HYDROGEN SULFIDE REMOVAL FROM BIOGAS WITH A FIXED BED OF
RUSTED IRON TURNINGS

by

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Canas, 1982

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF APPLIED SCIENCE

in

FACULTY OF GRADUATE STUDIES
Bio-Resource Engineering

We accept this thesis as conforming
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
October, 1986

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ABSTRACT

Biogas produced at farm level has many applications, however the hydrogen sulfide must be eliminated from the biogas to prevent any possible damage to equipment, users and operators, and the environment. Among the various options available to the farmer to clean hydrogen sulfide from biogas a fixed-bed of rusted iron turnings seems appropriate.

This study investigated the effectiveness of a fixed bed of rusted iron turnings in eliminating hydrogen sulfide. For that purpose, dynamic bench scale test were done to study the effects of flow rate (0.5 l/min, 0.75 l/min and 1.0 l/min) and hydrogen sulfide concentration (100 ppm and 200 ppm). The gas used was a mixture of saturated carbon dioxide and hydrogen sulfide. The iron turnings were made with a uniform thickness and width and allowed to oxidize under atmospheric conditions for 8 weeks.

The resulting breakthrough curves were well described by sigmoidal curves. The breakpoint time was affected by flow rate and hydrogen sulfide concentration. At the higher flows and concentrations the breakpoint times were smaller. In contrast, the mass of hydrogen sulfide removed up to breakpoint time was independent of flow rate and hydrogen sulfide concentration (0.83 g). Nevertheless, the maximum removal capacity was independent of hydrogen sulfide concentration but dependent on flow rate.
The rate data conformed well to a surface rate model, however the calculated pseudo-rate constants were different for the flow rates and hydrogen sulfide concentrations used in this study. Thus it was not possible to define a mechanism control for the rate of reaction.

The fixed-bed was able to eliminate hydrogen sulfide from the gas mixture, however only 30 to 44% of the iron oxide reacted.
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Invariance of the Rate Constant with the Hydrogen Sulfide Concentration Calculated from Breakthrough Runs for the Rusted Iron Turnings. Flow rate 0.75 l/min.

Invariance of the Rate Constant with the Hydrogen Sulfide Concentration Calculated from Breakthrough Runs for the Rusted Iron Turnings. Flow rate 0.50 l/min.

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ACKNOWLEDGMENT

I wish to thank my supervisor Dr. R.N. Bulley for his guidance and interest during this study. I would also like to thank Dr. K.V. Lo for his support, and Dr. R.M.R. Branion for his valuable assistance in proof-reading the final draft.

Finally I extend a special thank you to my wife, my daughter and my parents for their patience and support during the last three years. Also I thank my friends at BioE for their help and assistance, especially Alan, D.G. and Lily.
Chapter 1

INTRODUCTION

The disposal of farm animal wastes has become a serious problem in farms that raise animals on concentrated feedlots. This type of operation produces large quantities of manure that can not be handled by the traditional practice of land spreading, becoming then a potential hazard to the environment. One of the options that has been proposed to alleviate this problem is the anaerobic digestion of the animal wastes. This approach not only reduces the capacity of the raw wastes to pollute the environment, but also produces a gas mixture that can be used as a source of energy. In general this gas mixture or biogas can be defined as a fuel gas, rich in methane, produced through a biological route from a wide variety of substrate biomasses including animal wastes and plant residues.

A typical biogas contains about 60% methane and 40% carbon dioxide. However, small quantities of sulfide gases, hydrogen, ammonia, and other trace impurities can also be present in the biogas. In Table 1 the compositions for different biogases reported in the literature are shown. The typical biogas is a sort of average gas for which the methane can be 54 to 80% and the carbon dioxide 20 to 45 % of the total volume. In contrast, the trace components are seldom reported or measured and they cannot be fixed in any specific range. Nevertheless, hydrogen sulfide can be found
Table 1 Composition of Digester Gas

<table>
<thead>
<tr>
<th>Component</th>
<th>Composition (%V/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A¹</td>
</tr>
<tr>
<td>CH₄</td>
<td>54-80</td>
</tr>
<tr>
<td>CO₂</td>
<td>20-45</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.1</td>
</tr>
<tr>
<td>N₂</td>
<td>traces</td>
</tr>
<tr>
<td>NH₃</td>
<td>traces</td>
</tr>
<tr>
<td>CO</td>
<td>-</td>
</tr>
<tr>
<td>O₂</td>
<td>-</td>
</tr>
<tr>
<td>H₂</td>
<td>0-10</td>
</tr>
</tbody>
</table>

Source:
1 Wheatley (1979).
3 Stafford et al. (1980).
4 Maramba (1978) animal wastes.
5 Dasilva (1978).

in all the digesters in percentages as low as 0.01% and as high as approximately 1%.

The main use of biogas at the farm level is as a source of energy. As a fuel, biogas can be used to run boilers, space heaters, cooking stoves and stationary engines that can drive blowers, pumps or electricity generators.

Although biogas can have all those many applications on the farm, there are some problems in its use. The problems are caused by carbon dioxide, water vapor and sulfide gases present in the biogas. The high content of carbon dioxide lowers the calorific value of the mixture and the water vapor tends to condense in the supply lines. The sulfide gases, mainly in the form of hydrogen sulfide, can cause serious corrosion problems on the metal surfaces of handling
equipment, burners and controls. It has been reported that biogas plants in Switzerland experienced corrosion problems when electricity was generated from biogas that had been poorly treated or untreated (Demuynick et al., 1984).

In addition hydrogen sulfide is a toxic gas. Its toxicity is rated as slightly less than cyanide and more toxic than carbon monoxide (Ferguson, 1975). In Table 2 the physiological effects of the three main components of the biogas are shown. It is seen that the methane and carbon dioxide act as asphyxiating gases and the hydrogen sulfide as poison. However the most interesting fact is that even at the low concentrations in which the hydrogen sulfide is present in biogas it can cause injury or death to anybody exposed to the gas.

Plants are also affected by the presence of hydrogen sulfide in the air. Most of the symptoms of injury are limited to new foliage with the leaf margin being scorched (Linzon, 1978). The maximum concentration at which damage can be avoided for plants has been set at 10 ppm (Committee on Medical and Biological Effects of Environmental Pollution, 1978).

Primary air quality standards for hydrogen sulfide have not been formulated although some countries have limits to the amount of hydrogen sulfide that can be emitted to the environment. In the province of British Columbia, Canada, emission standards have been set for stack emissions from Kraft pulp mills. The objective level A has been set at 5
Table 2 Physiological Properties of the Main Components of Biogas

<table>
<thead>
<tr>
<th>Gas Component</th>
<th>Concentration(^1) (%V/V)</th>
<th>Exposure(^2) period</th>
<th>Physiological(^3) effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>50</td>
<td>-</td>
<td>Asphyxiating Headache, non toxic</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO(_2)</td>
<td>2</td>
<td>-</td>
<td>Asphyxiating Safe</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-</td>
<td>Increased breathing</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>30 min</td>
<td>Drowsiness, headaches</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>30 min</td>
<td>Heavy, asphyxiating breath</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>30 min</td>
<td>Could be fatal Poison</td>
</tr>
<tr>
<td>H(_2)S</td>
<td>0.01</td>
<td>Hours</td>
<td>Irritation of nose and eyes</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>60 min</td>
<td>Headaches, dizziness</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>30 min</td>
<td>Nausea, excitement, insomnia</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>-</td>
<td>Unconsciousness, death</td>
</tr>
</tbody>
</table>

\(^1\) Concentration in volume of pure gas in 100 volumes of atmospheric air.
\(^2\) Exposure period: The time during which the effects of the noxious gas are felt by an adult human being and an animal (especially a pig) of about 68 kg weight.
\(^3\) Physiological effects: These are found to occur in adult humans; similar effects would be felt by animals weighing 68 kg; lighter animals will be affected sooner and at lower levels; and heavier animals would be affected at later times and at higher concentrations levels.


ppm over a period of 24 hr; objective level B has been set at 20 ppm over a period of 24 hr; and objective level C is set at 70 ppm over a period of 24 hours (Committe on Medical and Biological Effects on Environmental Pollution,1978).

On the whole, hydrogen sulfide must be eliminated from biogas or reduced to tolerable levels to minimize the damage
to gas handling equipment, to health of the users and operators of the system, and on the environment.
LITERATURE REVIEW

2.1 PRODUCTION OF HYDROGEN SULFIDE UNDER ANAEROBIC CONDITIONS

Microorganisms are capable of carrying out a wide variety of sulfur transformations. The main sources of hydrogen sulfide in the sulfur cycle are the reduction of sulfates and the degradation of organic sources of sulfur (amino acids). Both of the above substances are present or form during the anaerobic degradation of animal excreta, vegetable wastes and domestic waste waters (Cooper, 1975; Carlson and Leiser, 1966).

Around 0.4 to 0.8% of the dry weight of microorganisms is in the form of sulfur (Postgate, 1968). Most of it is stored in the form of proteins and polypeptides (amino acids cysteine and methionine) and the rest in sulfur containing vitamins and cofactors, thiamin, biotin and coenzyme M) (Zinder and Brock, 1978).

Roy and Trudinger (1970) mention that most microorganisms use sulfate as their main source of sulfur for growth. Microorganisms reduce the sulfate to hydrogen sulfide intracellularly and replace the hydroxyl groups on serine and homoserine with sulfhydryl groups. This reduction is called *assimilatory* because all the hydrogen sulfide produced is incorporated into amino acids. In contrast, some microorganisms only utilize sulfur containing amino acids as
their sulfur source.

Goldhaber and Kaplan (1974) mention that although reduction of sulfate by organic matter is found in most anoxic habitats, there is no known chemical mechanism for that reduction under normal earth temperatures and pressures. Consequently they attributed the reaction to the microorganisms present in the habitat.

The hydrogen sulfide that appears in the environment comes from what has been called dissimilatory sulfate reduction. Under such circumstances, sulfate that is used as an electron acceptor for the oxidation of the organic matter is reduced to hydrogen sulfide and excreted by the cells.

There are three strains of bacteria that have been identified as sulfate-reducers. First, the Desulfovibrio which are small motile, heterotrophic, obligatory, spiral shaped organisms. Secondly, The Desulfomonas which are short, non-motile rods with physiological similarity to Desulfovibrio. And lastly, the Desulfomaculum which are large, motile, heterotrophic rods that form resistant spores.

