

CARBON DIOXIDE AND AMMONIA REMOVAL
FROM ANAEROBIC DIGESTION GAS

by

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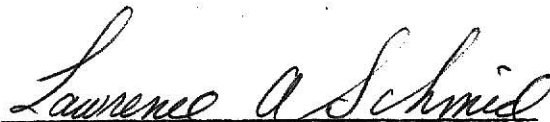
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INTRODUCTION

In a time when energy usage in the United States is increasing at a rapid rate, more efficient use of present sources and development of new energy sources is receiving much attention by researchers. One of this country's largest industries, agriculture, is also one of the biggest energy consumers. It is an absolute necessity that the farmer have sufficient fuel and chemicals to continue and possibly increase already high production efficiency. Ironically, the agriculture industry has at its disposal large quantities of one of man's oldest fuels, livestock manure. In making use of this "energy stockpile," agriculture could supply much of its own energy needs.

In the last twenty years or so, the feedlot concept of readying livestock for market has become a rather efficient method for finishing animals. The number of feedlots in the U. S. shows what a large industry it is (1)*. As an industry, its pollution problems

SIZE (no. of animals)	NO. OF LOTS
1000 - 2000	991
2000 - 4000	543
4000 - 8000	331
8000 - 16000	210
16000 - 32000	105
>32000	41

are finally coming under government regulations. Feedlots can no longer just flush their pens into the nearest watercourse. The waste from feedlots is much more concentrated and in larger quantities than has previously been encountered. The old method used on individual

*References listed by numbers in brackets.

farms of spreading raw or partially treated manure as fertilizer on croplands is not practical because it is present in such large amounts in feedlots. Trucking manure from the feedlot to distant croplands is probably only economical over a certain distance from the lot. Beyond that distance, costs would eventually outweigh income and thus, in many cases, a large amount of manure could not be disposed of in this manner. In addition, the manure is produced all year long while its distribution as fertilizer is only required a few times per year. Thus, stabilization of the manure for storage and subsequent storage facilities are needed. Both of these are problems which have not been satisfactorily solved.

A solution to the feedlot waste problem which has been tried quite extensively is the anaerobic digestion of the wastes. Anaerobic digestion will produce methane and stabilized solids. Its use as a treatment system for concentrated feedlot wastes has met with only limited success. The usual problems have been poor stabilization of the solids and low methane production (2). Swine wastes demonstrate this problem more than other types of livestock waste. Typically, daily swine waste production per 100 lbs. of animal weight is as follows (3):

Volume (gallons)	0.90
Total solids (lbs)	0.59
Volatile solids (lbs)	0.47
COD (lbs)	0.52
BOD _L (lbs)	0.20

As a partial solution to the treatment of swine feedlot wastes, it has been found that dilution of the waste concentration does allow more complete treatment. The one obvious drawback with this strategy

is the greatly increased waste quantities which, because of the larger facilities required for treatment, make the dilution technique uneconomical in most cases.

In order to treat swine wastes at the concentrated levels found in feedlot sewage without dilution, methods to remove substances toxic to the anaerobic organisms were studied. Swine wastes in particular have this toxicity problem because they contain relatively large amounts of nitrogen in the form of ammonia, which in concentrations of greater than 2000 mg/l have a very detrimental effect on the anaerobic digestion process (2). In fact, ammonia concentrations often are found to exceed 3000 mg/l in concentrated swine wastes. Because dilution generally is not a good method to reduce ammonia, the removal of ammonia or at least a reduction is desirable. The main reasons are that the dilution method increases plant costs and final disposal is more difficult. The recovery and use of this ammonia as a fertilizer is a possibility. Producing this fertilizer in a storable form would be an advancement over previous methods.

As has been mentioned, one of the products of anaerobic digestion is methane gas. Its discovery is credited to an Italian physicist in 1776. It was more accurately characterized by William Henry of England in 1806 (1). This gas has great potential as a substitute for natural gas or propane. The heating value of methane has been variously reported as 600-700 BTU/cu. ft. (1) for unpurified gas from an anaerobic digester and about 1000 BTU/cu. ft. (2) for pure methane. For an average animal weight of 100 lbs., gas produced could range from 1.5 - 2.0 cu. ft/day/animal, assuming 50% volatile solids reduction by digestion (2). This could be used to heat the digester

to the required temperature of 95°F with excess used elsewhere in lot operations or sold. One major problem with this gas is its high carbon dioxide concentration. It can range as high as 50% of the gas volume produced. This greatly reduces the fuel value of a given quantity of the gas because CO₂ has no heating potential. Its removal would make for a much more efficient fuel. The removal of CO₂ has been used for many years to improve the fuel value of natural gas and coal gas. There is a large variety of methods available to cleanse fuel gases of CO₂. Efficient removal of nitrogen from the waste as ammonia and removal of the CO₂ from the gas stream of an anaerobic digester are two processes which could enhance the feasibility of anaerobic digestion.

LITERATURE REVIEW

The most common applications of gas purification found in the literature are to purify coal gases and coke oven flue gases. Coal gas is being used in many parts of the world as a substitute for natural gas, notably in South Africa and Europe. The coke oven flue gases are usually a result of the steel production process. Thus, much of the literature on gas purification deals with clean-up of these particular gases. These gases contain many undesirable impurities in addition to ammonia and CO_2 . However, since the methane feed gas investigated here was considerably less complex than either coal gas or coke oven gas, purification processes can be greatly simplified when applied to the methane stream.

AMMONIA REMOVAL

There are three major processes typically used for the removal of ammonia impurities from synthesis gases. All three have changed minimally in the last forty years or so (4). All include washing the gas with water or a strong acid. This results in either an aqueous solution of ammonium hydroxide (water wash) or a salt of the acid absorbent (acid wash). From this point, the three processes diverge.

Indirect Process

The indirect process is the oldest of the three and is most popular in Europe (See Figure 1). Its main products are weak and strong ammonia liquors, anhydrous ammonia and ammonium salts of weak and strong acids. Several heating, cooling, and condensation steps are carried out mainly to remove coal tar which fouls equipment and

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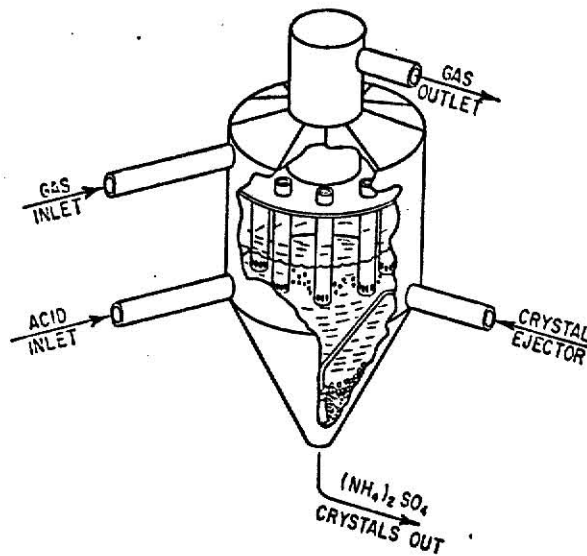


Fig. 2 - Saturator (4)

in higher steam consumption and thus higher costs for steam production; relatively high capital investment; ground space needed is larger than for other ammonia removal processes; and there is a loss of ammonia through successive steps of the process and during storage (4).

Direct Process

This process was first proposed by Brunck and the German Otto Co. for use on hot coke oven gases (5). The hot (90°C) gases are passed directly from the ovens into the saturator where the acid scrubbing occurs. About twenty years ago, it was thought that if steelmakers used phosphoric acid in the saturators to treat coke oven gases, a mixed fertilizer, diammonium phosphate, could be produced. Prior to that time, sulfuric acid was used which resulted in the production of ammonium sulfate. This salt in itself is not a fertilizer until it is mixed with other ingredients. Thus, it was seen as advantage to produce the diammonium phosphate. Such steel manufacturers as Kaiser

Steel and Ford Motor Co. have used this process. At the time this was first tried, however, the fertilizer industry was producing adequate supplies so coke manufacturers were reluctant to compete (6).

The problem with application of the direct process to coke gases is that the heavy tars in the gas, instead of being removed prior to scrubbing as in the indirect process, are carried into the acid and foul it rather rapidly. It also contaminates the acid salt produced making it nearly unusable (4). Since our methane feed gas contains no such tars, this would pose no problems as far as degrading the acid or contaminating any potentially recoverable salts of ammonia.

The gas exits the saturator minus ammonia at about 85°C which is above the dew point of water vapor. It enters a condensing unit for removal of ammonia-free liquor as an effluent, or for use in quenching of the coke (5). Since our gas temperature is more like 30-35°C, this last step would be eliminated. The biggest advantage of using this process is its relative simplicity compared to the indirect and semidirect processes.

Semidirect Process

This process is a combination of the direct and indirect methods previously discussed. It was developed by Koppers Co., Inc. and is the most popular method in the U. S. It differs from the direct process in that cooling occurs prior to acid scrubbing. However, unlike the indirect method in which cooling, reheating, and secondary cooling all occur prior to scrubbing, only one cooling step and reheating occur before scrubbing in the semidirect process. The second cooling takes place after the stripping in acid (5). The gas is cooled to 35°C before passing through the reheater and the saturator for actual

ammonia removal (See Figure 3). Unlike the indirect process in which bulk ammonia removal occurs in packed stripping towers, all ammonia removal in the semidirect process occurs in a saturator (4). Because no tar problems will exist with the methane feed gas, the necessity of using the semidirect process probably does not exist.

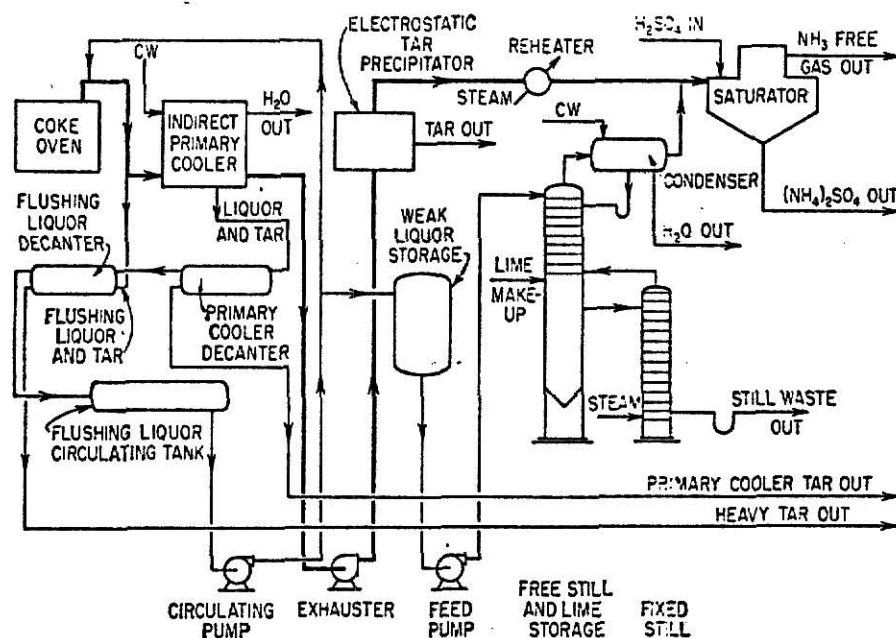


Fig. 3 - Flow sheet of semidirect process (4)

Miscellaneous Processes

Absorption of ammonia in water under pressure is one possibility for ammonia removal. This involves washing the gas at pressures of 100-200 atmospheres with water being injected into the pressure vessel. Solid salts are recovered from the solution after it is cooled. A variation developed in Germany uses injected dilute ammonia solution and operates at a pressure of four atmospheres and a temperature of 140°C. Ammonia is recovered as a 10% solution. The trace ammonia remaining is recovered in a water wash at 15°C (4).

