system depends on the total carrier concentration, the physically dissolved gas concentration on the upstream and downstream sides of the membrane thickness, the relative magnitudes of the diffusion coefficients (both solute and solute carrier complex), the magnitude of the reaction rate constants and the degree of reversibility of the reaction (Guha et., 1990).

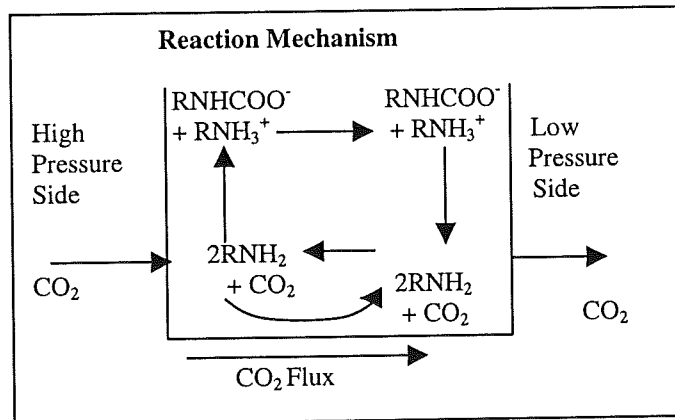


Figure 1. 2: CO_2 -MEA Facilitated Transport Reaction Mechanism

In applying this to a generalized reaction mechanism we get:



Overall Reaction:



In this system the condition of electro-neutrality is $[C^+] = [AB^-]$, therefore the conservation of amine results in the total amine concentration, C_T , being:

$$C_T = C_B + C_{AB^-} + C_{C^+} \quad (1.8)$$

The reaction rate for the overall reaction can be written:

$$r_A = k_1 C_A C_B^2 - k_2 C_{AB}^2 \quad (1.9)$$

$$r_A = 2r_B = -r_{AB} \quad (1.10)$$

The governing equations were based on the Fick's second law of diffusion, including the chemical reaction effects. The diffusion-reaction equations were written for the solute, A, the solvent or carrier, B, and the carrier complex, AB.

1.5 Governing Equations

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial X^2} - k_1 C_A C_B^2 + k_2 C_{AB}^2 - V_A \frac{\partial C_A}{\partial X} \quad (1.11)$$

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial X^2} - 2k_1 C_A C_B^2 + 2k_2 C_{AB}^2 - V_B \frac{\partial C_B}{\partial X} \quad (1.12)$$

$$\frac{\partial C_{AB}}{\partial t} = D_{AB} \frac{\partial^2 C_{AB}}{\partial X^2} + k_1 C_A C_B^2 - k_2 C_{AB}^2 - V_{AB} \frac{\partial C_{AB}}{\partial X} \quad (1.13)$$

Boundary Conditions

$$@ \quad t = 0 \quad C_A = 0 \quad C_B = C_T \quad \frac{\partial C_{AB}}{\partial X} = 0 \quad (1.14)$$

$$@ \quad x = x_1 \quad C_A = C_{A0} \quad \frac{\partial C_B}{\partial X} = 0 \quad \frac{\partial C_{AB}}{\partial X} = 0$$

$$@ \quad x = L \quad C_A = 0 \quad \frac{\partial C_B}{\partial X} = 0 \quad \frac{\partial C_{AB}}{\partial X} = 0$$

$$C_T = C_B + 2C_{AB}$$

$$D_B = D_{AB}$$

The above equations were converted into a dimensionless form. By developing the model with dimensionless equations and parameters, the results can be easily compared to similar studies, which are also dimensionless. The dimensionless parameters were defined as:

$$\Delta = \frac{D_{AB}}{D_A} \frac{k_1 C_T}{k_2} \quad \epsilon = \frac{D_{AB}}{k_2 L^2 C_T} \quad K = \frac{k_1 C_{A0}}{k_2} \quad X = \frac{x}{L} \quad (1.15)$$

$$\tau = \frac{t D_A}{L} \quad C_A^* = \frac{C_A}{C_{A0}} \quad C_B^* = \frac{C_B}{C_T} \quad C_{AB}^* = \frac{C_{AB}}{C_T}$$

$$V^* = \frac{V}{V_0}$$

Dimensionless equations:

$$\frac{\partial C_A^*}{\partial \tau} = \frac{\partial^2 C_A^*}{\partial X^2} + \frac{\Delta}{\epsilon} \left[\frac{1}{K} C_{AB}^{*2} - C_A^* C_B^{*2} \right] - V_A^* \frac{\partial C_A^*}{\partial X} \quad (1.16)$$

$$\frac{\partial C_B^*}{\partial \tau} = \left(\frac{D_{AB}}{D_A} \right) \left[\frac{\partial^2 C_B^*}{\partial X^2} + \frac{K}{\epsilon} \left(\frac{2}{K} C_{AB}^{*2} - 2 C_A^* C_B^{*2} \right) \right] - V_B^* \frac{\partial C_B^*}{\partial X} \quad (1.17)$$

$$\frac{\partial C_{AB}^*}{\partial \tau} = \left(\frac{D_{AB}}{D_A} \right) \left[\frac{\partial^2 C_{AB}^*}{\partial X^2} + \frac{K}{\epsilon} \left(C_A^* C_B^{*2} - \frac{1}{K} C_{AB}^{*2} \right) \right] - V_{AB}^* \frac{\partial C_{AB}^*}{\partial X} \quad (1.18)$$

Boundary Conditions:

$$@ \quad \tau = 0 \quad C_A^* = 0 \quad C_B^* = 1 \quad C_{AB}^* = 0 \quad (1.19)$$

$$@ \quad X = 0 \quad C_A^* = 1 \quad \frac{\partial C_B^*}{\partial X} = 0 \quad \frac{\partial C_{AB}^*}{\partial X} = 0$$

$$@ \quad X = L \quad C_A^* = 0 \quad \frac{\partial C_B^*}{\partial X} = 0 \quad \frac{\partial C_{AB}^*}{\partial X} = 0$$

$$1 = C_B^* + 2C_{AB}^*$$

The boundary conditions at C_B and C_{AB} represent that the carrier and solute carrier complex are non volatile and constrained to stay within the system. The boundary condition on A indicate that there is a constant source of A at one boundary and A is rapidly removed from the opposite boundary so that the concentration is zero at that point. This last boundary condition corresponds to a maximum flux of A through the membrane. For non-zero concentration of A at the outlet the total flux is reduced due to a decreased diffusion flux and decreased facilitation since the reverse reaction is slowed. Also, the exit concentration becomes time dependant [Folkner and Noble, 1983].

1.6 Barakat-Clark Model Formulation

The governing equations were solved using the finite difference technique proposed by Barakat and Clark (1966). In this formulation, Barakat and Clark discretize second derivative terms into two separate formats: One for forward difference and the other for backward difference. The true solution is then obtained by taking the average of two different equations. The Barakat Clark method has an accuracy of $O(\Delta x^4)$ and $O(\Delta t^2)$. The discretized format for the second derivative terms appearing in governing equations is as follows:

Forward Difference:

$$\frac{\partial^2 C}{\partial x^2} \Rightarrow \frac{C_{i+1}^n - C_i^n - C_i^{n+1} + C_{i-1}^{n+1}}{\Delta x^2} \quad (1.20)$$

Backward Difference:

$$\frac{\partial^2 C}{\partial x^2} \Rightarrow \frac{C_{i+1}^{n+1} - C_i^{n+1} - C_i^n + C_{i-1}^n}{\Delta x^2} \quad (1.21)$$

In using this approach, this project required the descretization of the three concentration equations presented earlier (1.16, 1.17, 1.18). When isolating for the future time step concentration variables, the individual equations become:

Forward:

$$C_{A_i}^{*n+1} = \frac{\frac{d\tau}{dx^2} (C_{A_{i+1}}^{*n} + C_{A_{i-1}}^{*n+1}) + \left(1 - \frac{d\tau}{dx^2} - \frac{d\tau\Delta}{\varepsilon} C_{B_i}^{*2}\right) C_{A_i}^{*n} + \frac{d\tau\Delta}{\varepsilon K} C_{AB_i}^{*n2}}{\left(1 + \frac{d\tau}{dx^2}\right)} - V_A^* (C_{A_{i+1}}^{*n} - C_{A_{i-1}}^{*n}) \quad (1.22)$$

$$C_{B_i}^{*n+1} = \frac{\frac{D_{AB}}{D_A} \frac{d\tau}{dx^2} (C_{B_{i+1}}^{*n} + C_{B_{i-1}}^{*n+1}) + \left(1 - \frac{D_{AB}}{D_A} \frac{d\tau}{dx^2} - \frac{2D_{AB}}{D_A} \frac{d\tau K}{\varepsilon} C_{A_i}^{*n} C_{B_i}^{*n}\right) C_{B_i}^{*n} + \frac{2D_{AB}}{D_A} \frac{d\tau\Delta}{\varepsilon} C_{AB_i}^{*n2}}{\left(1 + \frac{D_{AB}}{D_A} \frac{d\tau}{dx^2}\right)} \quad (1.2)$$

$$-V_B^* (C_{B_{i+1}}^{*n} - C_{B_{i-1}}^{*n})$$

$$C_{AB_i}^{*n+1} = \frac{\frac{D_{AB}}{D_A} \frac{d\tau}{dx^2} (C_{AB_{i+1}}^{*n} + C_{AB_{i-1}}^{*n+1}) + \left(1 - \frac{D_{AB}}{D_A} \frac{d\tau}{dx^2} - \frac{D_{AB}}{D_A} \frac{d\tau}{\varepsilon} C_{AB_i}^{*n}\right) C_{AB_i}^{*n} + \frac{D_{AB}}{D_A} \frac{d\tau K}{\varepsilon} C_{A_i}^{*n2} C_{AB_i}^{*n2}}{\left(1 + \frac{D_{AB}}{D_A} \frac{d\tau}{dx^2}\right)} \quad (1.24)$$

$$-V_{AB}^* (C_{AB_{i+1}}^{*n} - C_{AB_{i-1}}^{*n})$$

Backward Difference:

$$C_{A_i}^{*n+1} = \frac{\frac{d\tau}{dx^2} (C_{A_{i+1}}^{*n+1} + C_{A_{i-1}}^{*n}) + \left(1 - \frac{d\tau}{dx^2} - \frac{d\tau\Delta}{\varepsilon} C_{B_i}^{*2}\right) C_{A_i}^{*n} + \frac{d\tau\Delta}{\varepsilon K} C_{AB_i}^{*n2}}{\left(1 + \frac{d\tau}{dx^2}\right)} - V_{A_{i+1}}^* (C_{A_{i+1}}^{*n} - C_{A_{i-1}}^{*n}) \quad (1.25)$$

$$C_{B_i}^{*n+1} = \frac{\frac{D_{AB}}{D_A} \frac{d\tau}{dx^2} (C_{B_{i+1}}^{*n+1} + C_{B_{i-1}}^{*n}) + \left(1 - \frac{D_{AB}}{D_A} \frac{d\tau}{dx^2} - \frac{2D_{AB}}{D_A} \frac{d\tau K}{\varepsilon} C_{A_i}^{*n} C_{B_i}^{*n}\right) C_{B_i}^{*n} + \frac{2D_{AB}}{D_A} \frac{d\tau\Delta}{\varepsilon} C_{AB_i}^{*n2}}{\left(1 + \frac{D_{AB}}{D_A} \frac{d\tau}{dx^2}\right)} \quad (1.26)$$

$$-V_B^* (C_{B_{i+1}}^{*n} - C_{B_{i-1}}^{*n})$$

$$C_{AB_i}^{*n+1} = \frac{\frac{D_{AB}}{D_A} \frac{d\tau}{dx^2} (C_{AB_{i+1}}^{*n+1} + C_{AB_{i-1}}^{*n}) + \left(1 - \frac{D_{AB}}{D_A} \frac{d\tau}{dx^2} - \frac{D_{AB}}{D_A} \frac{d\tau}{\varepsilon} C_{AB_i}^{*n}\right) C_{AB_i}^{*n} + \frac{D_{AB}}{D_A} \frac{d\tau K}{\varepsilon} C_{A_i}^{*n2} C_{AB_i}^{*n2}}{\left(1 + \frac{D_{AB}}{D_A} \frac{d\tau}{dx^2}\right)} \quad (1.27)$$

$$-V_{AB}^* (C_{AB_{i+1}}^{*n} - C_{AB_{i-1}}^{*n})$$

1.6.1 Boundary Conditions

The boundary conditions for this problem are first order differential equations, therefore Neuman Boundary conditions were used in the model such that:

Inlet:

$$\frac{\partial C}{\partial x} \Rightarrow \frac{4C_{i+1}^n - C_{i+2}^n - 3C_i^{n+1}}{2dx} \quad (1.28)$$

Outlet:

$$\frac{\partial C}{\partial x} \Rightarrow \frac{C_{N-2}^n - 4C_{N-1}^n + 3C_N^{n+1}}{2dx} \quad (1.29)$$

In equation set (1.19), boundary conditions stipulate that all first derivative terms equal zero. Therefore, the boundary conditions for all concentrations C_A , C_B , C_{AB} , can be written as follows:

Inlet:

$$C_{X_1}^{*n+1} = \frac{4C_{X_{i+1}}^{*n} - C_{X_{i+2}}^{*n}}{3} \quad (1.30)$$

Outlet:

$$C_{X_N}^{*n+1} = \frac{4C_{X_{N-1}}^{*n} - C_{X_{N-2}}^{*n}}{3} \quad (1.31)$$

Where X is representing the species B, and AB.

1.7 Facilitation Factor

The facilitation factor is a measure of the enhanced permeation across a membrane due to the presence of a reacting carrier. Essentially it is the ratio of solute flux with facilitation to solute flux without facilitation. Despite the simple definition of the facilitation factor, a number of researchers have tried to define it mathematically in their research. The methods used for derivation vary widely as do the formulations. In this study a number of these formulations were tested but few produced acceptable results. Furthermore, the results from the different formulations were not acceptable amongst each other. This led to the conclusion that the development of a facilitation factor equation is specific to the system being studied. With this in mind, a simple formulation presented by Smith (et al., 1977), was finally used in the model. The derivation of this formulation is as follows:

$$F = \frac{N_{A_r}}{N_{A_0}} \quad (1.32)$$

$$N_{A_r} = -D_A \frac{dC_A}{dx} - D_{AB} \frac{dC_{AB^*}}{dx} \quad (1.33)$$

$$N_{A_0} = -D_A \frac{dC_A}{dx} \quad (1.34)$$

By substituting Equations 1.33 and 1.34 into Equations 1.32 we can write:

$$F = \frac{\frac{D_A(C_A^{*0} - C_A^{*L})}{L} + \frac{D_{AB}(C_{AB}^{*0} - C_{AB}^{*L})}{L}}{\frac{D_A(C_A^{*0} - C_A^{*L})}{L}} \quad (1.35)$$

$$F = 1 + \frac{D_{AB}(C_{AB}^{*0} - C_{AB}^{*L})}{D_A(C_A^{*0} - C_A^{*L})} \quad (1.36)$$

Earlier during this study the facilitation factor formulation developed by Jain and Schultz (1982) was tested. The results produced by this model were erroneous in that the values were less than one. Reconsideration of this situation led to the possible conclusion that the formula should have added a one to the predicted results. Basically the formula produces values for the facilitation factor that were above and beyond the standard flux value that was without facilitation.

