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**DETERMINATION OF THE EFFECTS OF SULFUR DIOXIDE
ON RECOVERY SYSTEMS FOR CO₂**

Final Report, 1977 - 1980

MASTER

Work Performed for the Department of Energy
Under Contract No. EF-77-S-05-5532

Date Published — January 1981

West Virginia University
Morgantown, West Virginia



U. S. DEPARTMENT OF ENERGY

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DETERMINATION OF THE EFFECTS OF SULFUR DIOXIDE
ON RECOVERY SYSTEMS FOR CO₂

Final Report
1977 - 1980

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ABSTRACT

The present study was initiated to investigate the problems associated with recovery of CO_2 from flue gases for enhanced oil recovery. In particular, the scope of this work may be stated:

- a.) Determine the type of impurities formed in ammonia, MEA, and potassium carbonate systems when extracting CO_2 from oxidizing flue gases containing nitrogen oxides and sulfur oxides.
- b.) Determine the levels of impurity build-up in the solvents.
- c.) Estimate the impurity level in the recovered CO_2 .
- d.) Evaluate the effect on corrosion in metals by these solvents in a flue gas environment.
- e.) Determine the carbon-dioxide absorption coefficients in solvents contaminated due to the pollutants present in the flue gas.
- f.) Evaluate the effect of particulate matter on absorption coefficients in the solvents.
- g.) Recommend potential absorption systems for CO_2 from flue gas and estimate the cost of recovery.

The results of this study indicate that in ammonia, ammonia sulfate is quickly formed to render that portion of the absorbent inactive. In MEA, amine sulfite and amine sulfate are the dominant impurities formed. However, higher oxidized forms of the amines and thiosulfates were found in very small quantities. In amine-activated potassium carbonate solutions, only sulfite and sulfates ions were found, without higher oxidation products. No nitrogen-oxide species were found in any solution.

The impurity levels obtained in the present experiments indicated no limit on contaminant build-up. The sulfate (with some sulfite, thiosulfate) levels in a commercial system could be expected to increase until the capacity for absorbing either CO_2 or SO_2 is exhausted. In amines, this occurs at a level

near 0.5 mole SO₂/mole MEA; in potassium carbonate, this occurs at complete displacement of carbonate ion by sulfite and sulfate ion.

The impurity level in the recovered CO₂ was estimated to be \leq 100 ppm non-condensable gases, 20-200 ppm SO₂, and $<$ 20 ppm NO_x.

Corrosion in the absorption systems will be similar to that observed in CO₂ absorption systems from reducing gas streams. However, corrosion will be slightly higher in the absorption tower than in present commercial plants.

The absorption rate of CO₂ in solutions decreases with increasing loading of CO₂ in almost a linear fashion. The absorption coefficients obtained were also almost linear with respect to active solution species; in agreement with theory of chemical-reaction control at low CO₂ partial pressures. MEA solutions showed much greater absorption rates than potash solutions. The coefficients ranged from 50×10^{-5} lb mole/ft²-sec for 20% MEA to 2×10^{-5} for 9% K₂CO₃ (8% K₂SO₄, 0.9% MEA) at zero CO₂ loadings. It was found that addition of EAE rather than MEA as an activator increased the absorption rate by a factor of 2-4. At high CO₂ loadings, the absorption rate of MEA and EAE-activated potassium carbonate have almost the same values.

The presence of particulates did not appear to appreciably affect the absorption rate of CO₂ in these solutions.

Several alternative absorption systems were evaluated in a preliminary cost evaluation. It is recommended that a K₂CO₃ (EAE activated) solution be the process of choice. However, there is little cost differential between an amine process and a K₂CO₃ process; the final decision should be based on operating experience, operating ease, and corrosion problem minimization. The estimated cost of recovery was 0.88¢/MCF CO₂ for extraction from a side stream of flue gas, 60% recovery of CO₂ in the flue gas, and some SO₂ absorption. The CO₂ is available at mean atmospheric pressure, and must be compressed for EOR. The cost estimate is thus low. The capital charges on equivalent electrical capacity of treated flue gas are roughly \$140/Kw, 40-50% greater than for SO₂ scrubbing alone.

I. INTRODUCTION

Carbon dioxide flooding of depleted oil reservoirs is an important process for recovering additional quantities of U.S. oil. Enhanced oil recovery (EOR) in the U.S. has the potential for recovery of an additional 18-52 billion barrels of oil, with 7-21 billion barrels obtainable by CO₂ flooding.⁽¹⁾ At present, the major sources of CO₂ are from natural gas wells with high CO₂ content,⁽²⁾ or alternatively from large ammonia production facilities. These sources are limited in volume and location, however. For the CO₂ quantities required in commercial EOR operations, the major untapped potential resource is CO₂ from combustion flue gas.^(2,3,4)

A rough cost calculation of physical-solvent recovery of CO₂ from atmospheric pressure flue gas shows it to be uneconomical.⁽⁵⁾ The use of a chemical-reaction solvent has been used in the early part of the century,⁽⁶⁾ but economic application to large-scale recovery of CO₂ has not been accomplished. The most promising systems are the alkanolamine, potassium carbonate, and ammonia systems.⁽²⁾

The ammonia system can remove CO₂ and SO₂,⁽⁷⁾ but it is unknown as to what oxidation problems exist in an oxidizing atmosphere. One major drawback is that for an atmospheric pressure flue gas the high vapor pressure of ammonia can lead to high chemical losses and air pollution problems.⁽⁸⁾ Also, ammonia absorbs and desorbs SO₂ which could be a potential contaminant in the CO₂ needed for secondary oil recovery.

Alkanolamines have good capacity for absorption of CO₂. Preliminary analysis indicates that diisopropanolamine (DIPA) might be a preferred absorbent, since it has a low vapor pressure for low potential solvent losses and air pollution, low reactivity with carbonyl sulfide, potentially low reactivity with SO₂, low corrosion, and low heat of reaction. However, the mass transfer coefficient is relatively low, so the design of an absorption tower leads to excessively large pressure drops and difficulty with draw and reinforcement of tower walls.⁽²⁾ In addition, nitrosoamines could be formed through reaction with nitrogen oxides. Thus, DIPA is not the first alkanolamine choice, but MEA (monoethanolamine) is chosen for analysis because of its much higher absorption coefficient. Because of its higher vapor pressure, a MEA system will probably require a water

wash after the absorption tower. Possible reactions of SO_2 with MEA are probable, but it is probable that only limited solvent losses and corrosion will be found.

Hot potassium carbonate could also be used for absorption of CO_2 from combustion flue gases. However, for good performance alkanolamines are often added as activators, so many of the same difficulties may be encountered as for alkanolamine systems. The absorption coefficient appears less for potassium carbonate than for the MEA system in atmospheric flue gases. When coupled with heat-of-reaction and liquid flow effects,⁽⁷⁾ the cost incentive appears questionable for hot potassium carbonate systems, e.g., there is rule of thumb which states that partial pressures of CO_2 should be above 20 psi for use of potassium carbonate systems.

It appears technically and possibly economically feasible to absorb CO_2 from flue gases for secondary oil recovery. Some systems historically have been used as CO_2 sources. However, large questions remain with respect to the influence of SO_2 and NO_x in an oxidizing atmosphere in absorption towers. In addition, dissolution of N_2 in the absorbing medium could also lead to possible problems in subsequent secondary oil recovery use. The present work addresses some of these questions.

A. Problems in Recovery of CO_2 from Flue Gas

Difficulties exist in the application of existing gas purification systems to the recovery of CO_2 from flue gases for secondary oil recovery. One potential problem is the level of impurities that may be contained in the regenerated CO_2 . For example, indications are that even very low percentages of N_2 can have substantial effects on increasing the miscibility pressure between CO_2 and crude oil.⁽⁹⁾ Another problem concerns the corrosion problems of amines and derivatives in an oxidizing atmosphere such as flue gas. Finally, the presence of SO_2 may initiate reactions to non-regenerable compounds, thereby decreasing solution effectiveness and causing loss of absorbing solution.

The absorption of N_2 in NH_3 is quite appreciable,⁽⁷⁾ and SO_2 is readily absorbed and regenerated.⁽⁷⁾ Thus a pure ammonia, or ammoniacal solution process might be expected to have severe problems of impurities in the captured

carbon dioxide. No data is available on N₂ dissolution in amine, but by analogy it might be expected that some N₂ solubility exists in the alkanolamines used for many CO₂ recovery processes.

Corrosion, already a problem for processes with MEA and potassium carbonate solutions with additives in reducing atmospheres, could be quite markedly changed with an oxidizing atmosphere and oxidation products. No data are available for corrosion in such an environment, as these processes have not generally been used other than in reducing environments.

Finally, the most important question concerns the effect of sulfur dioxide, since SO₂ is a stronger acid gas than CO₂ or H₂S and is readily absorbed into ethanolamine and carbonate solutions. The resulting absorption products in ethanolamines are sulfites, which are regenerable. During a high temperature amine regeneration, the sulfites may be partially reconverted to SO₂. However, a portion of the sulfites will be converted to non-regenerable products which will poison the amine solution. Indeed, most amine solutions which are in use industrially might even absorb all of the SO₂ with a resulting 100 % conversion to heat-stable (non-regenerable) compounds.⁽²⁾ However, some evidence exists which suggests a limit on the amount of conversion/degradation and utilization of the amines.⁽¹⁰⁾

The degradation of the amine occurs in two ways, the disproportionation of sulfite into thionates or the oxidation of sulfite to sulfate.^(10,11) These irreversible reactions may be temperature dependent,⁽¹¹⁾ and the temperature at which degradation becomes appreciable varies with each individual amine, probably between 200° and 300°F. The solubility of SO₂ in amines is independent of the partial pressure of SO₂ at high SO₂ pressures with saturation being reached when the system becomes neutral (pH 7),⁽¹¹⁾ but a saturation limit is reached for low pressures near a 50 wt% solution.⁽¹¹⁾ In the case of oxidation to sulfate the reaction is rapid and spontaneous even in the absence of air. Furthermore, when stabilization of amine solutions was attempted with the addition of 0.1% hydroquinone, the reaction still occurred rapidly.⁽¹²⁾

The absorption of SO₂ into carbonates is similar to that occurring in amines and absorption will occur according to the reaction



Removal efficiencies can be expected to be on the same order as H_2S , while oxidation of the sulfites results in the formation of sulfates and thiosulfates which are non-regenerable and will not be removed during regeneration.⁽²⁾

Because the degradation compounds will tend to continually build up, a method of controlling the level of contamination must be devised. Thermal regeneration and distillation appear unsatisfactory for removal of such compounds, although some systems are available for amine processes.⁽¹³⁾ An assured method for solution control is a continuous purge stream, resulting in the extra cost of replacing the fouled solvent and a waste disposal or treatment problem.

The effects of SO_2 on most physical absorption solvents are unknown. One solvent known to be inhibited by SO_2 is propylene carbonate (the Fluor solvent, the Fluor Oil and Gas Corp., Denver, Colorado). Two reactions may occur between SO_2 and propylene carbonate in water; 1) a conversion to sulfate or bisulfate, and 2) an acid hydrolysis. The former reaction is less probable than hydrolysis. Products resulting from an acid hydrolysis triggered by SO_2 are propylene glycol and propylene oxide which are non-regenerable and these degradation products require special reclaiming procedures. Vacuum reclamation and $CaCl_2$ treatment have been used. Without removal, the compounds will accumulate and result in reduced solvent absorption capacity.

It is important to note that no quantitative experiments have been conducted to study the effects of SO_2 on processes used for the absorption of CO_2 from gases. Absorption and desorption levels and operating difficulties (i.e., corrosion, foaming, erosion, etc.) resulting from use with SO_2 are unknown. One study suggests that the presence of sulfites/sulfates in alkali carbonates even increases the absorption rate,⁽¹⁴⁾ but quantitative absorption coefficients were not reported. Before CO_2 may be recovered from sources such as power plant stack gases, development work will have to be done in order to adapt existing processes or develop new ones. At the present time the application of contemporary CO_2 separation techniques is not recommended to a gas stream containing SO_2 , but rather it is suggested that SO_2 be removed from the gas prior to CO_2 separation.⁽¹⁵⁾ This work is a first step in the needed development work.

B. Study Scope

The scope of the present work may be stated:

- * Determine the type of impurities formed in ammonia, MEA, and potassium carbonate systems when extracting CO₂ from oxidizing flue gases containing nitrogen oxides and sulfur oxides.
- * Determine the levels of impurity build-up in the solvents.
- * Estimate the impurity level in the recovered CO₂.
- * Evaluate the effect on corrosion in metals by these solvents in a flue gas environment.
- * Determine the carbon-dioxide absorption coefficients in solvents contaminated due to the pollutants present in the flue gas.
- * Evaluate the effect of particulate matter on absorption coefficients in the solvents.
- * Recommend potential absorption systems for CO₂ from flue gas and estimate the cost of recovery.

II. EXPERIMENTAL PROGRAM

A. Measurement of Impurities

a.) Overview

Two different absorption columns were utilized to obtain the information necessary to investigate these objectives. One column was a packed tower - the other, a weeping sieve tray column. Stack gas was simulated in four ways; burning of gasoline doped with pyridine to supply nitrogen oxides and thiophene to supply sulfur dioxide; burning of "sour" fuel oil; mixing of compressed air, CO₂ and SO₂ with a manifold; and commercially mixed gas containing SO₂ and CO₂ with a balance of air or N₂. A reboiler was installed in the system in order to thermally regenerate the "fouled" solutions.

The absorption characteristics were examined by taking liquid and gas samples at the points of entrance and exit to the column. The gas samples were analyzed for CO₂ and SO₂ by infrared spectrophotometry or by gas chromatography. The liquid samples were analyzed for sulfate by turbidimetric spectrophotometry and by potassium permanganate titrations for sulfite. A solid sample was prepared by boiling off all volatiles. This solid was then tested for total sulfur using a Leco sulfur determinator. Upon determining all the inlet and outlet concentrations, material balances were performed to determine the capacity of each solution.

Identification of the various chemical species that are formed when SO₂ and CO₂ react with the absorption media was facilitated by the use of mass spectrometry, nuclear magnetic resonance and assorted wet chemistry qualitative analysis.

b.) Materials

Aqueous solutions of MEA, ammonium hydroxide and potassium carbonate activated with MEA were used as absorbing media. Stack gas was simulated in four ways: (i) Initially a commercially available leaded-type gasoline was doped with pyridine to give nitrogen compounds and thiophene to provide sulfur compounds. The gasoline was suction fed to a sonic nozzle where it was combusted with compressed air at a drive pressure of 20 psi. (ii) Another method for producing stack gas involved the burning of fuel oil. Gulf

Research and Development Corporation provided an Iranian Crude that contained both sulfur and nitrogen (See Table 1). The fuel oil was first heated to 135°F and it was then pumped to the nozzle and burned in the same manner as the gasoline mixture. (iii) Commercially compressed CO₂ and SO₂ supplied by Matheson were mixed in a manifold with compressed air to provide large quantities of simulated effluent gas. (iv) Matheson also supplied two types of commercially premixed gases, the compositions of which were known (shown in Table 2).

Table 1

<u>Ultimate Composition of Iranian Crude</u>
1.75 % S
86.1 % C
12.2 % H
0.15 % N

Table 2

<u>Premixed Gas Composition</u>	
<u>Cylinder 1.</u>	<u>Cylinder 2.</u>
0.3 % SO ₂	0.3 % SO ₂
11.0 % CO ₂	11.0 % CO ₂
Balance-Air	Balance-N ₂

Barium chloride, barium carbonate, sulfuric acid, standard solutions of iodine, permanganate and thiosulfate were used in the quantitative analysis of liquid samples.

c.) Equipment

The components of equipment used in the investigation were

<u>Absorption System:</u>	<u>Burner System:</u>	<u>Sample Analysis:</u>
1) Packed Column	1) Heat exchangers	1) Gas chromatograph
2) Weeping sieve tray column	2) Funnel	2) Visible spectrophotometer
3) 2 reboilers	3) Ultrasonic nozzle	3) Atomic absorption spectrophotometer
4) Heating elements	4) Pump	
5) Centrifugal pump		
6) Blower		
7) Distributor nozzle		
8) Flowmeters		

The packed bed absorption system used in this study is shown in Figure 1. The packed column consisted of a 4-1/2 foot plexiglass column with a 5-1/4 inch inside diameter. It was packed to a height of 4 feet with 1/2 inch ceramic intalox saddles supplied by Stoneware.

Figure 2 represents the absorption system that employed the sieve tray column. Process Supply, Incorporated supplied a 12 foot tall glass sieve tray column containing 3 teflon trays. The 3 trays were spaced 2-1/2 feet apart and each tray contained 69 holes, 3 millimeters (0.118 in.) in diameter. The holes were arranged in a triangular pitch and provided approximately 60% active area.

The reboiler connected to the packed column was a 5.0 liter round bottom flask with 3 access holes. The reboiler attached to the sieve tray column was a 4.8 liter jug with an exit port at the bottom. Initially the heating elements were nichrome wire wrapped around glass rods. These were replaced by a vicor immersion heater. A 1/15 horsepower centrifugal pump was used to circulate the absorbing media. A 1/6 horsepower self-priming pump transported the fuel to the burning nozzle. A blower provided by Tradewinds Motor Fans provided better exhaust for the gas leaving the top of the column. Water-cooled glass condensers were installed above the reboilers to prevent solution loss due to vaporization. Condensers were also used to lower the temperature of the liquid leaving the reboiler before it entered the column. A plexiglass distributor nozzle was used to provide an even distribution of the absorbing media over the packed column.

The Sonic Development Corporation of New Jersey provided the 0-52H acoustic atomizer that was used to combust the fuels. Metal-finned heat exchangers were used to cool the gases, produced by burning, to less than 200°F before they entered the column. A large metal funnel channeled the gases into the heat exchangers. Flowmeters supplied by Rodger Gilmont, Incorporated were used to measure gas and liquid flow rates when cylinder gas was supplied to the column.

Gas analyses were done with a Beckman Model 2A gas chromatograph and a Perkin Elmer 990 gas chromatograph. A Bausch and Lomb Spectronic 20 spectrophotometer was used for sulfate determinations. A Perkin-Elmer Atomic Absorption Spectrophotometer was used to determine the concentration of metal ions in the solutions.