All the above strains grow only on limited sources of carbon (alcohols and organic acids), but they can tolerate a wide variety of environmental extremes (temperature, salinity and pressure) (Zobell, 1958) with the exception of pH. Low pH limits sulfate reduction (Tuttle et al., 1969).

The degradation of organic sulfur compounds to either sulfate or hydrogen sulfide is called mineralization. The
enzymatic degradation of organic sulfur compounds (mostly protein) during anaerobic digestion gives a mixture of amino acids or groups of amino acids that can be further degraded. The anaerobic degradation of cysteine (Freney, 1976) and methionine (Zinder and Brock, 1978) leads to the production of hydrogen sulfide and some mercaptans.

2.2 HYDROGEN SULFIDE REMOVAL

For a long time the chemical industry has used different methods of removing hydrogen sulfide from gaseous mixtures. Most of the methods have found application in the purification of natural gas, manufactured gas, coke oven gas and synthesis gas. However, commercially available processes for separation of hydrogen sulfide are capital and technology intensive and are used only when large quantities of gas are available for processing—over 2000 m³/h (National Research Council, 1977).

Some reviews have been done to assess the applicability of different processes to eliminate CO₂ and H₂S from digester gas. For large quantities of gas, Ashere (1981) and Glaub and Diaz (1981) should be consulted.

For small scale farm digesters three methods have been pointed out as possible: a) water scrubbing, b) alkaline scrubbing and c) iron sponge scrubbing (Hobson et al., 1981; National Research Council, 1977).

Water scrubbing is also known as plain water washing. This process eliminates both the CO₂ and H₂S although the
process requires relative high pressures because of the low solubility of both gases in water. For instance, the solubility of CO₂ at 20°C is only 1.5 kg/100 kg of H₂O under 1 atm but under 50 atm of pressure the solubility increases to 6 kg/100 kg H₂O. Therefore, if low pressures are utilized the quantity of water needed is high. At the same time due to the low partial pressures of the hydrogen sulfide in the digester gas (around 0.001 atm for a gas with 0.1% H₂S at 1 atm) a very poor absorption could be expected (National Research Council, 1977). Some other problems present are the extremely corrosive nature of the CO₂-H₂S mixture dissolved in water compared to the individual systems, particularly under high pressures (Barbouteau and Galaud, 1972) and the immediate desorption of the acid gases from the water when exposed to the atmosphere. Hobson et al. (1981) state that for farm level systems, that store gas at low pressures, a column of water of a few inches can be enough to prevent the flow of the gas and also that unless pure water was used (because of possible reactions with metals to form insoluble sulfides) filtration would be required to avoid plugging the distribution system.

The second option is the use of alkaline scrubbing with NaOH, KOH or Ca(OH)₂ solutions. These processes are a combination of absorption and chemical reaction. For example, in a NaOH solution the CO₂ is absorbed by the alkaline solution and reacts with the NaOH to form Na₂CO₃ that establishes an equilibrium with the CO₂ in solutions.
The reaction are as follows:

\[ \text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \] \hspace{1cm} (1)

\[ \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{NaHCO}_3 \] \hspace{1cm} (2)

And if the contact time is enough \( \text{H}_2\text{S} \) reacts with the carbonate as follows:

\[ \text{H}_2\text{S} + \text{Na}_2\text{CO}_3 \rightarrow \text{NaHS} + \text{NaHCO}_3 \] \hspace{1cm} (3)

The above processes suffer from the same technical problems as the water wash process and are rarely used in small scale systems.

The iron sponge process is one of the oldest methods used to clean hydrogen sulfide from town gas. The typical process is the iron box process in which the gas is passed through a series of boxes filled with wood shavings coated with hydrated iron oxide. In the absence of air or sulfur dioxide the main reaction is known as sulfiding because it forms \( \text{Fe}_2\text{S}_3 \). The latter can be regenerated by exposing the sponge to air.

For systems that require only \( \text{H}_2\text{S} \) removal, e.g. digester gas, the iron-sponge process would seem to be more acceptable and easier to handle by the farmer than the other processes. Nevertheless, Hobson et al. (1981) reported that for a poorly run system the pressure drop can be as high as 22 cm \( \text{H}_2\text{O} \)/m of bed and for a plant that stores gas under low
pressures (less than 50 cm of H₂O) this could be a problem.

The iron sponge process finds its widest application in the treatment of gases where complete removal of the hydrogen sulfide is essential. Maddox and Burns (1968a) cite some of the advantages of the iron sponge process as: a) the process is selective towards H₂S, b) the CO₂ is not removed, c) the removal of H₂S is very good for small gas volumes, d) the process would operate equally well at almost any operating pressure, and e) the process is suitable for operation with minimal attention.

As previously mentioned iron oxide is the active material in the iron sponge. Griffith and Morcom (1945) found that when hydrogen sulfide reacts with any of the seven forms of ferric oxide (see Table 3), the reaction product is always hydrated ferric sulfide as represented by the following equations:

\[ 2\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O} + 6\text{H}_2\text{S} \rightarrow 2\text{Fe}_2\text{S}_3 \cdot \text{H}_2\text{O} + 6\text{H}_2\text{O} \]  \hspace{1cm} (4)

\[ 2\text{Fe}_2\text{O}_3 + 6\text{H}_2\text{S} \rightarrow 2\text{Fe}_2\text{S}_3 \cdot \text{H}_2\text{O} + 4\text{H}_2\text{O} \]  \hspace{1cm} (5)

Of all the seven ferric oxides only two types, \( \alpha - \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O} \) and \( \gamma - \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O} \) react immediately and rapidly with hydrogen sulfide.

The sulfide hydrate, \( \text{Fe}_2\text{S}_3 \cdot \text{H}_2\text{O} \), is stable in an atmosphere of inert gas at temperatures below 20°C, but at higher temperatures in the presence of hydrogen sulfide the sulfide hydrate is converted into \( \text{FeS}_2 \) and \( \text{Fe}_8\text{S}_9 \). An
Table 3 Forms of Ferric Oxide

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha Fe_2O_3$</td>
<td>Bright red, with low magnetic susceptibility; very stable on heating.</td>
</tr>
<tr>
<td>$\alpha Fe_2O_3\cdot H_2O$</td>
<td>Yellow brown, with low susceptibility, changes to $\alpha Fe_2O_3$ on heating at 250°-300°C.</td>
</tr>
<tr>
<td>$\beta Fe_2O_3\cdot H_2O$</td>
<td>Bright yellow with low susceptibility. Changes to $\alpha Fe_2O_3$ on heating above 100°C.</td>
</tr>
<tr>
<td>$\gamma Fe_2O_3$</td>
<td>Chocolate brown, intensively magnetic. On heating at 300°C changes to $\alpha Fe_2O_3$ with loss of magnetic properties, the conversion being complete in about 24 hours.</td>
</tr>
<tr>
<td>$\gamma Fe_2O_3\cdot H_2O$</td>
<td>Orange with low susceptibility. On heating at 300°C changes to $\gamma Fe_2O_3$ with great increase of magnetic properties, but on prolonged heating at this temperature slowly converts to $\alpha Fe_2O_3$ with a fall of susceptibility as for $\gamma Fe_2O_3$.</td>
</tr>
<tr>
<td>$\delta Fe_2O_3\cdot H_2O$</td>
<td>Dark red brown, intensely magnetic. On heating at 150°C is converted completely to $\alpha Fe_2O_3$ with a great drop in susceptibility.</td>
</tr>
<tr>
<td>Amorphous $Fe_2O_3$</td>
<td>Red brown, low susceptibility hardly changes on heating; at 100°C becomes $\alpha Fe_2O_3$ even under boiling water, when color become bright red</td>
</tr>
</tbody>
</table>


Alkaline pH seems to stop the decomposition of the sulfide hydrate even at temperatures near 90°C; however, alkaline pHs cannot prevent the dehydration of the sulfide hydrate that starts at 40-50°C (Hopton, 1948).

The oxidation of the sulfide hydrate under alkaline pH and temperatures below 40-50°C is fast and always gives the active $\alpha-Fe_2O_3\cdot H_2O$ under dry conditions and $\gamma-Fe_2O_3\cdot H_2O$ under wet conditions. On the other hand FeS$_2$ and Fe$_6$S$_9$,
oxidize slowly and the former compound, upon oxidation, gives iron sulfate and anhydrous \( \gamma-\text{Fe}_2\text{O}_3 \).

From stoichiometric considerations it can be said that 1 kg of ferric oxide reacts with 0.64 kg of hydrogen sulfide to form 1.30 kg of sulfide. Nevertheless, in practice, yields of 0.56 kg are among the highest values reported, but it is usually assumed that 50% of the stoichiometric yield is obtainable in the first cycle (Kohl and Reisenfeld, 1960).

The reaction rate between hydrogen sulfide and ferric oxide depends on the penetration of the gas into the mass (sponge), therefore it is related to the bulk porosity and to the pore structure of the oxide (Hopton, 1948; Ward, 1972).

2.3 DESIGN CRITERIA

Process design criteria for the iron-sponge method are based on empirical rules. In the following paragraphs these criteria will be shown.

Kohl and Reisenfeld (1960) and Ward (1972) consider that the best approach to design is the use of the following equation:

\[
R = \frac{F}{V}
\]

(6)

where,

\begin{align*}
R & \quad \text{Space velocity or R factor [hr}^{-1}] \\
F & \quad \text{Maximum flow of gas [ft}^3/\text{hr}] \\
V & \quad \text{Volume of the reaction chamber}
\end{align*}
where $R$ is known as the $R$ ratio and represents the number of bed volumes per unit time being treated in the box. Values of $R$ around 30 to 50 are used for the removal of hydrogen sulfide according to Ward (1972); however, Kohl and Reisenfeld (1960) recommend $R$ values between 20 and 50 for systems operating at atmospheric pressure with revivification in situ. One of the problems with the $R$ ratio as defined above is that the conditions at which the flow is calculated are usually not indicated. Box life of 60 days is considered a minimum but in practice they are designed to run up to 6 months before changing the oxide.