1.8 Model Results

This study consisted of a number of separate investigations. Initially the Barakat-Clark model formulation was compared to a standard explicit formulation. The results from the two models were very similar, thus verifying the Barakat-Clark model formulation. Secondly, the Barakat-Clark model was used to demonstrate the work reported by Folkner and Noble, 1983. This was done to show the model could generate the same results presented by the researchers in the area. The model generated satisfactory results for the concentration profiles across the membrane, however, the facilitation was not duplicated. Next, a set of runs was conducted to identify the effects of diffusion coefficients and their ratio on the facilitation factor. Finally, the model was run for different scenarios in an effort to identify the effects of system parameters on the facilitation factor. The effect of the inverse Damkohler number, ϵ , the mobility ratio, Δ , and the reaction equilibrium constant, K , were studied. Unfortunately kinetic and diffusion data for CO₂-alkanoamine systems is not well established. Diffusivity data for the parametric study was taken from Teramoto (et al., 1996), who studied a CO₂-MEA system.

Table 1.1: Values of parameters used in governing equation

ϵ	Δ	K	V_A	V_B	V_{AB}
0.1	5	0.1	0.1	0.1	0.1
1	15	1.0	0.5	0.05	0.05
10	25	10	1	0.01	0.01

$$D_{CO_2} = D_A = 1.97 \times 10^{-5} \text{ cm}^2$$

$$D_{RNH_2} = D_B = D_{AB} = 1.12 \times 10^{-5} \text{ cm}^2$$

1.8.1 Verify Model Output

Before presenting the facilitation factor results it is important to examine the fundamental system results to ensure that the model is working properly. This can be done by checking the concentration profiles of the diffusing species across the membrane thickness. This verification has been broken up into two parts: the first section examines a system that operates without facilitation and the second verifies a facilitated transport system.

1.8.2 Verify Mass Transfer Without Facilitation

When a system operates as a traditional solution-diffusion membrane there is no facilitation, or rather, no chemical reaction. Gas species diffuse across the membrane based on their solubility and diffusivity in the membrane. The current model only accounts for one diffusing species, solute A.

The concentration profile for solute A diffusing across the membrane is shown in Figure 1.3. In part (a) the concentration at various points throughout the thickness of the membrane is shown. Steady state conditions are indicated by the flat concentration trends

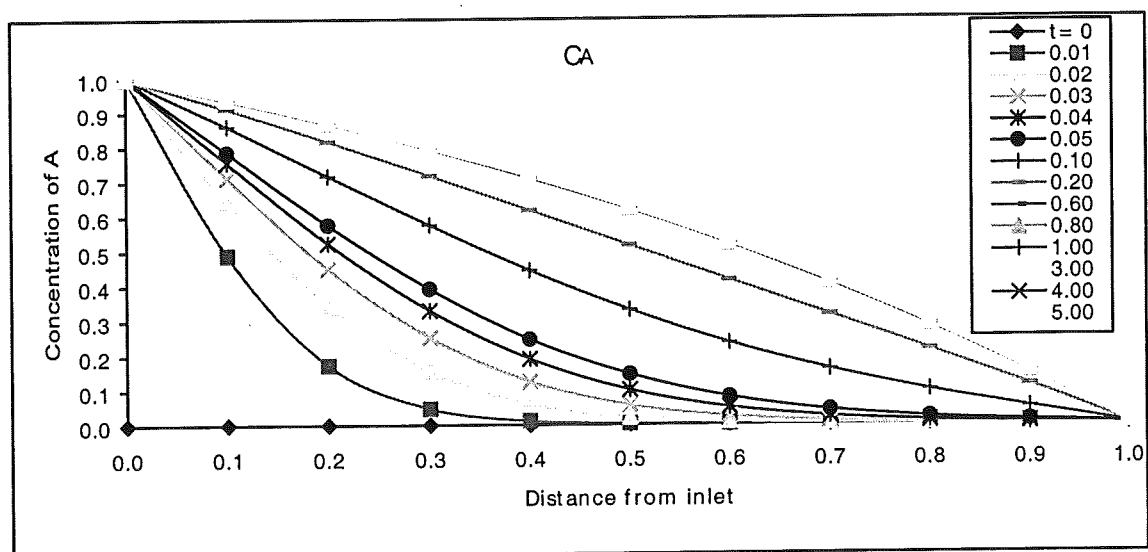
($dC/dx = 0$). At the inlet the concentration of C_A is 1.0 but this reduces to 0.0 at the membrane outlet.

The same results are shown in part (b) but this time the concentration is plotted against the membrane thickness. The steady state conditions are indicated by a straight-line profile. A regression on the black curve at $T = 5.0$ produces the equation $y = -x + 1$. This is expected since the concentration profile through the membrane should be linear in the absence of chemical reaction.

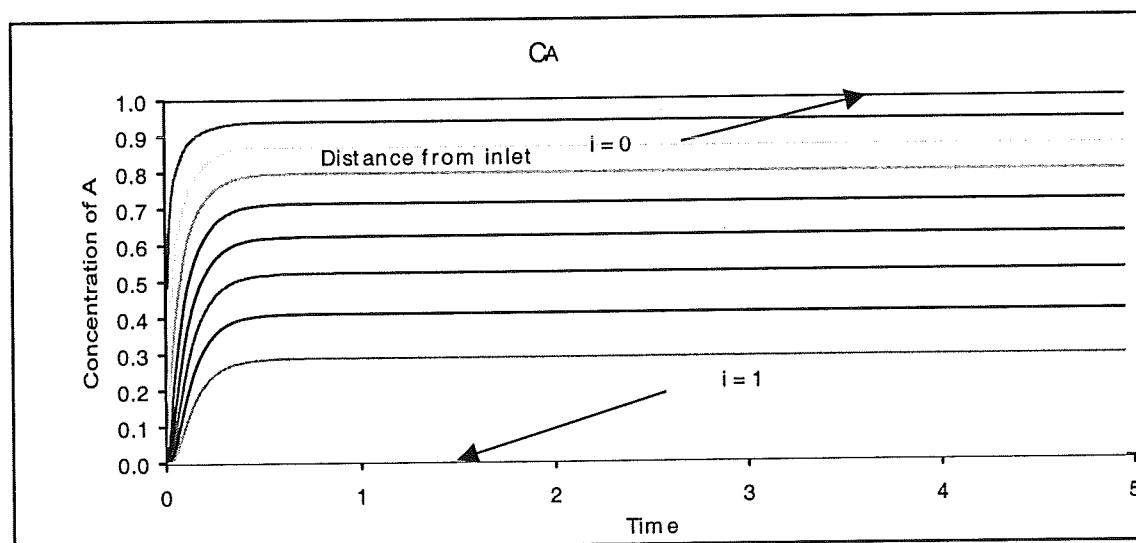
1.8.3 Mass Transfer With Facilitation

The model validity for a system with facilitation can be verified by examining the concentration profiles of the three reacting species across the membrane. The concentration profiles for the solute gas (A), the carrier (B), and the carrier complex (AB) across the membrane are presented in figure 1.4. There are six parts contained in this figure, two parts for each concentration profile. One chart plots concentration versus time and the other plots concentration versus location in the membrane (thickness).

Part (a) and (b) of the Figure 1.4 show that the concentration of A decreases across the membrane thickness with time, finally reaching zero at the outlet. Inside the membrane, the concentrations reach a steady-state value at each location. This is the desired behavior since the goal is to remove CO_2 . This happens through a reaction of A with B, therefore we should expect to see an increase in the concentration of B, the carrier, across the thickness of the membrane. This is in fact the case, and the behavior can be seen in parts (c) and (d). The concentration profile for B realistically predicts that it is consumed as it approaches the membrane inlet, but regenerated at the outlet upon the desorption of the carrier complex, AB. Finally, the concentration of AB is expected to decrease across the membrane. This is because it forms at the inlet of the membrane but reverts into A and B at the outlet of the membrane. The model successfully predicts this behavior, which is shown in parts (e) and (f).

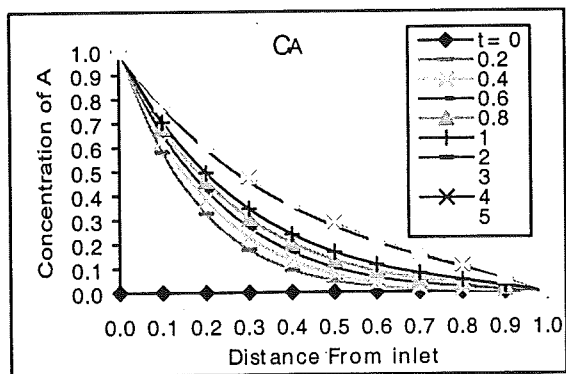


(a)

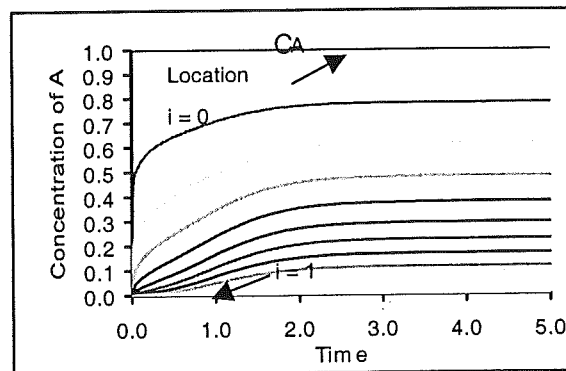


(b)

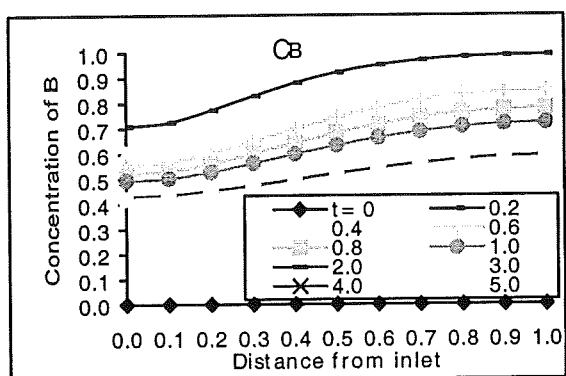
Figure 1. 3: Mass Transfer without Facilitation.



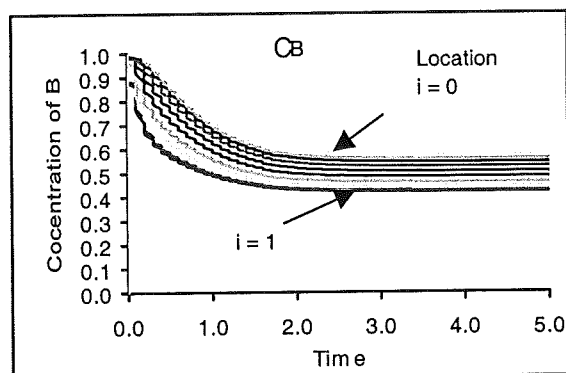
(a)



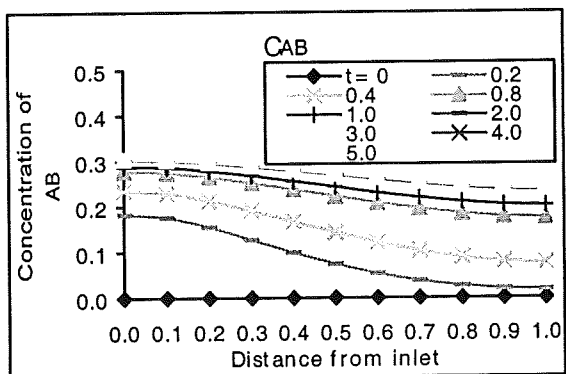
(b)



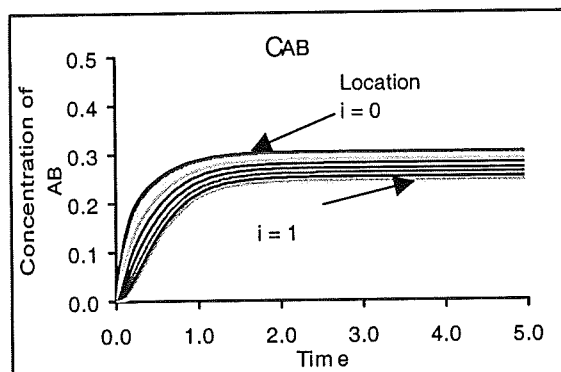
(c)



(d)



(e)



(f)

Figure 1. 4: Mass Transfer with Facilitation

1.8.4 Parametric Effects on Facilitated Transport

In general it can be said that increasing the inverse Damkohler number, ϵ , reduces facilitation; increasing the mobility ratio, Δ , decreases facilitation; and increasing the reaction equilibrium constant, K , increases facilitation. Figure 1.5 shows the effects of these parameters on the facilitation factor.

Part (a) shows that an increasing inverse Damkohler number, ϵ , has a negative effect on the facilitation factor. This result is expected and compares to the findings of Folkner and Noble, 1983. Since ϵ is inversely related to the total carrier concentration, C_T , an increase in ϵ means that C_T is reduced. Therefore, with less chemical solvent in the system, the facilitation transport is reduced.

The effect of the mobility ratio, Δ , on facilitation can be seen in part (b). An increasing Δ has a negative effect on the facilitation factor. This result was not expected, does not compare to the literature, and is currently under review. Normally it would be expected that an increasing Δ , would increase facilitation. This is because Δ is a measure of the carrier concentration and directly relates to the total amine concentration. When V increases C_T also increases. With more chemical solvent in the system there are more reactions between A and B, resulting in a higher concentration of AB. Therefore facilitation should be increased rather than decreased. One possible explanation for the unexpected results is the assumed values for D_A and D_{AB} . The effect of D_{AB} on the facilitation factor will be presented later in the report. It is possible that these values can affect whether the facilitation factor will increase or decrease with an increasing Δ value.