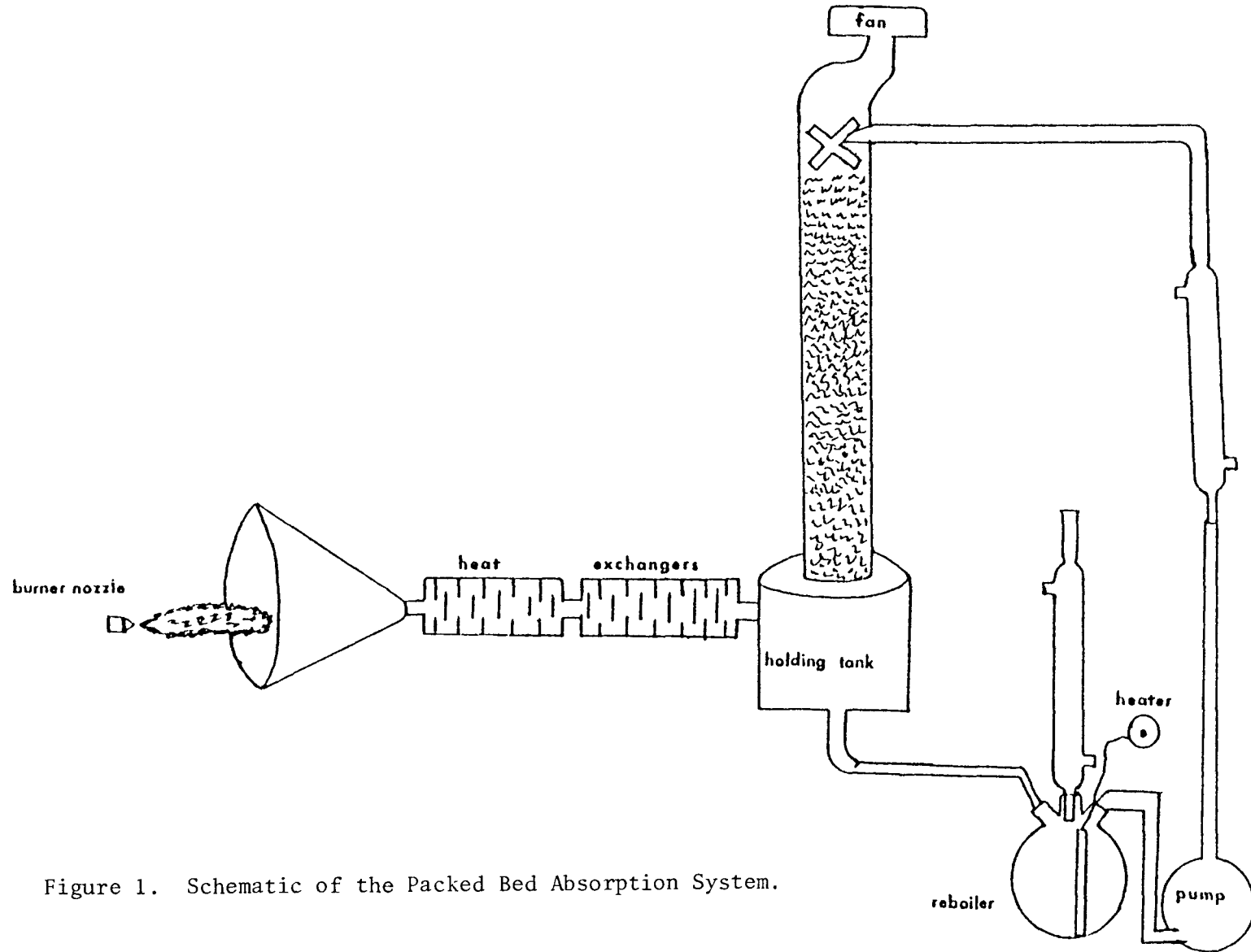


Figure 1. Schematic of the Packed Bed Absorption System.

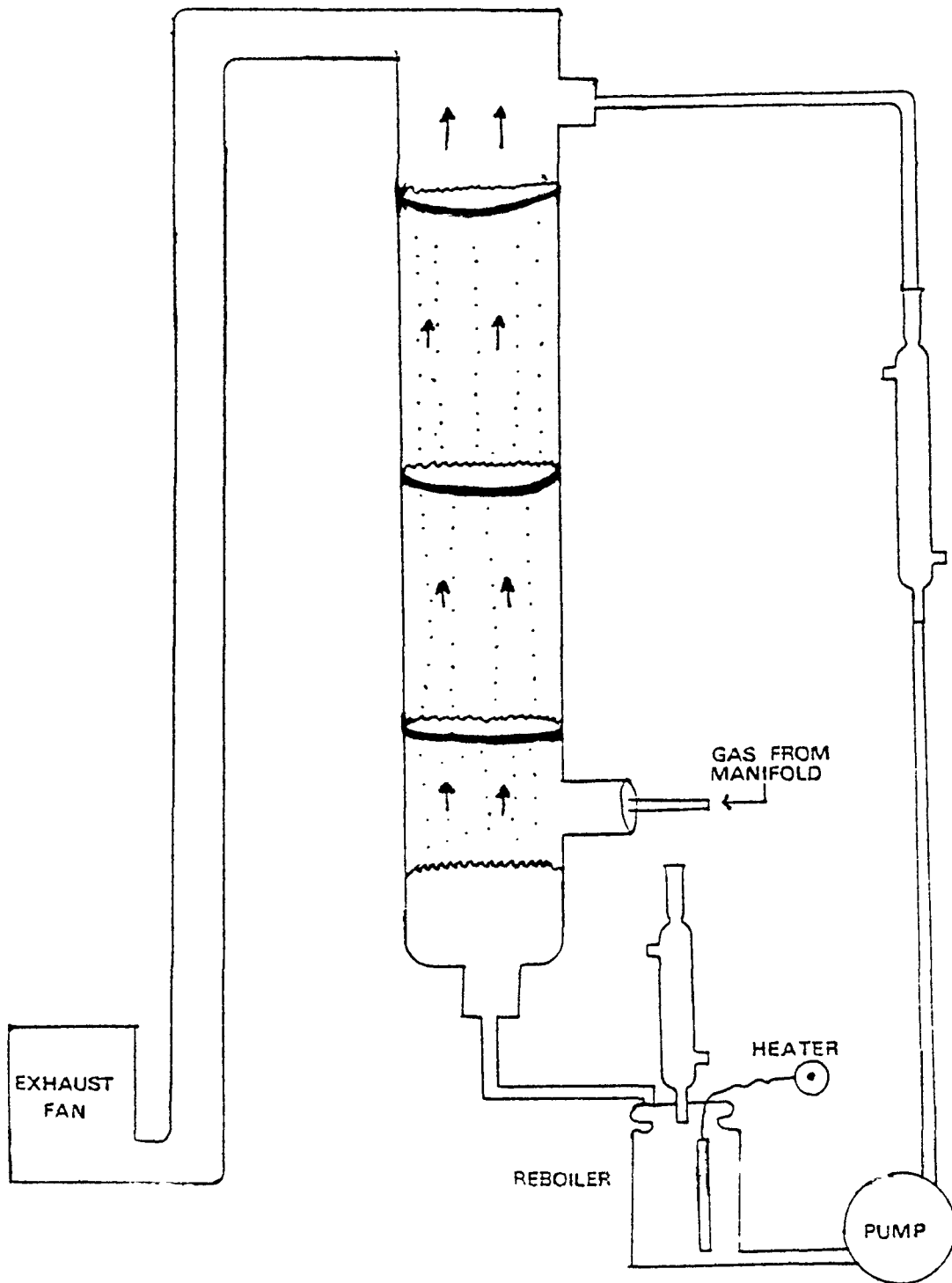


Figure 2. Schematic of Weeping Sieve Tray Column Absorption System.

c.) Procedures

The experimental procedure was divided into 3 sections:

1.) Absorption Experiments:

Packed Column. Preliminary absorption experiments with ammoniacal and MEA solutions were carried out in the packed column (see Figure 1). The absorbing liquid was circulated at a constant rate of 1.4 liters/min. Gas flow rates varied depending on the source of effluent gas. Fuel oil, doped gasoline and premixed gases were used in this column. Gas samples were taken every 10 to 15 minutes from the reboiler and every half hour from the bottom of column before the entrance to the reboiler. The temperature of the reboiler was constantly monitored as well as the pH of the solution in the reboiler.

Sieve Tray Column. Experiments utilizing MEA and MEA-activated potassium carbonate were performed in the weeping sieve tray column (see Figure 2). Liquid flow rates between 0.48 gal/min and 0.53 gal/min were used. Because of the need for large quantities of gas, the gas was predominantly supplied by manifold mixing of compressed CO₂, SO₂, and air. The premixed gas was also used, but to a smaller extent. Gas and liquid samples were taken in the same manner as for the packed column.

2.) Sample Analysis

Flue Gases. The gas samples were analyzed for CO₂, SO₂, N₂, and air using gas chromatography. Measurements taken in this manner had an error of $\pm 2\%$. MSA gas detector tubes were also used to measure quantities of CO₂, SO₂, NO₂, and CO present in the gas samples. Detector tubes had $\pm 10\%$ error.

Liquids. The quantitative determination of the sulfur concentration in the form of sulfate was determined turbidimetrically. Five milliliters of sample are treated with a conditioning reagent which aids in the suspension of particles. Barium chloride is added in excess to the sample. Barium sulfate, a white precipitate, forms immediately and causes the solution to become turbid. The absorbance of the prepared specimen, which is a function of concentration of BaSO₄, was determined with a spectrophotometer. A working curve of known concentration versus absorbance was used to obtain the concentration of S as

$\text{SO}_4^{=}$ in the sample. The numbers given by this determination should be considered to have approximately $\pm 8\%$ error, because of problems caused by interference of other ions present in the tapwater.

Quantitative determination of sulfur as sulfite was done by two methods. Initially a known amount of a standard iodine solution was added in excess to a certain volume of sample. The mixture was then titrated with standard sodium thiosulfate. This method of $\text{SO}_3^{=}$ determination has approximately $\pm 0.5\%$ error. Calculation of the quantity of S present as $\text{SO}_3^{=}$ was calculated by use of Equations 2 through 4.

$$(M_{\text{thiosulfate}})(\text{ml}_{\text{thiosulfate used}})\left(\frac{1}{M_{\text{iodine}}}\right)\left(\frac{1 \text{ mole iodine}}{2 \text{ mole } \text{S}_2\text{O}_3^{=}}\right) = \text{excess ml iodine} \quad (2)$$

$$[(\text{ml iodine used}) - (\text{excess ml iodine})](M_{\text{thiosulfate}})\left(\frac{\text{mole iodine}}{2 \text{ mole } \text{S}_2\text{O}_3^{=}}\right) = \# \text{ moles iodine} \quad (3)$$

$$\left(\frac{1 \text{ mole } \text{SO}_3^{=}}{1 \text{ mole iodine}}\right)(\# \text{ moles iodine})\left(\frac{1}{\text{ml sample}}\right)\left(\frac{32 \text{ g S}}{\text{mole } \text{SO}_3^{=}}\right)\left(\frac{1}{\rho_{\text{solution}}}\right)(10)^6 = \text{ppm S as } \text{SO}_3^{=} \quad (4)$$

Sulfite levels were also determined by titration with potassium permanganate. The permanganate ion oxidizes the sulfite to sulfate. When all the sulfite has become oxidized, the sample will turn pink due to the presence of excess permanganate. Equation 5 provides for the calculation of the concentration of S as $\text{SO}_3^{=}$ as determined by permanganate titrations. Permanganate titrations are relatively accurate and have an error of $\pm 0.1\%$.

$$(M_{\text{permanganate}})\left(\frac{3 \text{ moles } \text{SO}_3^{=}}{2 \text{ moles permanganate}}\right)\left(\frac{32 \text{ g S}}{\text{mole } \text{SO}_3^{=}}\right)\left(\frac{1}{\text{ml sample}}\right)(10^3)(\rho_{\text{solution}}) \\ = \text{ppm S as } \text{SO}_3^{=} \quad (5)$$

The following tests were used to qualitatively determine the products formed by the disproportion of absorbed SO_2 . The samples were tested for thiosulfates ($\text{S}_2\text{O}_3^{=}$) by the addition of sodium azide and iodine solution to the sample. If thiosulfate is present, the solution bubbles. If after the solution is heated to boiling, a white precipitate forms, and SO_2 is evolved upon

the addition of barium carbonate, trithionates ($S_3O_6^{=}$) are present. Tetra-thionates ($S_4O_6^{=}$) produce a yellow precipitate upon the addition of mercurous nitrate. Pentathionates ($S_5O_6^{=}$) will produce a precipitate of sulfur when 2N potassium hydroxide is added to the sample. A mass spectrogram was obtained to detect the presence of any organic sulfur compounds. A Leco sulfur determination was run to determine the total sulfur present in all forms except $SO_3^{=}$.

Qualitative determinations of nitrates and nitrites were done by oxidation of diphenylamine. In this procedure a reagent solution of water, acid and diphenylamine is prepared. A drop of the sample is added to 0.5 milliliters of reagent solution. A blue ring forms if there is as much as 0.5 micrograms nitric acid.

Regeneration Gases. The quantity of CO_2 in the H_2CO_3 , HCO_3^- , and $CO_3^{=}$ formed is determined in the following manner. Concentrated acid is added to the liquid sample, this lowers the pH and CO_2 gas is released. The quantity of CO_2 evolved is measured by monitoring the amount of water displaced by the gas. Figure 3 shows the set-up used for CO_2 determinations. Sulfur dioxide is not evolved because the pH is kept above 4 so that the SO_2 would remain in solution as HSO_3^- .

The presence of the other gases (N_2 , SO_2) in the regenerated carbon dioxide was determined in the following manner. Flue gas was passed through an absorbing solution for a given period of time to 0.5 moles CO_2 /mole active ingredient. A solution sample (in Figure 4) was then released into vacuum to drive off any gases, which were collected in the previously evacuated system of known volume. Carbon dioxide was frozen into the liquid-nitrogen cold finger. The pressure was recorded, and non-condensable gas release calculated. This was verified by heating the sample and finding no further non-condensibles.

3.) Corrosion Tests

Corrosion tests were conducted by placing copper and nichrome in MEA and NH_4OH solutions. These solutions were then heated to $100^\circ F$ and SO_2 , CO_2 , and air were bubbled through the solutions for several hours. Samples from these solutions were tested for the presence of copper, nickel, and chromium ions by atomic absorption. Monel, stainless steel, and carbon steel were placed in fresh MEA solutions. They were kept at a temperature of $160^\circ F$ for one week.

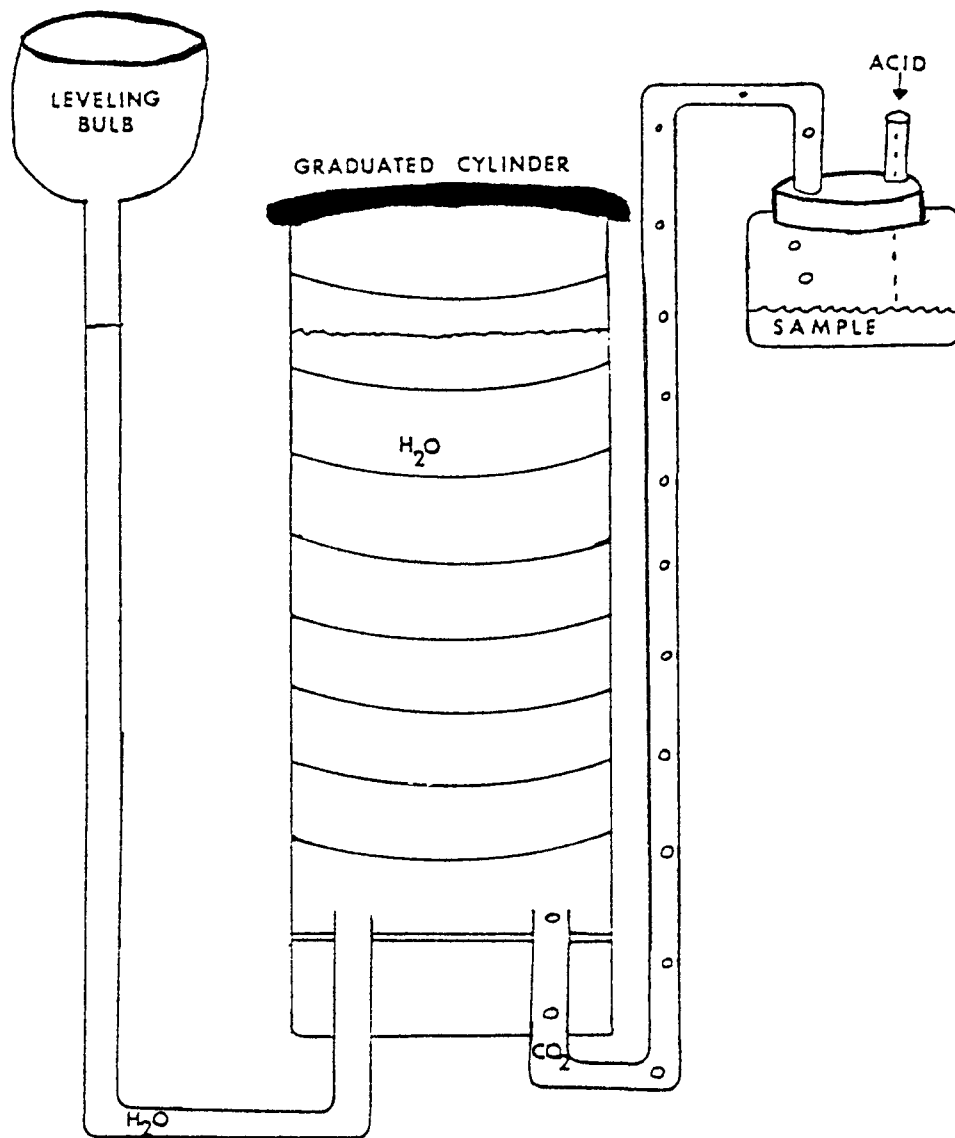


Figure 3. Schematic of Apparatus for CO_2 in Liquid Determinations.