A refrigeration technique has also been experimented with. When a typical coal gas is cooled to -10°C to 0°C , an aqueous solution of 20-30% ammonium carbonate can be obtained. To prevent formation of the solid crystals, however, the ammonium carbonate concentration is kept around 6%. The crude gas from the primary coolers (for tar removal) is contacted directly with a spray of refrigerated ammonia liquor and then washed with water for the removal of trace ammonia. Two advantages of this method are: 1) production of small liquid volumes and thus lower steam costs for ammonia distillation than with any other process, and 2) it is capable of production of a wide variety of end products, like the indirect process (4). Here again, this process could probably be simplified because no tar removal is needed.

CARBON DIOXIDE REMOVAL

Unlike the various ammonia removal processes discussed previously, there is a wide variety of proven processes available for the removal of CO_2 from synthesis gas. As with ammonia removal, most of the literature is written for the coal gas industry. Because coal gases contain many undesirable impurities not found in the methane feed gas, some of these processes are unnecessarily complex.

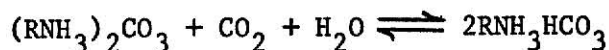
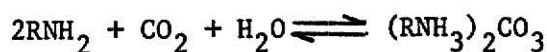
Ethanolamine Process

This process is frequently used on feed gases whose only impurities are carbon dioxide and hydrogen sulfide (7). It was first patented by R. R. Bottoms in 1930. Bottoms did much of the early work on using alkanolamines as absorbents for acidic gases like CO_2 and H_2S (4). The first of these compounds used for CO_2 absorption was triethanolamine (TEA). Several others have since displaced TEA as the prime CO_2 absorbent.

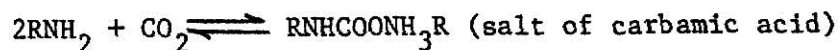
The two most commonly in use today are monoethanolamine (MEA) and diethanolamine (DEA).. Both MEA and DEA have much higher capacities for absorption of CO_2 than TEA (4).

Some other absorbents which have gained moderate acceptance are diaminoisopropanol, methyldiethanolamine (MDEA) and β , β' -hydroxyamino-ethyl ether (4). These three do have limitations which may prevent usage in all but special cases. For one, the ether compound is very expensive. All have been used when both CO_2 and H_2S removal is desired, as well as for CO_2 removal alone (4).

The MEA absorbent has been noted to react directly with CO_2 to form an amine salt of carbamic acid (4):



Net reaction:



A similar reaction is possible with DEA. It is believed that the relative inefficiencies of the tertiary amines, TEA and MDEA, for CO_2 removal are due to the fact that they cannot absorb CO_2 in this way (4). Titration curves for 2.5N solutions of these four amines, when neutralized with CO_2 also show MEA and DEA to be more efficient than TEA and MDEA (See Figure 4). This is due to the greater alkalinity of MEA and DEA. For comparison, a curve for titration of potassium hydroxide with CO_2 is included. It shows a steep curve because KOH is more highly ionized than the amines.

For economic reasons, MEA is generally the absorbent of choice, unless special conditions prevent its use. One such circumstance

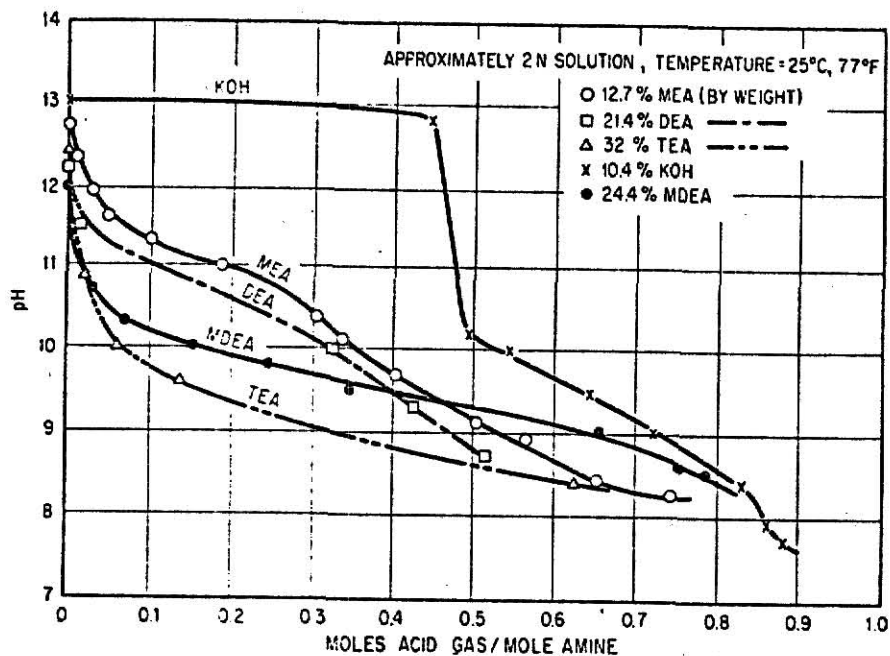


Fig. 4 - Titration curves showing neutralization of amines and KOH with CO_2 (4)

would be an irreversible chemical reaction which would not allow recovery of the MEA for reuse. The DEA absorbent very often is used in such cases. Another problem with MEA is its high vapor pressure. As for DEA, it does not yield as complete H_2S removal as MEA (7). Comparisons of all four amines are shown in Table 1.

Property	MEA	DEA	TEA	MDEA
Molecular weight.....	61.1	105.1	149.2	119.2
Concentration, lb/100 lb.....	15.2	25.5	36.0	28.0
Approximate cost, dollars/gal.....	0.35	0.49	0.76	1.83
Approximate vapor pressure of pure amine at 100°F, psia.....	0.03	0.0001	<0.0001	0.0004

Table 1 - Comparison of Ethanolamines (2.5N solution) (4)

Briefly, the basic flow scheme for CO_2 removal by ethanolamine absorption includes an absorber unit into the bottom of which the crude gas enters (See Figure 5). Purified gas is drawn off at the top of this unit. Countercurrently to this gas flow, a lean (low in CO_2) amine solution falls with a scrubbing action on the gas. The CO_2 -rich amine solution drawn off the bottom of the unit is heated in a shell and tube heat exchanger and then pumped to the upper part of the stripping unit where CO_2 is removed by a water wash. The now lean amine solution passes through the heat exchanger again, heating the CO_2 -rich amine solution entering the stripper, and back to the top of the absorption unit. Acid gas (CO_2) drawn off the top of the stripping unit is cooled to condense out water vapor which is returned to the top of the stripper unit to minimize amine losses. The acid gas is disposed of.

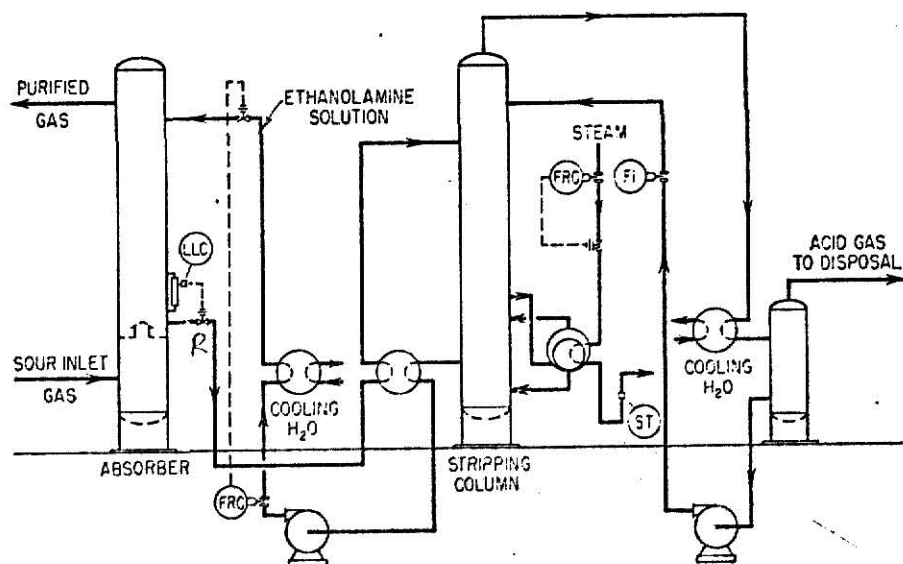


Fig. 5 - Flow sheet for alkanolamine process (4)

Alkaline Salt Solutions

This category includes a wide variety of methods and materials for CO_2 removal. In general, scrubbing with an alkaline salt solution will produce a gas which is essentially free of CO_2 (See Figure 6). The most common application of one of these techniques is as a final polishing process that follows bulk removal by some other method. The major problem with using caustic scrubbing for bulk CO_2 removal is the large quantities of chemical precipitate produced. In caustic stripping of CO_2 from a concentration of 300-400 mg/l down to less than 2 mg/l, as compared to using some other bulk removal technique to get the CO_2 down to about 25 mg/l then using caustic scrubbing to remove CO_2 down to near zero, the former method would produce far more chemical precipitate than the latter. This can pose quite a disposal problem. Further discussion of combining processes for better removal efficiency is covered later.

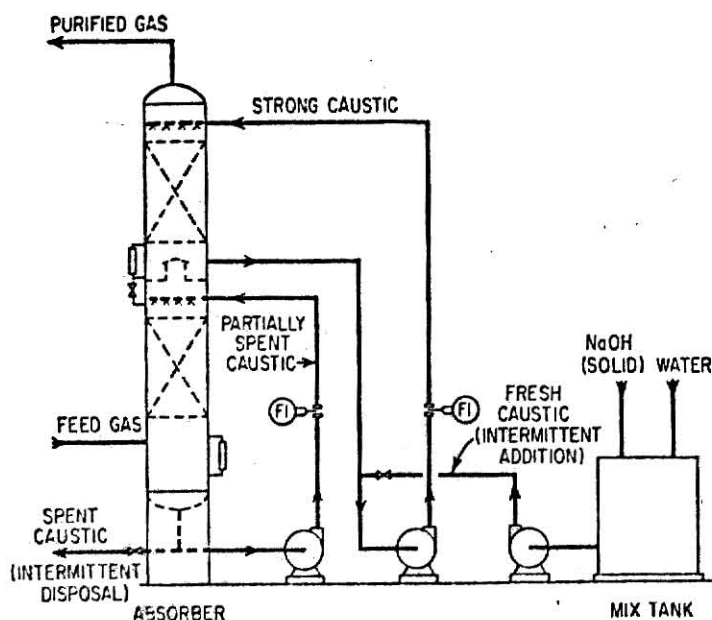


Fig. 6 - Flow sheet for alkaline salt scrubbing (4)

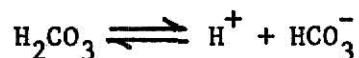
In some quarters it is felt that the use of strong alkalis, as opposed to alkaline salts is prohibitive because compounds formed during absorption are not readily dissociated and thus hinder or prevent regeneration of the solution (4). This would be true for a large installation of the type used to commercially purify natural gas, coal gas or other fuels on a large scale. In our feedlot situation, however, regeneration may be replaced by disposal because of the smaller quantities used. Thus, solutions of strong bases like NaOH and KOH may be considered. It has been found that a 2N solution of NaOH is optimum for CO_2 removal because the absorption coefficient is maximum at this concentration (7). Waste sludge is a problem, but disposal can be handled if the operation is not too large. The solution is usually discarded when it is 70-80% exhausted (7). Periodic addition of fresh caustic is made to maintain alkalinity. Solutions of lime are also a feasible absorbent.

Another variation is what is called the soda lime process (7). It is carried out in a batch process and is generally more expensive than NaOH scrubbing. It involves using a hydrated mixture, in granular form, which is manufactured by slaking quicklime with a NaOH solution (7). In removing CO_2 , the precipitate CaCO_3 is produced and the granules are not regenerable because they become irreversibly coated with CaCO_3 (7). Another limitation of the soda lime process is that removal is only practical from a moist gas because water is needed for the reactions. It has been noted that most efficient removals are obtained when the gas flows upwards through the bed; however, general practice is to use a downward gas flow to minimize dust problems due to agitation of

the bed (7). The absorptive capacity of soda lime is about 35% by weight, but this is very dependent on particle size (surface area available for absorption).