The effect of the equilibrium constant, K , on the facilitation factor is shown in part (C). The facilitation is improved when K increases. This parametric effect is quite interesting and deserves further investigation. Since K is a function of the initial concentration of solute gas, A, at the inlet, it will have an impact on the overall flux. A part of that flux will be due to facilitated transport, while the rest will be a result of regular diffusion

across the membrane. With a very high K value the carrier will operate near saturation capacity all the time, thus forcing all remaining gas to permeate across the system by diffusion only. When this happens, the facilitation factor will actually go down because the facilitated flux will reach a maximum value whereas the regular diffusion flux has no maximum. Thus the statement that facilitation increases with an increasing K should be accompanied by an upper limit for K because at very high K values the facilitation will actually decrease.

The effect of velocity on facilitation is shown in Fig: 1.6. It can be seen in part (a) that an increase in the velocity of A has no significant effect on facilitation factor. The increase in the velocity of B increases the facilitation factor rapidly, which can be noticed in part (b). The increase in velocity of AB does increase the facilitation factor, but the effect is not as intensive as in the case of B, as shown in part (c). This was the expected result because a higher velocity of the carrier complex will increase the facilitated flux.

A final comment is that the facilitation factor indicates the ratio between mass transfer with facilitation and without facilitation. Therefore, a high facilitation factor does not indicate a high mass transfer flux across the membrane. To obtain the mass flux across a membrane with facilitation, Equation 1.33 would have to be used. Alternatively, one could multiply the facilitation factor by NA_0 , the mass transfer flux without facilitation.

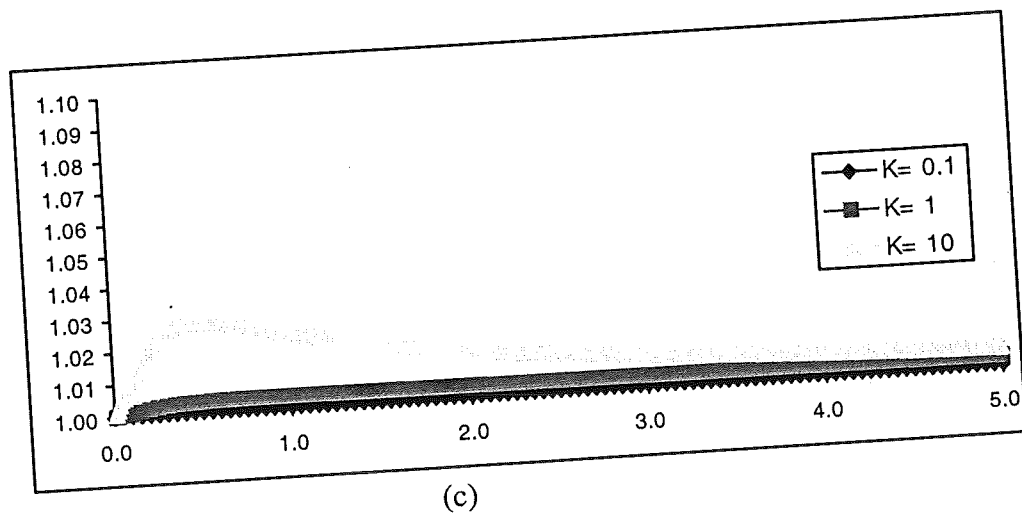
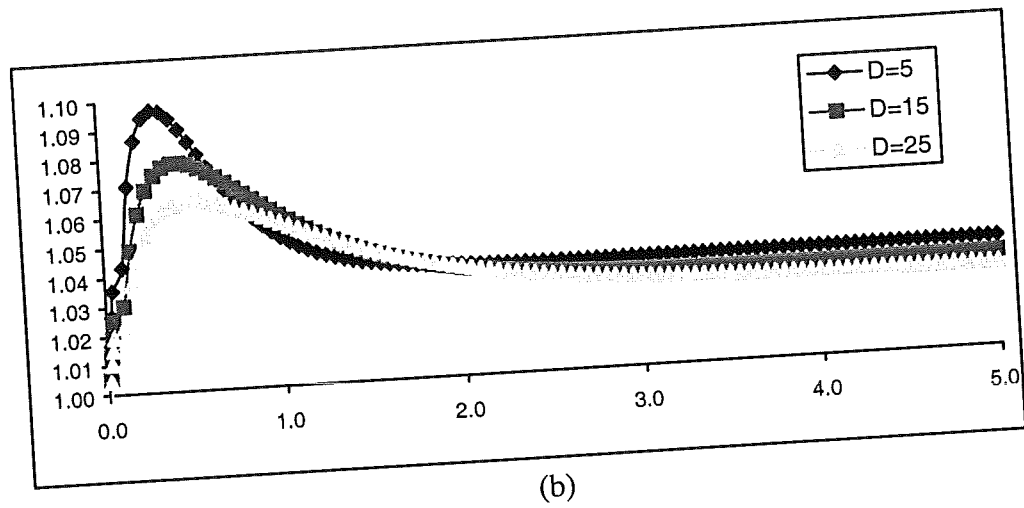
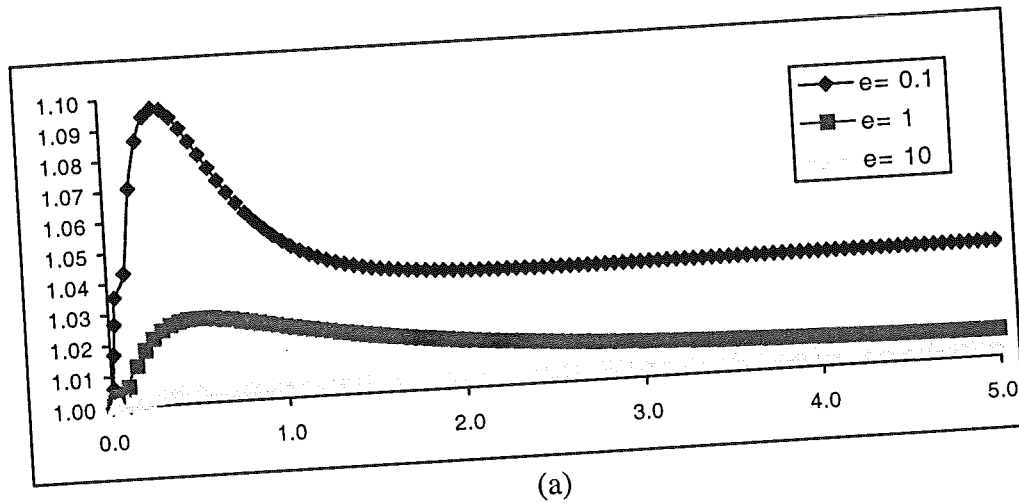
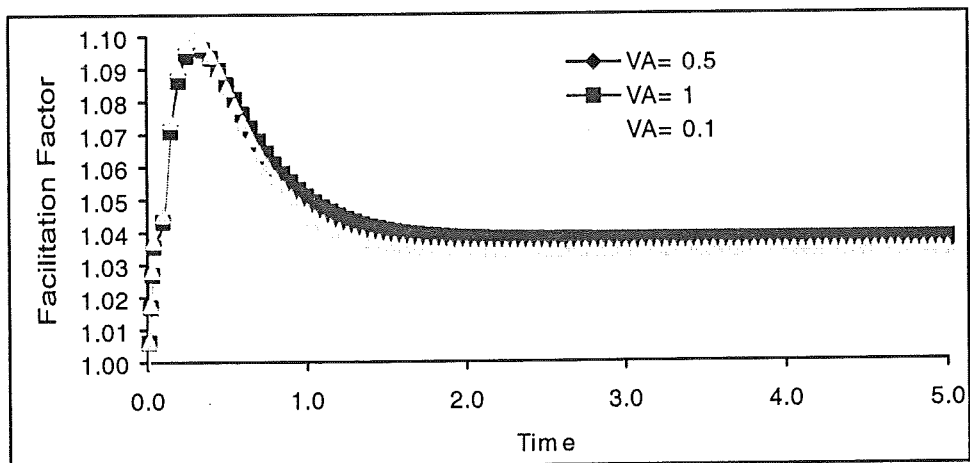
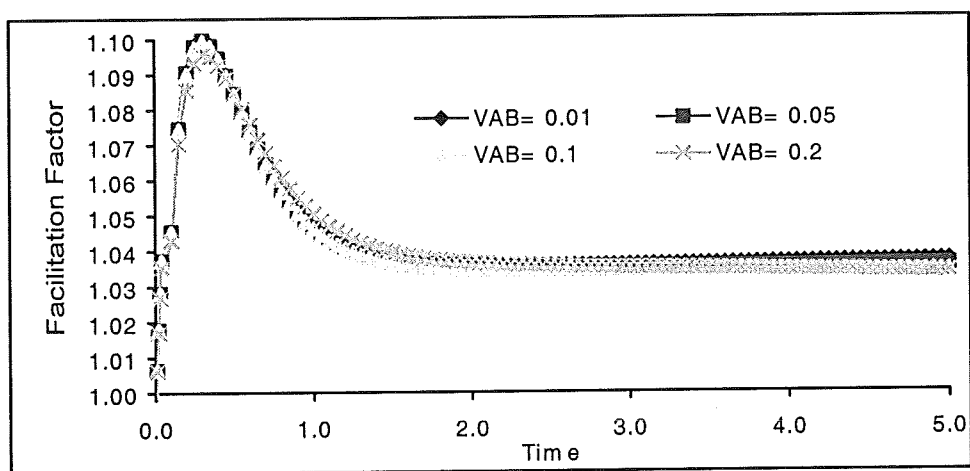


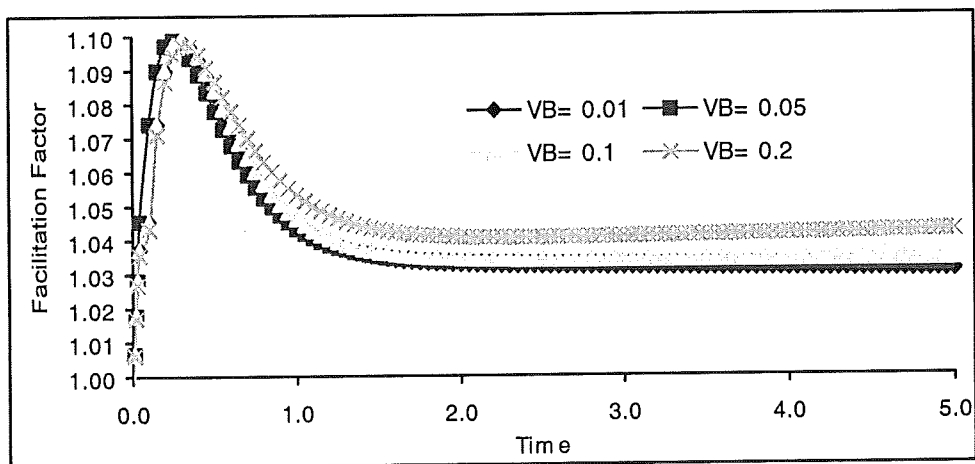
Figure 1.5: Effect of Parameters on Facilitation Factor ($D=\Delta$, $E=\epsilon$)



(a)



(b)



(c)

Figure 1.6: Effect of velocity of A, B, and AB on Facilitation Factor.

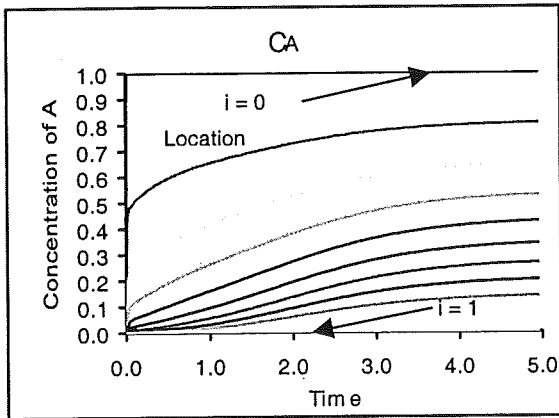
1.8.4.1 Effect of D_A and D_{AB} on the Facilitation Factor:

A small study was conducted to determine the effect of the diffusion coefficients, D_A and D_{AB} on the facilitation factor. Specially, the ratio between D_{AB} and D_A was evaluated, as was the overall magnitude of the coefficients. Table 1.3 lists the coefficient ratios in the runs that were conducted. Table 1.2 lists values of the coefficients used to study the effect of their magnitude on the facilitation factor. These values are compared to the base case, which was set as Run 2.

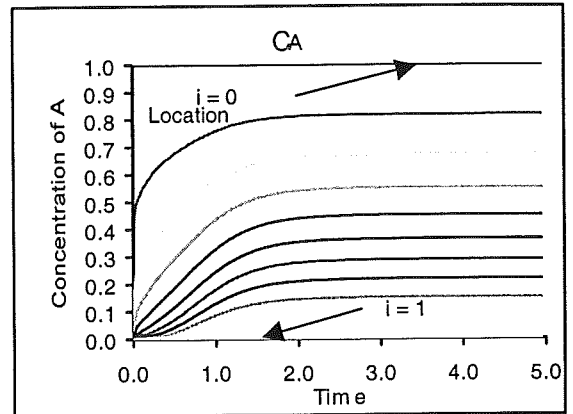
It was found that the value of the ratio between D_{AB} and D_A had a great impact on the facilitation factor. As the ratio increased, the facilitation factor also increased. This is due to a greater value of the D_{AB} coefficient, resulting in increased mass transfer flux of the carrier complex. If there was no facilitation, the D_{AB} coefficient would be zero, resulting in facilitation factor of one. Therefore, any value of D_{AB} greater than zero is beneficial to the system. Figure 1.7 shows the positive effects of having a greater D_{AB}/D_A ratio, as the concentration of C_A reaches a steady state more quickly.

The magnitude of the D_{AB} and D_A does not affect the facilitation factor. When making this comparison, it is imperative that the D_{AB}/D_A ratio remains constant among the runs being compared. One might expect that larger diffusion coefficients would result in a greater flux through the system, and therefore a higher level of facilitation. Although the flux levels may be larger, the ratio of the flux values with and without facilitation remains the same; therefore the facilitation factor also remains same. These results are confirmed in the plots shown in Figure 1.8. All of the results are identical, showing no benefit to the facilitation factor. It should be emphasized, however, that actual flux values would be higher, as explained earlier.