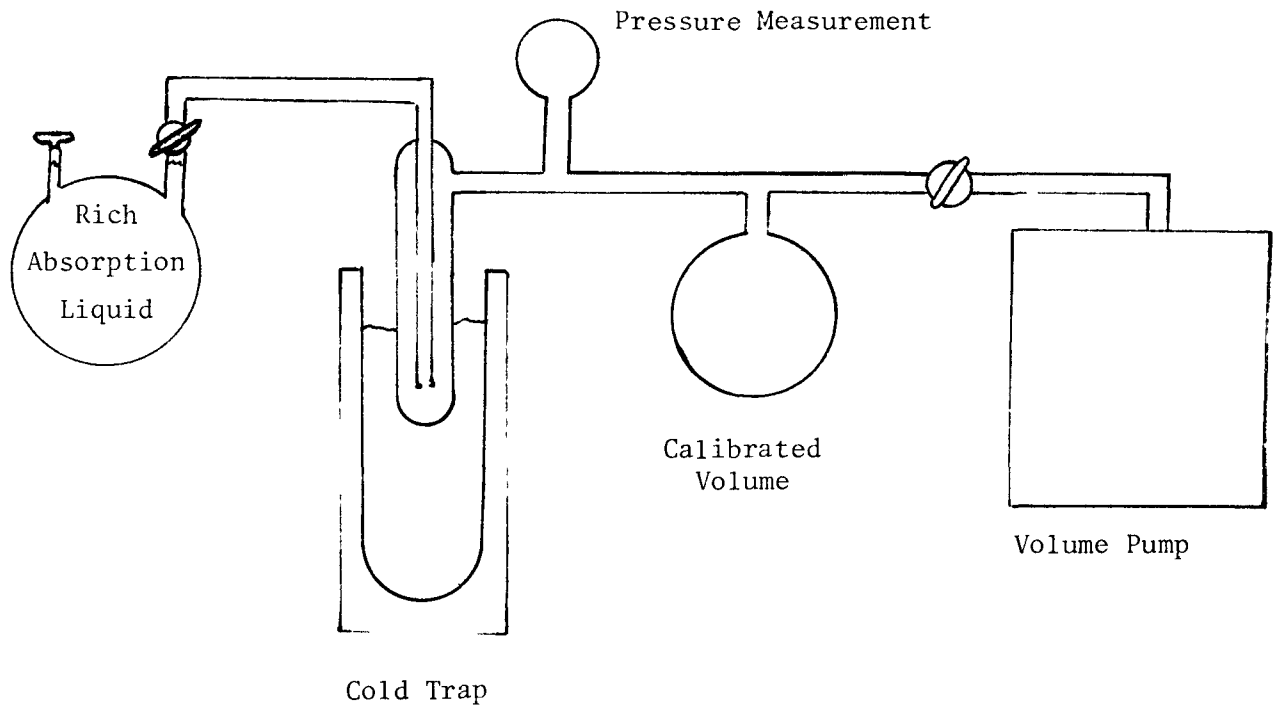


Figure 4. System to Measure Absorbed gases (condensable and non-condensable) from Liquid Solutions Used to Absorb CO_2 from Flue Gas.

The metals then sat in the solutions for 7-1/2 months. None of these solutions were loaded with acid gases. These solutions were also analyzed by atomic absorption.

B. Absorption Coefficients

The CO₂ absorption ability of chemically-reactive solutions will be affected by the contaminants. Two experimental systems were constructed to measure these effects.

Figure 5 schematically presents the system to obtain quantitative values of the absorption coefficient. It utilizes the same basic equipment as shown in Figure 2 and described earlier. The inlet gas is obtained by the mixture of carbon dioxide, air, and sulfur dioxide through a manifold. Gas composition is determined by calculation from the measured flow rates, and by measurement of gas from the plenum chamber by a Perkin Elmer gas chromatograph. Outlet gas is obtained by gas chromatograph measurement of the gas in the outlet mixing chamber. Temperature of the absorbing solution is measured on the absorbing tray by thermometer. The solution is continually recycled to a regenerator, where the solution is thermally heated to drive off CO₂ and other soluble gases.

The bubbles through the tray can be directly estimated by determining the portion of tray area which has bubbles. The bubble size can then be calculated from correlations. In addition, the bubble size has been obtained by photographing the bubbles with a telephoto camera at 1/500 second speeds. The bubble sizes can then be directly measured, and an average size determined (Appendix A).

As the system is continually regenerated, negligible CO₂ is absorbed and converted to carbonate or bicarbonate. The equilibrium CO₂ vapor pressure is thus essentially zero.⁽⁷⁾ The absorption coefficient can be calculated from

$$K_G = \frac{G}{A_B \cdot t_R} \left[\ln \frac{(y_{CO_2})_{in}}{(y_{CO_2})_{out}} \right] \quad \text{with units } \left[\frac{\text{lb moles}}{\text{ft}^2 \text{ sec}} \right] \quad (6)$$

G = Moles of Gas in One Bubble (lb moles)

A_B = Area of Bubble for Carbon Dioxide Mass Transfer (ft²)

t_R = Bubble Rise Time (sec)

y_{CO₂} = Mole Fraction Carbon Dioxide

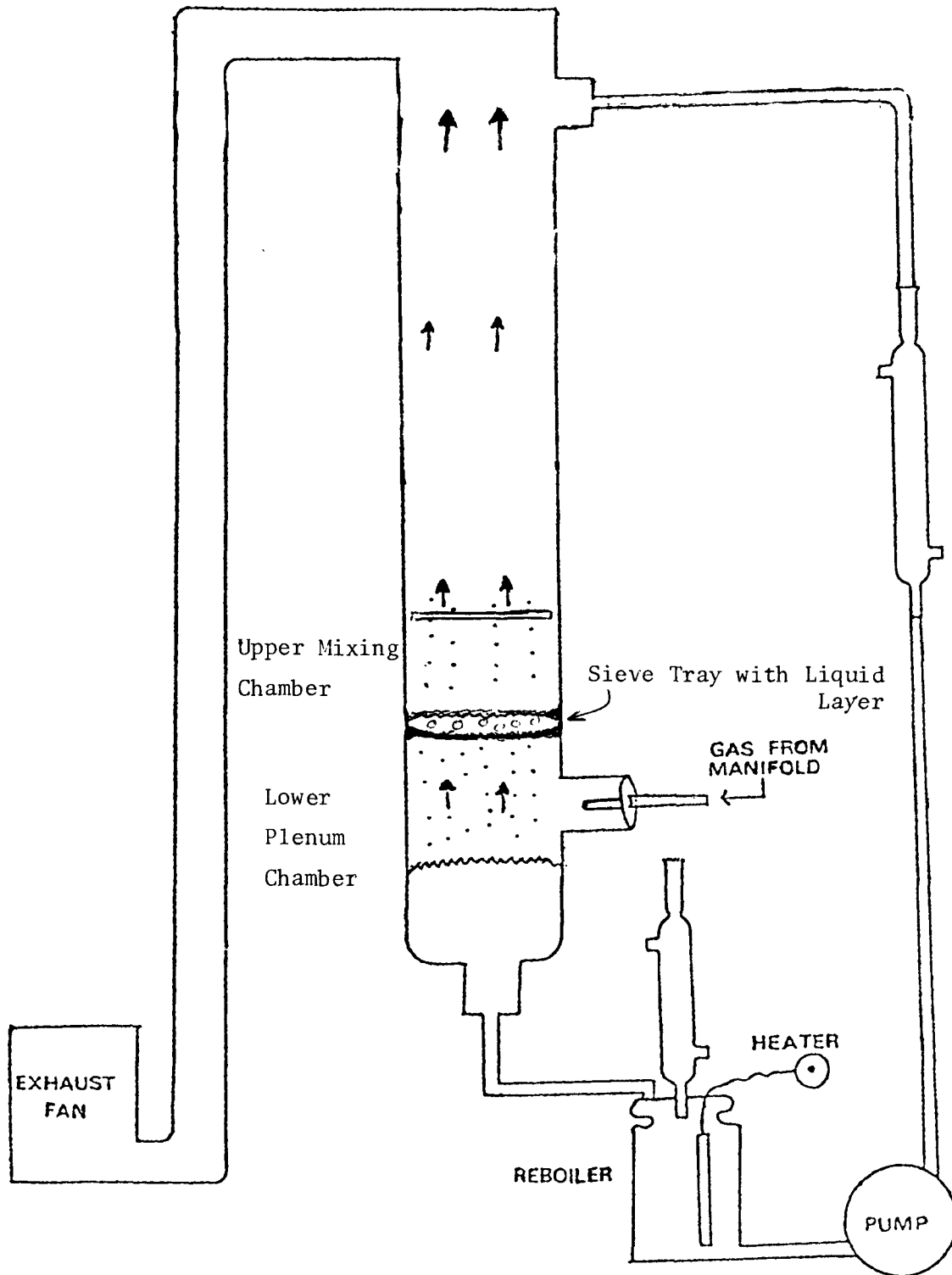


Figure 5. Schematic of Weeping Sieve Tray Column Absorption System.

Figure 6 presents the apparatus design to obtain relative absorption rates as a function of capacity. A precalibrated gas mixture enters through a flowmeter at (1000 l/minute) into a fritted-disc gas disperser. This disperser forms a multitude of bubbles which are then circulated through the solution by vigorous stirring. The stirring rate is maintained at constant speed, and verified by a strobe-light tachometer (150 rpm). The outlet gas is exhausted through a long line, from which a gas chromatograph sample is taken to measure outlet CO₂ concentration.

As the CO₂ level continually increases in the absorbing solution during the experiment, the equilibrium vapor pressure will also change. Then K_G will be given by

$$K_G(t) = \frac{G}{A_B \cdot t_R} \ln \left[\frac{(y_{CO_2})_{in} - y_{CO_2}^{(VP)}}{(y_{CO_2})_{out} - y_{CO_2}^{(VP)}} \right] \quad (7)$$

$y_{CO_2}^{(VP)}$ = Equilibrium mole fraction CO₂ over solution.

assuming psuedo-steady state for gas concentrations in the outlet gas chamber with respect to changes in the absorbing solution. As G, A_B, and t_R cannot be obtained accurately in this system, data is compared by the use of a relative absorption coefficient, R.A.C.

$$R.A.C. = \ln \left[\frac{(y_{CO_2})_{in} - y_{CO_2}^{(VP)}}{(y_{CO_2})_{out} - y_{CO_2}^{(VP)}} \right] \quad (8)$$

The solutions examined to determine K_G and R.A.C. for absorbing CO₂ from flue gas were: 20 wt% MEA, fouled MEA solution (including char solid), MEA-activated potassium carbonate solution, ethyl-amino-ethanol-activated potassium carbonate solution, and sulfate-fouled activated potassium carbonate solution. Absorption in ammonia was not accomplished, as the problem of fouling in ammonia indicated too difficult a solution-treatment problem.

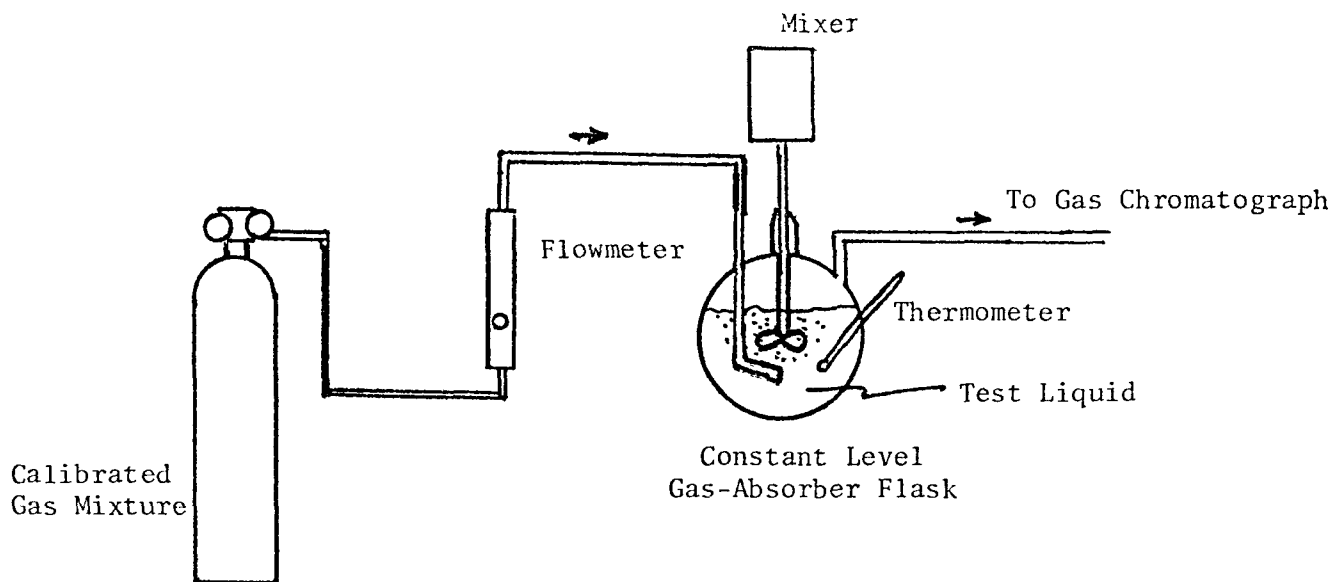


Figure 6. Schematic Diagram of Laboratory Flask Absorber to Compare Relative Absorption Rates of Test Liquid Solutions.

III. EXPERIMENTAL RESULTS

A. Impurities Formed

a.) MEA Solutions

Gas chromatography showed that aqueous solutions of 20 volume percent MEA absorbed ≥ 98 percent of the CO_2 that was present in the simulated stack gas in both the packed towers and the weeping sieve-tray columns. The chromatographs also demonstrated the absorbance of essentially all the SO_2 that was in the effluent gas. The chromatograms showed more percent SO_2 absorption than percent CO_2 absorption. Liquid analyses, which have an average of $\pm 3\%$ error, showed that ≥ 95 percent of the absorbed SO_2 was in the form of SO_3^- and SO_4^- in the liquid solution.

Figure 7 shows that in a packed column, at higher temperatures and in a predominantly inert atmosphere (N_2), most of the SO_2 absorbed was in the form of SO_3^- . This figure also shows that at the higher reboiler temperature, the amount of SO_3^- and SO_4^- formed increased. A leveling in the amount of SO_3^- formed was observed for both temperatures in Figure 7. The amount of SO_3^- and SO_4^- were expressed as ppm because the volume of solutions was not continually monitored. The concentrations of SO_3^- and SO_4^- are dependent upon the volume of solution present in the system. Caution is advised when comparing ppm concentrations from different experiments because the volumes are not the same for each run. Two solutions may contain the same mass of SO_3^- and SO_4^- , but the concentrations would be different if the volumes of solution were not equal.

Figures 8, 9, and 10 demonstrate that the majority of sulfur absorbed was in the form of SO_4^- for a weeping sieve tray column operated at lower temperatures (115°F) with an oxidative atmosphere of air. Figure 8 shows an increasing accumulation of SO_3^- and SO_4^- with respect to time. No leveling trends in quantity of SO_4^- and SO_3^- formed were noted over extended periods of time. Figure 7 shows that SO_4^- was formed even in the absence of oxygen. A Leco sulfur determination showed the existence of small quantities of polymeric sulfur compounds. Minor quantities of trithionate (S_3O_6^-) were detected using the barium carbonate test. A mass spectrum of the spent MEA solution denoted the

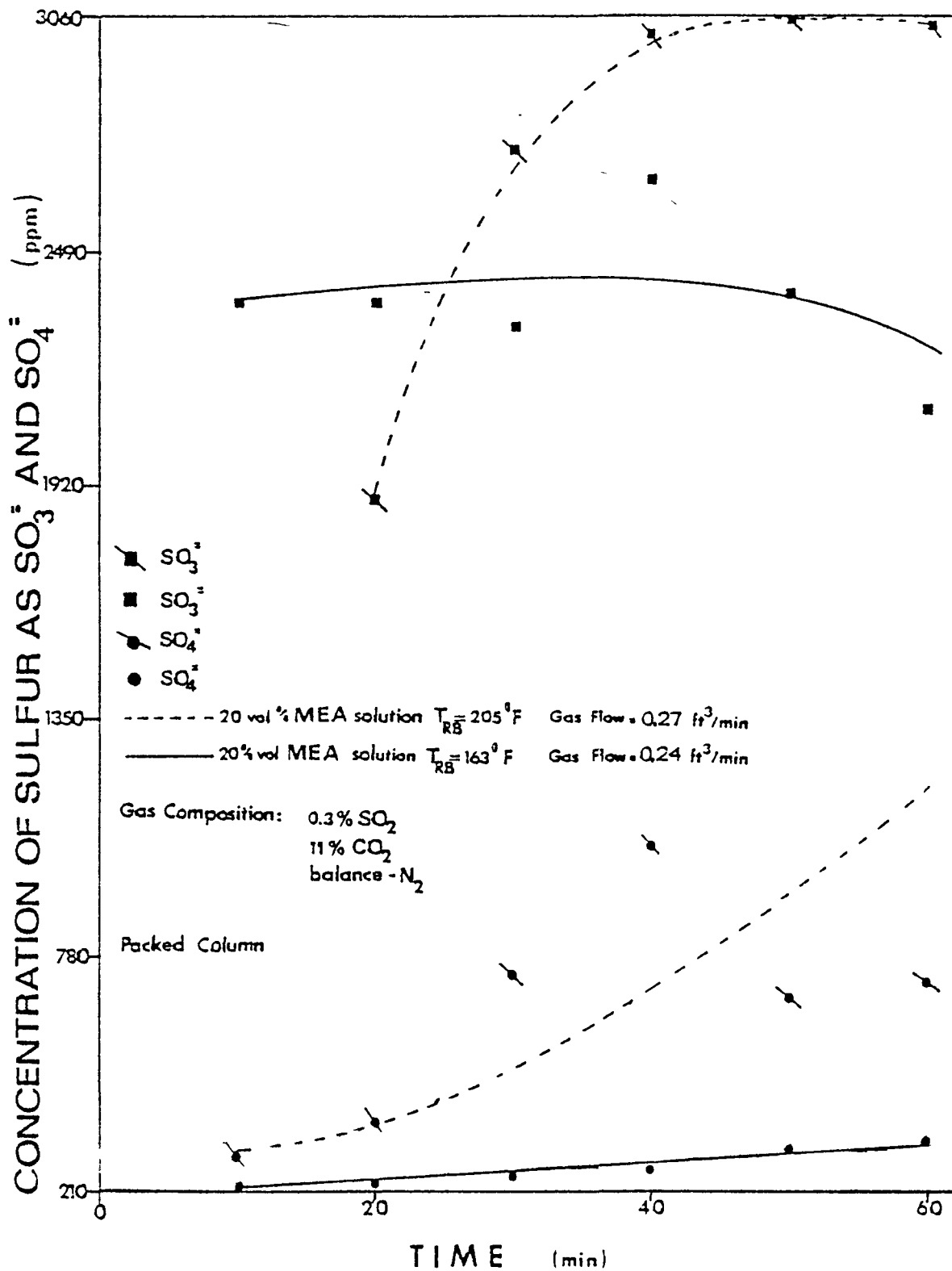


Figure 7. Concentration of Sulfur Absorbed as Sulfite and Sulfate as a Function of Operating Time for a Packed Column.