By far the most common alkaline salt solutions used are those of the carbonates of sodium and potassium. The strong alkalis operate at pH's of 12 or greater, which usually prevent their regeneration. The alkaline carbonate salts form an aqueous solution of a strong salt and a weak acid. These solutions can be easily buffered to a pH of between 9 and 11 (4). The salts Na_2CO_3 and K_2CO_3 are used also because of low cost due to ready availability (7).

The rate of CO_2 absorption is based on the reaction



for which $k = 4 \times 10^{-7}$ at 25°C . This reaction is actually slower than expected when compared with a similar reaction for H_2S absorption into carbonate solution ($k = 1 \times 10^{-7}$ @ 25°C). Based on k values alone, CO_2 should be absorbed faster than H_2S , but the reverse is true. This is possibly due to a slow chemical reaction between CO_2 and hydroxyl ions in solution. Thus it has been suggested that the CO_2 absorption rate is controlled not by diffusion mechanics, but by a chemical reaction. The use of catalysts to control this reaction has been proposed (4). Because of the slowness of the absorption, this process is not often used for bulk removal. It has found wide use as a final polishing step to remove trace CO_2 .

A very popular alkaline salt removal technique is known as the hot potassium carbonate process. This particular removal method was developed by the U. S. Bureau of Mines as part of a program to

develop a liquid fuel from coal. It generally permits higher CO_2 absorption rates than ordinary alkaline scrubbing. An added advantage is that it works under the conditions in which coal gas is synthesized, that is high CO_2 partial pressure and high temperatures. Some extensive studies have been carried out on temperature effects by Williamson and Matthews (4). The process consists of an absorption unit in which the CO_2 is stripped under pressure from the feed gas by a near-boiling K_2CO_3 solution (Figure 7). The CO_2 -rich solution is pumped to the

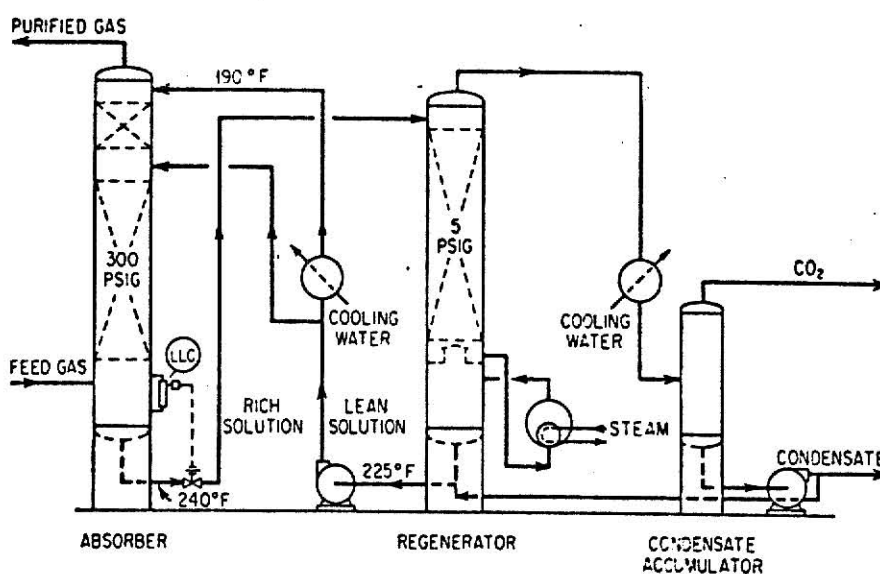


Fig. 7 - Flow sheet for hot K_2CO_3 process (4)

regenerator where the CO_2 is removed with steam stripping. The lean K_2CO_3 solution is then cooled from 225°F to 190° and recycled to the absorption unit. The stream from the regenerator is cooled and condensed, thus freeing the CO_2 gas (4). There are several variations on this process, but all require the feed gas to be at a high temperature.

As a result of these high temperature absorption conditions, steam to heat the feed gas is not needed, as well as any heat exchange equipment between the absorber and the regenerator. Also, the increased temperatures permit the use of more concentrated K_2CO_3 solution because of higher solubility.

Generally, the hot K_2CO_3 is used only for bulk CO_2 removal. High purity cannot be obtained by this process alone because it becomes uneconomical. As a bulk removal process, however, it is usually very competitive economically with other processes. In fact, the higher the CO_2 content to be removed, the more economical the process becomes (7). It has also been found that by the addition of certain amines (like MEA) to the K_2CO_3 solution, substantially increased rates of CO_2 absorption can be noted (8).

Another application of alkaline salt solutions for CO_2 removal is the Giammarco-Vetrocoke process developed in Italy. The flow scheme is basically the same as that of the hot K_2CO_3 process. The process uses an alkaline salt solution which is activated by the addition of organic or inorganic additives. Reportedly, the inorganic additives are more effective and are used in relatively high concentrations (4). Arsenic trioxide is a common inorganic additive. The rate of CO_2 absorption is increased, as well as the desorption rate. Thus, this process generally requires a smaller absorber and regenerator units than the K_2CO_3 process.

One of two methods of regeneration is usually employed. Steam regeneration like that used in the hot K_2CO_3 process can be used if CO_2 recovery is desired. If recovery is not needed, air regeneration

is used. This dispenses with the need for steam production and often results in a leaner carbonate solution for recycle (7). Usually, a product gas of high quality is obtained with only trace amounts of CO_2 in evidence. This process is easily followed by caustic scrubbing for trace CO_2 removal, if desired.

Water as an Absorbent

The use of water as an absorbent for gas impurities has been extensively investigated. As compared to other solvents, like the ethanolamines and caustic solutions, the solubility of CO_2 in water is relatively low. Also, some of the primary gas (methane, in this case) may also be absorbed into the water (4). The simplest plant consists of an absorption tower (See Figure 8) which operates at an elevated pressure and a flash chamber where the CO_2 is removed from the water at a lowered pressure. The water is recycled to the top of the tower for reuse in the absorption unit. A power recovery turbine could be added to use the energy available from pressure reduction and the expansion of the released CO_2 (4).

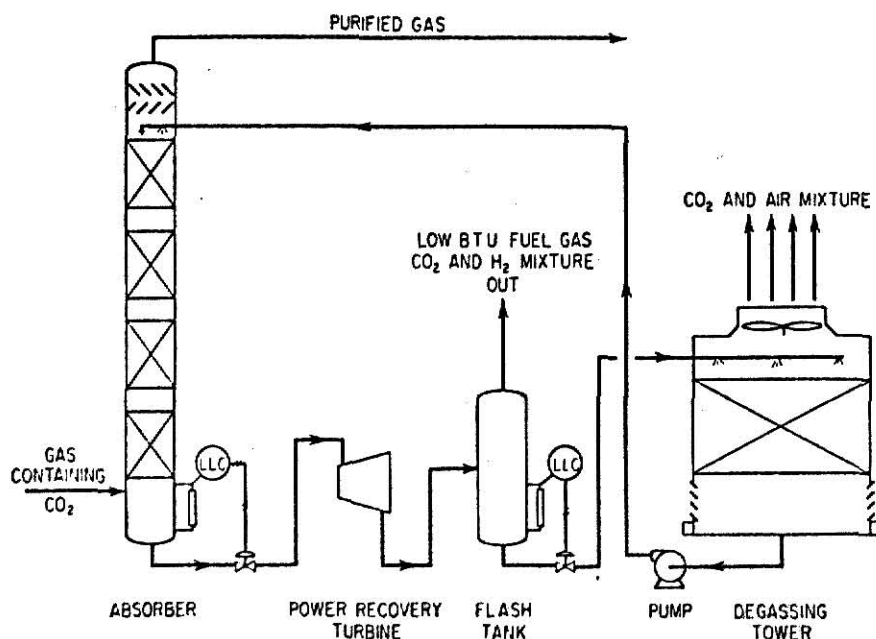


Fig. 8 - Flow sheet for water absorption of CO_2 (4)

This process is limited to gas streams containing CO_2 at a partial pressure greater than 50 psi to ensure an economical CO_2 capacity of the water.

Some advantages of this process over the MEA ethanolamine process are (4):

1. Simple plant design (no heat exchangers or reboilers)
2. Inexpensive solvent (water)
3. Solvent not reactive with most other trace impurities
4. No nitrogen vapors introduced into gas stream (as with MEA)

Some disadvantages include:

1. Excessive loss of H_2 or other valuable gas stream constituents
2. Very high pumping level
3. Poor CO_2 removal efficiency
4. Impure CO_2 by-product recovered

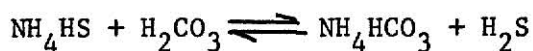
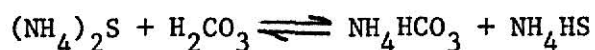
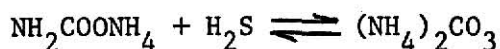
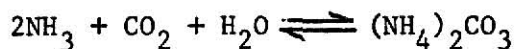
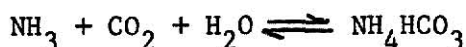
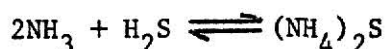
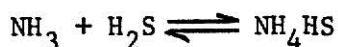
In general, when applied to industrial gas purification, if waste heat from other processes is available to use for steam generation, the amine process is considered to be a better choice (4).

Aqueous Ammonia Solution

When impurities such as organic acids and nitrogen-based compounds are present, a process like ethanolamines for CO_2 removal can be rendered useless. One reason is that these impurities can react non-regenerably with the amines. This prevents or impedes recovery of the amines from the fouled solution. Thus, ethanolamines are only effective for purifying gases containing H_2S and CO_2 impurities, as was discussed earlier. Coal gas often poses such a problem, as does our methane feed gas. The use of weak ammonia solutions to remove ammonia, as

well as H_2S and CO_2 has been demonstrated to work on some coal gases. In fact, maximum removals of ammonia and H_2S have been obtained using this method (4). This is due to the fact that H_2S and ammonia are absorbed faster than CO_2 , as noted earlier. The absorption of H_2S and ammonia is controlled by the liquid film resistance and that of CO_2 by gas film resistance (7).

The basic chemistry of the process can best be described by a series of chemical equilibrium equations (4):



Because our feed gas does contain a small amount of H_2S , this method might be feasible. However, our quantities of H_2S were not measured because they were very small and removal was not necessary. Thus, the dependence of this process on the presence of H_2S would probably determine whether it is feasible to remove CO_2 alone.

The use of ammonia solutions for CO_2 removal has been found to work well on synthesis gases containing 30% CO_2 (4). The major

advantage of this process, as has been noted, is the fact that the nitrogenous and other impurities do not affect its ability to remove CO_2 . Corrosion can, however, be a problem if some of these impurities are present in sufficient quantities. Carbonated solutions will cause such corrosion problems. This process generally has a more complex flow scheme than other CO_2 removal methods.