For high pressure processes Maddox and Burns (1968b) considered the following design criteria:

a) the depth of the bed should be at least 3 m, to produce enough pressure drop for a proper velocity distribution across the bed.

b) the bed diameter can be calculated by two methods: heat effects and contact time. The former method is based on the optimum sulfur deposition rate of 10 g per m$^2$ of cross-sectional area of the bed per minute, and the latter is defined by the following equation:

$$t = \frac{3600V}{W/p}$$ 

where,

$$t \quad - \quad \text{contact time [sec]}$$
\( V \) - reactor bed volume \([\text{ft}^3]\)

\( W \) - mass flow rate of gas \([\text{lb/hr}]\)

\( \rho \) - gas density \([\text{lb/ft}^3]\)

Values of \( t \) between 15 to 20 sec are used for beds with continuous revivification and values of at least 60 sec for beds without continuous revivification. Both methods should be used to check one another, for example if a bed is designed using the optimum sulfur deposition rate and the minimum depth of 3 m, the \( t \) value should be checked and if it is below 60 sec the height of the bed should be increased to approach a \( t \) value of 60 sec.

c) the bed life is obtained from the amount of sulfur in the gas and the type of operation used. For a bed using 9-lb-grade sponge and packed in such a way that there are 9 lb/ft\(^3\), the sponge is able to remove 5 lb of sulfur per ft\(^3\) of bed before the first regeneration. For continuous revivification the sponge removes 22 1/2 lb sulfur per ft\(^3\) of bed before change is required. If following the above criteria, the bed life is still less than 60 days, the size of the bed should be increased until it reaches a minimum of 60 days bed life.

Zapffe (1962) uses design criteria similar to Maddox and Burns (1968b), however he stresses the fact that the contact time should be calculated under actual operating conditions. He defines the contact time as the \( R \) ratio, which is not true, because one is the inverse of the other. However, he recommends \( R \) ratio values between 50 and 180,
but for gases with more than 50 grains of hydrogen sulfide per 100 ft$^3$ and no oxygen present R should be at least 90.

Hobson et al. (1981) state that even though the design of iron oxide purification systems depends on the sulfide concentration and the flow rate of the gas, a bed could be sized using as a criterion 400 g of oxide per m$^3$ per hour of gas flow rate.

The Biomass Energy Institute Inc. (1978) claims that 0.1 m$^3$ of iron sponge would clean 3300 m$^3$ of gas if its hydrogen sulfide concentration is 0.14 % V/V.

The National Research Council (1977) also claims that 0.0352 m$^3$ of iron sponge would eliminate the hydrogen sulfide from 2500 m$^3$ of gas if the concentration is 0.2 % V/V.

Ravishanker and Hills (1984) studied the performance of a bench scale static bed purifier and were able to fit a mathematical model to their data in order to predict the depth of the bed. They used the optimum sulfur deposition rate to set the diameter of the tower and according to them it worked well. The experiment was done with a synthetic biogas that had nitrogen instead of methane. However their model is limited to at least 4 days between regenerations, and partial pressures of hydrogen sulfide in the gas greater than $2.5 \times 10^{-4}$ atm. The equation can be written as follows:

$$\frac{1}{P} = 1.90 \times 10^3 [Z - 0.1(T - 2)] + \frac{1}{0.85P_0} \quad (8)$$
where,

\[ Z \quad - \quad \text{depth of bed [mm]} \]

\[ P \quad - \quad \text{desired partial pressure of hydrogen sulfide in treated gas [atm]} \]

\[ P_0 \quad - \quad \text{partial pressure of hydrogen sulfide in untreated gas [atm]} \]

\[ T \quad - \quad \text{time between revivification [days]} \]

2.4 IRON FILING SCRUBBER

Another type of scrubber that can be used to remove hydrogen sulfide is one that contains iron or steel filings as packing material (Maramba, 1978; Stanford et al., 1983; Economic and Social Commission for Asia and the Pacific, 1980; Meynell, 1976; Demuynick et al., 1984). The iron can be easily obtained from filings, steel cuttings, turnings and finely drawn wire. However, the absorption capacity is not easy to calculate because a sticky sludge forms on the surface of the iron that prevents the gas from contacting the material.

The only quantitative data reported for digester gas were given by Maramba (1978). He mentions that an hermetically sealed 55 gallon oil barrel with two layers, each 1 ft (0.30 m) deep, of iron filings, was used for a period of six months before changing the filings, when located before a 25 HP engine that worked 12 hours per day; however, no mention of the sulfide concentration or total flow of digester gas is given.
In the Guidebook on Biogas Development (Economic and Social Commission for Asia and the Pacific, 1980) the capacity for iron filings or ferric oxide (rust) is reported to be 2.5 kg of filings per m$^3$ of hydrogen sulfide (which is the same value used for the theoretical sulfiding capacity in the iron oxide process).

Nevertheless, there is not a clear position with regard to the activity of iron oxide obtained from atmospheric oxidation of iron (rusting). Ward (1972) reports that a mixed oxide made by mixing iron swarf and wood shavings and exposing it to the atmosphere for 2 weeks to 6 months was very active. In contrast, Hopton (1948) states that oxide produced by rusting of scrap iron or steel is of poor quality, and has limited value for hydrogen sulfide scrubbing.

2.5 THE RUSTING OF IRON

The formation of hydrated iron oxide in the presence of oxygen and water is known as rusting. Rust formed on atmospheric exposure is usually more adherent than that produced by immersion. Traditionally the mechanism for rusting iron has been seen as electrochemical process resulting from the presence of anode and cathode points on the surface of the iron (due to differences in stress, to lack of uniformity or to the presence of impurities) and reaction with carbon dioxide (Parkes, 1961; Wood and Holliday, 1963; Latimer and Hildebrand, 1951).
The mechanism is as follows: At the anodic points the iron is oxidized to iron II and at the cathodic points $\text{H}^+$ (hydrogen ions) are reduced to molecular hydrogen. The ferrous (iron II) and hydroxyl ions react to give ferrous hydroxide, which is converted by the carbon dioxide and water to ferrous bicarbonate. The latter is oxidized by the atmospheric oxygen and hydrolyzed to hydrated ferric oxide.

On the other hand, Evans (1967) states that although in earlier works carbon dioxide was held as responsible for the rusting of iron, sulfur dioxide is the main cause of atmospheric corrosion at inland locations, and that carbon dioxide could even retard the attack.

The absorbed sulphur dioxide combines with atmospheric oxygen and water at active catalytic points to give sulfuric acid that attacks the iron to produce iron sulfate (through electrochemical reactions). The ferrous sulfate is oxidized to the ferric state and hydrolyzed to produce ferric rust and sulfuric acid.

2.6 FIXED BED REACTOR PERFORMANCE

For the reaction to take place in a gas-solid reactor the material in the gas phase must move from the main body of the gas phase to the gas-solid interphase and into the solid phase.

The overall rate may be determined by any one or more of the following steps:

a) diffusion (mass transfer) of the material on the gas
phase to the gross surface of the solid,
b) diffusion of the molecules of the material into (or along the surface of) the large pores of the solid,
c) adsorption of the molecules on the interior surface of the solid,
d) chemical reaction of the adsorbed material with the solid.

If all the above steps are linear they can be combined in one expression; however, often one of the steps, the slowest, controls the rate and the rest of the steps can be ignored. Many heterogenous reactions are controlled by the rates at which the reacting substances are brought together to the interface and the rates of such reactions are controlled by mass transfer rates and not by chemical rates.

2.6.1 BREAKTHROUGH CURVE

For a fixed-bed reactor that contains a solid phase or catalyst which does not regenerate, because the products accumulate on the surface of the solid, the following effects can be noted:
a) the rate of reaction decreases with time,
b) the rate of escape of unused reactants increases with time,
c) the reaction mass products accumulate in the solid or catalyst bed at a decreasing rate.

Therefore, an unsteady condition prevails in the bed over the entire period of operation.
Figure 1 shows a plot of the dimensionless concentration of the effluent, \( C/C_0 \), against time or volume of gas treated (also known as throughput) for a complete run of a fixed bed reactor. It can be seen that at the beginning of the run the component in the gas phase is rapidly and effectively removed by the first layers of the solid in the upstream section of the column. In this section the solid is in contact with the gas at its highest concentration, \( C_0 \). Meanwhile, the small amounts that escape the first layers are removed by solid in the downstream end of the column, and the gas leaves the bed free of any reactive material. As the run continues the top layers become completely saturated and they do not react with the component in the gas phase; therefore, the effective zone of removal moves down in the column. The movement of the effective zone is accompanied by the movement of the effluent concentration front. However, the movement of effective zone is much slower than the linear velocity of the gas. The run reaches a point at which the concentration of effluent suddenly increases this point is called *breakpoint*. Nevertheless, the breakpoint can be arbitrarily chosen and its usually set as the maximum amount of effluent material allowed to exit the bed.

Due to the sudden increase in the effluent concentration when the breakpoint is reached the curve has received the name of *breakthrough curve*. Most of the breakthrough curves exhibit an \( S \) shape but with different degrees of steepness. Among the factors that can affect the
Feed Concentration $c_0$

Effluent Concentration $c_a$

$C/C_a$, $C/C_b$, $C/C_c$, $C/C_d$

Figure 1 Ideal Breakthrough Curve.
(Source: Treybal, 1980, p 624)
shape of the breakthrough curve are the initial influent concentration, the rate controlling mechanism, the particle size, the depth of the column, and the velocity of the flow.