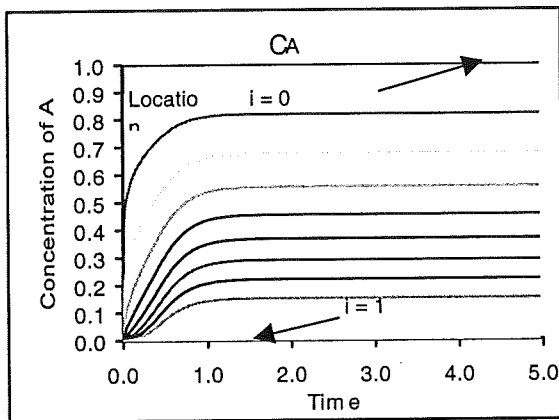
These facilitation factor values have been plotted in Figure 1.9. Part (a) shows that the facilitation factor is affected by the D_{AB}/D_A ratio. Part (b) shows that the magnitude of the D_{AB} and D_A value does not affect the facilitation factor.



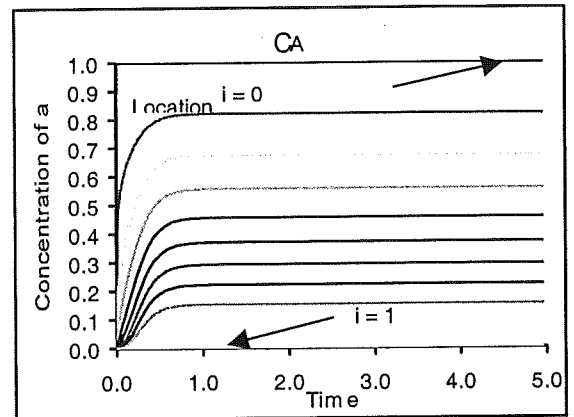
(a)



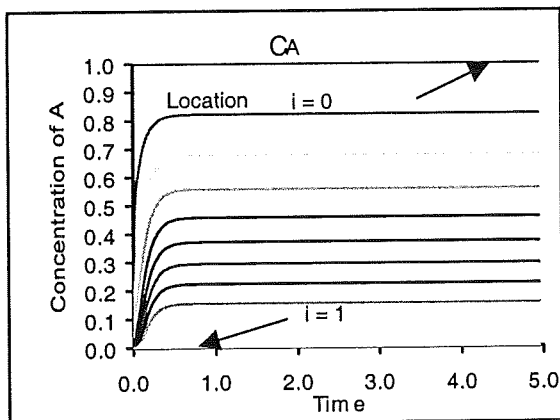
(b)



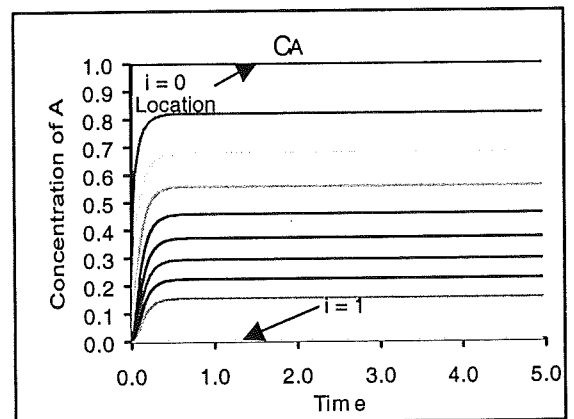
(c)



(d)



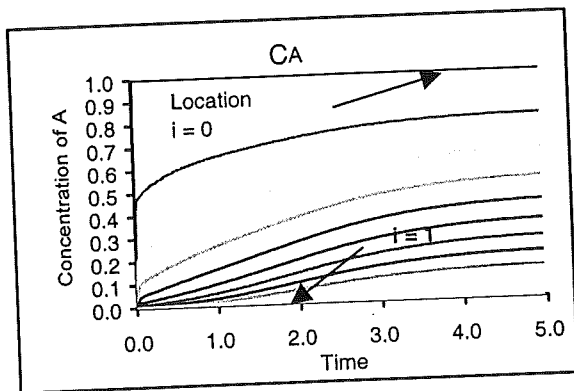
(e)



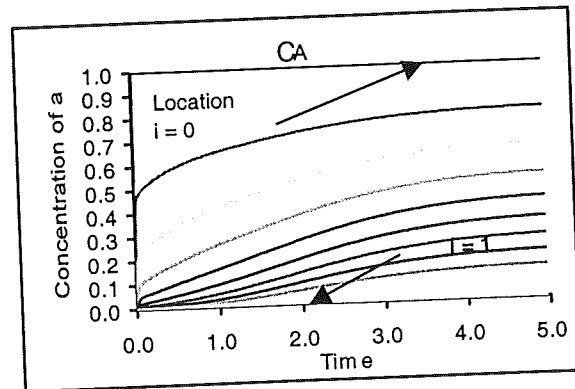
(f)

Figure 1.7: Effect of the ratio between D_{AB} and D_A

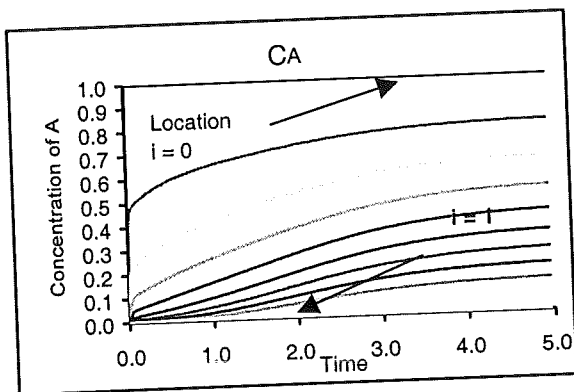
- (a) $D_{AB} : D_A = 0.2$ (b) $D_{AB} : D_A = 0.5$ (c) $D_{AB} : D_A = 1.0$
 (d) $D_{AB} : D_A = 2$ (e) $D_{AB} : D_A = 5$ (f) $D_{AB} : D_A = 10$



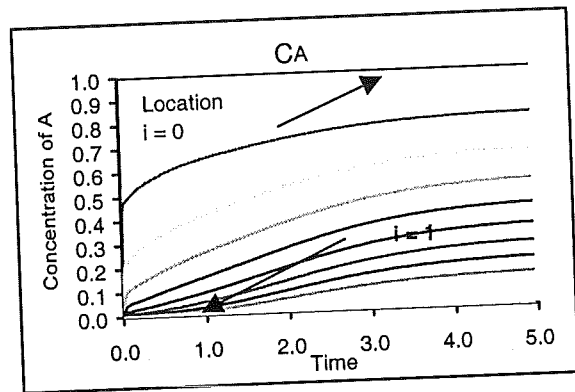
(a)



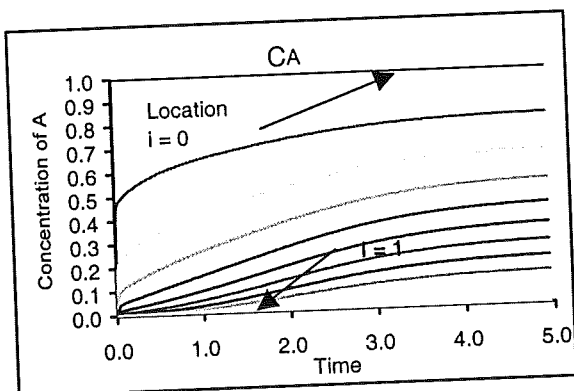
(b)



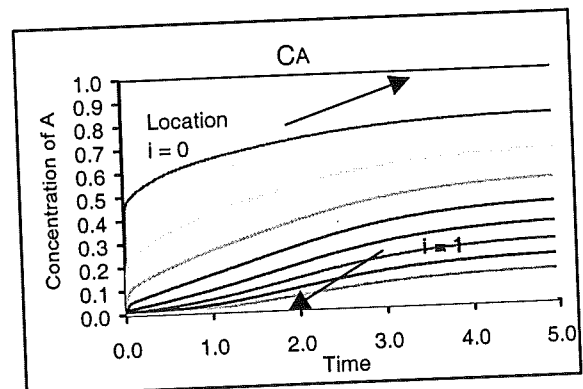
(c)



(d)



(e)



(f)

Figure 1.8 :Effect of the magnitude of D_A and D_{AB} . (Constant ratio of $D_A : D_{AB} = 0.2$)

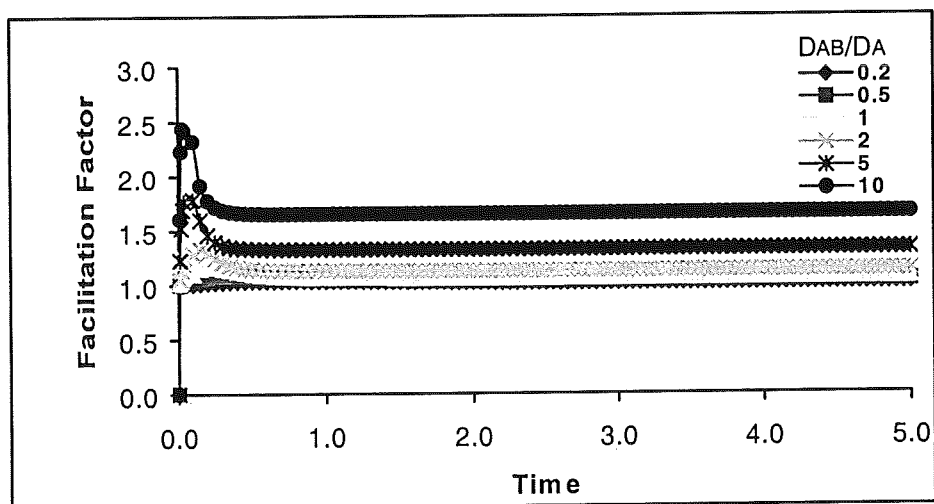
(a) Basis $D_A = 0.0000192 \text{ cm}^2/\text{s}$ $D_{AB} = 0.00000383 \text{ cm}^2/\text{s}$
 (b) $\times 0.1$ (c) $\times 0.5$ (d) $\times 2.0$ (e) $\times 10.0$ (f) $\times 100.0$

Table 1.2: Magnitude of D_{AB} and D_A Ratio Run List ($D_{AB}/D_A = 0.2$)

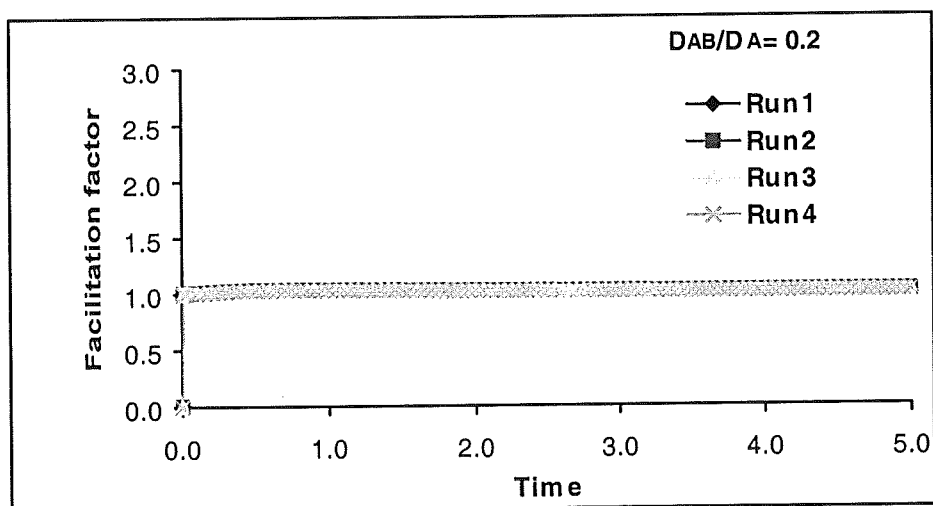
Run	D_A	D_{AB}	Factor
1	0.0000192	0.00000383	1
2	0.0000096	0.000001915	0.5
3	0.000192	0.0000383	10
4	0.00192	0.00083	100

Table 1.3: D_{AB}/D_A Ratio Run List

Run	D_A	D_{AB}	D_{AB}/D_A Ratio
5	0.0000192	0.00000383	0.2
6	0.0000192	0.0000096	0.5
7	0.0000192	0.0000192	1
8	0.0000192	0.0000383	2
9	0.0000192	0.000096	5
10	0.0000192	0.000192	10



(a)



(b)

Figure 1. 9: Effect of DAB/DA Ratio on Facilitation Factor

1.9 Conclusions And Recommendations

This work studied facilitated transport of CO_2 across a liquid membrane containing MEA using a homogeneous chemical-diffusion model. The Barakat-Clark method was used to solve the governing equations. The conclusions that can be made from this work are:

- Increasing the inverse Damkohler number reduces facilitation.
- Increasing the mobility ratio decreases facilitation.
- Increasing the reaction equilibrium constant increases facilitation.
- Increasing the D_{AB}/D_A ratio increases facilitation.
- Increasing the magnitude of D_{AB} and D_A ratio had no effect on facilitation.
- Increasing the velocity of V_A has a minor effect on facilitation.
- Increasing the velocity of V_B has significant effect on facilitation.
- Increasing the velocity of V_{AB} has an effect on facilitation but is not as significant as V_B .

Model validity was confirmed by examining the concentration profiles of the three reacting species across the thickness of the membrane. The facilitation factors were calculated using the method outlined by Smith et. al (1977).

CHAPTER 2

A NON-FICKIAN MODEL FOR SIMULATING POTASSIUM TRANSPORT IN CARBONATE FORMATIONS

2.1 Summary

Sophisticated prediction of aquifer performance requires numerical simulation. To date, no comprehensive simulation has been reported on ground-water modeling. Most available simulators are not applicable for fractured formations, and do not account for contaminant leaching and degradation, particularly in the vadose zone. Consequently, studying contaminant transport in a fractured or vuggy formation offers a formidable challenge.

This chapter addresses the problem of contaminant transport in carbonate formations, in the presence of fractures. A series of experiments was conducted using potassium nitrate as the contaminant. Dynamic adsorption and desorption tests were carried out using both homogeneous and fractured formation models. Initial modeling and experiments were carried out for a range of initial concentration values. The concentration at the outlet was measured with the Flame Ionization technique. A numerical model was developed using the surface excess theory, combined with a non-Fickian dispersion coefficient. Numerical results agreed favorably with experimental results. It was found that the non-Fickian model was necessary for modeling fracture flow results and with this version; there was no need to use the dual porosity/dual permeability formulation. Strong dependence of adsorption on initial concentration was observed and was justified with the numerical model.