Briefly, the flow of the process begins as the feed gas enters the bottom of the absorber unit and passes countercurrently to a falling 2-5% ammonia solution. The treated gas will contain about 150 mg/l of CO_2 , a small amount of ammonia and practically no H_2S (4) (See Figure 9). Before leaving the absorber, the CO_2 -free gas passes through a water wash to remove the ammonia, which is returned to the process. For more complete removal of CO_2 , a caustic scrubber will generally follow the absorber unit (7). The caustic scrubbing will reduce the CO_2 concentration to 10-25 mg/l. The carbonated ammonia

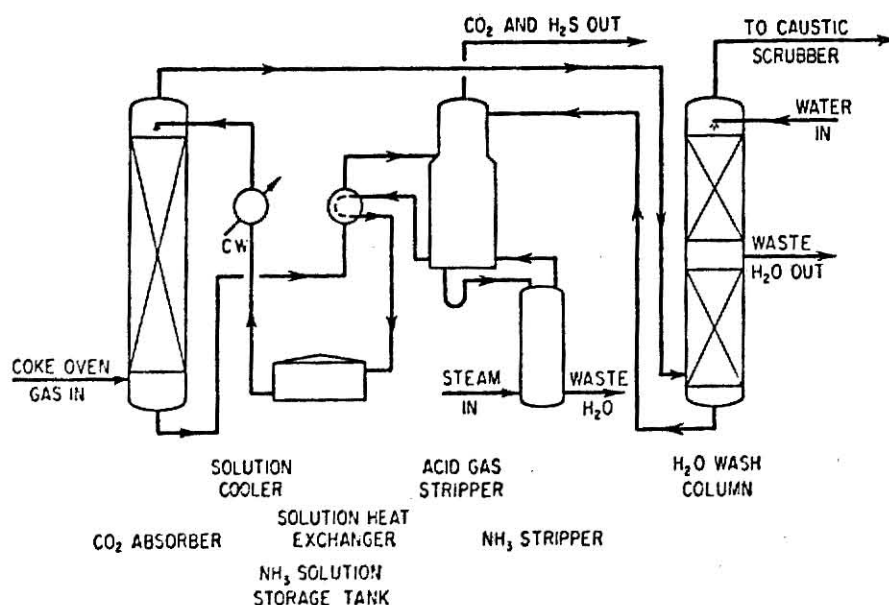


Fig. 9 - Flow sheet of CO_2 removal with NH_3 solution (4)

solution is withdrawn from the bottom of the absorber for regeneration. This solution is heated in a heat exchanger by the ammonia solution leaving the regenerator. In the regenerator, the acid gases (CO_2 and H_2S) are stripped by vapors from the ammonia stripper unit. The heating of ammonia solution with these vapors expels CO_2 from the top of the regenerator. Most of the regenerated ammonia solution is used to heat the CO_2 -rich solution incoming to the regenerator. It is then cooled to 100°F before re-entering the top of the absorption unit. The remainder of the regenerated ammonia solution enters the ammonia stripper where the ammonia is removed by direct contact with steam. This ammonia-steam mixture is the stripper exhaust vapor that is used to remove CO_2 from the carbonated ammonia solution in the regenerator. Water from the ammonia stripper is discarded to avoid buildup of the undesirable salts which it contains. This water is replaced by ammonia-containing water from the water wash treatment (4).

Catalytic Conversion

Another method which could be considered for CO_2 removal is catalytic conversion or methanation. Conversion, as it implies, involves the altering of the undesirable impurities to a more acceptable form. Thus, removal of the impurities from the raw gas is not usually involved. Instead, by the use of catalysts, the CO_2 can be chemically converted to a more desirable substance--in this case, methane. Some terminology about catalysts is in order here. A positive catalyst will increase a reaction rate while a negative one will decrease a reaction rate. Heterogeneous catalysts are in a different state of matter than the reactants present. A homogeneous catalyst is one which is in the same state as the reactants. In gas

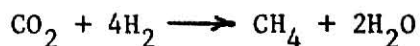
purification, positive, heterogeneous (usually solid) catalysts are used (4). Contact at the phase boundary of the reactants and the catalyst is very important. This contact is established by the adsorption of the reactants onto the catalyst surface. The mechanism of adsorption onto a catalyst surface can occur in several different ways (4):

- mass transfer of reactants from the fluid (gas) to the catalytic surface and of reaction products from the catalytic surface to the fluid
- diffusion of the reactants and reaction products into and out of the pores of the catalyst
- activated adsorption of the reactants and desorption of the reaction products at the phase interface
- surface reactions of adsorbed reactants to form chemically adsorbed products

Most catalysts used for gas purification are metal salts or metals. These catalysts must be supported on an inert carrier. Since catalysts are not, by definition, changed by the reaction, they should be usable for an indefinite period of time. Actually most catalysts do gradually deteriorate or deactivate and must be regenerated or replaced. Deterioration may be physical or chemical in nature. Deactivation occurs when the catalyst reacts with impurities in the gas stream. This is sometimes known as "catalyst poisoning" (4).

Specifically, the catalytic process of methanation is used to remove trace quantities of CO_2 after bulk removal by some other technique. For methanation of CO_2 (and CO), catalysts of a high nickel content (76-78% as Ni_2O_3) and aluminum (20-22% as Al_2O_3) are

often used. The basic reactions which occur in methanation are:



The use of the Ni-Al catalyst has an advantage in that regeneration is not frequently required. One of the few causes of catalyst poisoning with this catalyst is fouling by sulfur compounds. Thus, they must be totally removed before the Ni-Al catalyst can be used for methanation (4).

Physical Absorption of CO₂

Some thought has been given to considering a purely physical process for removing CO₂. Physical absorption of the CO₂ into a solvent could be induced by simply applying sufficient pressure. Because some processes are not economical for CO₂ contents of approximately 35% (or higher) at pressures of 350 psig, physical absorption could be an alternative (4). This process would require no heat energy addition for stripping of reaction products obtained like, say, in the MEA process. This is a very simple method that could probably be done economically only on moderate amounts of synthesis gas. Larger gas quantities would require great amounts of solvent to be recirculated, increasing energy requirements and costs for pumping. The literature talks of using organic solvents for such a procedure (4). Inorganic solvents may also be possible CO₂ absorbers under such conditions.

An example of such a physical absorption process using an organic solvent is the Rectisol Process. It involves the absorption of CO₂ (and many other impurities) from a synthesis gas into methanol (CH₃OH) at relatively low temperatures. The solubility of CO₂ is very high in methanol at elevated pressure. The CO₂ is released when the solvent

is returned to atmospheric pressure.

The absorption rate of CO_2 in methanol varies greatly with temperature, as is shown in Figure 10. Heat energy requirements are low because heat exchange methods can be used to heat the incoming gas with the outgoing purified gas. Overall, this process requires less energy than an equivalent ethanolamine treatment scheme.

Another advantage is that all undesirable impurities can be removed in one step because of the wide range of

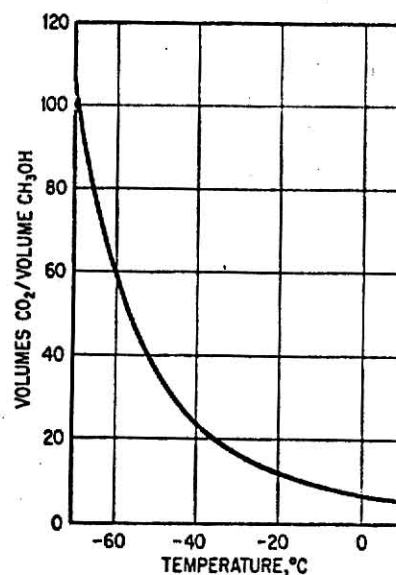


Fig. 10 - Solubility of CO_2 in methanol (4)

gaseous substances that can be absorbed by methanol. This process will also produce a gas very low in water content. For some situations, this is a very desirable result. Some disadvantages of Rectisol include its complex flow scheme, a high loss of methanol solvent due to its high vapor pressure at the required operating temperatures, and the lowest possible outlet CO_2 concentration is about 1%. In general, this method is good for bulk CO_2 removal at pressures above 150 psig (4).

The feed gas enters the bottom of a 2-stage absorber unit which operates at a pressure of about 300 psig. (See Figure 11 on next page). As the gas flows upward, it is washed countercurrently with the methanol solution which will remove most of the CO_2 and any H_2S present. The methanol enters the top of the first stage at a temperature of about -100°F . At the methanol outlet at the bottom of the absorber, the

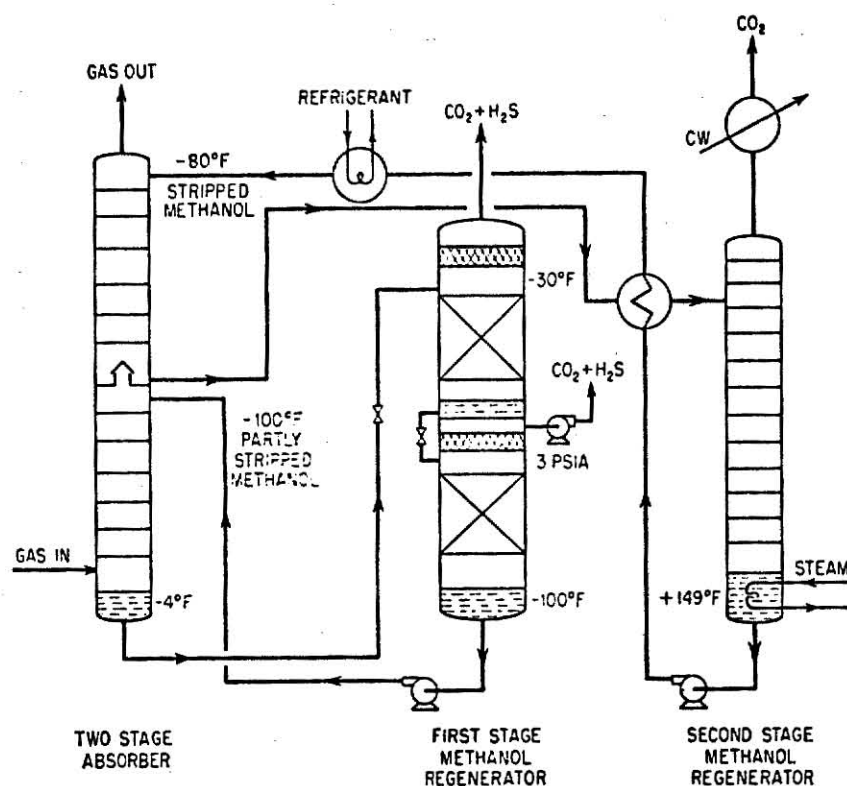


Fig. 11 - Flow sheet of Rectisol Process (4)

solution temperature is about -4°F due to heat of absorption. Purified gas leaves the top of the first stage and enters the second stage. The methanol is regenerated in a 2-stage process: 1) the temperature of the solvent is lowered to -30°F and the pressure to 15 psia, then 2) the pressure is lowered to 3 psia and the temperature to -100°F . The regenerated methanol still contains some CO_2 and is recycled to the top of the first stage absorber. In the absorber second stage, the partially purified gas from the first stage is again stripped by a small methanol stream at 80°F . This methanol has been thoroughly stripped of CO_2 , unlike that used in the first stage. It was stripped by heating with indirect steam to 149°F in the second stage regenerator

where virtually all CO_2 was removed. Thus, the product gas from the second stage absorber is nearly CO_2 -free.

Miscellaneous Processes

A device known as a regenerator (not to be confused with the like-named devices which are parts of other processes discussed) has been investigated by some researchers to evaluate its potential for gas purification. Basically a physical rather than chemical method, the regenerator cools the feed gas to its dew point by heat exchange with the product and waste gases. It is fundamentally a heat storage device that usually consists of two packed cylindrical vessels (See Figure 12). The warm feed gas and the cooler return gas are switched alternately between the vessels so that heat from the feed gas stored in the packing is used to heat the return gas, and vice versa. This

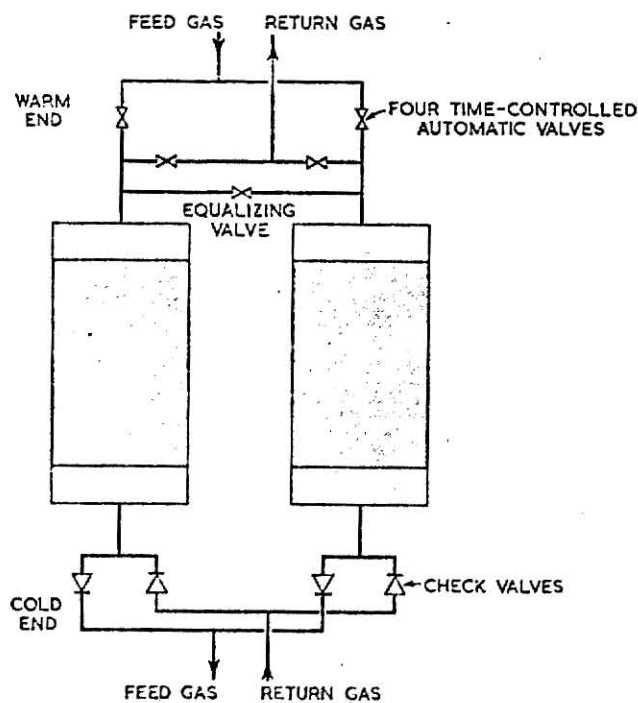


Fig. 12 - Regenerator operation (7)

device would be used on a low temperature plant because such plants must have a purification system which has the ability to handle very large gas flows, can remove impurities from the incoming feed gas by deposition on the packing, and of course economy (7). The regenerator system could meet all of these criteria. However, it is not suitable for high pressure plants because there would be high gas losses at changeover (movement of gas between the vessels) and because the cost of large pressure vessels could easily be prohibitive when comparing costs with other systems (7). Presently, the largest vessels in use have 12 foot diameters. Low capital costs of the regenerators method can be attributed to large surface areas per unit volume of packing (400-1000 sq. ft./cu. ft.) compared with that of a typical shell and tube heat exchanger (about 50 sq. ft./cu. ft.). One major drawback of the regenerator for use as a gas purification system is its complex operation (7). Some use of automated valves has been proposed, but not applied successfully.