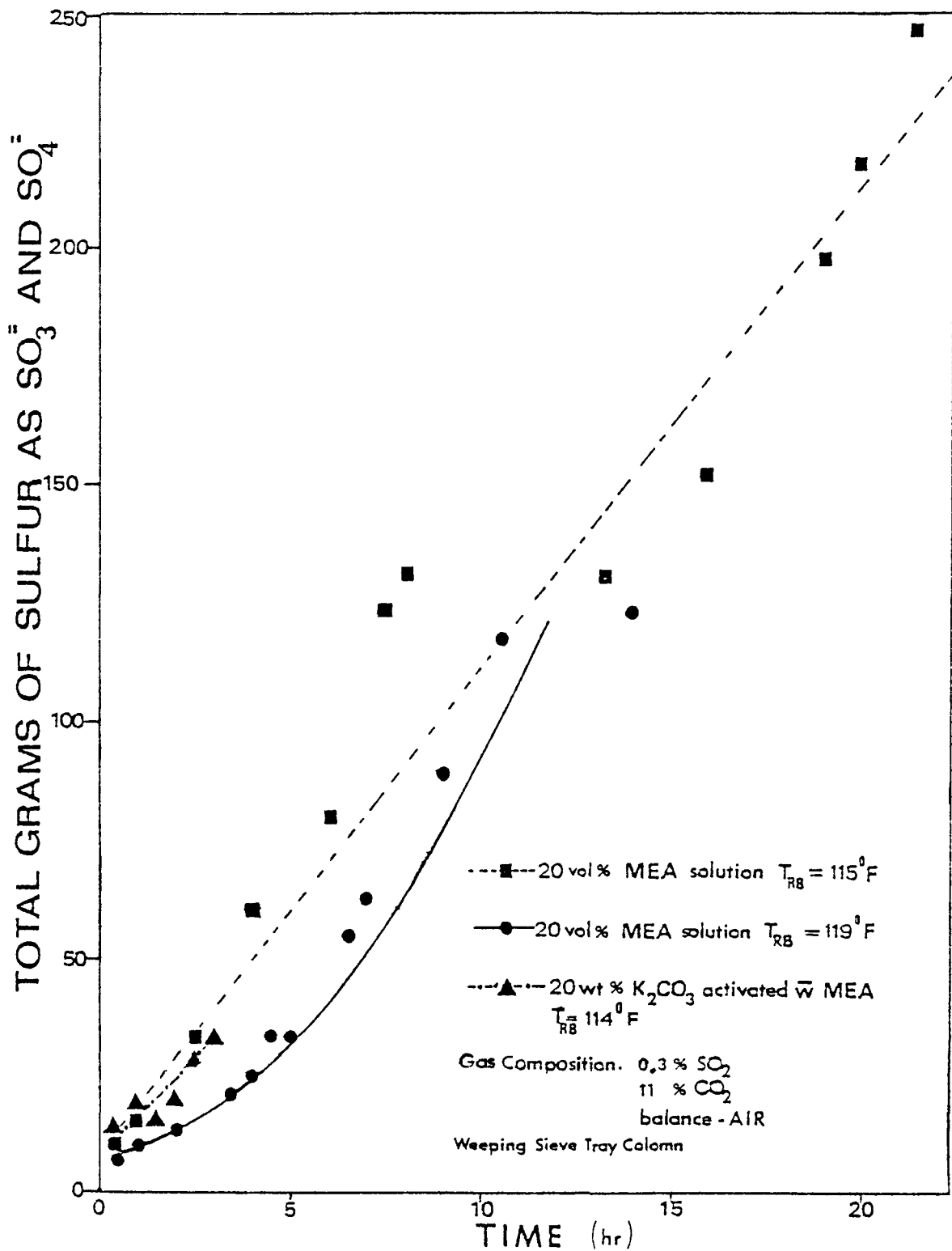


Figure 8. Total Grams of Sulfur Absorbed as Sulfate and Sulfite as a Function of Time for a Sieve Tray.

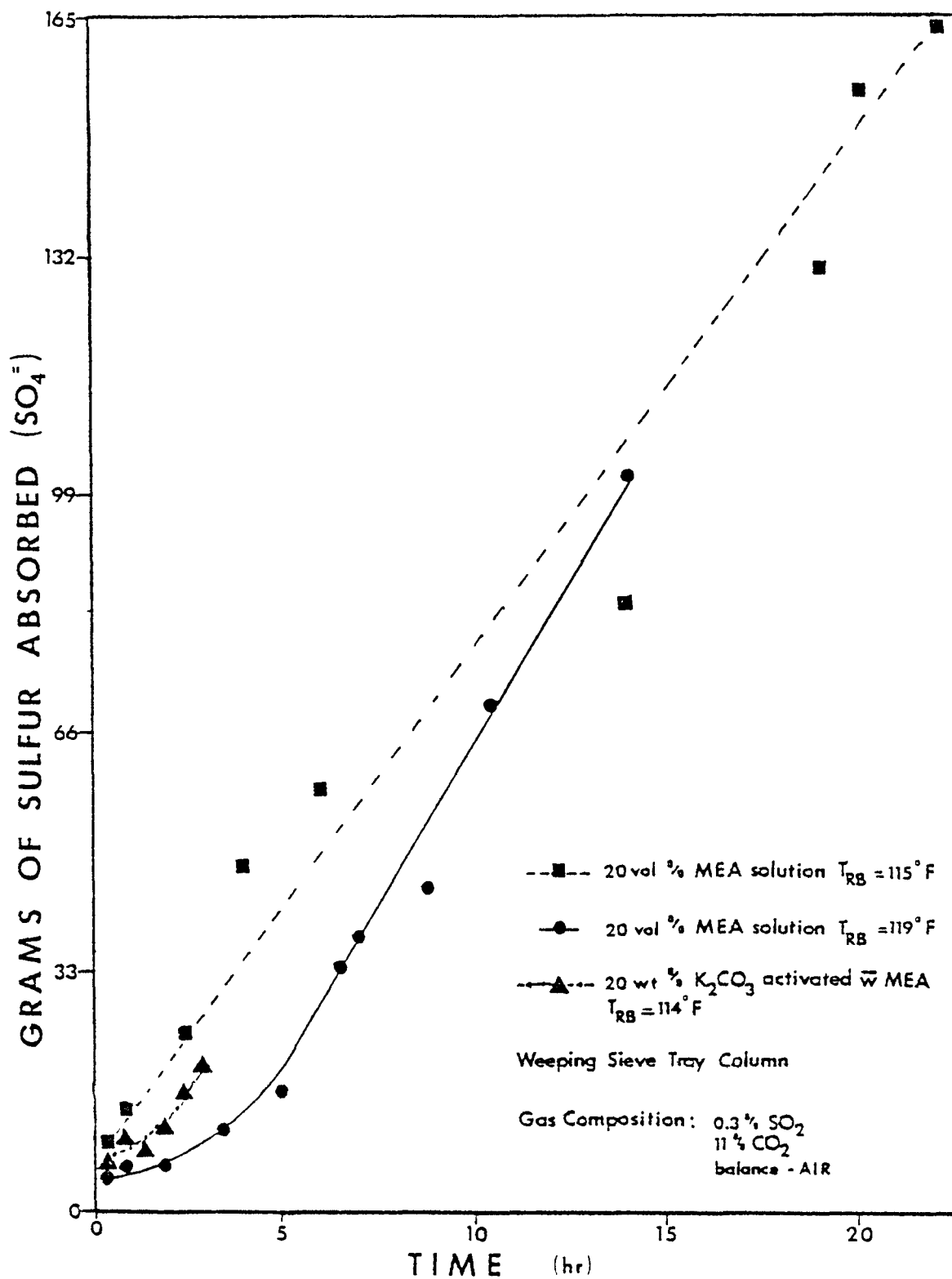


Figure 9. Grams of Sulfur Absorbed as Sulfate as a Function of Operating Time for a Sieve Tray Column.

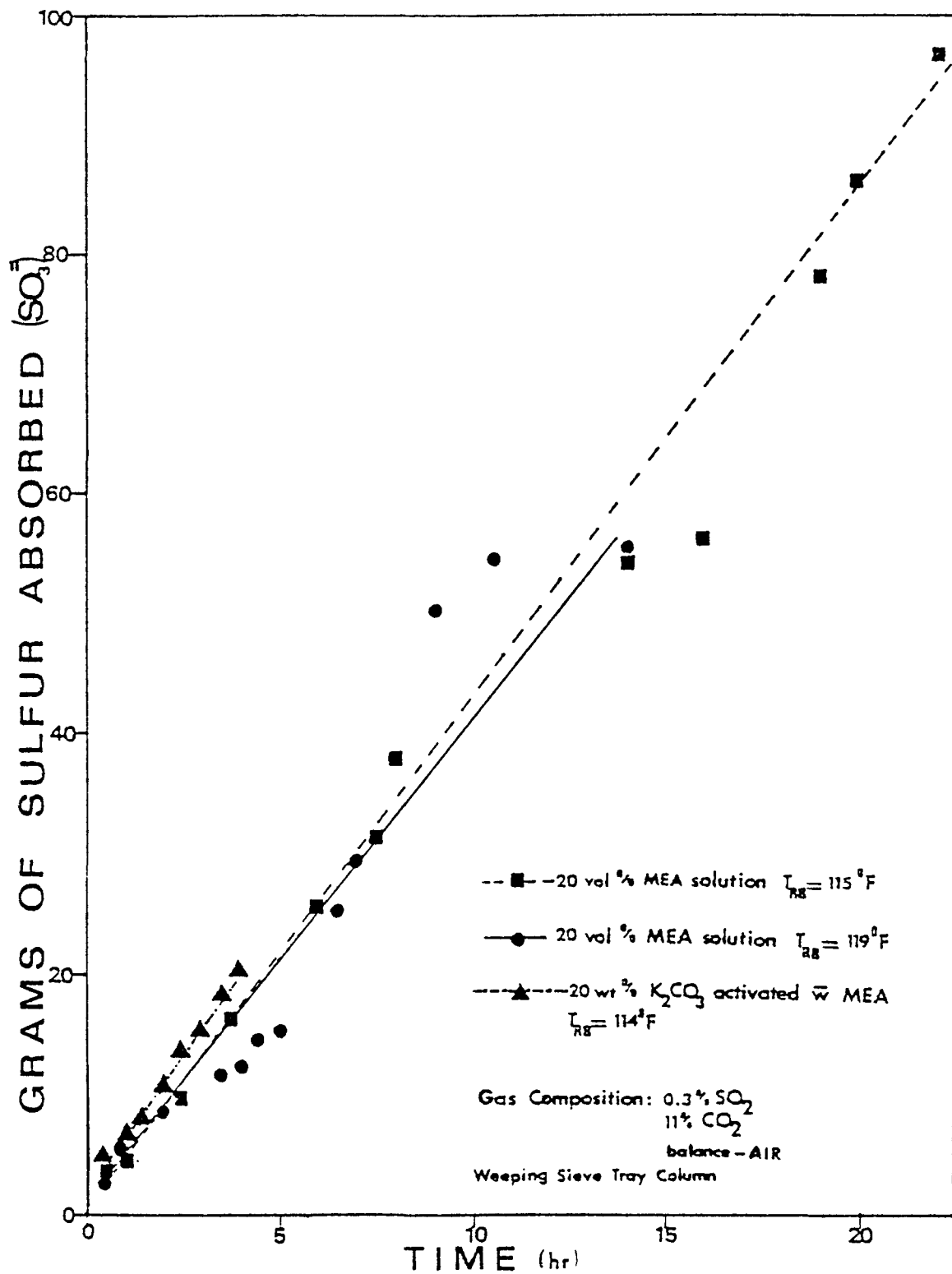


Figure 10. Grams of Sulfur Absorbed as Sulfite as a Function of Operating Time for a Sieve Tray Column.

presence of breakdown products of MEA such as oxazolidine and substituted ethylenediamine and imidazolidone, but no sulfur containing compounds. Colored solutions were produced when aqueous MEA was in contact with copper.

The decrease of solution pH as a function of the amount of sulfur present for 20% MEA solutions is shown in Figure 11. Figure 12 indicates a trend toward total saturation of the MEA with sulfur compounds.

Tests performed on the MEA liquid samples showed approximately 41 milliliters of CO₂ present in 1 milliliter of solution. This was after 14 hours of absorbing the simulated flue gas.

b.) Ammonium Hydroxide Solutions

Gas chromatography showed that NH₄OH solutions absorbed CO₂ similarly to the MEA solutions. No SO₂ was detected in the gas samples taken from the exit of the column. The ammonia solutions became colored upon prolonged contact with metal containing either copper or nickel.

Figure 13 shows that SO₄⁼ was formed in preference to SO₃⁼ in aqueous NH₄OH solutions operated at lower temperatures (100°F) in a relatively inert atmosphere of N₂. This agrees with the claim that auto-oxidation is caused by NH₃.⁽¹⁶⁾ The same figure shows a leveling trend in the formation of SO₃⁼ with time.

c.) Activated Potassium Carbonate

The gas chromatograph showed that the MEA-activated potassium carbonate solution absorbed 98 to 99% of the CO₂ put through the system. Essentially all the SO₂ that entered the column was absorbed. A comparison of Figures 9 and 10 shows that more SO₄⁼ was formed than SO₃⁼. Figure 9 denotes a greater formation of SO₄⁼ in the K₂CO₃ solution than in the MEA solution. Figure 8 demonstrates that no leveling trend was noted in the amount of SO₂ absorbed by MEA-activated potassium carbonate. Trithionate was detected qualitatively by the barium carbonate test.

Nitrogen was detected in small amounts in the evacuated system, but in very small amounts (< 1.5 x 10⁻⁴ mole/liter). This would be equivalent in a commercial operation to about 100 ppm N₂ in the regenerated CO₂ from a rich 2N K₂CO₃ solution.

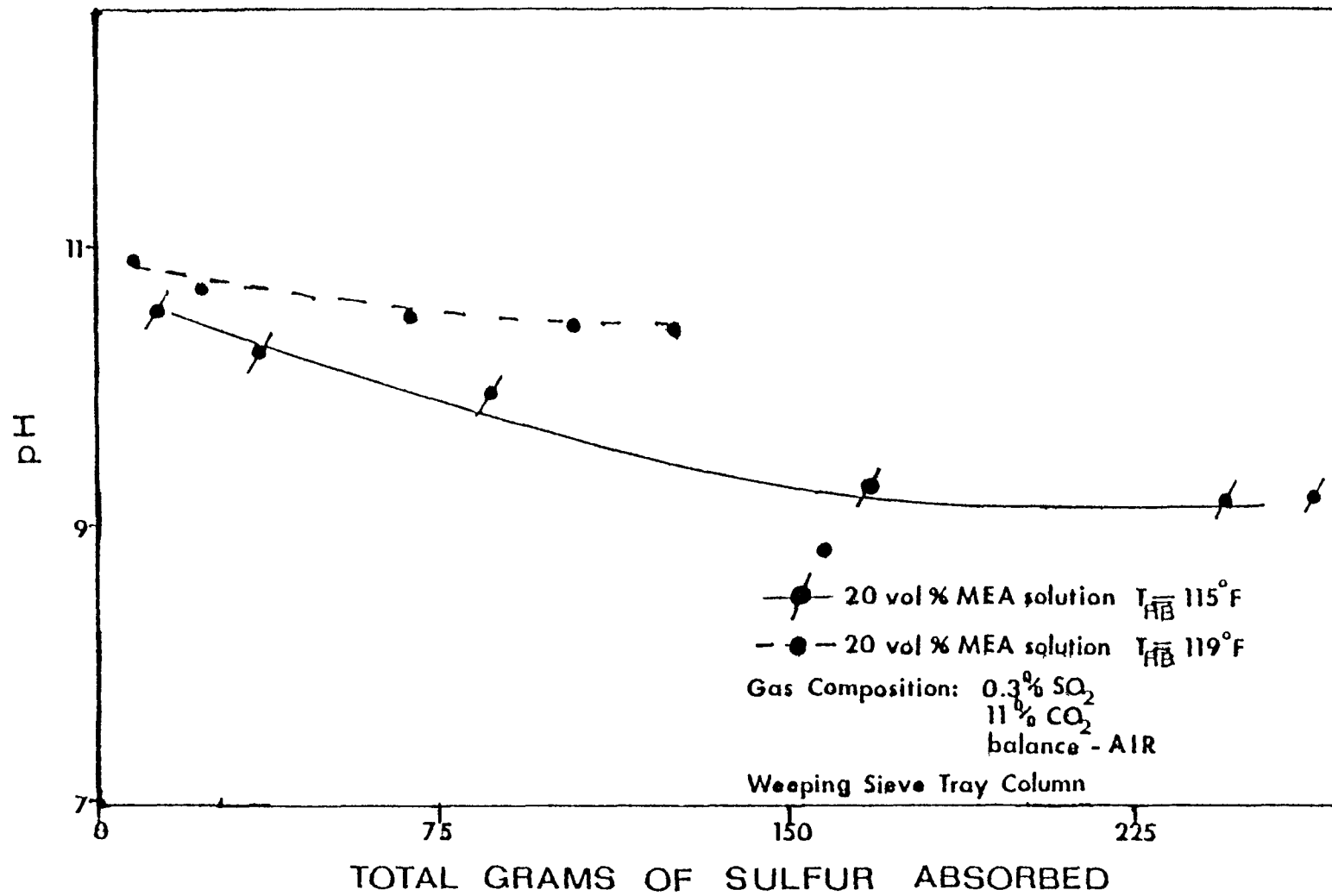


Figure 11. Total Grams of Sulfur Absorbed as a Function of pH.