2.2 Introduction

In the past three decades, fractured rock domains have received increasing attention by the researchers from a number of disciplines, including hydrogeology, petroleum engineering, and environmental engineering. The importance of fractures is particularly enhanced when one deals with carbonate formations, both in water flow and petroleum production, because most of these formations are known to be fractured. The subject has been investigated by petroleum engineers in connection with multiphase flow because many important petroleum reservoirs are in fractured rock formations. Of special interest are reservoirs composed of fractured porous rocks in which the matrix blocks, surrounded by the network of fractures, are porous. The permeability of such blocks is often rather low, but the porosity and the storage capacity for fluids are very high. Environmental engineers have been investigating the problem in connection with geological isolation of radioactive waste and remediation of ground water. Hydrologists deal with fractured formations because numerous deep aquifers are fractured. Chemical engineers mainly deal with chemical transport in limestone, but not necessarily in its fractured form (Arsic et al., 1991; Couturier et al., 1993).

In Canada, Switzerland, and Sweden large national research programs are underway to study radionuclide transport in crystalline rocks. Finland also intends to situate their repository in similar rocks and has a research program directed toward this end. Other countries, including Japan, France, Spain, the United Kingdom, and the USA have or have had research programs oriented towards crystalline rocks. In addition, an international field of research program is in progress in the Stripa mine in Sweden. The research is aimed at understanding the processes that determine the flow paths and the flow rates of water in the fractured rock masses.

Solutes that are dissolved in water will be carried by moving water, but various other mechanisms are involved in the process of solute transportation. Small molecules or ions diffuse in a concentration gradient and can move from one 'stream tube' to another. Different water volumes move with different velocities and may mix at more or less

regular intervals. The dissolved species may also experience kinetic effects caused by physical processes. One such process that may have a large impact for solute transport in fractured rock is the diffusion in and out of zones in which the water is moving so slowly that it can, for all practical purposes, be assumed to be stagnant. Such stagnant zones can be expected in fractures with uneven surfaces and with fracture-filling materials. In rocks with a connected matrix they can be very much larger than the mobile water volume in the fracture. Because the stagnant zones are reached by diffusion, the volume of stagnant water accessed depends on the residence time of the flowing water.

Different approaches to solute transport in fractured media have been attempted. These include the analysis of a single fracture (e.g. Grisak and Pickens, 1981; Tang et al., 1981; Sudicky and Frind, 1984). While some researchers considered the porous medium as comprised of equally-spaced fractures (Sudicky and Frind, 1984), others have used deterministic study of flow in an irregular network of fractures contained in an impermeable rock. Yet others (Schwartz and Smith, 1988) considered the same problem with a stochastic model. Recently, Choi et al. (1997) used a dual-permeability, dual-porosity approach to model fluid flow through a fractured formation. They built their model using non-Darcian flow through the fracture while allowing Darcian flow through the matrix. Even though this work was devoted to advancing the hydrodynamic aspect of fluid flow, no species transport was considered.

Adsorption and desorption are important phenomena in chemical transport. A Langmuir isotherm has been used most commonly to model adsorption at the solid/liquid interface. The widespread use of the Langmuir model arises from its ability to represent the general shape of many adsorption isotherms. However, more recently, the surface excess theory has been proven to be more theoretically sound and better apt in modelling adsorption (Islam and Chakma, 1991). Recently, Sarwar and Islam (1997) demonstrated that the surface excess theory is also capable of representing chemical transport through fractured formations. However, non-Fickian dispersion had to be introduced, along with non-equilibrium adsorption and desorption rates. They considered the transportation of several chemicals in silica sand formation and observed very good agreement between

experimental and numerical results, even for the regime with non-uniform adsorption and desorption profiles.

This research comprises of laboratory flow experiments and numerical modelling of KNO_2 transport in carbonate formations. Such flow is of relevance to agricultural applications for which run-offs from fertilisers constitute major contamination problems for groundwater. Also, in petroleum engineering applications, mathematical models of chemical transport are of importance, especially for the case of fractured carbonate formations.

2.3 Experimental Setup And Procedure

A glass column was used for all experimental tests. Because only hydrostatic pressure was used to maintain flow through the porous medium, little pressure was anticipated in the column and a glass column was sufficient. These samples were crushed in order to facilitate packing of this material in the column. The porosity of the crushed rock was approximately 15%. This was considered to be the result of adequate packing. The packed column was connected to an inlet (for injection of the contaminated water) and was released to the outside at atmospheric pressure. A two-folded aluminum foil was placed parallel to the axis of the cylinder to model a single fracture. The foil contains approximately 50 holes (performed with a 0.05-mm needle) per cm^2 , in order to assure cross flow as well as fracture flow. This was the procedure previously implemented by Sarwar and Islam (1997).

The Nitrate used was a solution of KNO_2 . This form of the potassium is considered to be difficult to remove from a water stream. Two different concentrations of nitrite, 50 and 150 PPM were used in this study. Standard solutions were prepared using laboratory-grade KNO_2 . Deionized water was used for all the experiments, as a solvent (adsorption tests) as well as a washing agent (desorption tests).

2.4 Procedure

In order to observe both adsorption and desorption, contaminated water was injected in each sample and was followed by fresh water after a high number of pore volumes of fluid injection. During this process, samples were collected at the outlet and were analyzed for potassium content in the effluent.

2.5 Theory

Adsorption of a chemical is considered to take place from the monomer phase. Surface excess is the measure of adsorption from liquid mixtures that describes the difference between the actual amount of component i adsorbed and the amount of component i that would be present in the adsorbed phase if the composition and the density of that phase were the same as those of the phase in equilibrium. For a binary system, the surface excess of component i is given by:

$$n_i^e = n^0(x_i^0 - x_i), \quad (2.1)$$

Where $i=1$ denotes chemical ($i=1$) and $i=2$ denotes the bulk phase carrying the chemical. If it is assumed that the liquid phase is directly in contact with the solid, the above equation assumes the following form

$$n_i^e = n'(x_i' - x_i). \quad (2.2)$$

Using the monomer adsorption model, the surface excess can be expressed as

$$\frac{1}{n'} = \frac{x_1'}{m_1} + \frac{x_2'}{m_2} \quad (2.3)$$

Where m_1 and m_2 represent the amounts of monolayer coverage for the chemical and the bulk phase, respectively. At this point the concept of selectivity can be introduced. Selectivity, S , is defined as follows:

$$S = \frac{x_1' / x_2'}{x_1 / x_2} \quad (2.4)$$

Even though the monolayer model is based on the assumption of monolayer adsorption, it has been taken for granted that the monolayer model is also suitable for multi-layered adsorption (Song and Islam, 1994). With selectivity, the expression of surface excess can be written as

$$n_a^e = \frac{m_1 x_1 x_2 (S - 1)}{S x_1 + (m_1 / m_2) x_2} \quad (2.5)$$

The amount of chemical adsorbed is given by

$$n_1' = \frac{m_1 x_1 S}{S x_1 + (m_1 / m_2) x_2} \quad (2.6)$$

Finally, the kinetic term is calculated as:

$$\frac{\partial n_1^e}{\partial t} = k_i (n_1^e - n_1^{ea}), \quad (2.7)$$

Where $k_i = k_1$ for adsorption and $k_i = k_2$ for desorption. This term introduces the possibility of desorption of a chemical in a dynamic displacement system.

2.6 Governing Equation

The one-dimensional mass transfer equation that includes the surface excess theory to describe adsorption in the solid/liquid interface is given as (Song and Islam, 1994):

$$\begin{aligned} \frac{\lambda q \rho_l}{A \phi} \frac{\partial^2 C}{\partial z^2} - \frac{q \rho_l}{A \phi} \frac{\partial C}{\partial z} &= \frac{1 - \phi}{\phi} \rho_r n_0 \frac{\partial C}{\partial t} \\ &+ \frac{1 - \phi}{\phi} \rho_r \left(\frac{\partial n_1^{ea}}{\partial t} \right) \end{aligned} \quad (2.8)$$

2.6.1 Numerical Solution Method and Accuracy

In order to discretize Eq. (8) the numerical scheme of Bracket and Clark (1966) was used. This scheme has been proven to be powerful in solving diffusive convection equation in the past. Numerical simulation was carried out in a linear grid system of 100 grid blocks. This number was selected after a series of trial runs for optimum accuracy. Time was discretized with a Δt of 50 seconds. This value was found to be appropriate considering that the spatial grid blocks were rather small. The following boundary and initial conditions were used:

$$C(z, 0) = 0 \quad \text{for } 0 \leq z \leq L$$

$$C(0, t) = C_0 + \lambda \left(\frac{\partial C}{\partial z} \right) \quad \text{for the adsorption test. For desorption, } C_0 \text{ is set to zero.}$$

$$\left. \frac{\partial C}{\partial z} \right|_{z=L} = 0 \quad \text{for } t > 0$$

Numerical simulation runs were conducted in order to obtain the best match between experimental and numerical results. The best match data are reported in Table 1. Note that the dispersion parameter was found to be a function of concentration. This aspect will be discussed later.

2.7 EXPERIMENTAL RESULTS AND DISCUSSION

Eight experimental runs were conducted with KNO_2 as the chemical with two different concentrations (50 and 150 ppm). Description of each run is given in Table 2. For each concentration, four runs were conducted in absence or presence of fracture and adsorption and desorption. Following is a discussion of various experimental runs.

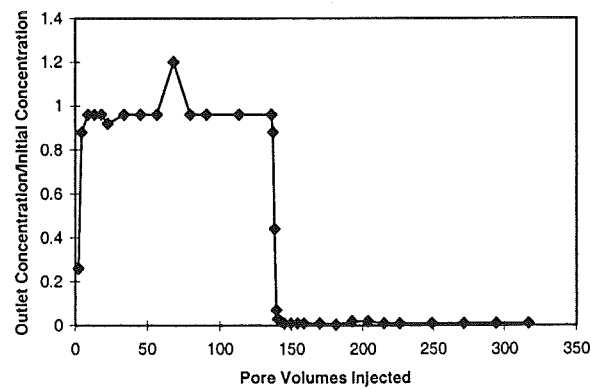


Figure 2.1: Chemical adsorption and desorption in absence of fracture (initial concentration=50ppm)

Figure 2.1 shows the results of Runs 1 and 2 (adsorption and desorption with 50 ppm solution).

These two runs were conducted on the same porous material. The adsorption test was simply followed by the desorption test that involved the injection of de-ionized water. As can be seen from Fig. 1, the outlet concentration rose to the same level as that of the inlet only after the injection of 10 pore volumes (PV) of water. This value is relatively higher as compared to the case using silica sand, for which saturation (to a dimensionless concentration of unity) was reached within two pore volumes of chemical injection (Sarwar and Islam, 1997). Indeed, carbonate formations exhibit much higher adsorptive capacity than do silica sands. Crushed carbonate has much greater surface area than silica sand. This is reflected in the fact that the permeability of crushed carbonate is several hundred times smaller than that of silica sand. The outlet concentration is measured in terms of potassium content. It was not possible in this study to determine the fate of NO_2^- in this study. It might be interesting to find the partition of NO_2^- in the solid and the liquid phases. The desorption trail in Fig. 1 shows much faster decline in outlet concentration than that of the adsorption curve. This was in contrast to silica sand for which slower desorption was observed (Sarwar and Islam, 1994). However, only limited amount of chemical was injected in their case and most likely nothing more than a monomer layer was allowed to be formed.

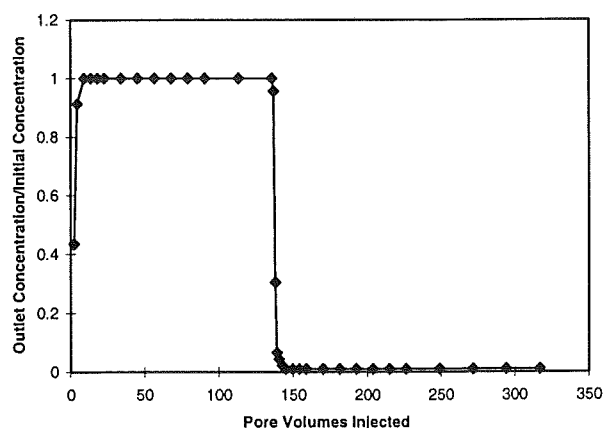


Figure 2.2: Chemical adsorption and desorption in presence of fracture (initial concentration=50ppm)

Figure 2.2 shows the adsorption and desorption profiles of Runs 3 and 4, respectively. These runs were conducted with 50-ppm nitrite solution during the adsorption phase. However, a single fracture was added to the system. This resulted in a smaller pressure drop across the porous medium in order to maintain the same flow rate as the homogeneous case (Fig. 1). However, the chemical transport was not particularly affected by the presence of the fracture. The saturation (the point of reaching concentration ratio of unity) took place at approximately the same time as that of the homogeneous case. It is conceivable that fractures will play a greater role at higher flow rates. This aspect of the study is currently underway.

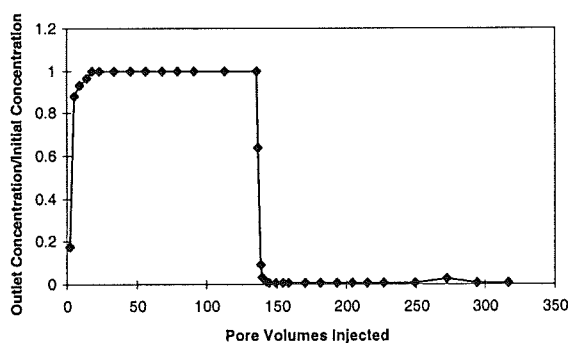


Figure 2.3: Chemical adsorption and desorption in absence of fracture (initial concentration=150ppm)

Figure 2.3 shows adsorption and desorption results of Runs 3 and 4 that were conducted with 150 ppm solution. The adsorption appears to reach steady state at a much slower pace than the one reached by lower concentration cases. Adsorption indeed

depends on the concentration gradient that is likely to be higher in this case than in the case of lower absolute concentration. This effect, however, cannot be observed unless a dynamic test is performed as done in this study. The effect of concentration on desorption is less pronounced.

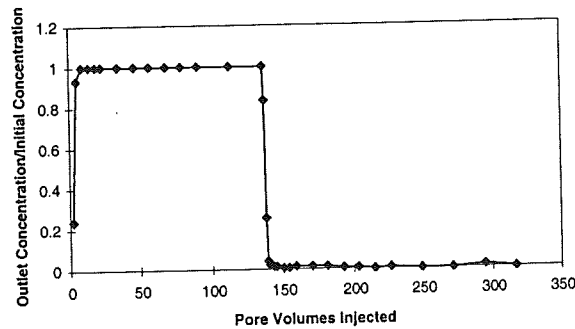


Figure 2.4: Chemical adsorption and desorption in presence of fracture (initial concentration=150ppm)

Figure 2.4 shows the adsorption and desorption profiles for the 150 ppm in presence of a fracture. For this case, the effect of fracture is clearly shown. The whole adsorption curve is moved to the left, in effect showing that chemical transport remain faster than the homogeneous case. Also, fractures play a greater role in the presence of higher concentration of the contaminant. This contribution of fractures can be modeled by non-Fickian dispersion (Sarwar and Islam, 1994). It is also conceivable that the adsorption and desorption rates are also affected. This will be discussed in the following section on numerical modeling.