2.6.2 SURFACE RATE CONTROL

For a surface rate control condition Chou and Hauser (1964) found that the performance of a fixed-bed reactor is given by the following equation:

\[
\ln\left(\frac{C_0}{C} - 1\right) = \frac{kSC_0}{m} \cdot \frac{v}{v} + \ln\left[\exp\left(\frac{kSx}{v}\right) - 1\right] - \frac{kSC_0t}{m} \quad (9)
\]

where,

- \(m\) - mass of \(H_2S\) absorbed [g/cm\(^3\) of bed]
- \(k\) - reaction rate constant [cm\(^3\)/cm\(^2\)day]
- \(C\) - concentration of reactant in the gas phase [g/cm\(^3\)]
- \(S\) - surface density [cm\(^2\)/cm\(^3\)]
- \(m\_\infty\) - maximum mass absorbed [g/cm\(^3\)]
- \(x\) - bed depth [cm]
- \(v\) - fluid velocity in the intertices of the bed [cm/day]

However, under experimental conditions the equation can be simplified to:

\[
\ln\left(\frac{C_0}{C} - 1\right) = \frac{kS}{v} - \frac{kS_0t}{m} \quad (10)
\]

Since the above equation is linear in time, \(t\), the rate constant, \(k\), can be calculated from the intercept, \(b_0\), of a
plot of the left hand side of the equation against time, then

\[ k = b_0 \frac{v}{xS} \]  
(11)

and the maximum capacity, \( m_\infty \), can be calculated from the slope, \( b_1 \), of the equation,

\[ m_\infty = \frac{kS \sigma_0}{b_1} \]  
(12)
3.1 OBJECTIVES AND EXPERIMENTAL DESIGN

3.1.1 RESEARCH OBJECTIVES

The objective of the experiment was to investigate the effectiveness of rusted iron turnings in eliminating hydrogen sulfide from biogas.

For this purpose, studies under dynamic conditions in a bench scale apparatus were conducted and the effects of variables such as total flow rate and initial hydrogen sulfide concentration were also studied.

3.1.2 EXPERIMENTAL DESIGN

The experimental units used iron turnings produced at the Bio-Resource Engineering workshop using the same machine and from the same steel bar. The turnings were allowed to rust under atmospheric conditions for a period of 8 weeks.

The variables manipulated were the total flow rate and the initial hydrogen sulfide concentration. The total flow rate is a continuous variable with 3 levels: 0.5 l/min, 0.75 l/min and 1.0 l/min. The hydrogen sulfide concentration was maintained at one of two levels: 100 ppm or 200 ppm. Therefore, a total of six experimental conditions were established—two variables with three and two fixed levels respectively. Each experimental condition was done in
The order in which the experimentation was conducted was completely randomized by giving a number to each experimental runs and drawing numbered papers from a box.

The response variables were the breakpoint time and the total mass of hydrogen sulfide removed by the bed when the breakpoint was reached.

Table 4 shows the experimental factors and their levels and Table 5 shows the results from the randomization.

### 3.2 EXPERIMENTAL APPARATUS

The breakthrough curves were obtained with the apparatus shown in Figure 2. The system provided a feed mixture that had known ratios of carbon dioxide to hydrogen.
Figure 2 Schematic Diagram of the Experimental Fixed-Bed Reactor System (Code in Table 6).
Table 6 List of Equipment

<table>
<thead>
<tr>
<th>Code in Figure 2</th>
<th>Item</th>
<th>Supplier</th>
<th>Model</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>Fixed-bed Reactor</td>
<td>Matheson</td>
<td>600</td>
<td>Clear plexiglass 10cm x 71cm</td>
</tr>
<tr>
<td>B2</td>
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<td>Matheson</td>
<td>604</td>
<td>Clear plexiglass 10cm x 71cm</td>
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<td>Matheson</td>
<td>603</td>
<td></td>
</tr>
<tr>
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<td>Rotameter</td>
<td>Matheson</td>
<td>603</td>
<td></td>
</tr>
<tr>
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<td>Rotameter</td>
<td>Matheson</td>
<td>603</td>
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</tr>
<tr>
<td>F4</td>
<td>Rotameter</td>
<td>Matheson</td>
<td>603</td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>Mixing Chamber</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>R1</td>
<td>Gas Regulator</td>
<td>Matheson</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R2</td>
<td>Gas Regulator</td>
<td>Union</td>
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<td></td>
</tr>
<tr>
<td>S</td>
<td>Saturation Vessel</td>
<td>Carbide</td>
<td></td>
<td>Clear plexiglass 76cm x 102 cm</td>
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<tr>
<td>Sp</td>
<td>Sampling Point</td>
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</tr>
<tr>
<td>T1</td>
<td>Carbon dioxide</td>
<td>Medigas</td>
<td>Cylinder K</td>
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</tr>
<tr>
<td>T2</td>
<td>Hydrogen sulfide</td>
<td>Matheson</td>
<td>Cylinder T</td>
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<tr>
<td>V1</td>
<td>Clamp</td>
<td>Matheson</td>
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<td></td>
</tr>
<tr>
<td>V2</td>
<td>High pressure valve</td>
<td>Matheson</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V3</td>
<td>High pressure valve</td>
<td>Matheson</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gas Bag</td>
<td>Environmental Measurements</td>
<td>10-011</td>
<td>du Pont Tedlar</td>
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<td></td>
<td>Hydrogen sulfide monitor</td>
<td>Energetic Science</td>
<td>ECOLYZER 6000 Series</td>
<td>Electrochemical detector</td>
</tr>
<tr>
<td>TH(1-3)</td>
<td>Thermocouple</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The flow of both the carbon and the hydrogen sulfide were drawn from high pressure gas cylinders that were
controlled with regulators and the flow rate was measured with calibrated flowmeters. Because the gas had to be wet (biogas is usually saturated) the carbon dioxide gas flow was sparged through liquid water. This stream was later brought together with the hydrogen sulfide in the mixing chamber.

The feed stream was divided in two and passed through the fixed beds. The beds were located inside a chamber. Each one of the beds had an upward flow. The gas leaving the beds was discharged into a chamber and further cleaned by passage through an activated carbon filter before being exhausted into the atmosphere.

The beds were constructed from clear plexiglass cylinders 10 cm diameter x 71 cm length. The packing material in each bed was supported by a pair of plexiglass plates that contained a thin layer of glasswool between them. Each plate had a diameter of 9.8 cm and had a total of 21 holes of 0.06 cm diameter drilled to allow the flow of gas. The plates were supported by three bars of 0.06 cm diameter and 20 cm long.

The sparger vessel was also made of clear plexiglass cylinder. The dimensions of the vessel were 7.6 cm diameter x 101.6 cm length. The vessel was filled to 3/4 of its capacity before each one of the runs started. The carbon dioxide entered through the bottom of the vessel and dispersed into the liquid by passage through a diffuser stone. The gas leaving the sparger was assumed to be
saturated at room temperature and barometric pressure.

The mixing chamber consisted of a glass bulb 2.5 cm diameter x 7.6 cm length. The gases entered the chamber in such way that the smaller flow was injected in the flow of the other gas.

3.3 MATERIALS

3.3.1 GASES

The gas mixture used during the experimental runs consisted of carbon dioxide and hydrogen sulfide. Because the methane is an extremely inflammable gas, if accidentally mixed with air, and is inert to the scrubbing material, it was decided to exclude it from the synthetic biogas. Although the percentage of carbon dioxide in the gas mixture is not representative of a typical biogas, it was thought that a gas containing only carbon dioxide could give results that represent a limiting value for the capacity of the scrubbing material to eliminate hydrogen sulfide, given that the carbon dioxide can react with the scrubbing material to form iron carbonate.

The carbon dioxide used was obtained from pressurized cylinders (size K) supplied by Medigas Pacific. The gas was USP siphon grade and it contained 1 ppm of hydrogen sulfide. The total weight of carbon dioxide was around 28 kg and each cylinder could last from 5 to 10 days depending on the flow rate used.
The hydrogen sulfide that was used was also obtained from pressurized cylinders (size P) supplied by Matheson. The gas had a concentration of 0.84% hydrogen sulfide and used nitrogen as balance gas.

The calibration gas for the hydrogen sulfide detector was also supplied by Matheson. This gas was in pressurized cylinders (size M) and had a certified standard quality of 26.5 ppm.

3.3.2 IRON TURNINGS

All the iron turnings used were produced at the Bio-Resource Engineering workshop with the same machine and from the same steel bar. The objective was to produce a uniform type of turnings with approximately the same thickness and width. The values chosen were 0.04 cm for the thickness and 0.30 cm for the width, however the values obtained averaged 0.03 cm for thickness and 0.25 cm for width.

The material prepared as described above was allowed to oxidize under atmospheric conditions for a period of 8 weeks by exposure to ambient weather conditions during the whole 8 week period. The oxidation was conducted in the gardens beside the Bio-Resource Engineering Annex.

The material was spread over plastic sheets of 75cm x 100cm each containing similar amounts of material. The material was turned every two weeks with the purpose of exposing all the material to the atmospheric conditions,
especially the material that was located at the bottom of the heap.

Once the oxidation period was over all the material was collected and stored at room temperature in closed propylene bags until it was needed.

The iron turnings had a grey color before being exposed to the atmospheric conditions but after the 8 weeks of oxidation the turnings took on an orange color. This new color was due to the cover of rust adhering to the surface of the turnings.

In Table 3, it was mentioned that the $\gamma$-$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ has a characteristic orange color; however, if the oxide is heated up to 300°C the color of the oxide changes from orange to chocolate brown, which is the characteristic color of the dehydrated $\gamma$-$\text{Fe}_2\text{O}_3$. Several samples (3) of the rusted iron turnings were exposed to temperatures of 300°C (in a LabHeat Muffle Furnace M154-1A, Blue M Electric Company) for a period of not less than one hour. After the one hour had expired the samples were taken out of the muffle furnace and checked for color. The change of color was from orange to chocolate brown, showing that the iron oxide formed by the atmospheric oxidation of the iron was the active $\gamma$-$\text{Fe}_2\text{O}_3$.

Visual inspection of the rusted iron turnings showed that the cover of rust was not uniformly distributed onto the surface of the turnings. Furthermore, the rust was not attached to the iron surface with the same strength in all areas. Some rust was so loose that could be removed just by
touching it, while some other had to be scraped off with a brush and sandpaper. The amount of rust on the iron turnings was determined by measuring lost of weight of predetermined samples (approximately 10 g) of rusted iron turnings after being scraped with a brush and sandpaper. The average percentage of rust in the iron turnings was of 1.4% (0.014 of rust per gram of iron turning ± 0.0011).

3.4 EXPERIMENTAL PROCEDURES

At the beginning of each experiment a weighed amount of iron turnings, 691 g, was placed into the beds. The procedure was as follows: The material was divided into approximately 6 equal parts, each one of the parts was introduced into the bed top and gradually forced down with the aid of a wooden bar that had attached at one of its ends a plexiglass plate that had a slightly smaller diameter than the diameter of the bed. The material was compressed as much as possible with the bar. The average density of the packed material was around 0.44 g/cm³. Once the bed was completely packed glasswool was placed over the top of the material and held in place with a plexiglass plate similar to the plates used to support the material at the bottom of the bed. The bed was closed and placed in the chamber. The procedure was repeated with the other column. Once the beds were in the vacuum chamber the gas lines were connected to the beds.