Molecular sieves have been proposed as a possible gas purification method. Mobil Oil has used a sieve to purify a mixed ethane-propane stream which also contains CO_2 in concentrations of 0.05-0.1% mole. Mobil has been able to separate out 85% of the propane and about 20% of the ethane from this stream by using molecular sieves (9). The feed gas enters at 110-115°F and 200-260 psia. The precisely sized pores of the sieve admit the impurity molecules (CO_2) which are smaller, and exclude the propane and heavier HC molecules like ethane. The purified gas is less than 1 mg/l CO_2 . In comparing a wet system (any of the stripping methods previously discussed) and a dry system (molecular sieve), the installed equipment costs, exclusive of absorbent or

chemicals, was nearly equal. In addition, the dry system was generally found to have lower operating and maintenance costs (9). Another factor in favor of the dry system, specifically the molecular sieve, is the fact that it can be totally automated.

One more process which has received limited acceptance so far is low temperature adsorption for CO_2 removal. It is known that the adsorption capacity of certain substances increases with decreased temperatures. The use of a silica gel as an adsorption media in a medium pressure range has been carried out successfully. The gel can be reactivated at a low or high temperature (7). At low temperatures, incomplete regeneration of the gel usually occurs, however. With high temperature regeneration, the main disadvantage is the increased refrigeration load on the plant (7). This method, however, does yield better regeneration levels.

Combined Processes

Another treatment scheme to be considered would be to combine some of the various processes already discussed. As has been noted, some of these processes are suited best for bulk removal of large quantities of CO_2 . Others are only efficient for removal of small amounts of CO_2 . Also, some are probably acceptable for removing large quantities of CO_2 to essentially zero concentrations. Four basic types of bulk removal processes have been discussed which have been most often used and best known (10). The first is the water wash which is good in a situation where cold water and cheap power are available. Second are the amine processes which generally work well in low pressure plants where fuel is cheap and/or CO_2 must be removed to low levels. Third are the other various chemical processes which

include hot K_2CO_3 and the Giammarco-Vetrocoke processes. These processes are generally good for intermediate pressures of 4-8 atmospheres where only bulk removal of CO_2 is needed. These three processes must be followed by some other final polishing technique like caustic stripping for removal of trace CO_2 . Finally, there are the various physical absorption and adsorption processes which are good at high pressures (greater than 70 atm) (10). The removal levels of these processes are variable and somewhat controllable by the operator.

Mullowney has studied combining these and other processes by setting up seven different treatment schemes and comparing them economically (Table 2). The feed gas flow was 12,000 SCF/day at 350 psig. It contains 34.3% CO_2 by volume and removal to a final concentration of 25 mg/l or less is needed. The study is based on a combination initial plant investment plus one year's operating and maintenance expenses. The most expensive initial cost was for an aqueous DEA plant (20-25% solution) followed by a caustic wash. The cheapest equipment investment was for a hot K_2CO_3 process followed by aqueous MEA.

As far as operating costs go, the utilities for an aqueous ammonia treatment followed by caustic scrubbing were easily the most expensive. At the other end of the scale, the cheapest (by nearly 4 1/2 times) was for water scrubbing followed by MEA. Other direct operating expenses including operating labor and maintenance were then added in and the total direct operating costs were lowest for the hot K_2CO_3 followed by MEA. Most expensive was the aqueous ammonia followed by caustic wash.

Indirect costs which include depreciation, taxes and insurance are then included with the initial investment and direct operating expenses to show that water scrubbing followed by MEA was the cheapest way to treat this particular gas stream to the required CO₂ level. The hot K₂CO₃ followed by MEA was only slightly more expensive. The value of this study today may be questionable, however, because it was made nearly 20 years ago, and costs of nearly everything have gone up greatly. The relative differences between the schemes would probably be the same.

Cost breakdown	Scheme No.†						
	1	2	3	4	5	6	7
Plant investment, thousands of dollars	607	921	543	396	619	778	793
Direct operating costs, thousands of dollars/year:							
Utilities:							
Steam @ \$0.55/1,000 lb.	262	252	93	97	96	10	366
Electricity @ \$0.01/kwhr.	19	29	19	18	21	41	19
Cooling water @ \$0.02/1,000 gal.	32	32	18	15	19	7	33
Process water @ \$0.10/1,000 gal.					1		11
Gas losses @ \$0.50/1,000 SCF.	4	3	7	8	5	37	3
Chemical losses @ 1957 cost.	2	17	11	26	26	3	3
Subtotal.	319	333	143	167	168	97	435
Operating labor:							
Foremen, \$3.50/hr; operators, \$2.75/hr; plus 22% payroll burden.	47	47	47	66	66	47	47
Maintenance @ 4% plant cost (60% labor, 40% material).	24	37	22	24	25	31	32
Plant general.	51	58	50	56	67	55	55
Subtotal.	122	142	119	156	158	133	134
Total direct costs.	441	475	267	323	326	230	569
Indirect operating costs, thousands of dollars/year:							
Depreciation @ 10% of plant cost.	61	92	55	60	62	78	79
Taxes and insurance @ 2.5% of plant cost.	15	23	14	15	15	19	20
Total indirect costs.	76	115	69	75	77	97	99
Total operating costs, thousands of dollars/year.	517	590	336	398	403	327	668
Treating cost (on stream 360 days/year):							
Dollars/MSCF gas treated.	0.12	0.14	0.08	0.09	0.09	0.08	0.15
Dollars/MSCF CO ₂ removed.	0.35	0.40	0.23	0.27	0.27	0.22	0.45

* Design conditions:

1. Feed gas, 12,000,000 SCF/day @ 350 psig, contains 34.3 per cent CO₂ by volume.

2. Product gas to contain less than 25 ppm CO₂ by volume.

† Cases studied:

1. Conventional aqueous monoethanolamine plant (15 to 20 per cent MEA).

2. Aqueous diethanolamine plant (20 to 25 per cent solution) followed by caustic wash.

3. Hot potassium carbonate process followed by aqueous MEA.

4. Hot potassium carbonate process followed by aqueous DEA, then by caustic wash.

5. Hot potassium carbonate process followed by aqueous ammonia treating, then by caustic wash.

6. Water scrubbing followed by aqueous MEA.

7. Aqueous ammonia followed by caustic.

Table 2 - Comparison of Combined Processes for CO₂ Removal

EXPERIMENTAL METHODS AND RESULTS

Some of the more promising removal procedures for ammonia and CO_2 were investigated in the laboratory. The first method investigated was the direct process since it is the simpler of these methods mentioned. Since no problem impurities like coal tars were known to exist in the methane stream, a direct stripping in phosphoric acid was studied. Several CO_2 removal techniques were tried. Stripping in caustics (NaOH, KOH, and lime) was carried out in field experiments using digester gas at the Kansas State University Boar Testing Station (2). That work is not extensively covered in this paper. In the laboratory, a study of physical absorption into a phosphoric acid solution under pressure was pursued.

AMMONIA REMOVAL

It is a well known principle that gaseous ammonia will be absorbed into a strong acid solution. This fact has been used in the fertilizer manufacturing industry for a long time. It can result in the production of ammonium sulfate, ammonium phosphates, and numerous other ammonium salts. The absorption of ammonia into these acids is a diffusion mechanism which occurs when a gas containing ammonia comes into contact with acid in which the ammonia concentration is less than some saturation value.

Because ammonia is considered to be highly soluble (12, 13) as compared to many gases, its rate of absorption is controlled by the gas film rather than the liquid film (13). In other words, it has been found that the rate of absorption of a gas is controlled by the rate of diffusion (the solubility) of the solute (in this case ammonia)

through the surface films of gas and liquid at the gas-liquid boundary. This is why the relative importance of the two films is determined by the gas solubility (13).

The next logical question is what factors affect gas solubility? It has been found that the rate of diffusion for ammonia is affected mainly by temperature, pH, viscosity, and to a lesser degree, some other variables (14). Other research has revealed that desorption of ammonia from water under quiescent conditions is affected by temperature and pH (15). The per cent concentration of ammonia nitrogen in a lagoon approximately doubled for either a 10°C rise in temperature or a 0.3 unit rise in pH. Whether these quantities for quiescent conditions could be applied to the agitated environment of a packed tower was not investigated. It does, however, point up the effects temperature and pH can have on absorption. In a study which did vary temperature over a range of 10-50°C in an unpacked tower, effects on liquid and gas film coefficients were noted (12). The liquid film coefficient, which controls absorption of a low solubility gas, was found to increase as the fourth power of the absolute temperature. On the other hand, the gas film coefficient which controls absorption of a highly soluble gas, was found to decrease as the 1.4 power of absolute temperature. This is due to the fact that the coefficients are based upon the ratio of density to viscosity of the fluid (12).

Some of the other variables might include effects of stirring and gas currents in the atmosphere surrounding the liquid solvent. Conflicting evidence has been noted about the effects of stirring on absorption. Lewis and Whitman (13) have noted that gas absorption

through a free liquid surface is greatly enhanced by stirring of the liquid. Another research effort by Hashimoto and Ludington (16) found that the rates of a mechanical stirrer (which varied from 100-400 rpm) had little effect on ammonia absorption rates. The absorption rates in this particular study are probably fairly low in comparison to equivalent agitation provided by gas diffusion.

The relative speeds of the gas and liquid as they move past one another have been noted to cause significant changes in absorption rates. One study (16) indicates that to maximize this velocity difference is a great advantage in a situation where the gas film coefficient is high, which implies a highly soluble gas like ammonia. In other words, for a gas of high solubility, maximizing the relative velocity between gas and liquid will yield the greatest absorption rate. Another study (12) quantifies this by saying that the gas film coefficient is proportional to the relative gas velocity to the 0.8 power. The researchers also noted that the gas velocity had no noticeable effect on the liquid film coefficient. Thus, the effect of gas velocity is greater with highly soluble gases (like ammonia) than a relatively insoluble one (like H_2S).

These are some reasons for investigating the packed tower method for removing ammonia in acid. Factors such as temperature, pH, and amount of agitation can be controlled fairly easily. For example, the amount of agitation which will control the relative velocities between the gas and liquid depends upon the type of packing used. This ability to control these factors is a great advantage.

Because of the potential for using ammonium phosphate compounds for fertilizer, a closer look at this process of converting phosphoric acid and ammonia gas into such a useful substance was needed.

Essentially, enough ammonia must be introduced into the acid to raise it to a pH of near neutrality. The main question is how much ammonia must be added to do this? Also investigated was the uptake rate of ammonia into phosphoric acid--how many grams of ammonia will be absorbed per gram of acid? The ammonia removal efficiency of such an acid stripping scheme was also of major interest.

Apparatus

The apparatus used to study absorption of ammonia in phosphoric acid is shown in Figure 13 on the next page. Since the methane present in the gas stream was assumed to have no effect on the ammonia absorption mechanism, air was substituted for this investigation. The reason for this is that large quantities of pressurized methane needed were not available. An air flow of approximately 30,000 ml/min was used throughout the run.