2.8 Discussion On Mathematical Modelling

Numerical simulation runs were conducted individually for each section of adsorption and desorption separately. This helped determine the adsorption and desorption rates independently. Following is a discussion on the mathematical modelling results.

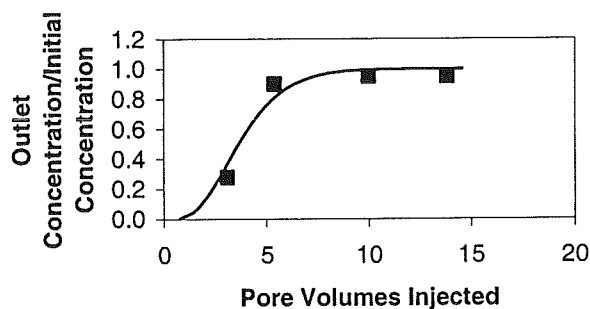


Figure 2.5: Comparison of experimental and numerical results of an initial concentration of 50 PPM (no fracture)

Figure 2.5 compares numerical and experimental results of Run 1 (adsorption with 50-PPM solution, in absence of fracture). The agreement between experimental and numerical results is excellent. Resulting best-fit parameters are listed in Table 1. Numerical modelling of such a process is further consolidated if the breakthrough values could be monitored. Unfortunately, breakthrough values were not monitored in the experimental study.

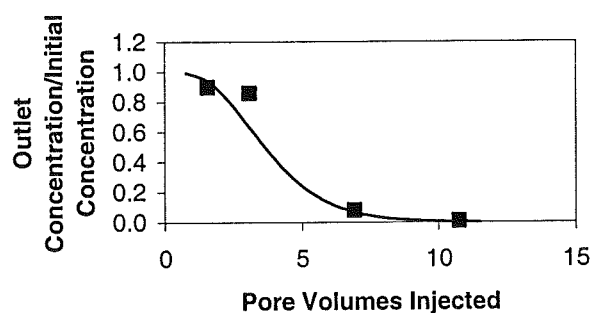


Figure 2. 6: Comparison of experimental and numerical results of an initial concentration of 50 ppm (no fracture)

The experimental and numerical results of Run 2 (desorption with 50 PPM solution in absence of a fracture) are shown in Fig. 2.6. A much lower desorption rate compared to adsorption rate had to be used in order to match the experimental desorption data. It commonly found that the adsorption rate is higher than the desorption rate. This, in fact, forms the basis for irreversible thermodynamics and the surface excess theory. In order

to obtain a better match between experimental and numerical results, the dispersion parameter used in the desorption phase was somewhat smaller than that of the adsorption phase. It is expected that the dispersion of fresh water into contaminated water (desorption test) be different than the dispersion of contaminated water into fresh water (adsorption test). This process is further complicated by the presence of tightly packed crushed carbonate rocks. No other variable was adjusted in order obtain the match between experimental and numerical results. Also, these numbers are significantly different from those of silica sand (Sarwar and Islam, 1994). Note, however, that the concentration of nitrate used by Sarwar and Islam was much lower than the one used in this study.

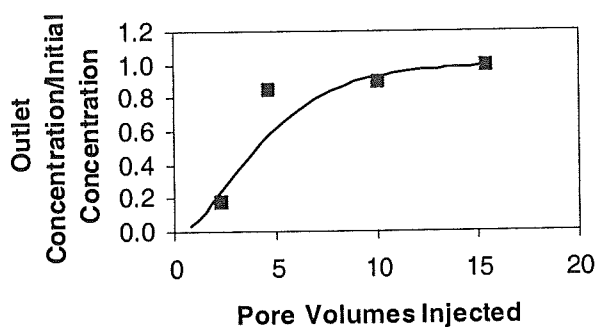


Figure 2.7: Comparison of experimental and numerical results for an initial concentration of 150 PPM (no fracture)

Figure 2.7 compares experimental and numerical results of Run 3. For this run, an adsorption test was performed using a concentration of 150 PPM, in the absence of fractures. For this numerical run no parameter was adjusted. Note that the agreement between experimental and numerical results is remarkably good, especially considering that no parameter was adjusted. In order to obtain a good match between experimental and numerical results of the desorption test, the dispersion rate was first modified. This alone did not improve the agreement that showed elongated desorption trail. In order to remedy this discrepancy, the rate of desorption was modified (see Table 2). It is not unusual to find that the desorption rate be a function of concentration

(Sarwar and Islam, 1994). It is particularly important to realise that at higher concentrations, the assumption of monolayer may not be applicable, in which case desorption will depend on the concentration, rather than on the surface properties of the solid.

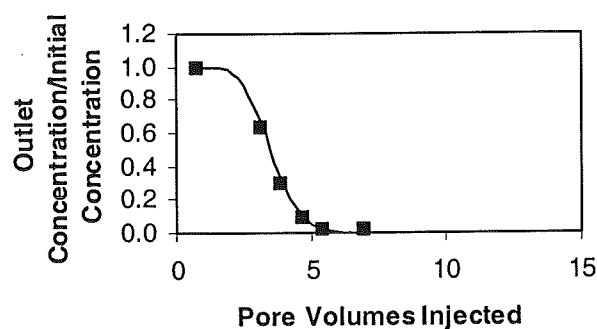


Figure 2.8: Comparison of experimental and numerical results for an initial concentration of 150 PPM (no fracture)

Figure 2.8 shows that the agreement between experimental and numerical results is greatly improved by modifying the desorption rate.

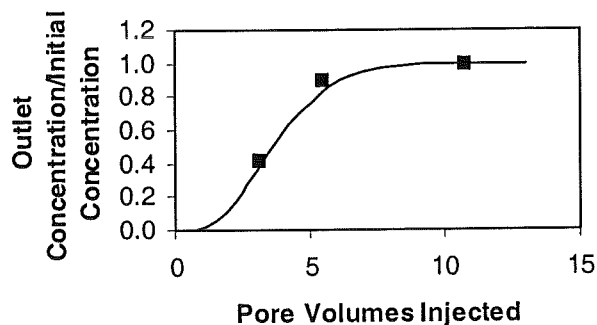


Figure 2.9: Comparison of experimental and numerical results for an initial concentration of 50 PPM (with fracture)

Figure 2.9 compares experimental and numerical results of Run 5 for which 50-PPM solution was used to conduct the adsorption test in presence of a single fracture. Excellent agreement between experimental and numerical results is obtained only after modifying the dispersion rate to one third of that of the previous adsorption tests. The

presence of fracture invokes an increase in permeability, hence creating a channel for chemical transport. This can result in decreased adsorption (due to bypassing of chemicals) or a decrease in dispersion (as convection is affected by an increase in permeability). Note that the adsorption or desorption rates were not changed due to the presence of the fracture.

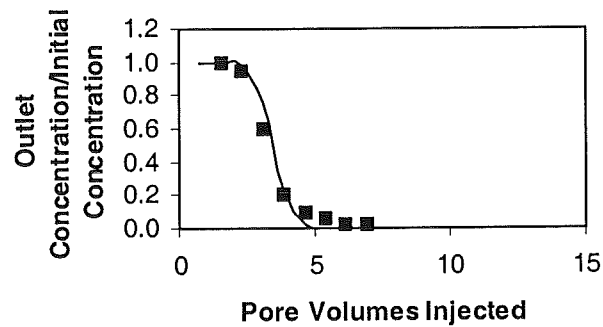


Figure 2.10: Comparison of experimental and numerical results for an initial concentration of 50 PPM (with fracture)

An excellent agreement between experimental and numerical results can be seen in Fig. 2.10. The agreement is particularly good during the quick change in outlet concentration during which the dynamic phenomena are most active. Considering that only the dispersion parameter was adjusted for this desorption case, the agreement between experimental and numerical results is impressive.

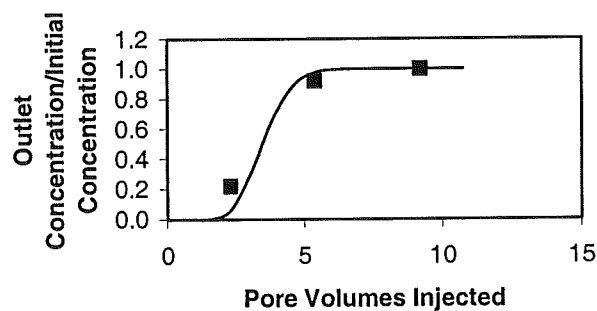


Figure 2.11: Comparison of experimental and numerical results for an initial concentration of 150 PPM (with fracture)

Figure 2.11 shows the comparison between experimental and numerical for Run 7 that was conducted with a 150-PPM solution using a fractured formation. Figure 12 shows the same for the desorption case. Note that the agreement between experimental and numerical results is obtained without making any adjustment to the adjustable parameters (see Table 2).

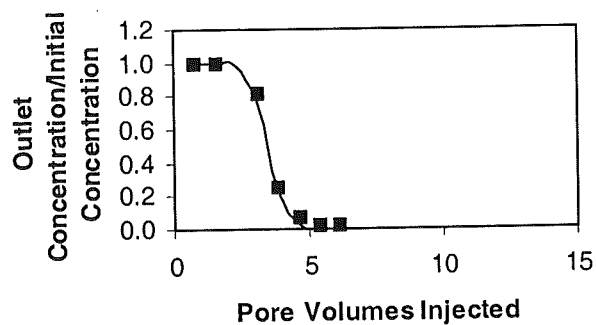


Figure 2.12: Comparison of experimental and numerical results for an initial concentration of 150 PPM (with fracture)

Table 2.1 Input Data

TABLE 1-Input Data			
C_0	50, 100 ppm	λ	Variable, see Table 2
k	11.3 mD	m_1/m_2	15
n_0	200 mg/g	S	25
q	10 ml/min	m_1	$0.05n_0$
ϕ	0.15	k_1	2/hr
ρ_l	1 cm ³ /ml	k_2	Variable, see Table 2
ρ_r	2.8 g/ml	PV	22 cm ³

Table 2.2: Experimental Runs Data

TABLE 2-Experimental Runs			
Run no.	λ	K_2	Description of runs
1	3	.03	50 ppm, adsorption test, no fracture
2	1.1	.03	50 ppm, desorption, no fracture
3	3	.03	150 ppm, adsorption test, no fracture
4	0.25	.01	150 ppm, desorption test, no fracture
5	1	.03	50 ppm, adsorption test, with fracture
6	0.1	.03	50 ppm, desorption test, with fracture
7	1	.03	150 ppm, adsorption test, with fracture
8	0.1	.01	150 ppm, desorption test, with fracture

2.9 Conclusions

A series of experimental and numerical runs was conducted in order to describe nitrite flow in a carbonate formation with or without the presence of a linear fracture. Experimental results show that the kinematics of adsorption and desorption depend on the concentration of the solute, leading to the use of a non-Fickian dispersion model. This model is coupled with the surface excess theory and showed excellent agreement with experimental results with a minimum number of adjustable parameters.

CHAPTER 3

ADSORPTION OF SULFUR IN LIMESTONE

3.1 Summary

The H_2S present in natural gas stream is highly poisonous and toxic even if its concentration is below 5%. Moreover the deposition of the elemental sulfur in tubular and flow lines can lead to decreased production, increased corrosion rate and higher filtration costs. So it is necessary to remove the sulfur gas in order to keep the gas at acceptable specifications. The conventional employed treatment techniques are chemical based and are expensive along with serious environmental concerns. Environmentally friendly, naturally occurring substance limestone was investigated for its sulfur adsorption capability in down-hole applications. It was found satisfactory for sulfur adsorption capability. The gas containing SO_2 was passed through limestone packed column and a change in concentration at the outlet was noticed by bubbling the exit stream through a water beaker. The pH of water was monitored throughout the experiment.

3.2 Literature Review

The published literature on "Separation of Sour Gas from Natural gas stream " is reviewed in this section. Many people have performed several studies on this issue and there are numerous reports on successful application of their techniques, published in different journals. Different processes developed by well known organizations for natural gas treatments which are proven good on an industrial scale, have also been discussed in this section.

3.2.1 Downstream Treatment

There are four categories of commercial processes available in general for the downstream treatment of natural gas.

3.2.1.1 Absorption of Regenerable Solvents: (Chemical Absorption)

Among the various acid gas removal processes, absorption by ethanolamine solution is the most commonly used. In this process the regeneration of the used solvent is carried out in a stripping column. This is the traditional method of removing H_2S from natural gas. In this process the sour natural gas is first treated with a solvent as Diethanol amine (DEA) or Monoethanolamine (MEA), and sulfur is recovered from a Claus plant. The Ethanolamine based process for treatment of sour natural gas was discovered by Bottoms in 1930. (Amit Chakma, 1985).

Sufficient information on acid gas solubility in solvents needed for the design of the gas plants at typical operating conditions is available in the literature. (Martin et al., 1978; Dingman et al; 1983; Mdax et al., 1987).

Due to limitations of experimental techniques employed, it is difficult to obtain an accurate experimental data under very low and very high partial pressure conditions (Astarita et al., 1983).

W. HU and A. Chakma (1990) developed a mathematical model for the prediction of equilibrium solubility of CO_2 and H_2S in aminoethanol aqueous solutions. Their approach is quite identical to that of Kent and Eisenberg (1976).

3.2.1.1.1 Nonregenerable Chemical Scavengers:

In a number of situations such as low volume and low-pressure gases the conventional ethanolamine process may not be economical. In such cases nonregenerable chemical scavengers are preferred for use (A.Chakma; 1985).

Dennis Leppin (1995) has evaluated three types of commercial scavengers: Nitite, nonregenerable amine and triazine. He has reported the successful application of afore mentioned agents, treating 16 MMscFD of natural gas with 19 PPM v H₂S and 0.5 percent CO₂ at 1000 psig; (SPE 29743).

But these scavengers are not usually environmentally friendly, they are toxic in nature and their safe disposal is costly. So with growing environmental concerns it is expected that this practice may no longer be allowed. If no economically viable technology is developed to handle these gases, the condensate producing wells may have to be shut down. Therefore there is a need to develop other alternate technologies capable of handling low volume gases in an economical manner.