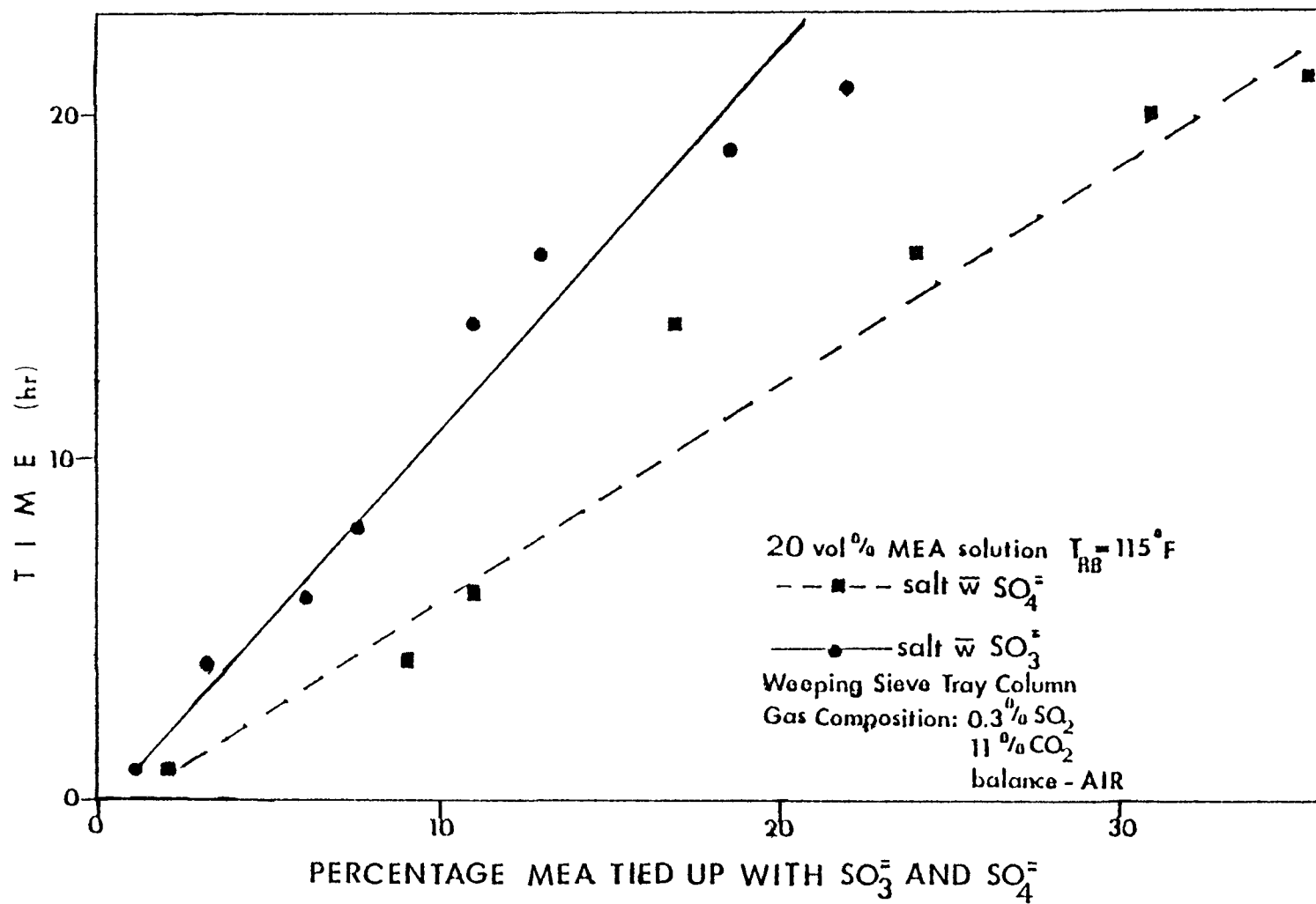


Figure 12. Percentage of MEA Tied Up with SO_3^- and SO_4^- as a Function of Operating Time.

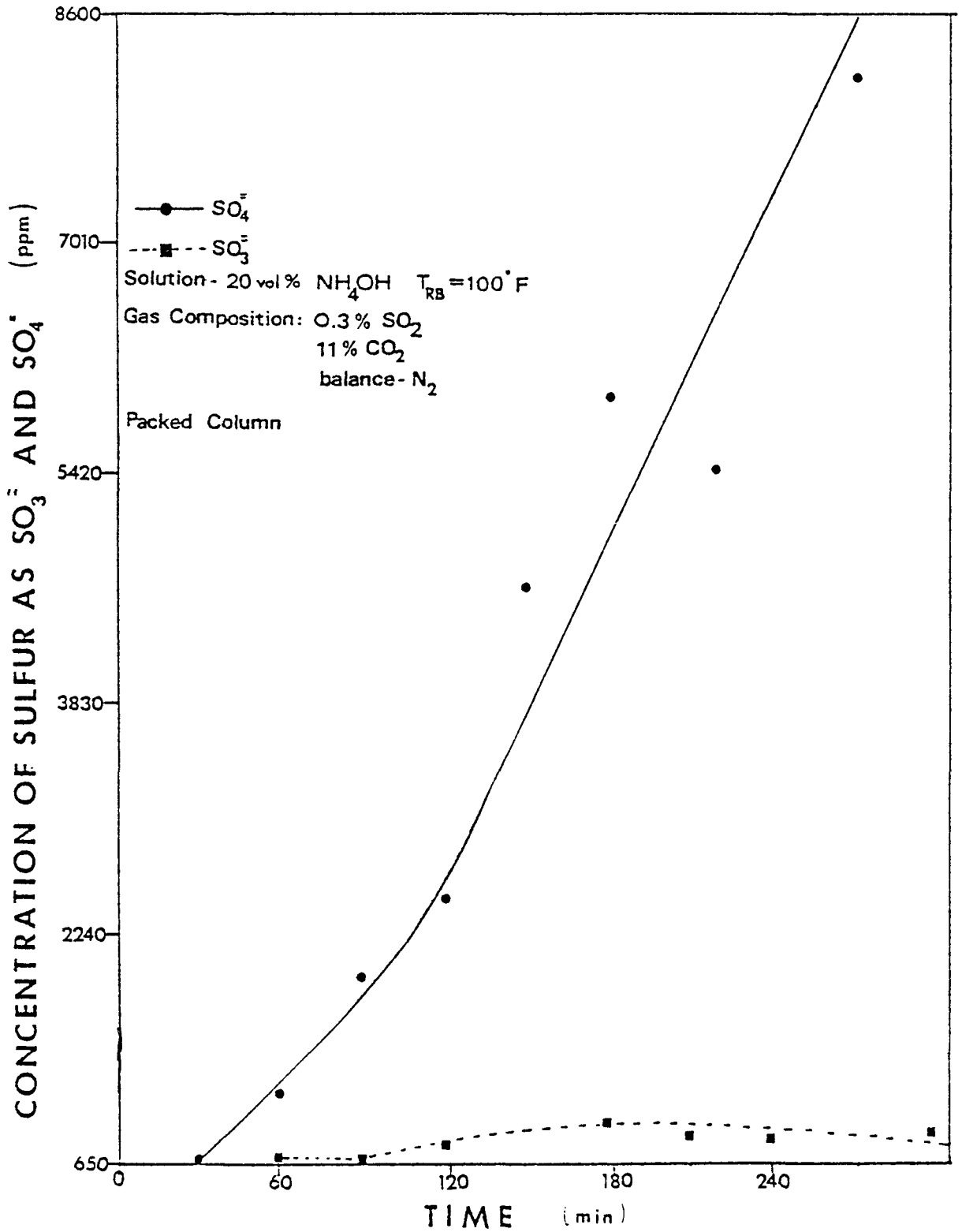


Figure 13. Concentration of Sulfur as SO_3^- and SO_4^- as a Function of Operating Time for Ammonium Hydroxide Solution.

d.) Corrosion Tests

Results of the corrosion tests for MEA and NH_4OH solutions are shown in Table 3. MEA and NH_4OH solutions were shown to be corrosive to copper. Both solutions became blue after short periods of exposure to copper. Atomic absorption (AA) showed the presence of 50 to 60 ppm of Cu in each of the solutions. MEA was inert to the nichrome but NH_4OH solutions turned green in the presence of nichrome. The AA denoted 160 to 170 ppm nickel in the NH_4OH sample taken after 5 hours of operation. Only stainless steel was unaffected by the MEA solution. Among the following metals tested, monel, stainless steel, and carbon steel, a brown metallic layer formed on the outside of the monel and the solution contained 19 ppm of nickel. The solution contacted with carbon steel contained 16 ppm of iron.

Table 3

Corrosion Tests

<u>Solution</u>		
MEA	Copper	Copper was oxidized by the MEA. 50 ppm of copper ions were noted in the solution.
MEA	Monel (Copper-Nickel)	Bronze colored coating formed on the surface of the metal. Produced 19 ppm nickel.
MEA	Stainless Steel	No deliterious effects.
MEA	Carbon Steel	Produced 16 ppm iron.
MEA	80% Nickel-20% Chromium	No deliterious effects.
NH_4OH	Copper	Copper was oxidized. Produced 60 ppm copper metal ions in solution.
NH_4OH	80% Nickel-20% Chromium	Nickel oxidized. 170 ppm nickel metal ions found in sample.

e.) NO_x Gases

No NO_x gases were obtained for experiments with nitrogen in the fuel supply. However, no detectable quantities of NO_x were found in the exhaust gas. This occurs because the flame was at too low a temperature to convert the organic nitrogen into NO_x, but the material is left as cyanides and organic nitrogen. As a result, no nitrogen compounds were found in the liquid samples.

B. Gas Absorption Coefficients

Preliminary K_G values were measured in the sieve tray column using only one tray. Temperatures of the system varied from 40-60°C. No variation of K_G with temperature was able to be verified. The values for various conditions of absorbing MEA and activated potassium carbonate solutions are presented in Table 4. Table 5 presents relative absorption for a variety of solutions as obtained in the laboratory flasks. Figure 14 presents the typical relative absorption as a function of CO₂ saturation. Figures 15-17 present the relative absorption coefficient, as defined by Eq. 7, as a function of CO₂ saturation. Note that as the absorption of CO₂ increases, the absorption coefficient drops slightly, indicating chemical reaction control. Note that the addition of EAE is slightly more effective than MEA as an activator, in accordance with the prediction of Danckwertz and Shrier.⁽¹⁷⁾

C. Discussion of Formation of Solution Impurities

a.) MEA Solutions

Figure 7 shows that in a packed column operating at relatively high reboiler temperatures and in an inert atmosphere of N₂, the SO₂ is absorbed mostly in the form of SO₃²⁻. The predominance of SO₃²⁻ is probably due to the absence of any large quantities of oxygen which promote SO₄²⁻ formation.⁽¹⁸⁾ Note that the sulfates do form and the level continues to increase with time. A leveling trend is noted in the concentration of SO₃²⁻ as a function of time. This is most likely because the reboilers are operating at temperatures high enough to facilitate thermal stripping of the SO₃²⁻. This stripping converts the SO₃²⁻ to SO₂ gas, which exits through the condensor. Figure 7 also demonstrates the effect of reboiler temperature upon SO₃²⁻ and SO₄²⁻ formations. At a reboiler temperature of 205°F, it appears that more SO₂ is absorbed in the

Table 4

Initial Gas Absorption Coefficients* for Various Solutions

<u>Solution Condition</u> [†]	<u>K_G ($\frac{\text{lb mole}}{\text{ft}^2\text{-sec}}$), avg. value</u>	<u>pH</u>	<u>Comments</u>
4 wt % MEA - Unfouled	$10 \times 10^{-5} \pm 25\%$		
20% MEA - Unfouled	$48 \times 10^{-5} \pm 50\%$	10.8	
20% MEA - Fouled (35% SO_4^-) (22% SO_3^-)	$16 \times 10^{-5} \pm 15\%$	9.5	Added char did not change K_G value.
18% K_2CO_3 - 1% MEA	$7 \times 10^{-5} \pm 10\%$	10.8	
14% K_2CO_3 - 4.5% K_2SO_4 - 0.9% MEA	$4.5 \times 10^{-5} \pm 10\%$	10.8	
9% K_2CO_3 - 7% K_2SO_4 - 0.9% MEA	$2 \times 10^{-5} \pm 10\%$	10.8	
18% K_2CO_3 - 4.5% K_2SO_4 - 0.9% MEA	$5.4 \times 10^{-5} \pm 15\%$	10.8	

T = 40-60°C

* V = 0.48 ft³/min

† System continually regenerated to maintain (mole CO₂ absorbed)/(mole Active Species) ≈ 0.

Table 5

Relative Gas Absorption for Various Solutions

$$\text{R.G.A. (Relative value)} = \frac{(P_{\text{CO}_2})_{\text{ln mean}}}{\text{Rate Absorption}}$$

<u>Solution</u>	<u>RGA Initial</u>	<u>RGA (Mole CO₂/Mole Active Species = 0.5)</u>
20 wt% MEA	7.0	1.1
14.2% K ₂ CO ₃ , 0.9% EAE	4.0	0.9
20 wt% MEA (16% SO ₄ ⁼ fouled)	2.7	Does not absorb. Capacity for CO ₂ exhausted at 0.25 mole CO ₂ /mole MEA
15% K ₂ CO ₃ , 0.9% EAE (20% SO ₄ ⁼ fouled)	3.5	0.45
15% K ₂ CO ₃ , 0.87% MEA	2.1	0.7
11.5% K ₂ CO ₃ , 0.9% EAE	2.7	0.4