Ammonia was added by bubbling metered air into a bottle of ammonium hydroxide (NH_4OH) where the air became saturated with ammonia. This air-ammonia mixture was then mixed with the compressed air at an average rate of about 420 ml/min. Next, a sample of the mixed gases was drawn off to be analyzed for ammonia content. This was accomplished by bubbling some mixed gas into a container of acid. By monitoring the amount of gas entering the acid using a wet test gas meter, the amount of ammonia added to the acid in a given time could be computed. This rate was assumed to be the same for the larger quantity of mixed gas entering the main ammonia stripper column. The main column was

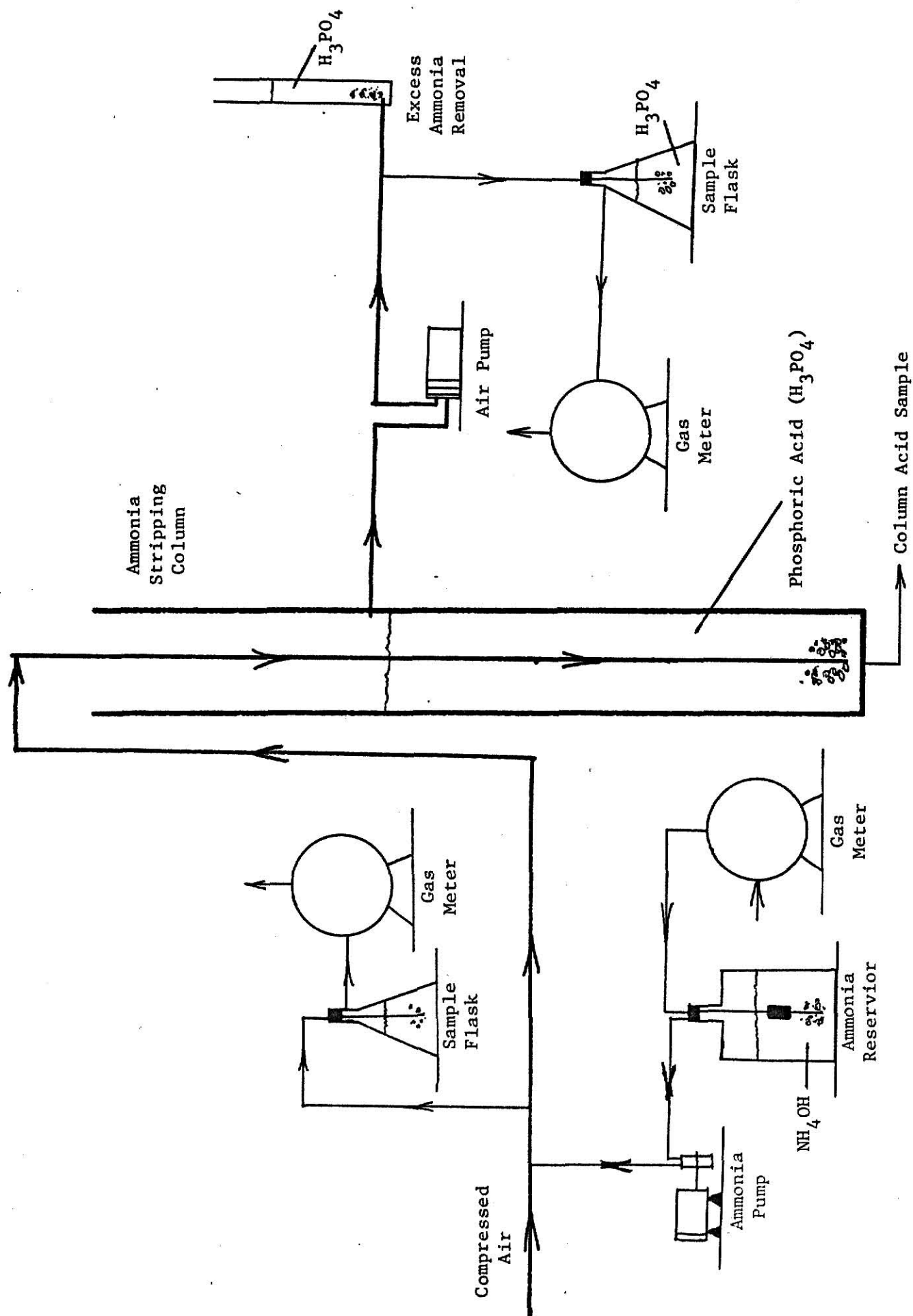


Fig. 13 - Laboratory apparatus for study of ammonia removal in phosphoric acid

of 6" diameter plexiglas construction. It contained an average of 20 liters of 85% H_3PO_4 over the testing period. The gas entered the column as shown and served as a mixing mechanism to promote absorption, as well as a transport method for getting the ammonia to the acid solution.

To complete the check on the removal efficiency of the stripper column, the amount of ammonia in the atmosphere above the acid surface was monitored using the same technique as for sampling the mixed gases before they entered the column. This sample was obtained using an air pump which continuously drew off the gas and pumped it into a flask of acid. A sample of acid from the bottom of the stripper column itself was also analyzed for ammonia content to keep track of ammonia buildup there.

Sampling

Depending upon how fast ammonia levels were increasing in the column acid, one, two, or three sets of samples were analyzed per day. Most of the time, uptake of ammonia was slow enough that only one or two samples were required. From each of the two sampling flasks, 1 ml of acid was pipetted out. A larger quantity (25-35 ml) of acid was taken from the bottom of the column. This larger sample was needed for the pH meter. A large sample of NH_4OH was also taken for a pH check.

Sample Preparation and Analysis

The flask samples, as well as 1 ml of the column sample were diluted to 100 ml each with distilled water. Each of these samples, which now had a pH in the range of 1.2-1.3, was treated with 1 ml of 0.62M zinc sulfate solution, followed by an amount of 6N NaOH

solution sufficient to raise the pH of the sample to 10.5 or higher (17). This resulted in a white precipitate of various calcium and magnesium compounds that might have precipitated upon nesslerization, causing incorrect spectrophotometer readings for ammonia concentration. The samples were then centrifuged for about 20 minutes at 4400 rpm. They were diluted in various proportions, depending upon expected ammonia concentrations, to 50 ml in Nessler tubes. One drop (~ 0.1 ml) of Rochelle salt and 1 ml of Nessler reagent were added to the 50 ml diluted samples. A blank sample was also set up using ammonia-free distilled water and the same quantities of Rochelle and Nessler that were added to the samples. The Rochelle salt acted as a coagulant for any trace impurities that might interfere with light readings. The tubes were stoppered and shaken moderately, then allowed to stand for 10 minutes to permit color development. The samples were placed in a Coleman model 6C spectrophotometer at a wave length of 410 microns. Per cent transmittance was set at 100% for the blank, then each sample was placed in the spectrophotometer for comparison. Using a previously prepared calibration curve, which plotted per cent transmittance vs. grams of N in a series samples of known ammonia concentrations in 50 ml, the concentrations in each sample could be computed by multiplying the amount read from the curve by the dilution factor for that particular sample.

The remainder of the column acid sample, as well as the NH_4OH sample were tested for pH and then returned to their respective places in the apparatus. This pH check was done to monitor the progress of neutralization occurring in each of these solutions. The acid was being neutralized by ammonia addition and the NH_4OH was depleted by

removal of ammonia from solution. When the pH of the NH_4OH dropped below about 10.5, the air passing through no longer picked up ammonia for transport to the acid column. At this time, fresh NH_4OH solution had to be used in its place.

Results

Based on the ammonia concentrations found in the three samples and the gas flow measurements taken as indicated on Figure 13, the quantity of ammonia added to the acid column and carried off in the exhaust gases could be computed (Appendix A). Approximately 1.16×10^7 mg of ammonia was added to the acid column while running at the previously stated air and ammonia flow rates for 31 days. In the exhaust gases, 7.99×10^4 mg was carried from the column. This resulted in a 99.3% removal of ammonia in the acid solution. Starting from a concentration of 640 mg/l ammonia on the first day, the concentration increased to approximately 85,000 mg/l by the 31st day. As has already been noted, the degree of neutralization of the acid by ammonia was monitored by pH changes. On the first day, the pH was zero. It did show some slight increases, sometimes approaching 1.0. However, these readings tended to fluctuate and on the 31st day, the pH reading was essentially zero again; it was assumed that neutralization had not yet begun to occur to any measurable degree.

Looking back through the data (Appendix A), it shows that no substantial increase of ammonia in the acid column occurred for the last nine days of operation, even upon replacement of the spent NH_4OH with fresh solution. During this same period, thick encrustations of white crystals began forming on the inside surfaces of the column above the liquid level. For the last four or five days, these crystals

also appeared, undissolved, in the acid itself. It was found that they were very soluble in non-ammoniated acid and only slightly less soluble in water. After final shut down on the 31st day, the solution in the column was left undisturbed for several days. At the end of this time, 4 to 5 inches of precipitate could be noted at the bottom of the column. The most likely possibility for this crystal was obviously some ammonium phosphate compound. Upon dissolving a known weight of the crystal in distilled water, it was found to be about 25% ammonia by weight. Using the Hach method (18) for total phosphate analysis, significant phosphate was found to be present also. The CRC Handbook of Chemistry and Physics (19) listed three ammonium orthophosphate compounds which could have been formed in this situation. They are $(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$. Some characteristics of these three compounds are shown in Table 3.

Comp.	Color	Molecular Weight	% NH_3 (By Wt.)	Solubility (gm/100 ml Water)	Calculated Solubility Prod.
$(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$	White	203	26.6	7.48×10^1	26.1
$\text{NH}_4\text{H}_2\text{PO}_4$	Colorless	115	15.6	3.88×10^0	22.7
$(\text{NH}_4)_2\text{HPO}_4$	Colorless	132	27.3	3.32×10^2	57.5

Table 3 - Characteristics of Three Ammonium Orthophosphate Compounds

Based on Table 3, it was felt that the most likely form of the crystal found in the stripping column is $(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$. The main reasons for this choice are 1) the white color, and 2) the ammonia content was approximately equal to that found in sample crystals

tested. Because the solubility of $\text{NH}_4\text{H}_2\text{PO}_4$ was nearly the same, it is possible that there was some of this compound present also. For the most part, however, it was probably $(\text{NH}_4)_3\text{PO}_4$ because of the white color.

The possibility does exist that the acid solution could have become saturated with crystals before it was neutralized to a pH near 7. This could be what happened once the ammonia concentration reached 80,000-85,000 mg/l. Finding the saturation value of ammonia in phosphoric acid would tell which controls, the saturation or neutralization process.

Special Tests

Because some slight decrease in the acid level in the column was noted, analysis of some of the physical properties was desired. It was felt that this decrease might be due to evaporation of water from the acid solution. This could happen because the column was not sealed and any process of evaporation would be promoted by the mixing action of the gases entering the column.

The first characteristic checked was specific gravity. The incident that prompted this investigation was the difficulty experienced in pipetting the 1 ml sample of column acid from the larger sample obtained from the bottom of the column. This parameter was checked for three different samples of acid withdrawn from the column at different times during the run. One was a sample of stock acid that contained no ammonia. The second was withdrawn from the column when the ammonia concentration was 4,600 mg/l. The third was obtained when the column concentration was 80,000 mg/l.

To obtain specific gravity, equal volumes (100 ml) of the acid

samples were weighed and compared with a like sample of distilled water. The results are noted in Table 4.

Weights (gms.)	Distilled Water	N = 0	N = 4600	N = 80,000
Full wt.	154.4	215.7	220.3	212.3
Empty wt.	54.4	48.1	59.3	56.7
Net wt.	100.0	167.7	161.0	155.6
Specific Gravity	1.000	1.676	1.610	1.556

Table 4 - Specific Gravity of Acid Solutions
(100 ml samples @ 25°C)

These results were exactly the opposite of what was expected. If pipetting was becoming more difficult, one might expect an increase in specific gravity. Thus, the change in density was probably not responsible for the difficulty. One cause of the decrease in specific gravity was the entrainment of air bubbles from mixing of the acid. The samples were allowed to stand for several hours in hopes of negating such effects. Apparently this period of time was not sufficient. After a period of several days the analysis was run again with essentially the same results.