3.2.1.1.2 Newly Developed Techniques

The mixed amine process is more suitable at large-scale gas plants, because amine/ Claus processes have operating difficulties for small sulfur capacities (up to 5 tones/day).

The process developed by VIIGAS, Russia, treats sour gas using an electric arc method which is an alternate to Claus unit coupled with alkanolamine solution treatment. The essence of the arc method is that sour gas is delivered to arc reactor through plasmatron where H₂S is dissociated at 2200-2370 °F. Downstream, the mixture containing H₂, CO, CO₂, non dissociated H₂S and sulfur, passes to the heat exchanger where it is water cooled down to 1300 °F. The mixture is then passed through a condenser and sulfur is condensed there and cool gas is then subjected to burning in a furnace.

3.2.1.1.3 Liquid Redox Process

Low concentrations of H_2S in sour gases at high H_2S/CO_2 ratios are generally removed by liquid redox processes using transition metals, e.g. Sulfolin and Stretford. VNIIGAS (Russia) has developed a technique based on iron chelate solution where H_2S reacts with an aqueous solution containing Fe^{3+} - EDTA (FeY), and H_2S is oxidized to elemental sulfur. This technology was first applied to the natural gas treatment in 1989. It can handle a stream of natural gas containing 6 % CO_2 , 0.1 % H_2S at 5.5 MPa.

3.2.1.1.4 Physical Solvents

Physical solvents are usually used for selective removal of H_2S over CO_2 and the process can be designed for either bulk acid gas removal or selective H_2S removal with specified degree of removal. Dimethyl Ether of Polyethylene glycol (Selexol), n-methyl pyrrolidone (Purisol), Methanol (Rectisol) and Propylene carbonate (Fluor) have been successfully used for NG treatment. Refrigerated methanol is well known as a selective physical solvent for the removal of H_2S from gases. Methanol being a physical and not a chemical solvent, absorbs by a selective solubility the acid components present in the gases; not by chemical reactions as with amines (Minkkinen and J.P.Jonchere; Institut Francais du petrole, France). Claus type recovery projects are complementary to this project if high H_2S loads are to be handled, which is complicated in its operation already.

3.2.1.2 Adsorption on Solids

Low concentrations of H_2S in natural gas can also be handled well by regenerable adsorbents such as activated carbon, activated alumina, silica gel and synthetic zeolites (Molecular sieve; MS). Non-Regenerable adsorbents i.e. zinc and iron oxides, have been used for natural gas sweetening.

Lee and Chi (1973) initiated an experimental study of natural gas purification using a 5A zeolite. In their work it was suggested that this sorbent could be used in an adsorption process to remove H_2S from natural gas. The study on successful application of these

sorbents has been performed by different scientists (et. al; E.S.Kikkinides, and R.T.Yang ,1995). They have also reported the removal of H_2S compounds from natural gas by pressure swing adsorption (PSA) using 5A zeolites as sorbent. A typical integrated processing scheme is to hydrodesulfurize sulfur compounds over Co-Mo catalyst to H_2S and chemisorb H_2S over ZnO. This scheme is good for desulfurization on off shore platforms before pipeline transport of the gas. Mercaptans can be removed from natural gas by adsorption on NaX zeolites, pretreated with 5-10 % aq. NaOH.

3.2.1.3 Membrane Separation

The separation of natural gas by thin barriers termed as membranes is a dynamic and rapidly growing field, and it has been proven to be technically and economically superior to the competing technologies. This superiority is due to many advantages which membrane technology benefits from, including low capital investment, low weight and space requirement and high process flexibility. In the past ten years the membrane gas separation has made great advances and can now be regarded as a competitive industrial gas separation method. However, membrane processes are found to be cost effective for treating low conc. NG (Abdulreza Tabe-Mohammadi, 1999).

3.2.1.3.1 Membrane Separation Principle

A synthetic membrane is a thin barrier between two phases through which differential transport can occur under a variety of driving forces including pressure, concentration and electrical potential across the membranes. Pressure difference across the membrane can facilitate RO (reverse osmosis), ultrafiltration, microfiltration, gas separation, and pervaporation. Temperature difference across the membrane can facilitate distillation, whereas concentration difference can be used for dialysis and extraction. Electrodialysis can also be performed with the help of membranes when an electric potential across the membrane is maintained. Differential transport occurs when the membrane restricts the transport of different species in some specific way. The transport is a non-equilibrium process and the separation of chemical species results from differences in transport rates through the membranes. Membrane separation is considered a non-equilibrium process

because it is based on the selective permeation rate of the feed components. If a membrane system is allowed to go to equilibrium, permeation would continue until the pressure and concentration of gases on both sides are equal. (Koros, W.J; Ma, Y.H, 1996).

The two main parameters defining the performance of a membrane are separation factor and permeance. In a binary system consisting of gases "a" and "b" with gas "a" as fast permeating gas, separation factor is defined as the concentration ratio of "a" to "b" in the permeate, and X_a and X_b are the concentration of the gases "a" and "b" in the feed.

$$\alpha_{a/b} = Y_a/Y_b / X_a/X_b$$

Where α is the separation factor, Y_a and Y_b are the concentration of the gases "a" and "b" in the permeate and X_a and X_b are the conc. of gases "a" and "b" in the feed.

Permeance is defined as the volume of the feed passing through a unit area of membrane at unit time and under unit pressure. $P = V/At \Delta P$ Where P is permeance, V is vol. of gas, A is area, t is time and ΔP is pressure difference. (Abdulreza Tebe-Mohammadi, 1999).

3.2.1.3.2 Membrane Application Review

Thomas Graham in 1929 performed the first recorded experiment on the transport of gases and vapors in polymeric membranes. A few years later he observed the separation of gases using natural rubber via Knudsen diffusion (M.Stanley, 1996). Despite many experimental works, the progress of membrane separation techniques was very slow in early stages. The progress in membrane science and technology was accelerated during the 1980s by the development and refinement of polymeric membranes. Membrane gas separation emerged as commercial process on a large scale during the 1980s. (Kesting R.E, 1985). The commercial use of membrane for acid gas removal started in 1984 with the installation of the SACROC unit by Cynara (D. Paro, 1984).

C. Thaeron; D.J. Parrilo and B.B. Pruden (1998) have reported their study performed on the separation performance of hydrogen sulfide- methane mixtures by a nonporous carbon membrane called selective surface flow (SSF) membrane. The H_2S rejection - CH_4 recovery data can be empirically correlated using a simple equation with a single adjustable parameter which is a function of feed gas partial pressure of H_2S in moderate (>0.2 Mpa) even if the total feed pressure is low (0.45 Mpa).

Steven Ray Alexander and Jack Winnick (1994) have developed an advanced process for the separation of H_2S from natural gas through an electrochemical membrane. In this process the electric field is employed as an alternative to the chemical potential driving force, developed due to pressure or concentration difference. H_2S is removed from natural gas by reduction to the sulfide ion and H_2 at cathode. Sulfide ions from anode are oxidized to elemental sulfur and are swept away by an inert gas stream. No absorbents are used and there is no need for subsequent treatment of a concentrated H_2S stream as with gas sweetening technology.

While membranes are good for bulk acid gas removal, they are inferior to, or must be combined with other processes when the acid gases are present in low concentration. That is because at low levels the partial pressure of acid gases and therefore the driving force of the process is decreased.

3.2.1.4 Direct Oxidation to Sulfur

Lower concentration of H_2S in natural gas can be selectively oxidized over an activated carbon catalyst to elemental sulfur, water and a small fraction of sulfur. Direct conversion or H_2S processes are basically used for H_2S removal in sulfur recovery and tail gas treating applications. A.I Chaudhry and Eric.L. Tolefsson (1990) have reported their research to optimize the reaction conditions to develop a process for a commercial unit capable of processing sour natural gas containing 1.0 % H_2S .

The LO-CAT II hydrogen sulfide oxidation process developed by ARI USA offers an environmentally sound, one step process for removing H_2S selectively from gas stream

and producing elemental sulfur. In the LO-CAT II autocirculation unit, the acid gas is sparged through the LO-CAT solution in the absorption portion of the vessel. The H_2S is absorbed into the aqueous solution of chelated iron, and the resultant sulfide ions are oxidized to elemental sulfur (Hydrocarbon Engineering Journal, Feb., 1999).

The other well known process is Stretford (British Gas), which is based on catalytic liquid phase oxidation of H_2S using sodium metavanadate and anthraquinone disulphonic acid to obtain elemental sulfur.

3.2.2 Down-hole / Upstream Treatment

The studies reported in the previous pages talk about the surface treatment of natural gas. It is beneficial also to focus the study on the down-hole treatment of natural gas because otherwise deposition of elemental sulfur in tubular and flow lines can lead to decreased production, increased corrosion and higher filtration /water disposal costs. These problems have been experienced at different fields even though H_2S is present at level of 5% which is below the level where sulfur deposition is normally a concern. The field experiences with sulfur deposition from different locations have been reported in the literature, and deposition behavior of sulfur in the well bore has been explained through experimental data and mathematical models.

The deposition of sulfur at La Barge field is reported by E.R.Thomas and R.J. Voohees, according to their report. Within six months of initial production in 1986, three of the seventeen tubing strings showed significant flow restrictions. This was unexpected since the 5% H_2S concentration in the gas was below that where sulfur deposition is normally a concern. The corrosion of flow lines was also observed.

Peng & Roinson developed a model similar in principle to Tomcej (1989) to determine where sulfur could be expected to deposit over the life of the field as a function of flowing conditions. It can be concluded from their study that phase behavior and well bore hydraulic models can be used to predict where and how much sulfur can be expected

to deposit. The reports further state that sulfur deposition concerns will grow as the field is produced.

Another study on experimental and numerical modeling of sulfur plugging in carbonate reservoirs has been performed by J.H.Abu-Kassem and M.R.Islam (1999) which presents experimental results along with a comprehensive bore model that predicts sulfur precipitation as well as plugging in carbonate cores. Their study concludes that both flow rate and the history of the production have a profound impact on plugging with sulfur.

3.2.2.1.1 Down-hole Gas Treatment Processes

The down-hole gas treatment processes reported in the literature are generally based on chemical treatment. The membrane application has been reported for the enrichment of natural gas wells (Hissham.m.Ettuney; Ghazi Al-Emzi 1994). The information on membrane application for removal of H_2S down-hole is lacking in the literature.

3.2.2.1.2 Diaryl Disulfide (DADS)

Diaryl Disulfide was first used successfully as a solvent to remove sulfur from tubular and flow lines at Exxon Co. USA's La Barge field in Wyoming, where there was the aforementioned the problem of tubular plugging. DADS in its application is found preferable for sulfur deposition problems because it is cheaper and less volatile with no disposal needed when compared with commonly used solvent Dimethyl disulfide (DMDS). The sulfur uptake of DADS is observed far better than that of amine chemicals in the presence of a large amount of CO_2 . The DADS treatment process applied at La Barge was batch wise in application (Robert J. Voorhees, and J. Kenlly, 1991).

3.2.2.1.3 Scavengers and Biocides

The use of scavengers and biocides is effective for H₂S control. These chemicals have been both in topside equipment and down-hole applications. Though typically effective, these chemicals are costly in application and may exhibit unintended toxicity in produced fluids. (P.J. Sturman and D.M. Goeres, 1999; SPE 56772).

3.2.2.1.4 Treatment with NO₂ / NO₃

The down-hole injection of nitrite containing solutions into sour oil and gas wells under controlled conditions has been observed to effectively remove hydrogen sulfide (H₂S) from aqueous and gas phases. Souring control using nitrite has been successfully applied to a gas well in the San Juan Basin of New Mexico (SPE 56772, 1999). In a 36- hour down-hole squeeze in a gas well, injected NO₂- removed H₂S from produced gas for a period of seven months. This treatment has proven an effective means of controlling H₂S in oil and gas wells and of removing iron sulfide scale for the near well bore.

It can be concluded from the literature review that there are a variety of processes for surface treatment of natural gas for sulfur removal, based on chemical treatment and mechanical separation as well. But studies performed on down-hole sulfur removal from natural gas streams are very limited and are mostly focused on chemical treatment. The information about the membrane application for down-hole gas treatment is lacking in the literature. Moreover, the chemical treatment processes employed down-hole are not continuous in their operation.

The membrane performance has been proven superior to conventional chemical treatment methods, as in the past ten years membrane gas separation has made great advances and can now be regarded as a competitive industrial gas separation method. The membranes developed for sour gas treatment are mostly made of polymeric material and are expensive in their preparation. So it is necessary to investigate some inorganic material

and evaluate its sour gas separation characteristics for down-hole natural gas treatment applications.

3.3 Experimental Setup

A glass column packed with glass balls was used for all experimental tests. A calcium carbonate sample was obtained in powder form. The glass column was packed with a limestone sample along with the glass balls. The packed column was connected to a cylinder of SO_2 gas with a concentration of 5000 PPM carried by N_2 gas and the gas released from this column was bubbled through a distilled water beaker. The electrode of pH meter was inserted in this beaker to monitor the pH change in distilled water. The experiment was carried out at STP conditions. A manometer was used to measure the pressure drop across the column. The limestone sample was impregnated with Monoethanol Amine solution for different compositions and packed with glass balls in the column.

3.4 Procedure

In order to observe the adsorption of SO_2 in limestone, the Sample N_2 gas carrying 5000 PPM of SO_2 was passed through the glass column packed with limestone. The gas released from this column was bubbled through distilled water contained in a beaker of 1-liter volume. The change in pH of water was monitored with the help of a pH meter for the same time period and at fixed flow rate. The experiment with packed column was repeated by packing it with limestone impregnated with different concentrations of MEA (Monoethanolamine). Then the gas with the same flow rate was directly bubbled through the water, without passing through the adsorption column. The change in pH was monitored in this case too.

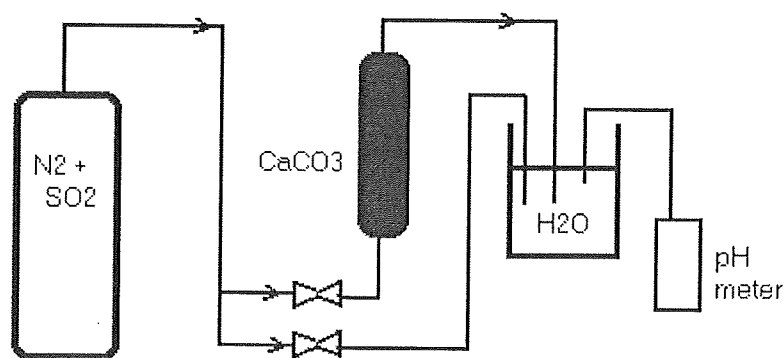
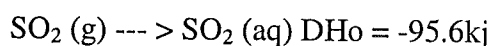


Figure 3.1: Experimental setup

3.5 Theory

Sulfur dioxide is highly soluble in water. At room temperature, the dissolving process is exothermic:

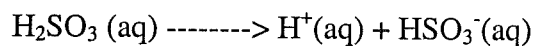


At room temperature, the solubility of SO_2 is approximately 200 g SO_2/L . Thus, 1 ml of water could dissolve 76 ml SO_2 . The solubility of SO_2 in water is highly temperature dependent and is about 400 times more soluble at 0°C (228 g/L) than it is at 90°C (5.8 g/L).