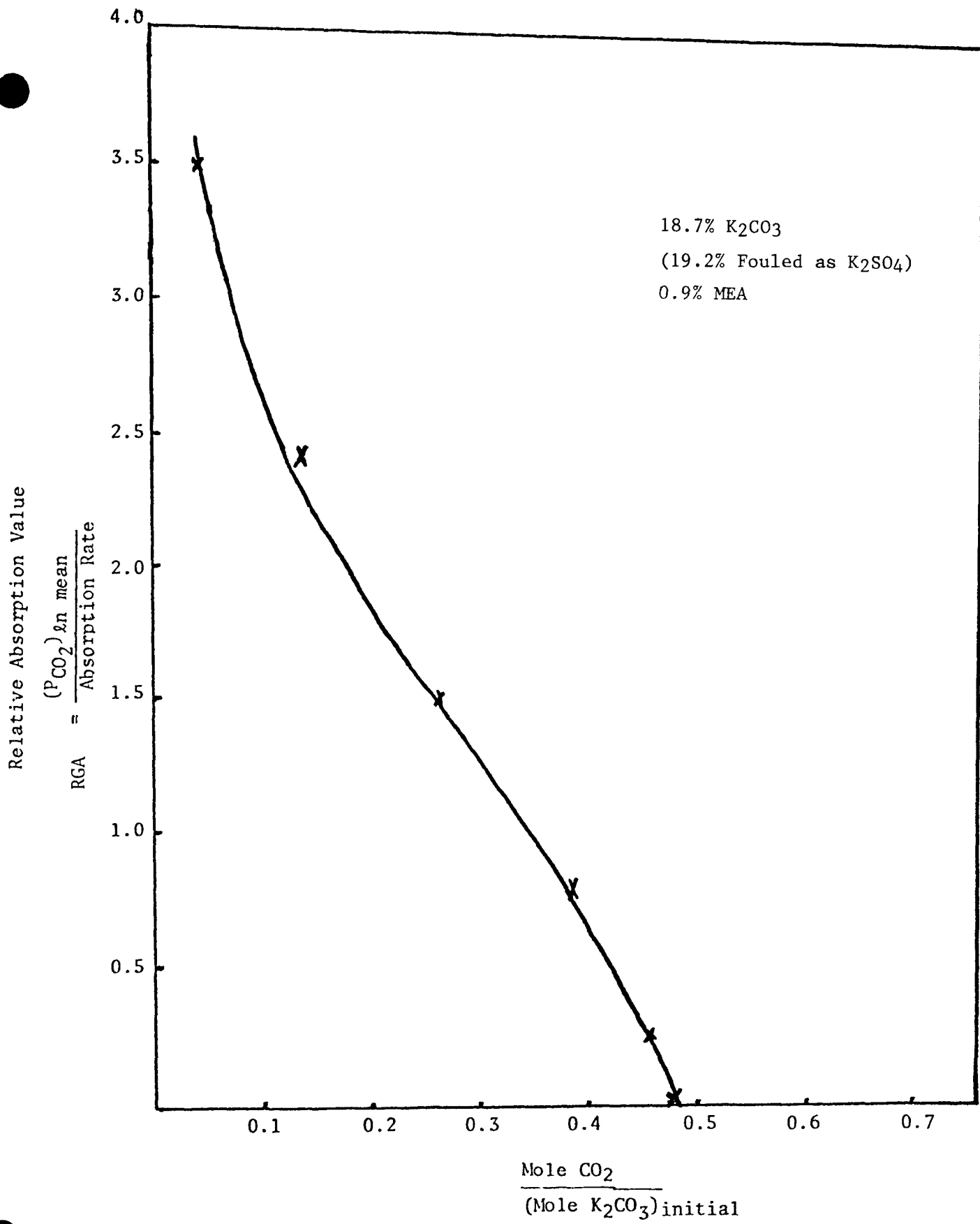
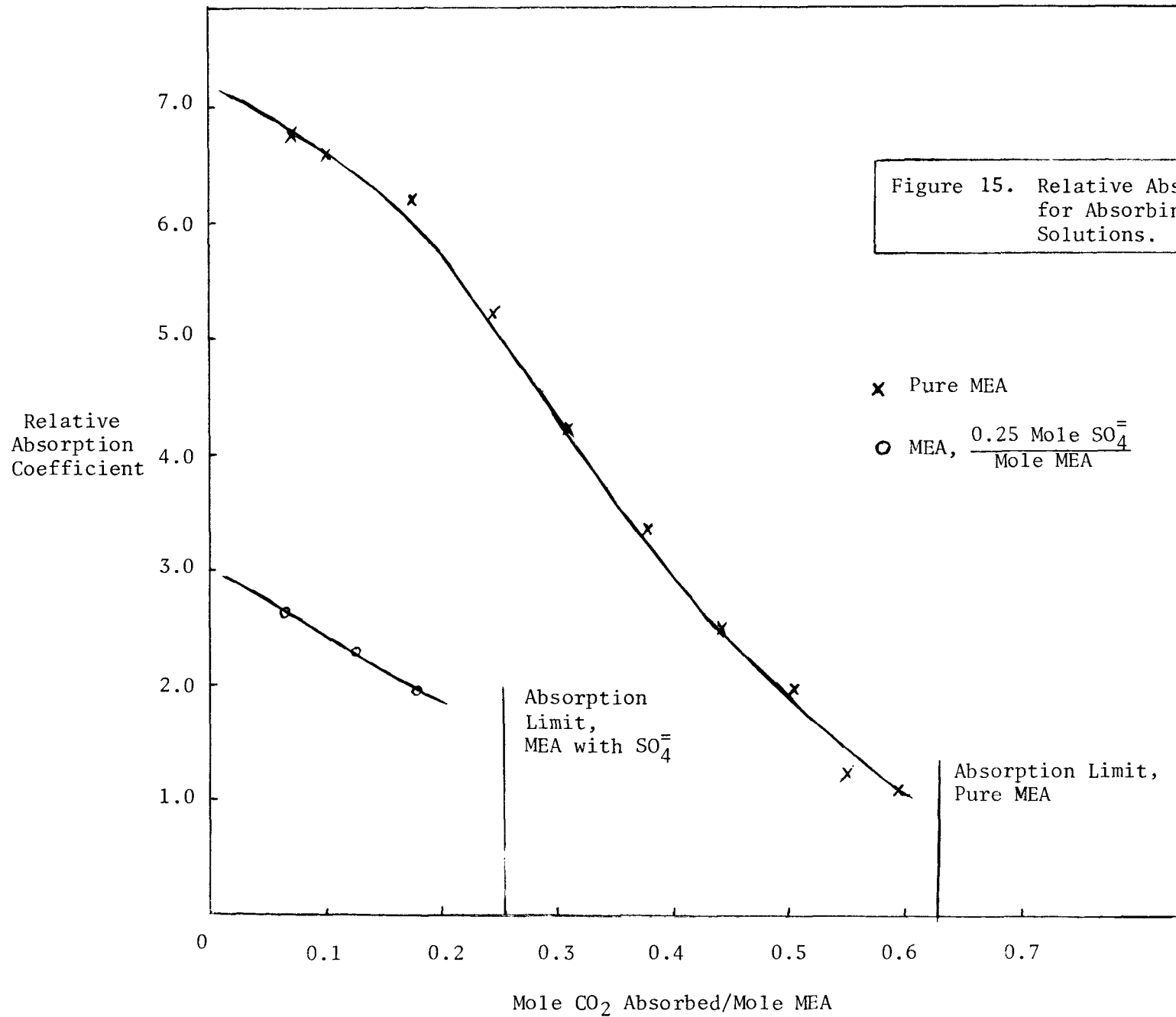
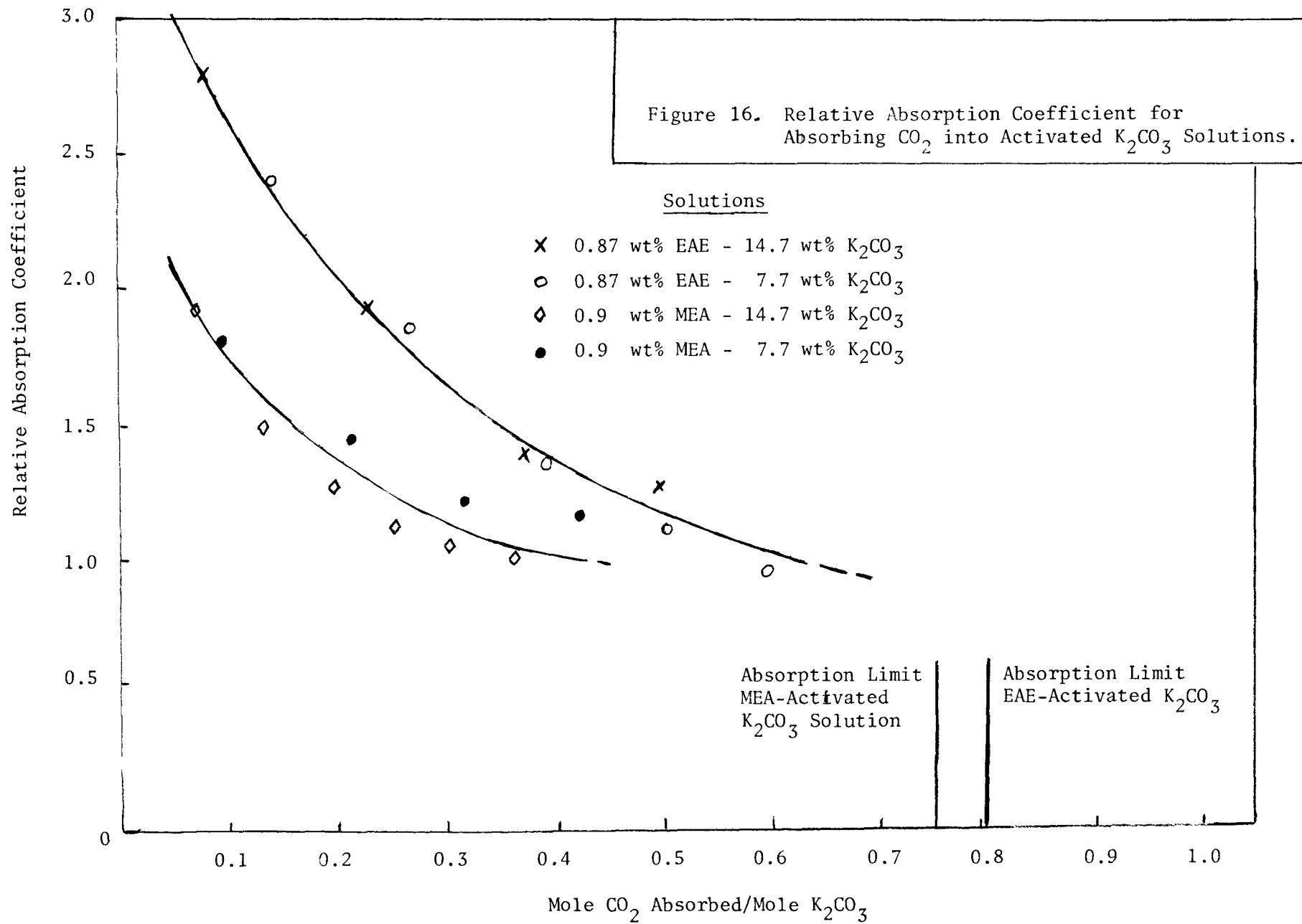
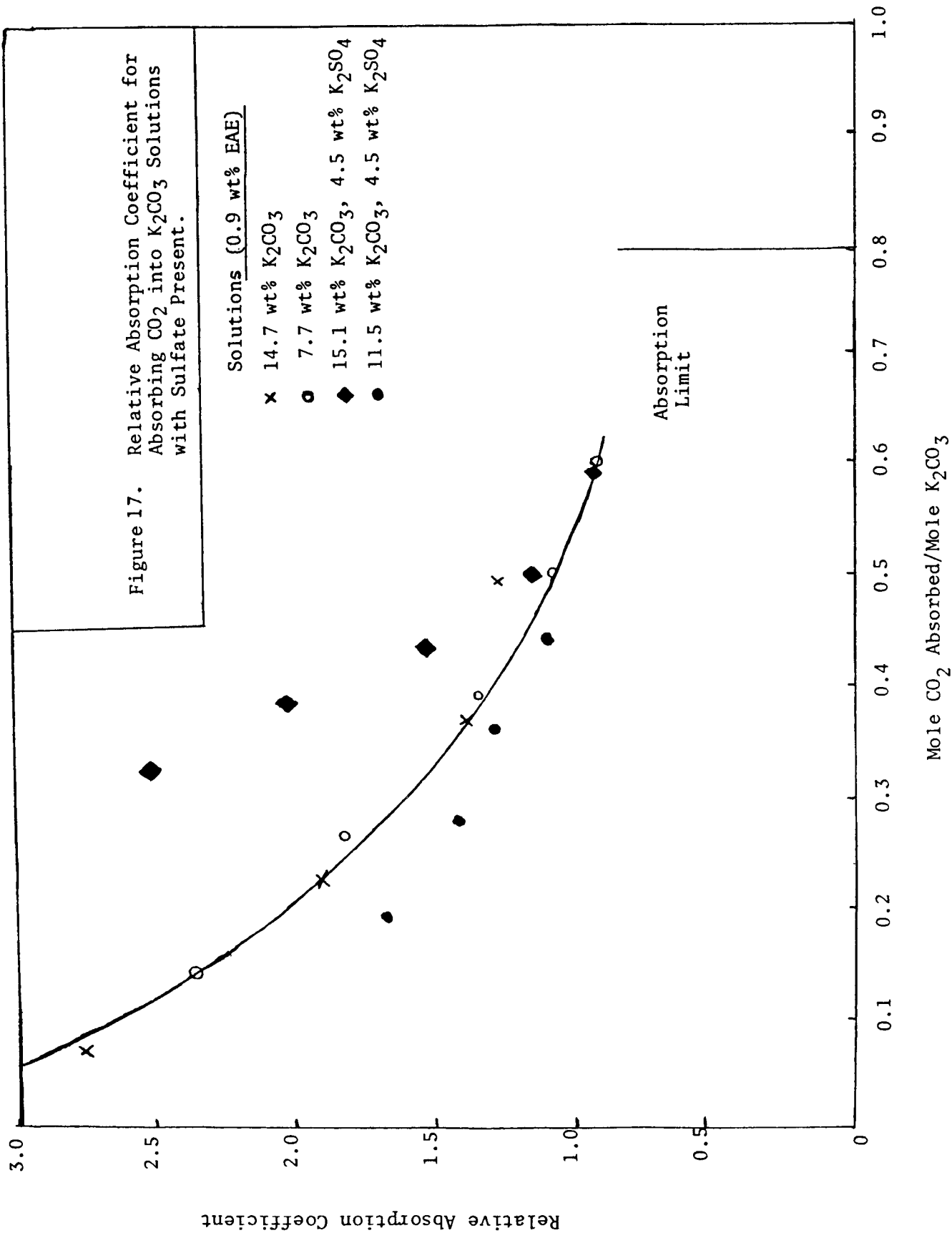


Figure 14. Relative Absorption of CO₂ in K₂CO₃ Solution as a Function of Loading. (Typical Curve).







form of SO_3^- and SO_4^- than at a temperature of 160°F. The difference in concentrations of SO_3^- and SO_4^- between the two runs may be due to a difference in the volume of MEA solution in the system. At the higher reboiler temperatures, the concentration of SO_4^- formed appears to be considerably greater than at the lower temperature, especially as the time of operation increases. A possible explanation of this phenomenon is that the SO_3^- is oxidized to SO_4^- more rapidly at higher temperatures. This observation is in agreement with Slack who said high solution temperatures tend to increase SO_4^- formation.⁽¹⁸⁾ The formation of SO_4^- in the presence of minimal oxygen appears due to the MEA present. MEA has been reported to cause oxidation under inert atmospheres.⁽¹⁹⁾

A comparison of Figures 9 and 10 denotes the predominance of SO_4^- formation over SO_3^- formation in a sieve tray column operated at lower reboiler temperatures. This can be explained by the excessive quantity of air present in the system and the oxydation-promoting MEA. The oxygen in the air provides an oxidative atmosphere which converts SO_3^- to SO_4^- . Figure 10 shows no leveling in the amount of SO_3^- produced. This is probably because the reboiler is not operating at a high enough temperature to strip all the SO_3^- that is being absorbed and thus the amount present in the solution continues to rise.

Gas chromatograms showed that all the SO_2 and ≥ 95 percent of the CO_2 in the flue gas was absorbed by the MEA solution. A material balance around the system, using inlet and exit gas flow rates and concentrations, and concentrations of SO_3^- and SO_4^- in the liquid, showed ≥ 96 percent of the SO_2 absorbed was in the form of SO_3^- and SO_4^- . Wet chemistry tests showed that absorbed SO_2 appears in one other chemical form, trithionate (S_3O_6^-).

Figure 11 shows the change in solution pH as a function of the amount of the sulfur present as SO_3^- and SO_4^- . It should be noted here that the solution pH is a function of the amount of CO_2 absorbed, as well as the amount of SO_2 absorbed. Table 6 shows how the pH of 20% solution of MEA falls as the amount of CO_2 absorbed increases. The more SO_2 and CO_2 absorbed, the lower the pH of the solution becomes. When the solution pH drops below 10.25, absorbed CO_2 is predominantly found in the HCO_3^- form. Note that at the lower pH, one mole of MEA can absorb one mole CO_2 , while 2 moles MEA for every one mole CO_2 is required when the absorbed CO_2 is in the form of CO_3^- .

Figure 12 demonstrates the effect of operating time on the percentage of MEA tied up as a salt with SO_3^- and SO_4^- . The trend is toward increased amounts of MEA becoming chemically bonded with sulfur compounds. This figure shows that approximately 57% of the MEA is chemically associated with the sulfur compounds after 22 hours of operation. The gas chromatographs showed all the SO_2 absorbed and 95 to 98 percent of the CO_2 absorbed. Thus, the SO_2 is absorbed preferentially to the CO_2 .

The mass spectrum showed the presence of MEA degradation products. This means that the MEA is not only being nonregenerably associated with sulfur groups, but is also being irreversibly converted to inactive forms by thermal oxidative breakdown. Eventually it is probably that all the MEA absorptive power will be lost due to degradation and to the formation of compounds with non-regenerable sulfur groups. As a result, no further removal of CO_2 or SO_2 would be expected.

MEA solutions are still a potential medium for simultaneous CO_2 and SO_2 removal if an inexpensive method for removal of non-regenerable sulfur compounds can be found which reclaims the amine. An ion exchange is a likely method for removing these compounds.

Table 6

pH of 20% MEA Solution for Various Amounts of Absorbed CO_2

<u>Amount of CO_2</u>	<u>Solution pH</u>
0.2 mole CO_2 /mole MEA	10.0
0.4 mole CO_2 /mole MEA	9.25
0.6 mole CO_2 /mole MEA	8.1

Solution temperature = 110°F

b.) Ammonical Solutions

The ammonia solutions were tested in a packed column at low solution temperatures and in an atmosphere of N_2 . These solutions performed as well as those of MEA in CO_2 and SO_2 removal. Figure 13 shows that the SO_2 absorbed was found mostly in the form of SO_4^- . Sulfite levels were considerably lower

than those of the SO_4^- . This is probably because most of the SO_2 absorbed is oxidated immediately. The leveling in the concentration of SO_3^- is probably caused by small amounts of SO_3^- being thermally regenerated. The SO_4^- was formed in large quantities even though the solution was subjected to low temperatures and in a mostly inert atmosphere. Formation of SO_4^- was probably enhanced by the presence of small quantities of air inherent in the system as well as the catalytic action of NH_3 .⁽²⁰⁾ The quantity of sulfate formed would probably be even larger in actual operations because the flue gas would contain a considerable quantity of air and there would be higher reboiler temperatures. Both of these situations promote SO_4^- formation.⁽¹⁸⁾ Ammonium sulfate can not be regenerated by the reboiler and thus permanently fouls the solution. The ammonium sulfate can be precipitated out as a solid and sold to fertilizer manufacturers. The economics of ammonical solutions depend on the cost of the ammonium hydroxide solution and the expense of preparing the sulfate for marketing versus the selling price and market for ammonium sulfate. The market is presently overloaded with ammonium sulfate and it is not economical to produce large amounts of this product.

c.) MEA Activated K_2CO_3 Solutions

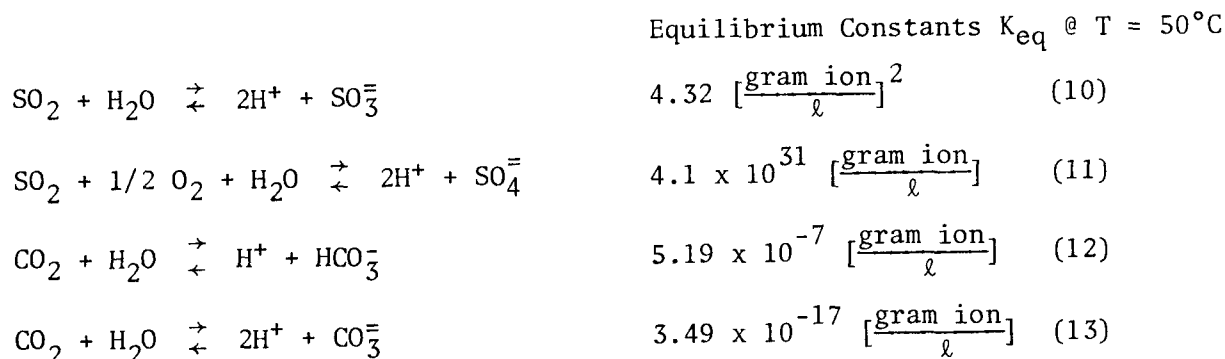
Gas chromatographs showed that all the SO_2 and ≥ 96 percent of the CO_2 in the simulated flue gas was absorbed by the activated K_2CO_3 solution. Figures 9 and 10 show the increasing amounts of SO_3^- and SO_4^- that were formed. Material balances showed that $\geq 95\%$ of the SO_2 absorbed was in the form of SO_3^- and SO_4^- . Here, as in the MEA solutions, more SO_4^- was formed than SO_3^- . This is due to the oxidizing atmosphere in the system and the presence of MEA which promotes oxidation.⁽¹⁹⁾ As with the MEA in the sieve tray column, there was no leveling in the amount of SO_3^- present. Apparently, the reboiler was not operating at a temperature high enough to thermally remove all the SO_3^- formed.

Figure 8 shows no evidence of a leveling trend in the amount of sulfur compounds absorbed. A leveling trend might occur for this particular solution because of the minimal quantity of MEA available to combine with the sulfur groups. Only one percent of the solution is MEA. Calculations show that more than 100% of the MEA present in the activated carbonate solution would be required to form compounds with all the SO_3^- and SO_4^- present after five hours of operation, if the sulfur groups preferentially formed compounds with the amines.

In fact, the SO_3^- and SO_4^- replace CO_3^- and HCO_3^- , electrically balancing the potassium ions (K^+), as well as forming compounds with the MEA. The replacement of CO_3^- and HCO_3^- by SO_3^- and SO_4^- can be explained by the concept of electroneutrality, when the number of positive charges is equal to the number of negative charges. Equation 9 represents an abbreviated form of the equation of electroneutrality for MEA-activated potassium carbonate solutions, initially. Because of the pH, there are minimal quantities of hydrogen ions and MEA ions and they are not listed in Equation 9.

$$[\text{CO}_3^-] = 1/2 [\text{K}^+] \quad (9)$$

Before any acid gases are absorbed, the concentration of K^+ equals twice the concentration of CO_3^- . The absorbed SO_2 reacts to form SO_3^- and SO_4^- , while the absorbed CO_2 reacts with the CO_3^- present to form HCO_3^- . Equations 10 through 13 represent the reactions for absorption and desorption of CO_2 and SO_2 .