Approximately one hour before the start of an experiment, the flow of carbon dioxide was set and allowed
to go through the saturation vessel. The gas was not passed through the beds initially but was exhausted to the atmosphere. After 15 minutes the lines to the beds were opened and the beds were allowed to purge for at least 15 minutes. Once this period of time had elapsed the gas mixture was bypassed from the beds and the flow of hydrogen sulfide turned on and allowed to mix with the saturated carbon dioxide. After a period of approximately 15 to 20 minutes the gas mixture was sampled and the concentration of hydrogen sulfide determined. If the concentration was near the expected value the gas mixture was again bypassed to the beds and the experiment started. However, if the concentration was far from the expected value the flow of hydrogen sulfide was readjusted and the concentration measured again. The procedure was repeated until a satisfactory concentration was found.

3.5 SAMPLING

The sampling system consisted of gas bags and clamps. The bags were connected with tubing to an outlet located at the top of each bed. The clamp closing the flow through the tubing was removed and the bags were allowed to fill up to a predetermined volume, approximately 10 liters. The clamp was used to stop the flow of the gas out of the bed and force it to go into the bag. The system is based on the fact that the flow pattern in the column was not changed by the backpressure exerted by the bag.
The assumption that the sampling system exerted hardly any backpressure was checked by attaching an open end manometer to the bottom of the bed and measuring the increase of the backpressure due to the bag being filled. The changes in backpressure were too small to be considered if the bags collected around 10 to 12 liters of gas.

Before any sample was taken, the bags were connected to the beds, allowed to fill to approximately 1/2 of the sample volume and emptied through the vacuum chamber until the bags were completely collapsed. Immediately afterward the samples were taken.

Because of the flow being different for each run the sampling time varied between 10 to 15 minutes. For the influent concentration a similar procedure was followed; however, to avoid a change on the flow pattern in the columns a smaller sample per unit time was taken. The sampling time for this case was about 1 hr.

3.6 ANALYSIS

A hydrogen sulfide detector Ecolyzer 600 Series MOD III Hyster was chosen as the method of analysis because it is fairly simple, relatively rapid and inexpensive.

The hydrogen sulfide monitor it is capable of measuring on a dual range, from 0 to 50 ppm and from 0 to 250 ppm of hydrogen sulfide. Its accuracy is stated to be 2% of the full scale range and its stability for the zero 2% of the full scale per day. For the calibration the accuracy is 2%
of range. The response time is stated at 90% of the signal within 45 seconds, however the response was slightly slower.

The hydrogen sulfide monitor was connected to a digital display and the response signal could be followed during the duration of the analysis.
Chapter 4

RESULTS AND DISCUSSION

4.1 INTRODUCTION

The results obtained for the different runs of the experimental design are shown in Figures 3 and 4. These curves result from plotting the dimensionless concentration, C/Co, against time. In other words, they are the breakthrough curves. An inspection of the breakthrough curves in Figures 3 and 4 for the raw data showed that the dimensionless concentration passed through three different stages. The first stage was characterized by low effluent concentrations and it was during this period that the bed removed a constant amount of hydrogen sulfide. However, a slow increase in the effluent concentration can be noticed.

The second stage started when the effluent concentration experienced a sudden increase that made the dimensionless concentration rise rapidly. The amounts of hydrogen sulfide removed during this period also rapidly decreased.

The third stage, that is not noticeable in all the curves, began when the effluent concentration started to increase slowly and steadily again until the bed was exhausted.

An interesting observation was that the displacement of the concentration front, C/Co vs time, was accompanied by a change in color of the iron oxide from orange to black (when
Figure 3 Breakthrough Curves for Removal of Hydrogen Sulfide by Rusted Iron Turnings at Various Flow Rates. Hydrogen Sulfide Concentration 197.0 to 202.6 ppm.
Figure 4 Breakthrough Curves for Removal of Hydrogen Sulfide by Rusted Iron Turnings at Various Flow Rates. Hydrogen Sulfide Concentration 81.8 to 109.0 ppm.
the iron oxide reacted with the hydrogen sulfide to form the sulfide). This front or stain moved through the bed at a constant velocity that was lower than the empty bed velocity of the gas through the column.

The results can also be plotted as a function of the total volume of gas treated or throughput. The results of such plots are shown in Figures 5 and 6. When Figures 3 and 4 are compared to Figures 5 and 6, the same general trend can be observed in the breakthrough curves. However, the order of the curves has been reversed. For example in Figure 1 the bed that had the highest flow broke through the column last, but in Figure 3 it broke through first.

4.2 CORRELATION OF RATE DATA

From the description of the experimental curves given in the previous section it was thought that the experimental curves followed an S shaped curve and could be correlated to a sigmoidal function.

A simple sigmoidal curve of the following form was tested:

\[
\frac{C}{C_0} = \frac{1}{1 + me^{at}}
\]  \hspace{1cm} (12)

where,

- \( \frac{C}{C_0} \) - dimensionless concentration
- \( t \) - time [day]
- \( a \) - constant [day\(^{-1}\)]
Figure 5 Breakthrough Curves for Removal of Hydrogen Sulfide by Rusted Iron Turnings at Various Flow Rates as a Function of Throughput. Hydrogen Sulfide Concentration 197.0 to 202.6 ppm.
Figure 6 Breakthrough Curves for Removal of Hydrogen Sulfide by Rusted Iron Turnings at Various Flow Rates as a Function of Throughput. Hydrogen Sulfide Concentration 81.8 to 109.0 ppm.
\( m \) \quad \text{constant}

However, the above equation was transformed to a linear form so a linear regression algorithm could be used to find the best fitting curve.

The transformed equation was:

\[
\ln(C_0/C - 1) = \ln m + at
\]

or

\[
Y = b_0 + b_1t
\]

where,

\[
b_0 = \ln m
\]
\[
b_1 = a
\]

An example of the method used to determine the regressed sigmoidal curves is shown in the following paragraphs; however, for the rest of the experimental runs Appendix A must be consulted.

The following example is one of the replicates of the experimental runs (1.00 l/min and 197.0 ppm). In columns 1 and 2 of Table 7 the numerical results of the breakthrough curve are shown, and in column 3 the transformed variable \( \ln(C/C_0 - 1) \) is also shown.

Once the data were transformed as shown in Table 7 the \( \ln(C_0/C - 1) \) values were plotted against time (see Figure 7) to see how well the data conformed to the straight line. For
Table 7 Breakthrough Concentrations for 0.98 l/min and 197.0 ppm

<table>
<thead>
<tr>
<th>Time</th>
<th>C/C₀</th>
<th>ln(C₀/C - 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>0.07</td>
<td>2.5865</td>
</tr>
<tr>
<td>2.6</td>
<td>0.09</td>
<td>2.3136</td>
</tr>
<tr>
<td>3.6</td>
<td>0.11</td>
<td>2.0907</td>
</tr>
<tr>
<td>4.6</td>
<td>0.41</td>
<td>0.3639</td>
</tr>
<tr>
<td>5.6</td>
<td>0.56</td>
<td>-0.2412</td>
</tr>
<tr>
<td>6.6</td>
<td>0.64</td>
<td>-0.5754</td>
</tr>
<tr>
<td>7.8</td>
<td>0.79</td>
<td>-1.3249</td>
</tr>
<tr>
<td>8.6</td>
<td>0.85</td>
<td>-1.7346</td>
</tr>
</tbody>
</table>

In this case the data conformed well to a straight line (r²=0.9596). The data were regressed with the aid of a pocket calculator, Sharp EL-512, that had an inbuilt program to solve linear regressions for one independent and one dependent variable. For the data shown in column 3 of Table 7 the following result was obtained:

\[ Y = 3.8735 - 0.6709t \]  \hspace{1cm} (15)

The above equation when retransformed to its original form is as follows:

\[ \frac{C}{C_0} = 1 / (1 + 48.1104e^{-0.6709t}) \]  \hspace{1cm} (16)

In Figure 8 the regressed line for the experimental points in Table 7 is shown. The fitted curves and the experimental points for all the runs are shown in Figures 9, 10 and 11. These Figures have the results for experimental conditions using the same flow rate but different
concentrations.

4.3 **INFLUENCE OF THE FLOW RATE AND THE INITIAL HYDROGEN SULFIDE CONCENTRATION ON THE BREAKTHROUGH CURVE**

For a fixed-bed reactor the breakthrough curve usually takes a S shape. From the results shown in Figures 9, 10 and 11 it can be seen that the breakthrough curves for all the experimental conditions follow an S shape. However, the shape of the S curve can be affected by the flow rate and the initial hydrogen sulfide concentration.

The above effects can be seen by comparing the curves in Figures 9, 10 and 11. Nevertheless, in order to note the effect of flow rate and initial hydrogen sulfide concentration on the breakthrough curve, the slope of the curve at midpoint, $C/C_0 = 0.5$, was used as a measure of the steepness of the curve and of the effects of the former variables.

In Figure 12 the slopes of the breakthrough curves at $C/C_0 = 0.5$ are shown as a function of the initial hydrogen sulfide concentration. From Figure 12 it can be seen that there is an evident difference between the slopes at $C/C_0 = 0.5$ for the two levels of concentration. Therefore, it is possible to conclude that the initial concentration affects the shape of the breakthrough curve in such a way that as the concentration increases the slope at $C/C_0$ increases and the curve becomes steeper. It was also observed that the data follow a linear relation.
Figure 7 Regression Line for the Transformed Breakthrough Data. Hydrogen Sulfide Concentration 197.0 ppm and Flow Rate 0.98 l/min.
Figure 8 Regressed Sigmoidal Curve and Experimental Points for the Data in Table 7.
Figure 9 Regressed Sigmoidal Curve and Experimental Points for the Breakthrough Curve Obtained at a Hydrogen Sulfide Concentration of 109.0 and 197.0 ppm and a Flow Rate of 0.981/min.
Figure 10 Regressed Sigmoidal Curve and Experimental Points for the Breakthrough Curve Obtained at a Hydrogen Sulfide Concentration of 97.6 and 202.6 ppm and a Flow Rate of 0.751/min.
Figure 11 Regressed Sigmoidal Curve and Experimental Points for the Breakthrough Curve Obtained at a Hydrogen Sulfide Concentration of 81.8 and 201.3 ppm and a Flow Rate of 0.501/min.
Figure 12 Effect of Hyrogen Sulfide Concentration in the Shape of the Breakthrough Curves.