SO_2 is often thought of as the 'anhydride of sulfurous acid', H_2SO_3 . However, it is questionable if sulfurous acid exists at all. If it does, the equilibrium constant is so small that less than 1 molecule per billion is in the form of sulfurous acid.



The H_2SO_3 upon being dissolved in water undergoes the following reaction.



Since H_2SO_3 is a weak acid, it is only slightly dissociated in water, and concentration of H^+ can be calculated for it using its ionization constant value K_a .

For H_2SO_3 $K_a = 1.54 \times 10^{-2}$ (et. al. Richard E. Dickerson, 1979)

pH for 1.0 M solution of H_2SO_3 is :

$$(X)(X)/1.0-X = 1.54 \times 10^{-2}$$

Where X represents unknown equilibrium concentration of H^+ .

Since H_2SO_3 is weak acid it can be assumed that $1.0 - X = 1.0$.

$$\text{So } X = [H^+] = (1.54 \times 10^{-2})^{1/2} = 0.124$$

$$\text{pH} = -\log_{10}(0.124) = 0.91$$

$$\text{Similarly for Conc. 2.0 M, } \text{pH} = 0.6$$

The sharp decrease in the pH is caused by the formation of H_2SO_3 on the dissolution of SO_2 in water. As $CaCO_3$ captures the SO_2 in the packed column the outlet concentration of SO_2 from the column is decreased and hence the pH of water remains more stable.

3.6 Experimental Results and Discussions

The sharp decrease in pH in fig 3.1 shows the higher concentration of SO_2 in the exit stream. As the SO_2 is captured by limestone, the concentration of SO_2 in the exit stream is decreased so the less amount of SO_2 is dissolved in water and hence the change in pH is minor. The pH of water remains more stable when the limestone is impregnated with MEA because the capture rate of SO_2 is increased and hence the formation rate of H_2SO_3 is decreased, which actually causes the change in pH of water.

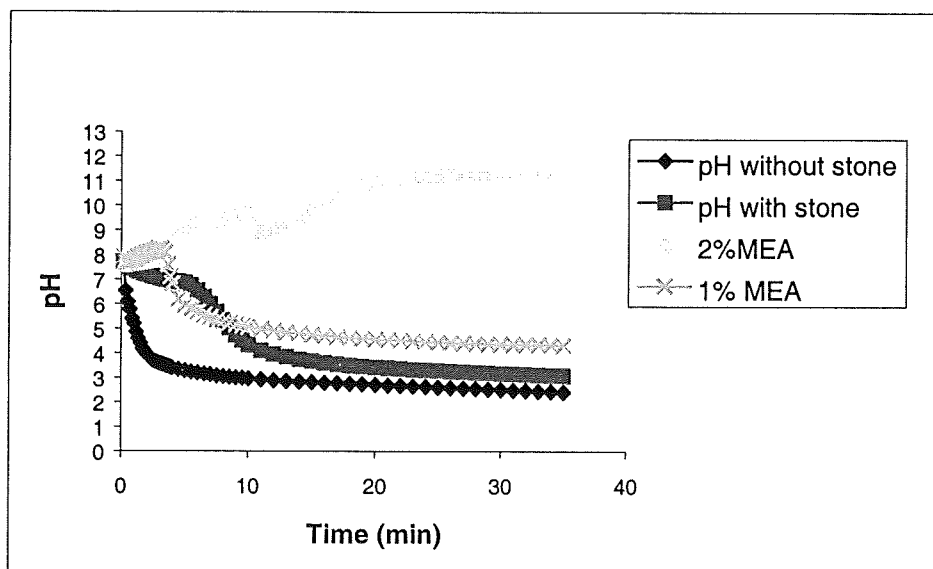


Figure 3.2: Concentration profile of SO_2 through and without limestone adsorption column

CHAPTER 4

A NUMERICAL MODEL FOR THE SIMULATION OF SO₂ ADSORPTION IN LIMESTONE

4.1 Summary

A numerical model was developed to simulate the adsorption of sulfur on limestone. The surface excess theory has been discussed in detail in Chapter 2 of this report. The governing equations were solved using the finite difference Barakat-Clark scheme. Results were used to determine the break through time of outlet concentrations of gas for different values of parameters involved in the governing equation. The results of the parametric study were helpful to explain the adsorption phenomenon.

4.2 Governing Equation

$$\begin{aligned} \frac{\lambda q \rho_g}{A \phi} \frac{\partial^2 C}{\partial z^2} - \frac{q \rho_g}{A \phi} \frac{\partial C}{\partial z} = \frac{1-\phi}{\phi} \rho_r n_0 \frac{\partial C}{\partial t} \\ + \frac{1-\phi}{\phi} \rho_r \left(\frac{\partial n_g^{ea}}{\partial t} \right) \end{aligned} \quad (4.1)$$

Boundary Conditions

$$C(z, 0) = 0 \quad \text{for } 0 \leq z \leq L$$

$$C(0, t) = C_0$$

$$\left. \frac{\partial C}{\partial z} \right|_{z=L} = 0 \quad \text{For } t > 0$$

Values of parameters used in governing equation:

Table 4. 1: Input Data

A	ϕ	N0	K1	ρ_r	λ	N1E	q
80 cm ²	0.3	100mg/g	1/hr	0.3	1 cm	100mg/g	7 L/min

4.3 Results and Discussions

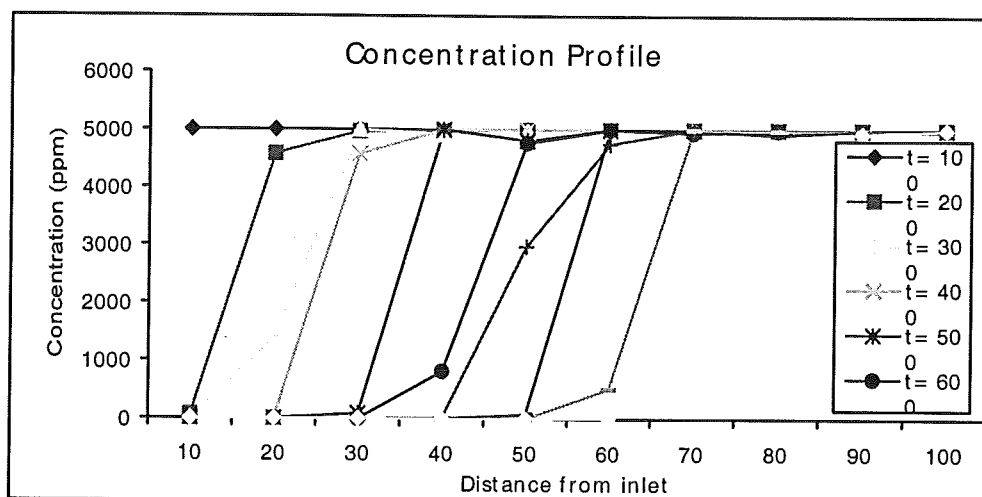


Figure 4.1: Concentration Profile of SO_2 at different time intervals

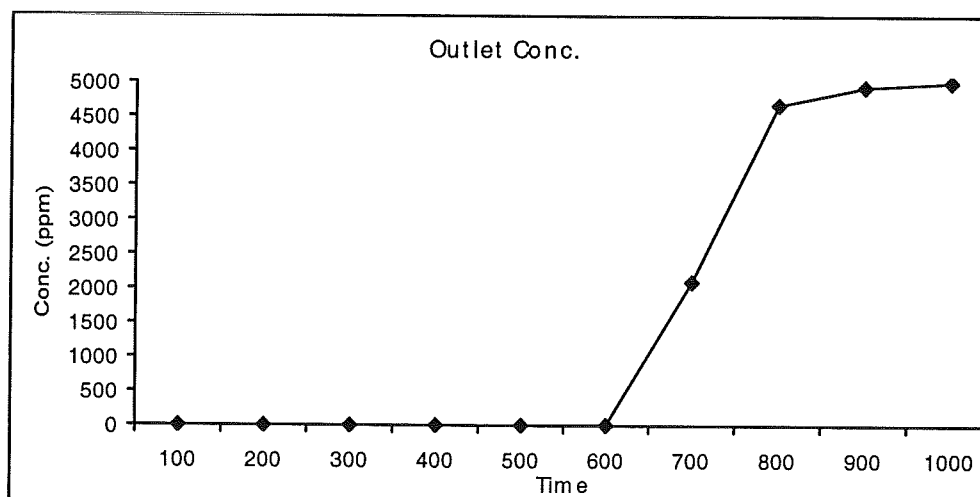


Figure 4.2: Outlet Conc. of SO_2 .

4.4 Parametric Effects

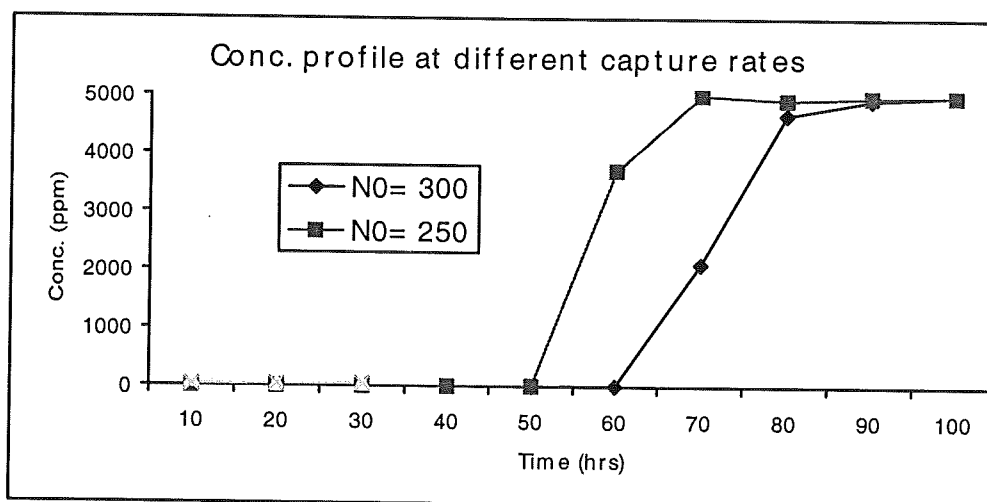


Figure 4.3: Conc. profile of SO_2 at different capture rates of carrier gas

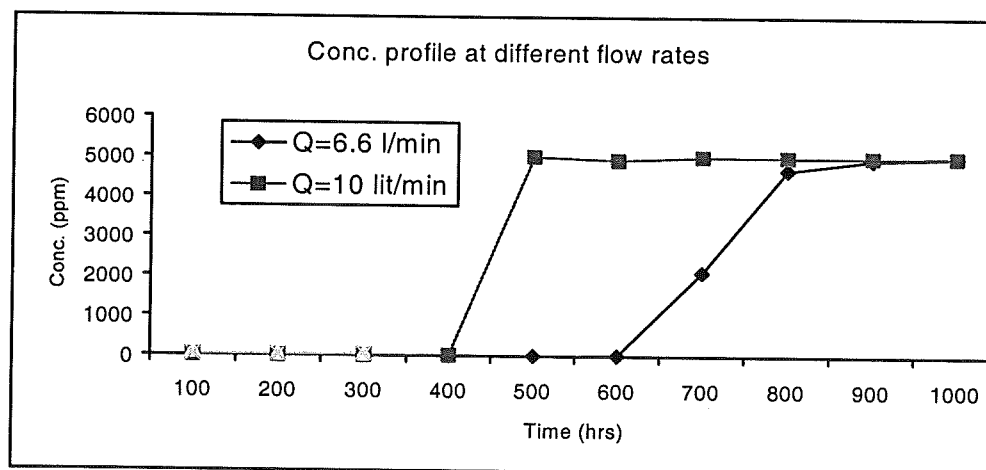


Figure 4.4: Conc. Profile of SO_2 at different flow rates

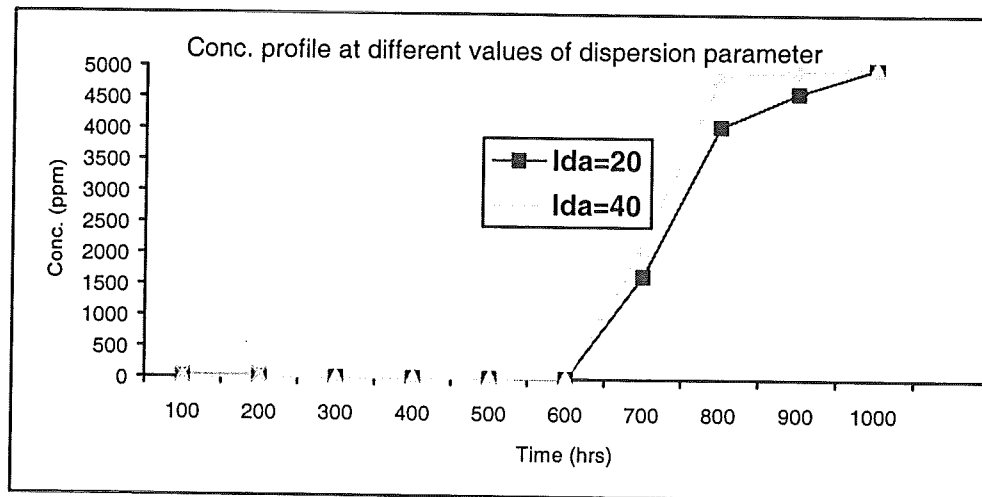


Figure 4.5: Conc. Profile of SO_2 at different values of dispersion parameter ($l_{da} = \lambda$)

4.5 Conclusions and Recommendations

- The model based upon the 'surface excess theory' is accurate in describing the adsorption of sulfur on solid surfaces.
- The Barakat Clark formulation is a proven powerful technique to solve diffusion equations based upon surface excess theory.
- An increase in flow rate Q decreases breakthrough time
- An increase in N_0 increases breakthrough time.
- An increase in dispersion parameter decreases the breakthrough time.
- Experimentation is required to determine values of parameters independently.

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