Equation 14 represents the equation of electroneutrality for the carbonate solution after the acid gases have been absorbed.

$$1/2[\text{K}^+] = [\text{CO}_3^-] + 1/2[\text{HCO}_3^-] + [\text{SO}_3^-] + [\text{SO}_4^-] \quad (14)$$

The concentration of the positively charged potassium ion is always constant for a given solution. To maintain electroneutrality, some of the negative ions present in the solution must be removed to allow for the production of other negative ions by Equations 10-13. An equilibrium between the negative

ions present must be achieved. The small equilibrium constants for Equations 12 and 13 show that at equilibrium the concentration of HCO_3^- and CO_3^{2-} are much lower than the concentration of SO_3^{2-} and SO_4^{2-} . The equilibrium constant for Equation 10 is very large and once the SO_4^{2-} is formed it remains in solution. The SO_3^{2-} will also be removed, but not until the quantity of CO_3^{2-} and HCO_3^- reaches a minimum. Eventually, the solution will predominantly contain nonregenerable SO_4^{2-} which results in a solution that has a minimal capacity for SO_2 and CO_2 absorption.

Amine-activated K_2CO_3 solutions do offer a possible means for simultaneous removal of CO_2 and SO_2 from stack gas. Because the amine is known to promote oxidation, it is suggested that the carbonate solution might be activated with another compound such as arsenite.

d.) Corrosion Studies

Aqueous solutions of MEA and ammonia were both shown to be highly corrosive to copper. This is in agreement with corrosion properties listed in Perry's Chemical Engineering Handbook which states that copper is unsuitable for use with alkaline solutions such as NH_4OH and amines.⁽²¹⁾ The corrosion of monel by MEA also coincides with Perry's listing that considers monel to be a poor choice for use with amines. Corrosion of the carbon steel by MEA is minimal but still evident. It is stated that mild steel is good for use with amines. Stainless steel is considered to be an excellent choice for use with amines and the results obtained by the study agree with this. Ammonium hydroxide solutions were highly corrosive to nichrome, an 80% nickel-20% chromium alloy.

e.) Regeneration Gases

Measurement of non-condensable gases indicates ≤ 100 ppm N_2 (or O_2) in the regenerated CO_2 . Calculations for SO_2 released at reboiler temperatures also indicate a small quantity maximum (≤ 200 ppm). Thus these impurities do not appear to be a major problem for EOR.

D. Discussion of Absorption Coefficients

The data in Table 4 and Figures 15-17 indicate that K_G in MEA solution for zero mole CO_2 /mole MEA is considerably greater than K_G in activated K_2CO_3 solution at zero mole CO_2 /mole K_2CO_3 . This agrees with literature findings.⁽⁷⁾ As the MEA becomes fouled, the absorption coefficient decreases appreciably (Table 5 and Figures 15-17). This is also true for activated- K_2CO_3 solutions, although the decrease in K_G and relative absorption coefficient (R.A.C.) is less.

Note that the R.A.C. data given in Figures 15-17 are based on Equation 8. This equation requires knowledge of the equilibrium vapor pressure of CO_2 over sulfite/sulfate fouled solutions. The approximation is made that the presence of sulfite/sulfate affects the solution with respect to VP_{CO_2} the same as the presence of H_2S . The consistency of the R.A.C. values indicate that this is a reasonable approximation, even though some minor variations are expected because of the difference in strength of the acids H_2S , H_2SO_3 , H_2SO_4 . Calculations of carbonate/bicarbonate ion-activity coefficients indicated little change in activity with either H_2S or SO_2 , further verifying the hypothesis.⁽²²⁾

As CO_2 is absorbed by the solutions, the R.A.C. decreases. Note that the R.A.C. is similar for fouled, loaded MEA solution and for fouled, loaded K_2CO_3 solution. This indicates negligible advantage to MEA absorption ability at reasonable loadings of the solutions. In addition, the total moles of CO_2 that can be absorbed by the fouled 20% MEA is less than or equal to the moles that can be absorbed by fouled 20-30% K_2CO_3 solution. This occurs because each mole of SO_4^{2-} ties up two moles of MEA, but only one mole of K_2CO_3 is tied up as K_2SO_4 .

In Figures 16 and 17, it is seen that EAE is a better activator for K_2CO_3 solution than is MEA. The R.A.C. are up to a factor of two larger; this is similar to literature predictions at low P_{CO_2} .⁽¹⁷⁾ The enhancement is less than found previously at low pressures for pure CO_2 . Apparently the presence of nitrogen and oxygen produces a gas film retarding CO_2 absorption. But the enhancement also indicates that chemical reaction control of absorption is still dominant. The presence of EAE helps to react with CO_2 near the gas-liquid interface, then transport the $\text{CO}_3^{2-}/\text{HCO}_3^-$ into the bulk liquid more rapidly than ordinary diffusion of the ionic species. As the CO_2 loading increases, the enhancement of EAE over MEA activation decreases as the MEA

and EAE are themselves chemically bound with the carbon dioxide.

Note that the R.A.C. for K_2CO_3 solutions fouled by SO_3^-/SO_4^- is at least as large as for pure K_2CO_3 solutions if we only consider the remaining $K_2CO_3/KHCO_3$ species. Differences (Figure 17) can be attributed to an ionic strength phenomenon, which at high concentrations of solution tends to maintain the K_G even with sulfate fouling. This fact lends an easy method of analysis for absorption coefficients of activated potassium carbonate, based on published data.

In summary, the absorption ability and capacity of EAE-activated K_2CO_3 solutions is as high as any solution at normal operative CO_2 loadings when extracting CO_2 from atmospheric flue gas.

IV. ECONOMIC EVALUATION

A. Design Procedure

It was ascertained to examine the costs of absorbing CO_2 from flue gas in MEA and K_2CO_3 aqueous solutions, which are the two most promising solutions for absorption from atmospheric gases. A 1% S coal power-plant flue gas was chosen as an available gas. (A similar sulfur-oxide gas level would be obtained if a high-sulfur fuel were used and then scrubbed.) It was assumed that the flue gas to the system represented the equivalent flow from a 200 MW unit, but that the system was attached to a 1000 MW plant. The cooled gas from the absorption tower could then be recombined with either the remaining untapped flue gas or the flue gas from a package boiler producing regeneration steam in order to provide effluent plume gas rise.

a.) MEA Process

A 30 wt%-MEA system was chosen to obtain high capacity solutions, as SO_2 is permanently absorbed as sulfite and then amine-catalyzed oxidized to sulfate ($\approx 50\%$) which reduces extensively the capacity as compared to original MEA solution. A 30% contaminated MEA (0.15 mole sulfite/mole MEA) was chosen as a sulfur loading tolerable for absorption, but high enough to allow ready slip-stream purification. Absorption temperature was set at 120-130°F to reduce MEA losses to the flue gas and allow for high enough equilibrium CO_2 vapor pressure for absorption. Lean loadings of 0.15 mole CO_2 /mole MEA and rich loadings of 0.25 mole CO_2 /mole MEA were set by vapor pressure needs to keep steam-stripping requirements low and solution capacity at entering flue gas concentrations. A basic flow scheme for MEA processes was thus chosen,⁽⁷⁾ but modified for purification and application to flue gas. (Figure 18).

The absorption tower is packed with 1 inch ceramic saddles; a water wash absorber is utilized to reabsorb vaporized MEA in the flue gas; the flue gas must be cooled to near absorption temperature for adequate control. The tower was designed by standard packed-tower design, with 0.5 in/ft packing pressure drop. The overall absorption coefficient, $K_G \cdot a$, for fouled MEA solution at the design CO_2 loadings was estimated at 6.5 lb moles/hr-ft³-atm by literature correlation^(7,22) by assuming H_2SO_3 acts similar to H_2S , and from estimates from the present results. Sixty percent absorption of the flue gas stream was to be absorbed, thus keeping a high CO_2 vapor driving force.

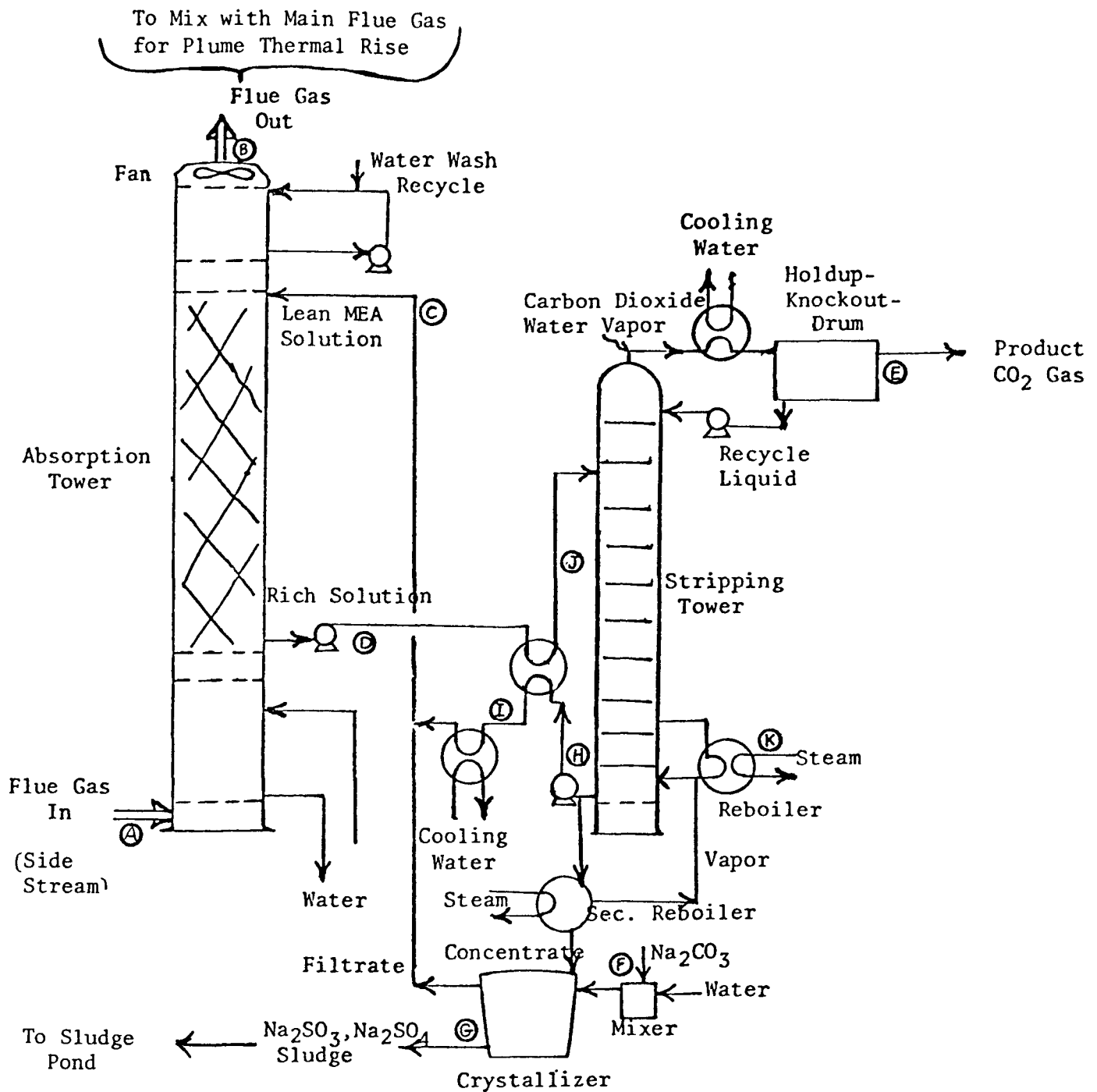


Figure 18. MEA Flowsheet. Schematic diagram of MEA system for absorption of CO₂ from flue gas. See attached list for conditions and flows.

Material Flow - Figure 18

<u>Stream</u>	<u>Flow Rate</u>	<u>Temp.</u>	<u>Comment</u>
A Flue Gas	25,380,000 SCFH 16.5% CO ₂ 64.6% N ₂ 5.6% O ₂ 13.3% H ₂ O 0.08% SO ₂	T = 300°F	Gas Pressures ≈ 1 atm Roughly 20% of the maximum flow of 1000 MW station.
B Flue Gas	21,650,000 SCFH 7.65% CO ₂ 75.7 % N ₂ 6.6 % O ₂ 10.0 % H ₂ O 0.02% SO ₂ 0.02% MEA	T = 130°F	
C MEA Solution	10,600,000 lb/hr 30 wt% MEA 0.15 mole CO ₂ /mole MEA 0.15 mole SO ₂ /mole MEA	T = 125°F	
D MEA Solution	10,940,000 lb/hr 29 wt% MEA 0.275 mole CO ₂ /mole MEA 0.15+ mole SO ₂ /mole MEA	T = 135°F	280,000#CO ₂ /hr absorbed
E Carbon Dioxide	302,000 lb/hr 92.5 % CO ₂ 7.5 % H ₂ O < 200 ppm vol SO ₂ , < 100 ppm N ₂	T = 105°F	P = 15 psia
F Sodium Carbonate	5,160 lb/hr	T = ambient	
G Sodium Sulfate Sludge	10,000 lb/hr Sodium Salts 60,000 lb/hr water	T = 220°F	
H MEA Solution	10,600,000 lb/hr (Conc. as in C)	T = 215°F	
I MEA Solution	10,600,000 lb/hr (Conc. as in C)	T = 145°F	
J MEA Solution	10,900,000 lb/hr (Conc. as in D)	T = 200°F	
K Steam	535,000 lb/hr	T = 265°F	

The stripper was assumed to operate at a reboiler temperature of 215°F. This provided a P_{CO_2} of 6 psia, $P_{\text{H}_2\text{O}} \approx 8.7$ psia for the rich solution, and $P_{\text{CO}_2} \approx 0.2$ psi for the lean solution.⁽⁷⁾ With λ_{CO_2} in this solution = 825 Btu/lb, vaporization of CO_2 , H_2O , and heating the absorption solution to stripper temperature, the estimated steam rate is 84 lb steam/mole CO_2 . This is comparable to the rates reported for operating installations of 74-140 lb steam/mole acid gas. The tower was assumed to be 15 trays for stripping with 6 trays for water wash to reabsorb MEA, as ascertained by experience.⁽⁷⁾ The diameter was assumed limited by vapor velocity to avoid entrainment. The reboiler and column were set to be stainless steel, as at the higher temperatures, high MEA concentrations, and free CO_2 gas obtained at the reboiler, high corrosion rates have been reported.

The purification system calls for a secondary reboiler to concentrate the solution, the vapor being recycled to the stripper column. Sodium carbonate is then added to the liquid concentrate in the crystallizer, and Na_2SO_3 and Na_2SO_4 are precipitated (see Table 7).

Table 7
Sodium and Potassium Salts Solubilities in Water

Salt	T(°C)	Solubility (g/100 g H_2O)			
		0°C	35°C	60°C	100°C
K_2CO_3		105.5	115.3	126.8	155.7
KHCO_3		22.4	42.2	60.0	---
K_2SO_3		---	---	---	126.0
K_2SO_4		7.35	13.9	17.0	24.1
Na_2CO_3		7.0	40.0	---	---
NaHCO_3		6.9	11.8	16.4	---
Na_2SO_3		---	≈ 28.0	28.8	≈ 28.0
Na_2SO_4		---	≈ 45.0	45.3	42.3

A heat exchanger between the recycled lean solution and rich solution from the absorber is present to reduce heat requirements. The solution is further cooled by water before being returned to the absorber. The heat transfer coefficients for these exchangers and for the reboilers were taken as typical for aqueous systems [$U = 250 \text{ Btu/hr-ft}^2\text{-}^\circ\text{F}$]⁽²³⁾ and checked by individual coefficient calculation.

The power boiler was assumed to be modified to reduce low-pressure steam turbine use in order to utilize the least expensive steam in one analysis. In another cost analysis, separate steam generation was assumed. Pumps handling the MEA solution should be corrosion resistant.

b.) Activated-K₂CO₃ Process

A 25 wt% K₂CO₃ system was chosen to obtain maximum capacity without causing precipitation of either KHCO₃ or K₂SO₄ in the absorber or stripper. The absorber temperature was set at 120-130°F. Cooling the solution for purification causes solidification of K₂SO₄ at 10% conversion of K₂CO₃-to-K₂SO₄ & trithionates @95°F. Thus a sulfate loading of 0.1 mole K₂SO₄/mole original K₂CO₃ is desirable, but minimum sulfite is desired as it does not readily precipitate (Table 7). Thus 0.2 wt% K₂Cr₂O₇ is added as a corrosion inhibitor and oxidation agent for sulfite to sulfate. An activator is added to enhance $K_G \cdot a$. Ethylaminoethanol (EAE) is chosen as it causes an increase in K_G of 2-4 over unactivated solutions in low pressure CO₂ systems. Determined by the same restrictions as for the MEA system, the loadings were 0.1 mole CO₂/mole K₂CO₃ lean and 0.67 mole CO₂/mole K₂CO₃ rich. Under these conditions it is estimated $K_G \cdot a)_{\text{MEA}} \approx K_G \cdot a)_{\text{K}_2\text{CO}_3 \text{ activated}}$. Thus, the same $K_G \cdot a = 6.5 \text{ lb mole/ft}^3 \text{ hr atm}$ is used as in the previous alternative for the packed-bed absorber. The basic flow scheme is similar to the MEA system, but with a different unit for purification of the contaminated solution (Figure 19).

The absorption tower is similar to the MEA system unit, except that a water wash is not required as EAE has a very small vapor pressure.

The stripper unit operates at 230°F, where $P_{\text{CO}_2} = 10 \text{ psi}$, $P_{\text{H}_2\text{O}} = 15 \text{ psi}$ for the rich solution. The unit has 15 trays for stripping, 1 water-wash tray. The corrosion should be reduced, so only the reboiler is made of stainless steel. With $\Delta H_{\text{CO}_2} = 263 \text{ Btu/lb CO}_2$, the stripper steam requirements for vaporization and solution heating are 58 lb steam/lb mole CO₂.