Figure 12 Effect of Hydrogen Sulfide Concentration in the Shape of the Breakthrough Curves.
In Figure 13, the slopes of the breakthrough curves at C/Co=0.5 are shown as a function of the flow rate. In Figure 13, line b shows that as flow rate decreases the slope also decreases hence the breakthrough curve tends to flatten out as the flow rate decreases. For line a the data are more dispersed than for line b, although the general tendency of the data is also to decrease the slope as the flow decreases.

To sum up, the shape of the breakthrough curve is influenced more by the initial concentration than by the flow rate.

4.4 BREAKPOINT TIME

The value for the breakpoint time is arbitrarily chosen. After looking through the information about the effects that the hydrogen sulfide has on the health of humans and animals, and the life of plants it was decided to set the breakpoint concentration at 10 ppm.

The breakpoint concentration was chosen to be 10 ppm for all the runs. The breakpoint time for each experimental run was obtained by setting the appropriate initial hydrogen sulfide concentration and the effluent concentration, 10 ppm, in the regressed sigmoidal curve. Table 8 shows the values obtained for the different experimental runs.

Because the results in Table 8 come from a completely randomized design a two way analysis of variance (ANOVA) can
Figure 13 Effect of Flow Rate on the shape of the Breakthrough Curves.
be performed with these data. Table 9 shows the Anova for the results in Table 8.

The results in Table 9 demonstrate that for a level of significance of 5% both of the factors, flow rate and initial hydrogen sulfide concentration, affect significantly the breakpoint time and they also interact significantly.

In Figure 14 the breakpoint time is plotted as a function of the flow rate and the initial hydrogen sulfide concentration to corroborate the above conclusions. It can be seen that both factors affect the breakpoint time. An increase in the flow rate decreases the breakpoint time for both concentrations, a decrease in the initial concentration increases the breakpoint time. However, the factors interaction causes the difference between the two concentration lines to vary differently when the flow rate
Figure 14 Breakpoint Time Versus Flow rate at Fixed Hydrogen Sulfide Concentrations.
Table 9 Anova for Breakpoint Time

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>df</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>Fc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate, Fi</td>
<td>2</td>
<td>43.64</td>
<td>23.32</td>
<td>55.53</td>
<td>5.14</td>
</tr>
<tr>
<td>Concentration, Cj</td>
<td>1</td>
<td>47.47</td>
<td>47.47</td>
<td>113.02</td>
<td>5.99</td>
</tr>
<tr>
<td>FxCInteraction, FiCj</td>
<td>2</td>
<td>12.78</td>
<td>6.39</td>
<td>15.21</td>
<td>5.14</td>
</tr>
<tr>
<td>Error, ( \epsilon_{ijk} )</td>
<td>6</td>
<td>2.52</td>
<td>0.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Totals</td>
<td>11</td>
<td>106.41</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

is decreased.

4.5 HYDROGEN SULFIDE REMOVED UP TO BREAKPOINT

The total mass of hydrogen sulfide removed by the rusted iron turnings was calculated under the following assumptions:

a) the influent hydrogen sulfide concentration curve is defined by the line \( C/C_0 = 1.0 \)

b) the linear regressed lines represent the effluents hydrogen sulfide curves (breakthrough curves)

c) the total amount of hydrogen sulfide removed by the fixed-bed reactor is given by the area \( \Delta A \), that is the area between the influent concentration curve and the effluent concentration curve limited by the breakpoint time, \( t_b \), as shown in Figure 15.

To transform the values of the area \( \Delta A \) to mass values the following equation was used:

\[
Y = 2.0592 \times 10^{-3} \Delta AFC_0
\]  
(17)
Figure 15 Graphical Representation of the Mass of Hydrogen Sulfide Removed by the Fixed-Bed.
where,

\[
\begin{align*}
Y & \quad \text{Total mass of hydrogen sulfide removed [g]} \\
\Delta A & \quad \text{area between curves [day]} \\
F & \quad \text{Flow rate [l/min] at 21°C and 1 atm} \\
C_0 & \quad \text{influent hydrogen sulfide concentration [ppm] at 21°C and 1 atm}
\end{align*}
\]

At breakpoint time, \( t_b \), \( Y \) is equal to \( Y_b \) and \( \Delta A \) equal to \( \Delta A_b \). Using the breakpoint values obtained in the previous section is possible to calculate \( Y_b \). For example for the following data:

\[
\begin{align*}
t_b & = 1.48 \text{ day} \\
F & = 1.00 \text{ l/min} \\
C_0 & = 197.0 \text{ ppm} \\
\Delta A_b & = 3.3333
\end{align*}
\]

and

\[
Y_b = 2.0592 \times 10^{-3} (197.0)(1.00)(3.3333) \quad (18)
\]

\[
Y_b = 0.57 \text{ g} \quad (19)
\]

The results of the calculations for the rest of the experimental runs are shown in Table 10.

The Anova for \( Y_b \) is shown in Table 11.

For a level of significance of 5% both of the factors, flow rate and initial hydrogen sulfide concentration, do not significantly affect the the mass of hydrogen sulfide removed at breakthrough and they do not interact
Table 10 Mass of Hydrogen Sulfide Removed at Breakthrough

<table>
<thead>
<tr>
<th>Flow Rate 1/min</th>
<th>Concentration ppm</th>
<th>Breakpoint Time day</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.98</td>
<td>197.0</td>
<td>0.57</td>
</tr>
<tr>
<td>1.00</td>
<td>197.0</td>
<td>0.89</td>
</tr>
<tr>
<td>0.76</td>
<td>202.6</td>
<td>1.01</td>
</tr>
<tr>
<td>0.74</td>
<td>202.6</td>
<td>0.67</td>
</tr>
<tr>
<td>0.49</td>
<td>201.3</td>
<td>0.77</td>
</tr>
<tr>
<td>0.50</td>
<td>202.3</td>
<td>0.84</td>
</tr>
<tr>
<td>1.00</td>
<td>109.0</td>
<td>0.79</td>
</tr>
<tr>
<td>1.02</td>
<td>109.0</td>
<td>0.63</td>
</tr>
<tr>
<td>0.74</td>
<td>97.6</td>
<td>1.01</td>
</tr>
<tr>
<td>0.76</td>
<td>97.6</td>
<td>0.87</td>
</tr>
<tr>
<td>0.57</td>
<td>81.8</td>
<td>1.02</td>
</tr>
<tr>
<td>0.50</td>
<td>81.8</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Table 11 Anova for the Mass of Hydrogen Sulfide Removed at Breakpoint

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>df</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>Fc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate, Fi</td>
<td>2</td>
<td>0.0165</td>
<td>0.0082</td>
<td>0.349</td>
<td>5.14</td>
</tr>
<tr>
<td>Concentration, Cj</td>
<td>1</td>
<td>0.0739</td>
<td>0.0739</td>
<td>3.147</td>
<td>5.99</td>
</tr>
<tr>
<td>FxCinteraction, FiCj</td>
<td>2</td>
<td>0.0146</td>
<td>0.0073</td>
<td>0.319</td>
<td>5.14</td>
</tr>
<tr>
<td>Error, εijk</td>
<td>6</td>
<td>0.1409</td>
<td>0.0235</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Totals</td>
<td>11</td>
<td>0.2459</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

significantly.

The results are shown graphically in Figure 16 and it can be seen that for the ranges of flow rate and initial concentration studied the mass of hydrogen sulfide picked up by the rusted iron up to the breakpoint is not much different and a horizontal line can be drawn through the
Figure 16 Mass of Hydrogen Sulfide Removed Up to Breakpoint Time.
points. The mass removed, given by the average of all the experimental results, is 0.83 g ± 0.10.

4.6 REMOVAL EFFICIENCY AND CAPACITY

The capacity of the oxidized iron turnings to remove hydrogen sulfide can be calculated from the breakthrough curves. Equation (17) was also used to calculate the total removal capacity of the packing material. However, the ΔA is given by the time for bed exhaustion, ts, that was calculated from the regressed sigmoidal curves for C/Co=0.9999.

An example of the calculation is given for the following conditions:

\[ts = 19.5 \text{ day}\]
\[F = 0.98 \text{ l/min}\]
\[Co = 197.0 \text{ ppm}\]
\[ΔA = 5.8 \text{ day}\]

then,

\[Y = 2.0592 \times 10^{-3} (197.0) (0.98) (5.8)\]  (20)

\[Y = 2.3 \text{ g}\]  (21)

The results for all the experimental results are shown in column 5 from Table 12 and an Anova for those results are shown in Table 13.
Table 12 Total Mass of Hydrogen Sulfide Removed

<table>
<thead>
<tr>
<th>Flow Rate (l/min)</th>
<th>Concentration (ppm)</th>
<th>ts (day)</th>
<th>ΔA (day)</th>
<th>Y (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.98</td>
<td>197.0</td>
<td>19.5</td>
<td>5.84</td>
<td>2.30</td>
</tr>
<tr>
<td>1.00</td>
<td>197.0</td>
<td>22.4</td>
<td>7.01</td>
<td>2.85</td>
</tr>
<tr>
<td>0.75</td>
<td>202.6</td>
<td>22.8</td>
<td>7.99</td>
<td>2.50</td>
</tr>
<tr>
<td>0.74</td>
<td>202.6</td>
<td>20.7</td>
<td>6.72</td>
<td>2.08</td>
</tr>
<tr>
<td>0.49</td>
<td>201.3</td>
<td>30.2</td>
<td>10.28</td>
<td>2.09</td>
</tr>
<tr>
<td>0.50</td>
<td>201.3</td>
<td>22.5</td>
<td>8.59</td>
<td>1.78</td>
</tr>
<tr>
<td>1.00</td>
<td>109.0</td>
<td>43.1</td>
<td>11.68</td>
<td>2.62</td>
</tr>
<tr>
<td>1.02</td>
<td>109.0</td>
<td>37.0</td>
<td>9.82</td>
<td>2.25</td>
</tr>
<tr>
<td>0.74</td>
<td>97.6</td>
<td>53.6</td>
<td>16.04</td>
<td>2.38</td>
</tr>
<tr>
<td>0.76</td>
<td>97.6</td>
<td>48.2</td>
<td>14.16</td>
<td>2.16</td>
</tr>
<tr>
<td>0.57</td>
<td>81.8</td>
<td>66.1</td>
<td>20.97</td>
<td>2.01</td>
</tr>
<tr>
<td>0.55</td>
<td>81.8</td>
<td>53.7</td>
<td>17.67</td>
<td>1.64</td>
</tr>
</tbody>
</table>