The next logical step of the investigation was to examine viscosity changes. This could definitely cause problems pipetting. An electric rotating spindle viscometer was used. A sample of each of the three acids was placed in a 600 ml beaker. It was necessary to use this size beaker with this particular instrument. Sample volume itself was not important, just as long as the spindle was at the specified depth in the sample. A speed of 100 rpm was used with

a No. 2 spindle. This resulted in a conversion factor of 4. By multiplying the instrument reading by this factor, the viscosity in centipoises (cps) was obtained (See Table 5).

Trial No.	N = 0	N = 4600	N = 80,000
1	28.5	23.4	27.2
2	28.6	23.5	27.4
3	28.7	23.4	27.4
4	28.7	23.4	27.4
Average	28.6	23.4	27.4
Viscosity (cps)	114.5	93.6	109.6

Table 5 - Change in Viscosity of Acid Solution @ 25°C

Though some differences in these values can be seen, they are not considered to be significant (20). However, if conclusions were to be drawn from this data, it could be said that viscosity decreased slightly with increased ammonia concentration. Here again, this is exactly the opposite of what was expected, in view of the difficulties of pipetting the acid samples at higher ammonia concentration. It is not meant here to imply that there is any connection between ammonia concentration and viscosity, and there probably is no such connection.

This problem with pipetting was noted mainly once the ammonia content approached 70,000 mg/l and crystals were visible in the acid. The only other explanation available at this time is that the crystals themselves caused difficulties in pipetting. Because the samples for both specific gravity tests and the viscosity tests were left undisturbed for a time, any crystals present would have settled out. This, of

course, would have no effect upon the specific gravity test, but could have an effect on the results with the viscometer. Therefore this, plus the fact that pipetting difficulties were encountered only when crystals were in evidence, suggests that the crystals were probably responsible.

Evaluation of Results

The main problem with this investigation was that in using this laboratory set-up, a neutralization value for ammonia concentration in acid was not reached. The fact that a large amount of crystal formation occurred in the stripper is an indication that not all of the ammonia entering the acid was being absorbed by it. In fact, if the average acid volume (20 liters) is divided into the total amount of ammonia pumped into the column (1.16×10^7 mg), a theoretical ammonia concentration of 580,000 mg/l should have been in the acid on the 31st day. It was only 85,000 mg/l. Much of this could probably be accounted for in both the crystals on the inside walls of the column and the precipitate in the acid itself. This would probably not cover all of the discrepancy, however. Some error was introduced by the method used to introduce ammonia into the system. The period between samples usually was in the range of 8 to 12 hours, sometimes higher, sometimes lower. As the ammonia concentration in the NH_4OH decreased gradually over this time, the ammonia pumped from the NH_4OH bottle to the acid column also decreased. However, the ammonia input over that time was averaged and did not take into account the fact that the fresh NH_4OH depleted rapidly at first and then more slowly later on. The data in Appendix A shows this, in that when ammonia in the acid did increase, especially right after a new bottle of

NH_4OH was put on line, it usually did so very rapidly. Thus, the effect of averaging out ammonia input rate over several hours may have resulted in higher theoretical inputs than were actually occurring.

CO_2 REMOVAL

The choices available for CO_2 removal are much more extensive than for ammonia removal. It was desirable to study a process which would be compatible with acid stripping of ammonia in a packed tower. Alkaline stripping of CO_2 was the first method examined. The methane gas stream from the anaerobic digester at the KSU Boar Testing Station was used as a feed (2). After ammonia removal in the phosphoric acid, stripping of CO_2 was tried with a 2N NaOH solution. Many problems were encountered, mainly due to clogging of pipes and valves with the precipitate formed by CO_2 absorption. Jar studies done in the lab revealed that 2N KOH would produce less precipitate than 2N NaOH for the same CO_2 quantity removed (21). These were strictly qualitative observations; no data was taken by the investigators. However, some quantitative work has been done on comparing NaOH and KOH as absorption media for CO_2 (22). Below a concentration of 3.5N, KOH absorbed CO_2 twice as fast as NaOH. Above 9N, KOH showed a rapid increase in CO_2 uptake rate for reasons unknown by the researchers. They also found that beyond concentrations of 3 or 4N, NaOH absorption rates decreased. According to the investigators, this could probably be explained by low solubility of carbonate and bicarbonate in NaOH.

Lime was also evaluated as a CO_2 removal solvent at the KSU Boar Testing Station (2). Like NaOH and KOH, the reaction products also created problems with clogging and disposal. The main advantage

of lime over the other two solvents, however, was its comparatively low cost. Whether this is enough to outweigh the disadvantages of lime is still to be determined.

Because of all the mechanical difficulties caused by the caustic scrubber tested at the Testing Station, a process which would produce little or no such problem-causing chemical by-products was investigated as an alternative. Physical absorption would avoid that problem and it could hopefully be incorporated with acid stripping of ammonia. Thus, the most available media for physical absorption, phosphoric acid solution, was investigated for its ability to absorb CO_2 under moderate pressure.

Apparatus

A device was constructed to study the uptake of CO_2 into a H_3PO_4 solution under pressure (See Figure 14). It consisted of two cylindrical vessels made of laminated layers of PVC pipe and connected together as shown by $\frac{1}{2}$ " diameter galvanized pipe. Gate valves were installed at each outlet and one in the connection between the two vessels. The vessel labeled A had a volume of 2.68 liters and vessel B had a volume of 2.77 liters. A plugged hole was also installed on the A side of the center valve. Pressure gages were located as shown.

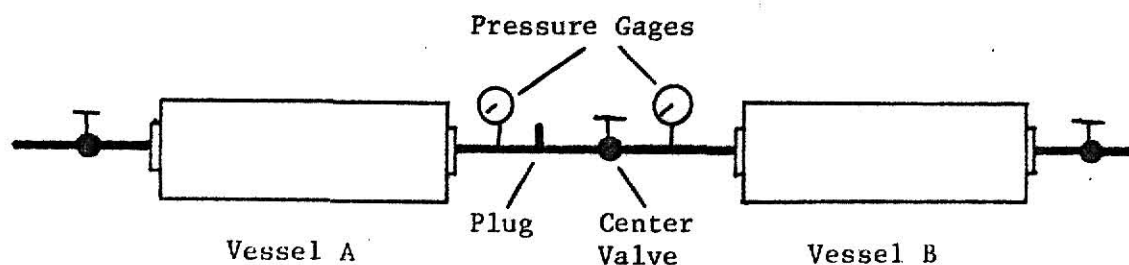


Figure 14 - Apparatus used to study CO_2 uptake into H_3PO_4

Procedure

Testing was done on a batch basis. A program was set up to investigate the absorption of CO_2 into a solution of acid and ammonia under various pressures. Also, the effect different concentrations of CO_2 in the atmosphere above the acid had on the absorption mechanism was examined. Thus, the program was to investigate CO_2 uptake at one, two, and three atmospheres (gage) pressure from atmospheres of zero, 10, 50, and 100% CO_2 . In those runs where CO_2 was less than 100% of the environment, helium was used as an inert filler gas because it was assumed that it would not be absorbed along with the CO_2 . This caused some problems which will be discussed later.

A typical run would start by placing 500 ml of acid solution (225 ml of stock, 85% H_3PO_4 , 225 ml distilled water, and 50 ml NH_4OH whose ammonia concentration was 25,000 mg/l) into vessel A. If this particular test was to be of a 50% CO_2 mixture at 2 atm, helium was added to vessel A at a pressure of 15 psig. With the center valve still closed, 45 psig of CO_2 was placed in vessel B. The center valve was then opened, allowing the gases to mix in A. The initial pressure in A was noted. Then the entire device was agitated by rolling it like a rolling pin on a flat surface for ten minutes. Pressure readings in vessel A were taken every minute. After ten minutes, a sample of the acid was drawn off and its CO_2 content was determined.

Sampling and Analysis

Upon completion of a run, an analysis of the CO_2 content of the acid was desired. A simple device for doing this (See Figure 15 on next page) involved the use of a 500 ml Erlenmyer flask with an evacuation nozzle. A balloon was stretched over the mouth of the

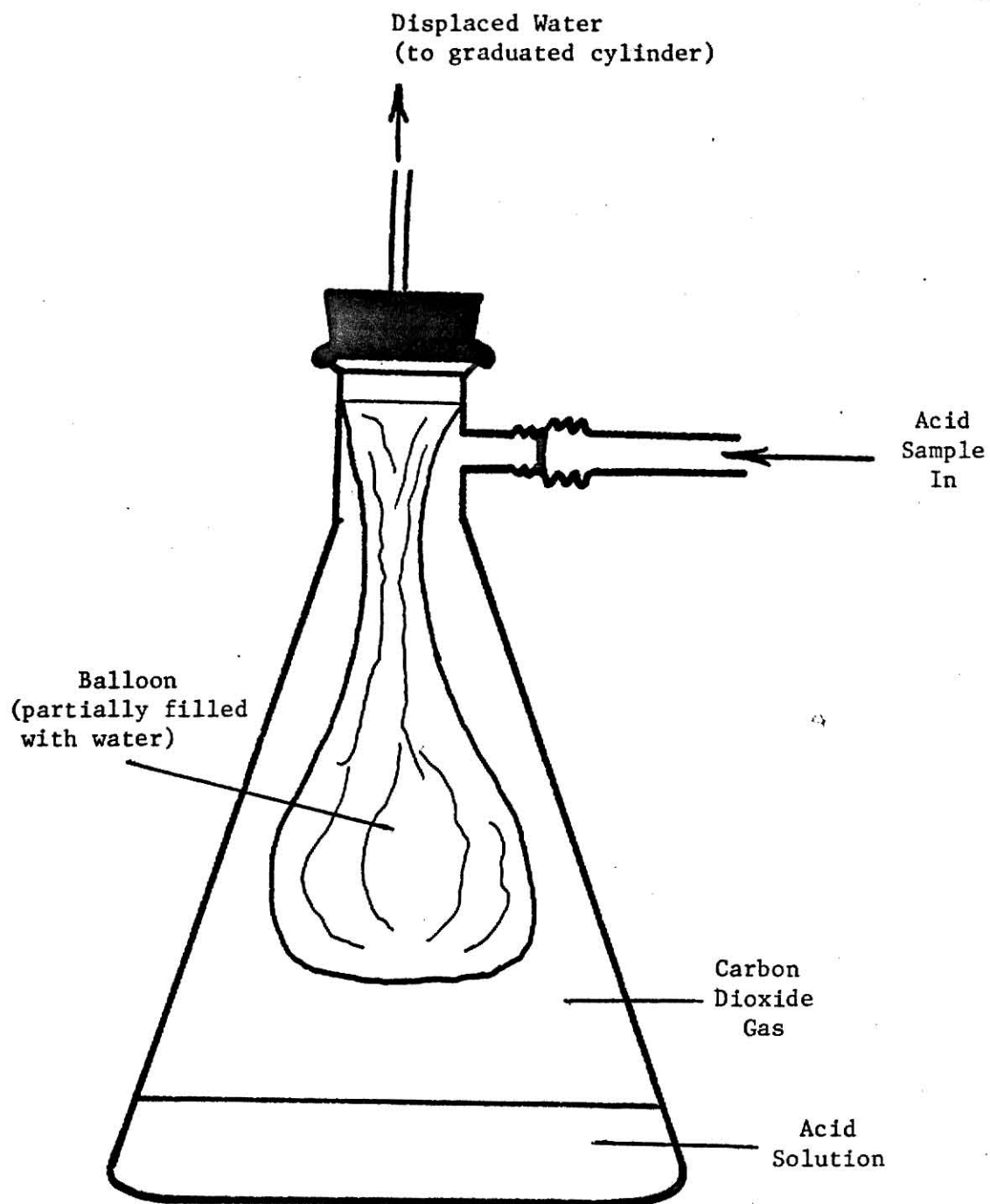


Fig. 15 - Sampling apparatus for CO₂ absorption test after sampling is completed

flask and the flask was evacuated through the nozzle, drawing the balloon into the flask. The tube used for evacuation was pinched off and detached from the vacuum pump. The balloon in the flask was then completely filled with tap water and plugged with a one-holed rubber stopper. Through the hole of the stopper, a tube was inserted which led to a graduated cylinder that captured any water forced from the balloon. Next, after the sample had been agitated for ten minutes as previously described, the tube on the nozzle of the flask was attached to the nozzle on the end of vessel A. The pinch clamp was removed from the tube, allowing a small amount of water to be displaced which was equivalent to the air volume in the tube. If water continued to flow after the clamp was removed, but before the valve on A was opened, this signified a leak which was admitting air into the system. This was not permissible and had to be repaired.