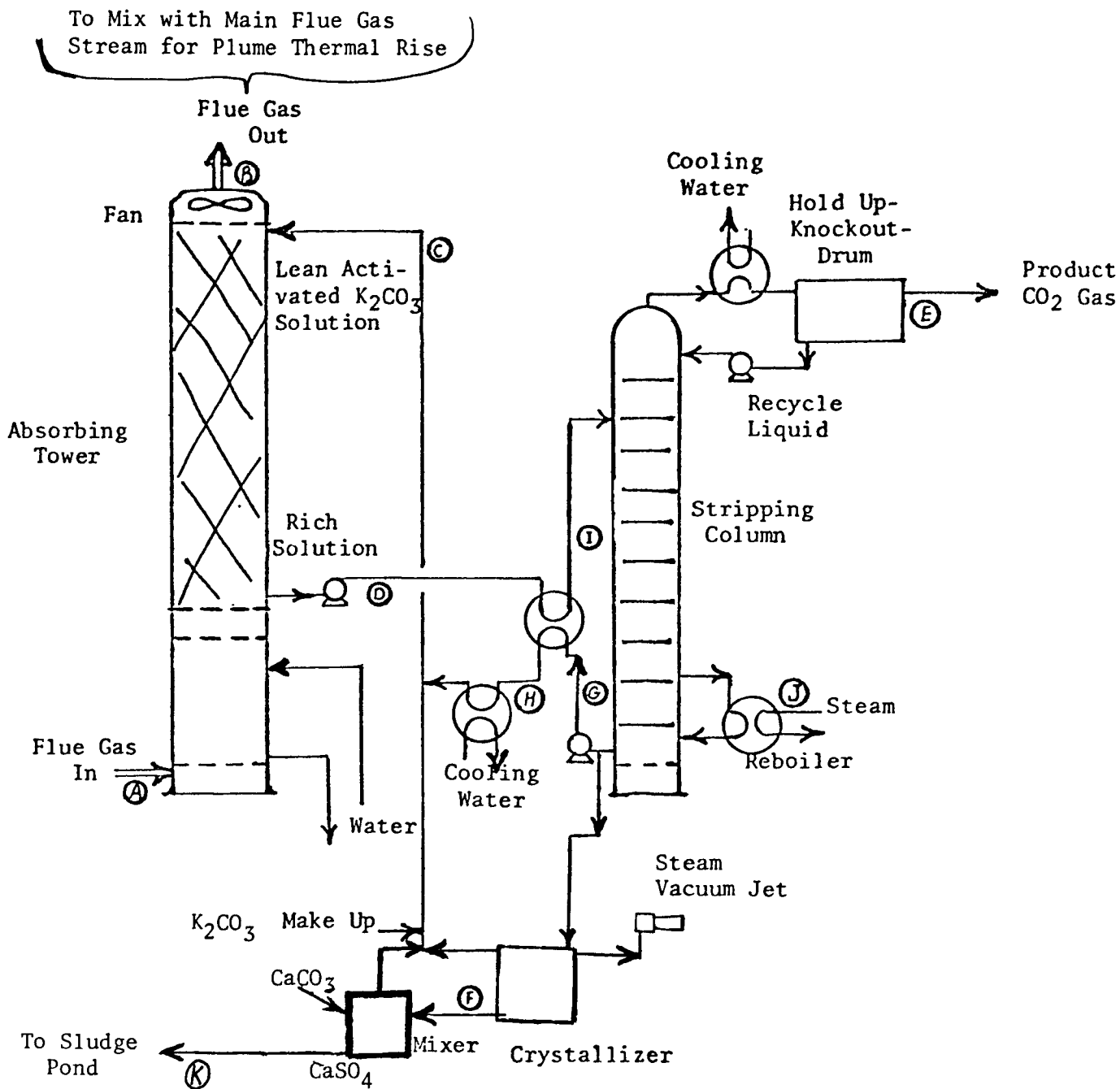


Figure 19. K_2CO_3 Flowsheet. Schematic diagram of activated- K_2CO_3 system for absorption of CO_2 from flue gas. See attached list for conditions and flows.

Material Flows - Figure 19

<u>Stream</u>	<u>Flow Rate</u>	<u>Temp.</u>	<u>Comment</u>
A Flue Gas	25,380,000 SCFH 16.5 % CO ₂ 64.6 % N ₂ 5.6 % O ₂ 13.3 % H ₂ O 0.08% SO ₂	T = 300°F	P = 1 atm.
B Flue Gas	21,650,000 SCFM 7.7 % CO ₂ 75.7 % N ₂ 6.6 % O ₂ 10.0 % H ₂ O 0.02% SO ₂	T = 130°F	P = 1 atm.
C K ₂ CO ₃ Solution	7,800,000 lb/hr 20.0 % K ₂ CO ₃ 1.0 % EAE 0.2 % K ₂ Cr ₂ O ₇ 3.0 % K ₂ SO ₄ (K ₂ SO ₃) 4.0 % KHCO ₃	T = 125°F	
D K ₂ CO ₃ Solution	8,140,000 lb/hr 8.0 % K ₂ CO ₃ 1.0 % EAE 0.2 % K ₂ Cr ₂ O ₇ 3.0 % K ₂ SO ₄ (K ₂ SO ₃) 20.7 % KHCO ₂	T = 134°F	280,000 lbs CO ₂ absorbed/hr
E Carbon Dioxide	295,000 lb/hr 5.0 % H ₂ O 95.0 % CO ₂ 20-200 ppm vol SO ₂ , < 100 ppm N ₂	T = 110°F	P = 25 psia
F K ₂ SO ₄	6,390 lb/hr	T = 95°F	
G K ₂ CO ₃ Solution	7,800,000 lb/hr (Conc. as in C)	T = 230°F	
H K ₂ CO ₃ Solution	7,800,000 lb/hr (Conc. as in C)	T = 145°F	
I K ₂ CO ₃ Solution	8,140,000 lb/hr (Conc. as in D)	T = 215°F	
J Steam	370,000 lb/hr	T = 280°F	
K CaSO ₄ Sludge	4,900 lb/hr (solids) 50,000 lb/hr (water)	T = 95°F	

The purification system is a K_2SO_4 crystallizer which, upon cooling the solution from 230°F to 95°F, results in a decrease in the solubility for the present system of 0.12 mole K_2SO_4 /original mole K_2CO_3 to 0.05 mole K_2SO_4 /original mole K_2CO_3 . After K_2SO_4 is precipitated, it is sent to a secondary mixer for addition of $CaCO_3$ to recover K_2CO_3 and form $CaSO_4$ sludge.

The heat exchange system in the K_2CO_3 system is similar in design and function to the MEA system. Pumps probably should have stainless steel at impellers units and other crucial units.

c.) General

The impurities, particularly sulfur compounds, that occur in absorption of CO_2 from flue gas must be removed on a continuous basis. Without purification, in about 100 hrs. the capacity of the solution would be exhausted, no CO_2 absorption would occur, and salt deposits would form throughout the system. The high MEA content in that process could be reduced in order to lessen the corrosion problems, but this would increase steam requirements. The addition of dichromate in potash solutions is not normally recommended for sulfur-containing gases, because of solution oxidation problems; however, in this instance it is desirable.

The sulfate salts collected may be further processed, sold, or discarded. The local situation will dictate the appropriate action.

The specified power boiler modification was costed to ascertain if reductions could be obtained by using exhaust steam from the turbine, rather than using an independent boiler and separate fuel. This latter could be important, as total SO_x and particulates are limited at a given power plant location. For comparison, an independent boiler system is examined, which allows easier control.

Based on data from a Bureau of Mines report,⁽¹⁰⁾ there will be some SO_2 vapor pressure in aqueous-amine solutions. Best estimates are SO_2 levels of 20 ppm from the stripper, but the levels may be as high as 200 ppm. Nitrogen oxides (primarily NO_2) should not readily absorb, so NO_x in the carbon dioxide should be minimal. This can be almost controlled to negligible levels if the flue gas comes from a fluidized-bed boiler. The SO_2 levels from the K_2CO_3 solution may be as high as that from the amine system, but should be considerably less if the sulfite is effectively oxidized.

The estimated labor is 4 operators/shift plus supervision. The system is assumed to operate 8000 hr/year.

The emphasis in this process design has been conceptual in developing the flowsheets and expected difficulties; therefore, detailed design of components has not been pursued and costs are \pm 30-40%. Further data would be needed from pilot plants or experience to more closely specify units.

B. Costs

Based on the flowsheets depicted in Figures 18 and 19, an equipment list was prepared (Table 8). Capital costs were estimated from Guthrie's estimates⁽²⁴⁾ based on this equipment list, and these costs can be found in Table 9.

The operating costs were calculated and are given in Table 10. If the power plant can be modified to draw off low pressure steam, perhaps savings can result. This can probably only be accomplished on a new power plant, as backfitting the steam draw-off pipes, absorption system, etc., is generally too expensive and difficult at most existing plants. The net increased coal use to maintain the same power output is only about 10% of that required if a separate boiler is needed.

In dealing with the solids sludge, a waste disposal and settling pond are required. The product carbon dioxide will be produced at near-atmospheric pressure, and must be compressed if it is to be used in Enhanced Oil Recovery. It is assumed that only a portion of the flue gas is diverted to these scrubbers, and mixing with the main stream will provide $> 250^{\circ}\text{F}$ gas temperature necessary for thermal rise of the effluent plumes.

Table 8
Equipment List

	<u>MEA Process</u>	<u>K₂CO₃ Process</u>
Absorption Tower	50 ft. dia. 30.5 ft. packing 8 ft. wash 8 ft. cooler contact Carbon steel	50 ft. dia. 30.5 ft. packing 2 ft. wash 8 ft. cooler contact Carbon steel
Stripping Column	19 ft. dia. 22 trays Stainless steel	19 ft. dia. 16 trays Carbon steel
Reboiler	Steam, 50 psig Kettle Stainless steel	Steam, 50 psig Kettle Stainless steel
a.) Steam from elect. plant	37,000 ft. ² heat transfer area	27,800 ft. ² heat transfer area
b.) Steam from Package Boiler	17,000 ft. ²	12,000 ft. ²
Condenser	Fixed Cooling water 80-125°F 13,000 ft. ²	Fixed Cooling water 80-125°F 8,900 ft. ²
Secondary Reboiler	Stainless steel Kettle 1000 ft. ²	
Solution Heat Exchangers	Floating heads 15°F approach ΔT 200,000 ft. ²	Floating heads 15°F approach ΔT 178,000 ft. ²
Cooling Heat Exchanger	Floating head Cooling water 80-125°F 20,000 ft. ²	Floating head Cooling water 80-125°F 16,700 ft. ²
Pumps	Stainless steel Centrifugal 850 hp-circulation to tower 500 hp-circulation to stripper 50 hp nozzle	Stainless steel Centrifugal 650 hp-circulation to tower 380 hp-circulation to stripper 50 hp nozzle

Table 8. Equipment List (cont'd)

	<u>MEA Process</u>	<u>K₂CO₃ Process</u>
Pumps (cont'd)	2 hp condenser return 180 hp cooling water circulation 2 hp Sludge pumps 2 hp water wash recycle	2 hp condenser return 125 hp cooling water circulation 2 hp Sludge pumps
Fans	Induction 25 in. H ₂ O	Induction 25 in. H ₂ O
Package Boiler, Modified Coal(12,500 Btu/lb)@80% eff.	5.4 x 10 ⁸ Btu/hr load Coal-fired 27 tons/hr	3.9 x 10 ⁸ Btu/hr load Coal-fired 20 tons/hr
Cooling Tower	6 x 10 ⁸ Btu/hr	5 x 10 ⁸ Btu/hr
Continuous Staged Crystallizer with Steam Ejector	60 tons/day	77 tons/day
Mixer, Lined for CaSO ₄ Formation		60 tons/day

Table 9

Capital Costs⁽²³⁾ of MEA and K₂CO₃ Processes

Costs are estimates of installed equipment with instrumentation. Option (a) considers a new power plant modified to allow low pressure steam (25 psig) to drive regeneration. Option (b) assumes package boiler for regeneration steam.

Item	Cost (Dec. 1979 Dollars)		Cost	
	<u>MEA Process</u>		<u>K₂CO₃ Process</u>	
	(a)	(b)	(a)	(b)
Fixed Capital				
Absorption Tower with Packing of Water Wash and Contact	\$ 4,700,000	\$ Same	\$ 4,600,000	\$ Same
Induction Fan	100,000	Same	100,000	Same
Pumps	1,200,000	Same	850,000	Same
Stripper Tower	750,000	Same	575,000	Same
Reboiler	3,400,000	1,550,000	2,850,000	1,230,000
Condenser	300,000	Same	250,000	Same
Purifiers	1,260,000	Same	1,110,000	Same
Stream Heat Exchanger	5,500,000	Same	5,000,000	Same
Cooling Heat Exchanger	920,000	Same	820,000	Same
Boiler Modifications*/Package Boiler	17,000,000	1,550,000	17,000,000	1,200,000
Cooling Towers for Cooling Water	1,250,000	Same	975,000	Same
Capital Equipment	\$36,380,000	\$19,080,000	\$34,030,000	\$16,600,000
Indirect Capital				
Coal, Chemical Storage (30+ days)	\$ 1,300,000	\$ Same	\$ 1,200,000	\$ Same
MEA/K ₂ CO ₃ Initial Charge	700,000	Same	200,000	Same
Land (Approx. 7% Process)	1,400,000	Same	1,400,000	Same
Interest During Construction* -10%	1,950,000	1,900,000	1,700,000	1,660,000
Engineering Fees* - 5%	1,000,000	Same	1,000,000	Same
Contingency* - 15%	2,900,000	Same	2,500,000	Same
Total Capital (Rounded)	\$45,600,000	\$28,300,000	\$42,000,000	\$24,660,000

Costs taken from Guthrie, Process Plant Estimating, Evaluation and Control, Graftsman Book Co., and updated.

† Railroad/Truck loading facilities not included. Retrofitting costs for flue-gas are not included.

* Redesign of the 1000 MW plant might cost 2% of the plant cost (\$850/Kw). The interest, fees, and contingency do not include a charge for this re-design.

Table 10

Yearly Operating Costs of MEA and K₂CO₃ Processes

	Cost (Dec. 1979 Dollars)			
	MEA Process		K ₂ CO ₃ Process	
	(a)	(b)	(a)	(b)
Electric Power (3¢/Kw hr)	\$ 750,000	\$ Same	\$ 520,000	\$ Same
Coal (\$40/ton - Extra steam use in power plant)	1,190,000	---	810,000	---
Package Boiler		8,640,000	570,000	6,400,000
Water - Purification Chemicals	250,000	Same	250,000	Same
Labor (\$10/hr)	350,000	Same	350,000	Same
Overhead, Supervision (75% labor)	265,000	Same	265,000	Same
Na ₂ CO ₃ (3.4¢/lb)	1,070,000	Same	---	---
K ₂ CO ₃ (18¢/lb)	---	---	70,000	Same
CaCO ₃ (\$10/ton)	---	---	1,400,000	Same
MEA (56¢/lb) Lost to Stack	10,000	Same	---	---
Salt Discard	100,000	Same	100,000	Same
Equipment Maintenance (5%/yr)	950,000	950,000	850,000	850,000
Taxes, Insurance (3% Cap.)	1,050,000	600,000	1,000,000	500,000
ROI @ 25%	11,400,000	7,100,000	10,500,000	6,100,000
	<u>\$17,400,000</u>	<u>\$19,600,000</u>	<u>\$17,180,000</u>	<u>\$16,100,000</u>

	Cost of CO ₂ Produced @ 1 atm.			
	MEA Process		K ₂ CO ₃ Process	
	(a)	(b)	(a)	(b)
	(\$/ton CO ₂)	(\$/MSCF)	(\$/ton CO ₂)	(\$/MSCF)
a. Steam from Power Plant	\$15.50	0.95	\$15.20	0.93
b. If coal in separate boiler is needed for steam to reboiler.	\$17.50	1.07	\$14.40	0.88

NOTE: Total Production Rate = $\frac{140 \text{ tons CO}_2}{\text{hr}}$

C. Summary

Preliminary cost estimates of processes for absorbing 3000 tons/day CO₂ from a 1% S coal-combustion flue gas have been accomplished. Two alternatives were analyzed: (1) Absorption in monoethanolamine (30%) solution and (2) absorption in activated potassium-carbonate (25%) solution. These absorption media and concentrations were chosen for maximum absorption capacity without precipitation fouling and for low utility use. Each alternative was costed for steam obtained from (a) a side stream of the power plant and (b) a separate package boiler. The difference in net operating costs between (a) and (b) are small; thus the best alternative is the non-interactive system (b) of separate absorption and electrical-power generation, which reduces possible operating difficulties. Location of the flue-gas absorption system is unspecified. If associated with a power plant, 20-100% of the flue-gas from a 1000 Megawatt station is used, depending on the time of day. If the power system operates at low load, all the flue gas is used as feed; at peak power loads, only about 20% of the flue gas is required as feed. Land requirements at the station may be difficult to obtain, and retrofitting costs could be appreciable and prohibitive.

Capital charges and operating costs for carbon dioxide production at 25% ROI were \$28,300,000; \$17.50/ton CO₂ and \$24,600,000; \$14.40/ton CO₂ respectively for MEA process (1b) and activated potassium carbonate process (2b). The difference may not be significant at the $\geq 30\%$ error limits on these estimates. However, the activated potassium carbonate process is recommended due to (a) less potential corrosion, (b) less steam use, (c) faster cost reduction at low-sulfur levels in the flue gas, and (d) smaller cost increases with rising fuel prices.

The carbon dioxide produced is expected to have 20-200 ppm SO₂, some trace of NO_x, and need drying. The MEA process, when operated for extended periods, must be purified by Na₂CO₃ addition of MEA-sulfite/sulfate and amine forms such as oxazolidone and higher degradation products. The potassium carbonate process should be purified of sulfates and sulfites (through oxidation to sulfates), by crystallization of the K₂SO₄ which has a lower solubility than the other potassium salts, then treated with CaCO₃.

APPENDIX

Measurement of Bubble Sizes in Absorption Column

Photographs were taken of the gas bubbles rising through the absorption solution in the experimental apparatus at the experimental gas flow rates. The size of distribution and average size were determined by measurement of the bubbles found on the photographs. Four-eight photographs were taken at each liquid level and for each variation in the number of gas ports generating bubbles. The number of bubbles in each photograph were 10-15. Using this, the average diameter was determined both for surface-area and volume averaging by the following relations:

$$\bar{D}_{\text{surf}} = \sqrt{\Sigma (D^2)/n}$$

$$\bar{D}_{\text{vol}} = \sqrt[3]{\Sigma (D^3)/n}$$

The data is listed below in Table 11.

Table 11

Average Bubble Diameter in Absorption Column (Figure 4.)

<u>Liquid Level (in)</u>	<u>Gas Ports</u>	<u>\bar{D}_{surf} (in)</u>	<u>\bar{D}_{vol} (in)</u>
3	2	0.49	0.49
3	3	0.40	0.42
2	2	0.52	0.52
2	3	0.45	0.45

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