Table 13 Anova for the Maximum Removal of Hydrogen Sulfide

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>df</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>Fc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate, Fi</td>
<td>2</td>
<td>0.77</td>
<td>0.385</td>
<td>5.37</td>
<td>5.14</td>
</tr>
<tr>
<td>Concentration, Cj</td>
<td>1</td>
<td>0.03</td>
<td>0.030</td>
<td>0.41</td>
<td>5.99</td>
</tr>
<tr>
<td>FxC interaction, FiCj</td>
<td>2</td>
<td>0.01</td>
<td>0.005</td>
<td>0.07</td>
<td>5.14</td>
</tr>
<tr>
<td>Error, eijk</td>
<td>6</td>
<td>0.01</td>
<td>0.005</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Totals</td>
<td>11</td>
<td>1.24</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For a significance level of 5% the total capacity is independent of the initial hydrogen sulfide concentration but is significantly affected by the flow rate. A Newman-Keuls test shows that the difference is between the 1.00 l/min and 0.5 l/min level.

The percentage of iron oxide in the rusted iron turnings was 1.4% therefore the total amount of oxide in
the turnings was 9.7 g. For the previous example a total of 0.24 g of hydrogen sulfide were removed per gram of iron oxide and the percentage of iron oxide consumed was 39.7%. Columns 3 and 4 of Table 14 show the grams of hydrogen sulfide removed per gram of oxide and the percentage of iron oxide consumed for the experimental runs.

When the yields shown in Column 3 of Table 12 are compared with the yields reported by Johnson et al. (1962) (56% for a 15cm bed) and Ravinshankser and Hills (1984) (59% for a 30 cm bed) for the iron oxide process, the results are low.

The capacity can also be expressed as a function of the mass of packing material. For all the experimental runs the total weight of rusted iron turnings in the column was 691.0 g. Then the capacity for the above example would be 0.0033 g of hydrogen sulfide per gram of rusted iron turning. The latter capacity is small and shows that most of the material is not used. Therefore, if the total weight of the packing material were reduced (a thinner turning) the surface area would increase and the total weight of rust could also be increased (due to more area being exposed to atmospheric oxidation) and the capacity of the rusted iron turnings could be improved. In column 5 of Table 14 the capacities for the experimental runs are shown.
### Table 14 Yields of Hydrogen Sulfide Removal

<table>
<thead>
<tr>
<th>Flow Rate (1/min)</th>
<th>Concentration (ppm)</th>
<th>R1 (%)</th>
<th>R2 (g/g)</th>
<th>Capacity (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.98</td>
<td>197.0</td>
<td>39.7</td>
<td>0.24</td>
<td>0.0033</td>
</tr>
<tr>
<td>1.00</td>
<td>197.0</td>
<td>48.9</td>
<td>0.29</td>
<td>0.0042</td>
</tr>
<tr>
<td>0.75</td>
<td>202.6</td>
<td>43.0</td>
<td>0.26</td>
<td>0.0036</td>
</tr>
<tr>
<td>0.74</td>
<td>202.6</td>
<td>35.7</td>
<td>0.21</td>
<td>0.0030</td>
</tr>
<tr>
<td>0.49</td>
<td>201.3</td>
<td>35.9</td>
<td>0.22</td>
<td>0.0030</td>
</tr>
<tr>
<td>0.50</td>
<td>201.3</td>
<td>30.6</td>
<td>0.18</td>
<td>0.0026</td>
</tr>
<tr>
<td>1.00</td>
<td>109.0</td>
<td>45.1</td>
<td>0.27</td>
<td>0.0038</td>
</tr>
<tr>
<td>1.02</td>
<td>109.0</td>
<td>38.6</td>
<td>0.23</td>
<td>0.0032</td>
</tr>
<tr>
<td>0.74</td>
<td>97.6</td>
<td>41.0</td>
<td>0.25</td>
<td>0.0035</td>
</tr>
<tr>
<td>0.76</td>
<td>97.6</td>
<td>37.2</td>
<td>0.22</td>
<td>0.0031</td>
</tr>
<tr>
<td>0.57</td>
<td>81.8</td>
<td>34.6</td>
<td>0.21</td>
<td>0.0029</td>
</tr>
<tr>
<td>0.55</td>
<td>81.8</td>
<td>28.1</td>
<td>0.17</td>
<td>0.0024</td>
</tr>
</tbody>
</table>

R1: Percentage of iron oxide removed.
R2: Grams of H₂S removed per gram of oxide.

### 4.7 SURFACE RATE MODEL

In the literature review it was stated that for a fixed-bed reactor controlled by a surface reaction rate a linear equation can be obtained to describe its performance. To prove the validity of such a model for this case it is necessary to find out if the equation would hold under different experimental conditions.

The equation used was equation (10). A plot of the left hand side of equation (10) against time should give a straight line. Comparing equation (10) with equation (13) we come to the conclusion that both equations have the same form, therefore the results obtained for the sigmoidal curve are also applicable to equation (10). In that case, all the experimental points follow a straight line. In Figures A.1 and A.2 of appendix A the plots of such lines are shown. These Figures show that the intercept, \( b_0 \), of the lines
increased as the flow rate increased. On the other hand for a given flow rate an increase in the hydrogen sulfide concentration increased the slope, \( b_1 \), of the line. However, the agreement between the experimental points and the expected linear behaviour confirms the assumption of the validity of equation (10).

The invariance of the rate constant with respect to the hydrogen sulfide concentration can be checked by plotting the left hand side of equation (10) against \( C_0 x t \). Such a plot should give a straight line for all the concentrations for a constant flow rate. In Figures 17, 18 and 19 the \( \ln(C_0/C - 1) \) is plotted against \( C_0 x t \) for the three different flow rates.

The data presented in Figures 17, 18 and 19 show that the points fall on the same straight line, although the initial points behave differently. However the equation seems to be valid for certain section of the data and the rate constant is invariant with initial hydrogen sulfide concentration (the coefficients of correlation for the lines were 0.93436, 0.94015 and 0.97228 respectively).

Because the ratio of surface to volume of the oxidized iron oxide, \( S \), was not measured the rate constant, \( k \), and ratio \( S \) were combined to form a pseudo-rate constant \( K \). The rate constants were calculated following the procedure explained in the literature review. For example in Figure 18 the pseudo-rate constant, \( K \), is plotted as function of the flow rate and the initial hydrogen sulfide concentration. It
Figure 17 Invariance of the Rate Constant with the Hydrogen Sulfide Concentration Calculated from Breakthrough Runs for the Rusted Steel Turnings; Flow Rate 1.00 l/min (at 21°C).
Figure 18 Invariance of the Rate Constant with the Hydrogen Sulfide Concentration Calculated from Breakthrough Runs for the Rusted Steel Turnings; Flow Rate 0.75 l/min (at 21°C).
Figure 19 Invariance of the Rate Constant with the Hydrogen Sulfide Concentration Calculated from Breakthrough Runs for the Rusted Steel Turnings; Flow Rate 0.50 l/min (at 21°C).
Figure 20 Effect of Flow Rate and Initial Hydrogen Sulfide Concentration on the Value of the Pseudo-Rate Constant, $K$, when Calculated with Equations (10) and (11)
can be seen that the rate constants for the higher concentration, line a, have higher values than the lower concentration, line b. The flow rate seems a linear relationship with the pseudo-rate constant for both concentrations.

The above equations are:

for concentration $\approx 200.0$ ppm

$$K = 1317.7 + 2641.3(F) \quad (22)$$

for concentration $\approx 100.0$ ppm

$$K = 1506.9 + 1643.8(F) \quad (23)$$

From the above analysis it can be said that although the data conform well to a straight line as required by the model and the data seem to be independent of the initial hydrogen sulfide concentration, the pseudo rate constant is not constant for all the experimental conditions. However, the invariance of the pseudo rate constant or certain region of the curves, as shown by Figures 15, 16 and 17, may indicate that the model is valid but that at the start of each run another mechanism may be controlling.

On the other hand, the dependence of the constant on flow rate may indicate that the diffusion or mass transfer are influencing the results.

Because of the influence of both the initial hydrogen sulfide concentration and flow rate on the pseudo-rate constant for the model, it appears that no simple or single theory is adequate for the explanation of the breakthrough curve. However if the variance of the pseudo-rate constant
with the initial concentration of hydrogen sulfide is accepted equation (10) may be used knowing that the pseudo-rate constant is a linear function of the flow rate for the ranges studied in this work.

### 4.8 BED SIZE

If equation (10) is written in terms of the half life, \( t_{0.5} \) (time when the effluent concentration is half of the influent concentration, \( C/C_0 = 1/2 \)), the left side of the equation becomes zero, giving the following relationship:

\[
t_{0.5} = m \frac{A \lambda X}{FC_0} \tag{24}
\]

For the experimental runs \( m \) is independent of the initial concentration but dependent on the flow rate; thus

for 1.00 l/min
\[
t_{0.5} = 57.4(X/C_0) \tag{25}
\]

for 0.75 l/min
\[
t_{0.5} = 70.3(X/C_0) \tag{26}
\]

for 0.50 l/min
\[
t_{0.5} = 80.7(X/C_0) \tag{27}
\]

Consequently the above equations would give a straight lines passing through the origin.
Dividing equation (9) by (21) we have:

\[ t = \{1 - \frac{F}{KX}\lambda[\ln(C_0/C - 1)]\}t_{0.5} \]  \hspace{1cm} (28)

Where \( K \) is given by equations (22) and (23).

The depth of the bed can be calculated with the aid of equations (22) to (28) as long as the empty bed velocity in the bed is not changed (Treybal, 1984).

The diameter of the bed can be determined from the empty bed velocity as follows:

\[ D = \left( \frac{4xF}{\pi Ve} \right)^{0.5} \]  \hspace{1cm} (29)

**Example**

The hydrogen sulfide concentration must be reduced from 200 ppm to 10 ppm for a particular Biogas. The scrubber will use rusted iron turnings that have been exposed to the atmospheric weather for 8 weeks. The scrubber must have a bed life of at least 60 days. The production of Biogas is 35 \( \text{m}^3 \) /day (all the volumes and concentrations for the gas are expressed at 21°C and 1 atm.

To minimize the diameter of the bed the maximum empty bed velocity would be used (or the highest flow rate, 1.00 l/min).

The empty bed velocity is given by:

\[ Ve = \frac{F}{A} \]  \hspace{1cm} (30)
Ve = (1.00)(1000)/78.54 = 12.7 (cm)/(min)

The flow rate is:

\[ F = \frac{(35)(1000)}{(1440)} = 24.3 \text{ (l)/(min)} \]

and the diameter of the bed is

\[ D = \left[ \frac{(4)(24.3)(1000)}{(\pi)(12.7)} \right]^{0.5} \]

\[ D = 49.4 \text{ (cm)} \text{ or } 0.5 \text{ (m)} \]  

Assuming a bed depth of 2.5 m the half life is calculated with equation (25)

\[ t_{0.5} = \frac{(57.425)(250)}{(200)} \]

\[ t_{0.5} = 71.8 \text{ (day)} \text{ or } 72 \text{ (days)} \]  

And K is calculated with equation (22)

\[ K = 1317.7 + 2641.3(1.00) \]

\[ K = 3958.9 \]  

Substituting (34) and (35) into (28) and taking C=10 for t=tb

\[ t_b = 68 \text{ (day)} \]
Therefore, the specifications of the bed are:

Bed diameter = 0.5 m
Bed depth = 2.5 m
Bed life = 68 days
Mass of rusted iron turnings = 216 kg
CONCLUSIONS

- The results of the study indicate that using rusted iron (or steel) turnings to reduce the content of hydrogen sulfide from biogas is feasible.
- The breakthrough curves were influenced more by the initial hydrogen sulfide concentration than by the flow rate.
- The breakpoint time is affected by the flow rate and the initial hydrogen sulfide concentration.
- The percentage of rust (in the form of $\gamma$-Fe$_2$O$_3$) in the iron turnings after oxidation was low (1.4%). This indicates that a longer period of time is necessary to produce a richer packing material.
- The results indicate that only 30 to 44% of the iron oxide (assuming that all the rust is in the form of $\gamma$-Fe$_2$O$_3$) reacted. Therefore, around 60 to 70% of the iron oxide was totally ineffective. When the former data are compared with the yields reported by Johnson et al. (1962), 78%, and by Ravinshanker and Hills (1984), 56%, it is observed that the rusted iron turnings are less effective in removing hydrogen sulfide than the iron-sponge process.
- The maximum removal capacity (theoretical) of the rusted iron turnings is dependent of the flow rate in the range studied but independent of the hydrogen sulfide concentration.
- The amount of hydrogen sulfide removed up to the
occurrence of the breakpoint time was independent of the flow rate and hydrogen sulfide concentration.

Regression equations of a linear form [equation (10)] were adequate in describing the breakthrough curves. Although the rate data conform well to the surface rate linear equation, the pseudo rate constant varies with the flow rate and the hydrogen sulfide concentration. The influence of the flow rate on the rate constant may indicate the effects of mass transfer. However, it is not clear which mechanism controls the rate.
LITERATURE CITED


Zapfere, F., 1962. Three Ways to Sweeten Gas. The Oil and Gas Journal, September, p 135,137-139.

Environment Part II: Ecological Impacts, J.O. Nriagu (ed). John Wiley and Sons, USA.

APPENDIX A

This appendix has the results of the linear regression applied to the experimental runs. Table A.1 shows the slopes, intercept and r values and Table A.2 shows the parameters of the sigmoidal curves. Figure A.1 and A.2 show the regressed lines.

<table>
<thead>
<tr>
<th>Flow Rates L/min</th>
<th>Concentration ppm</th>
<th>Slope</th>
<th>Intercept</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.98</td>
<td>197.0</td>
<td>-0.6709</td>
<td>3.8735</td>
<td>-0.9796</td>
</tr>
<tr>
<td>1.00</td>
<td>197.0</td>
<td>-0.5970</td>
<td>4.1710</td>
<td>-0.9849</td>
</tr>
<tr>
<td>0.76</td>
<td>202.6</td>
<td>-0.6057</td>
<td>4.8059</td>
<td>-0.9949</td>
</tr>
<tr>
<td>0.74</td>
<td>202.6</td>
<td>-0.6593</td>
<td>4.4229</td>
<td>-0.9947</td>
</tr>
<tr>
<td>0.49</td>
<td>201.3</td>
<td>-0.4622</td>
<td>4.7406</td>
<td>-0.9913</td>
</tr>
<tr>
<td>0.50</td>
<td>201.3</td>
<td>-0.6663</td>
<td>5.6710</td>
<td>-0.9689</td>
</tr>
<tr>
<td>1.00</td>
<td>109.7</td>
<td>-0.2906</td>
<td>3.3497</td>
<td>-0.9942</td>
</tr>
<tr>
<td>1.02</td>
<td>109.7</td>
<td>-0.3374</td>
<td>3.2743</td>
<td>-0.9928</td>
</tr>
<tr>
<td>0.74</td>
<td>97.6</td>
<td>-0.2455</td>
<td>3.8955</td>
<td>-0.9942</td>
</tr>
<tr>
<td>0.76</td>
<td>97.6</td>
<td>-0.2697</td>
<td>3.7758</td>
<td>-0.9946</td>
</tr>
<tr>
<td>0.57</td>
<td>81.8</td>
<td>-0.2400</td>
<td>4.2540</td>
<td>-0.9741</td>
</tr>
<tr>
<td>0.55</td>
<td>81.8</td>
<td>-0.2565</td>
<td>4.4916</td>
<td>-0.9852</td>
</tr>
</tbody>
</table>

Table A.1 Parameters obtained from the linear regressed lines
<table>
<thead>
<tr>
<th>Flow Rate (l/min)</th>
<th>Concentration (ppm)</th>
<th>Equation</th>
</tr>
</thead>
</table>
| 0.98             | 197.0              | \[
\frac{1}{1 + 48.1104 \times e^{-0.6709t}}
\] |
| 1.00             | 197.0              | \[
\frac{1}{1 + 64.7802 \times e^{-0.5970t}}
\] |
| 0.76             | 202.6              | \[
\frac{1}{1 + 122.2294 \times e^{-0.6057t}}
\] |
| 0.74             | 202.6              | \[
\frac{1}{1 + 83.3451 \times e^{-0.6593t}}
\] |
| 0.49             | 201.3              | \[
\frac{1}{1 + 114.0288 \times e^{-0.4621t}}
\] |
| 0.50             | 201.3              | \[
\frac{1}{1 + 290.3247 \times e^{-0.6663t}}
\] |
| 1.00             | 109.7              | \[
\frac{1}{1 + 28.4942 \times e^{-0.2906t}}
\] |
| 1.02             | 109.7              | \[
\frac{1}{1 + 26.4247 \times e^{-0.3374t}}
\] |
| 0.74             | 97.6               | \[
\frac{1}{1 + 49.1806 \times e^{-0.2455t}}
\] |
| 0.76             | 97.6               | \[
\frac{1}{1 + 43.6324 \times e^{-0.2697t}}
\] |
| 0.57             | 81.8               | \[
\frac{1}{1 + 70.3863 \times e^{-0.2400t}}
\] |
| 0.55             | 81.8               | \[
\frac{1}{1 + 89.2641 \times e^{-0.2400t}}
\] |
Figure A.1 Regression Lines for the Transformed Breakthrough Data for a Hydrogen Sulfide Concentration of 197.0 to 202.6 ppm.
Figure A.2 Regression Lines for the Transformed Breakthrough Data for a Hydrogen Sulfide Concentration of 81.8 to 109.0 ppm.
APPENDIX B

The slopes of the experimental curves were obtained by differentiating the regressed linear equations and substituting $Co/C = 2$.

$$
\ln(Co/C - 1) = a - bt \quad (b.1)
$$

$$
-\frac{d(C/Co)}{[(Co/C - 1)(C/Co)^2]} = -bdt \quad (b.2)
$$

$$
d(C/Co)/dt = (Co/C - 1)(C/Co)^2(-1)(-b) \quad (b.3)
$$

for $C/Co = 1/2$

$$
d(C/Co)/dt = b/4 \quad (b.4)
$$

Table B.1 shows the results of applying equation (b.4)

<table>
<thead>
<tr>
<th>Flow Rate 1/min</th>
<th>Concentration ppm</th>
<th>Slope day⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.98</td>
<td>197.0</td>
<td>0.1677</td>
</tr>
<tr>
<td>1.00</td>
<td>197.0</td>
<td>0.1493</td>
</tr>
<tr>
<td>0.76</td>
<td>202.6</td>
<td>0.1514</td>
</tr>
<tr>
<td>0.74</td>
<td>202.6</td>
<td>0.1648</td>
</tr>
<tr>
<td>0.49</td>
<td>201.3</td>
<td>0.1155</td>
</tr>
<tr>
<td>0.50</td>
<td>201.3</td>
<td>0.1666</td>
</tr>
<tr>
<td>1.00</td>
<td>109.7</td>
<td>0.0727</td>
</tr>
<tr>
<td>1.02</td>
<td>109.7</td>
<td>0.0843</td>
</tr>
<tr>
<td>0.74</td>
<td>97.6</td>
<td>0.0613</td>
</tr>
<tr>
<td>0.76</td>
<td>97.6</td>
<td>0.0674</td>
</tr>
<tr>
<td>0.57</td>
<td>81.8</td>
<td>0.0600</td>
</tr>
<tr>
<td>0.55</td>
<td>81.8</td>
<td>0.0641</td>
</tr>
</tbody>
</table>