Finding the system to be sealed, the device was placed in a vertical position, with vessel A below B. The valve on A was slowly opened, allowing the pressure above the liquid surface in A to force the acid out into the tube and then into the flask. As the acid-gas mixture flowed into the flask and outside the balloon, water was displaced from the balloon into the graduated cylinder. Usually about 275-300 ml of water displacement was used. The valve was then closed, the pinch clamp replaced and the device detached from the tube leading to the flask.

The stopper was removed from the flask and the water remaining inside the balloon was discarded. The balloon was removed from the flask and the acid sample was poured into another graduated cylinder. The volumes of the displaced water and the acid sample were recorded.

The difference between these volumes was assumed to be equal to the volume of CO_2 absorbed by the acid. The acid was returned to vessel A with some minor losses. These losses were taken into account by checking the total acid volume every few trials and averaging the discrepancy over that number of trials. Thus, the total volume of acid present during each test was known.

Results

The volume data taken at the time of sampling was converted to units of mg CO_2 uptake per gram phosphoric acid present. These computations and data are presented in Appendix B. Also shown is the per cent of the acid volume drawn off that was CO_2 gas. This was needed for the conversion computations. As expected, the highest pressure conditions yielded the largest gas uptake into the acid. In a 100% CO_2 atmosphere, the uptake rate at 3 atm pressure ranged around 1.7 mg CO_2 /gm acid. However, high CO_2 conditions like these are not too likely in the gas produced by an anaerobic digester. A CO_2 content of 10-50% is a more reasonable range. At one atm, the uptake for 50% CO_2 was about 0.17 mg/gm, and for 10%, was only about 0.01 mg/gm. At a pressure of 2 atm, the uptake for 50% was about 0.30 mg/gm and for 10% was 0.06 mg/gm. Finally, for 3 atm pressure and 50% CO_2 , uptakes averaged 0.58 mg/gm, and for 10%, they were 0.08 mg/gm. Another way of presenting this information is to plot the per cent volume of the sample which was gas against the CO_2 partial pressure. See Appendix B. The data plots as a straight line and the plot can be used to predict the amount of CO_2 that will be absorbed for a given partial pressure. (See Figure 16 on the next page.) Thus, at 3 atm and say, 50% CO_2 in the gas stream, the amount of acid needed to remove most of

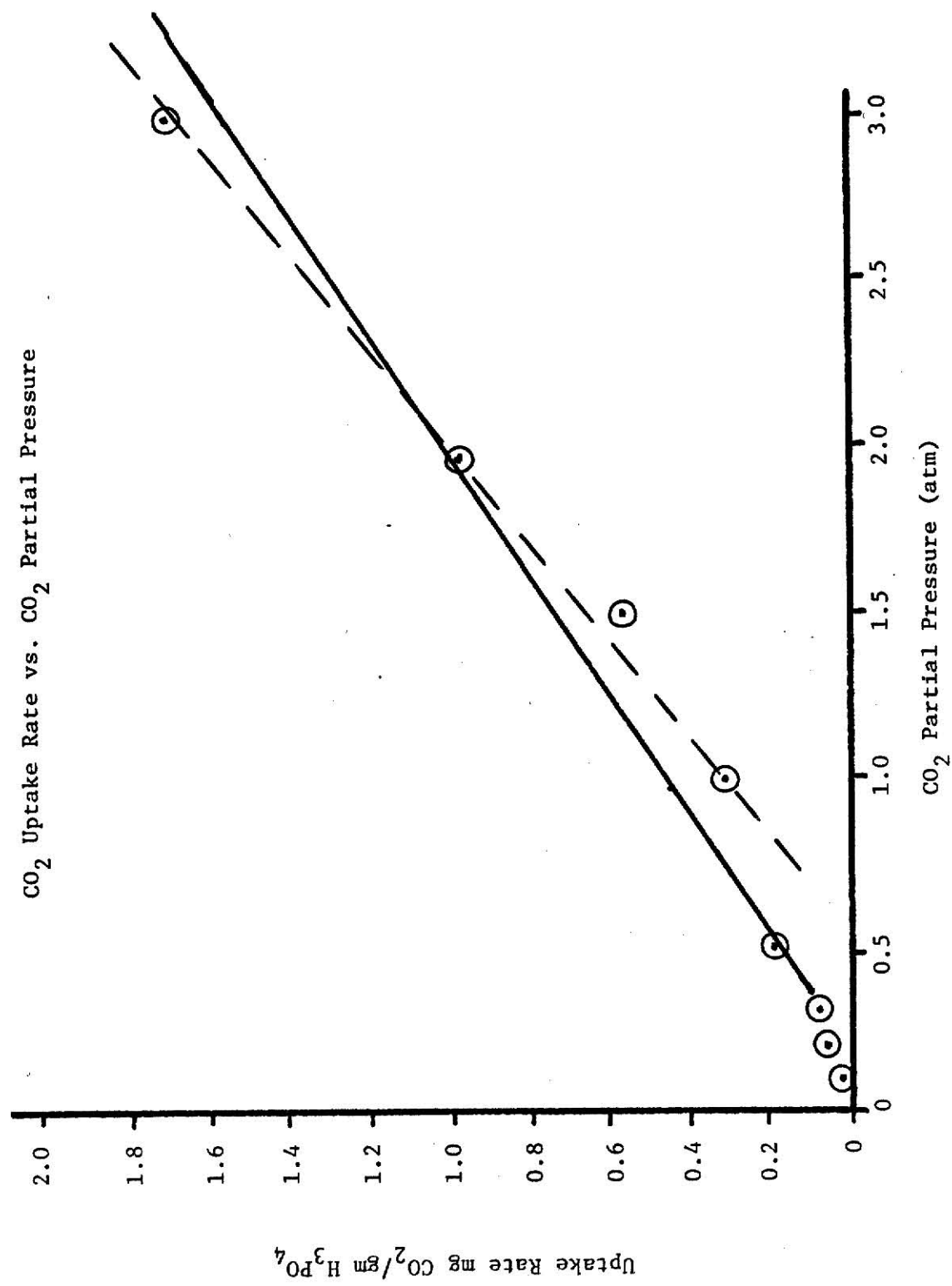


Fig. 16 - Plot of data of Appendix B

the CO_2 from the stream could be computed. The results do show that CO_2 removal by physical absorption into an acid solution is feasible.

Special Tests

There was a result that was rather unexpected. The reason helium was used in conjunction with CO_2 to create atmospheres that had less than 100% CO_2 was that it was assumed that helium would not absorb into the acid in any significant amounts. As is noted in the data of Appendix 2, some helium was absorbed by the solvent when runs were made with 100% helium (0% CO_2) at the specified pressures. This ranged around 7.4% for pressures of 1 and 2 atm, and was 9.3% for 3 atm. Thus, the question was raised, would methane also be physically absorbed into the acid solution? If so, excessive losses of methane could render the whole process useless because sufficient quantities of methane could not be recovered to make it worthwhile.

One reason methane had not been used earlier was that difficulty was experienced in finding a supply of methane at pressures of 2 or 3 atm. The lab natural gas (NG) available was only 2 or 3 psig, far too low to get any significant absorption. Surprisingly, chemical and welding suppliers in the area did not handle pressurized methane either. Thus, a method was developed to pressurize methane right in the absorption device using the lab NG. Without acid in the vessels, NG was used to flush out the device from one end with all three valves open. Then the valve on the end of vessel B was closed and the device allowed to fill with NG to the line pressure. Both the center valve and the one on vessel A were then closed. The NG line was then disconnected and a water line connected to the water tap was attached to the nozzle on A. Simultaneously turning on the water and opening the

valve allowed water into vessel A without letting NG out. The water continued to run until the pressure in A was 55-60 psig.

At that point the valve was closed and the water was turned off and disconnected. The device was then placed in a vertical position with vessel A below B and the valve between them was slowly opened, allowing the pressurized NG to flow from A to B. The center valve was closed after the pressures equalized and the device was inverted 180°, so that vessel A was directly above B. The valve on A was opened to relieve the pressure and then closed. Placing the device in a horizontal position, the plug next to the center valve was replaced by a nozzle. Now the NG line was reattached to the nozzle on the end of A and the NG tap turned on. In order to remove the maximum amount of water and prevent air from entering A, the device was again placed in a vertical position so that A was above B. The force of gravity plus the slight NG pressure above the liquid forced nearly all of the water out with minimal contamination of A by air. The plug was replaced with the gas still flowing out the plug hole and A was filled with NG ready to be pressurized by the same procedure as just outlined.

This entire process had to be repeated six to eight times to attain the 45 psig needed in B to get an overall pressure of 2 atm for the test to be run. It was not possible to do runs at three atmospheres because it would have required 5 atm of NG in B at the start of the test. It was felt that this was beyond the pressure limits of the device and so was not attempted.

To detect the amount of methane carried out in the acid after ten minutes of agitation, gas chromatography (GC) was used. First, a sample of NG straight from the lab tap was analyzed by GC for its

content of carbon dioxide, oxygen, nitrogen, and methane. See Table 6. By summing peak heights and then dividing each individual peak by that sum, a good estimate of the per cent each constituent (by volume) that was in the sample can be obtained. These are the figures that appear in Table 6. The numbers shown for the raw NG are actually an average of four separate analyses. The sample for the two tests which were taken at about two atm show that very little CH_4 is absorbed into the acid solution. Thus, the methane does not absorb as readily as helium and little loss of methane could be expected when the phosphoric acid is released to atmospheric pressure to desorb CO_2 .

Gas	% CO_2	% O_2	% N_2	% CH_4
Raw NG	8.4	1.2	19.3	71.0
Test 1	0	21.9	78.1	0
Test 2	0	23.6	75.0	1.4

Table 6 - Uptake of Various NG Constituents in H_3PO_4

CASE STUDY

From the experimental data that has been discussed and based on some assumptions made by earlier investigators, a preliminary design of a full scale feedlot facility can be undertaken. The combination of stripping ammonia in phosphoric acid and physical absorption of CO_2 could be carried out in a single unit, as shown on the next page in Figure 16. By stripping ammonia with acid under pressure in a packed tower, CO_2 could also be removed from the methane stream. This is what would happen in the absorber unit in Figure 16. The acid would then flow under pressure to another packed tower which would be open to the atmosphere. Here, under the lower pressure conditions, CO_2 would be released from the acid as it is agitated in its fall to the bottom of the tower. The acid (containing ammonia) would then be pumped back to the top of the absorber unit to be used again for removal of CO_2 and more ammonia. The methane from the top of the absorber would still contain about 10% CO_2 and would be used for mixing the contents of the digester.

There are four by-products of this treatment scheme which have possibilities for reuse. The first is methane. Besides its use for mixing, excess amounts can be bled off and used as a fuel to heat the digester and for other purposes. When the acid becomes neutralized by ammonia, it can be valuable as a liquid fertilizer, utilizing both the nitrogen and phosphorus. The stabilized solids from the digester would also be a good fertilizer. Finally, the supernatant from the digester can be used to flush the confinement area of the lot and transport the fresh wastes to the digester.

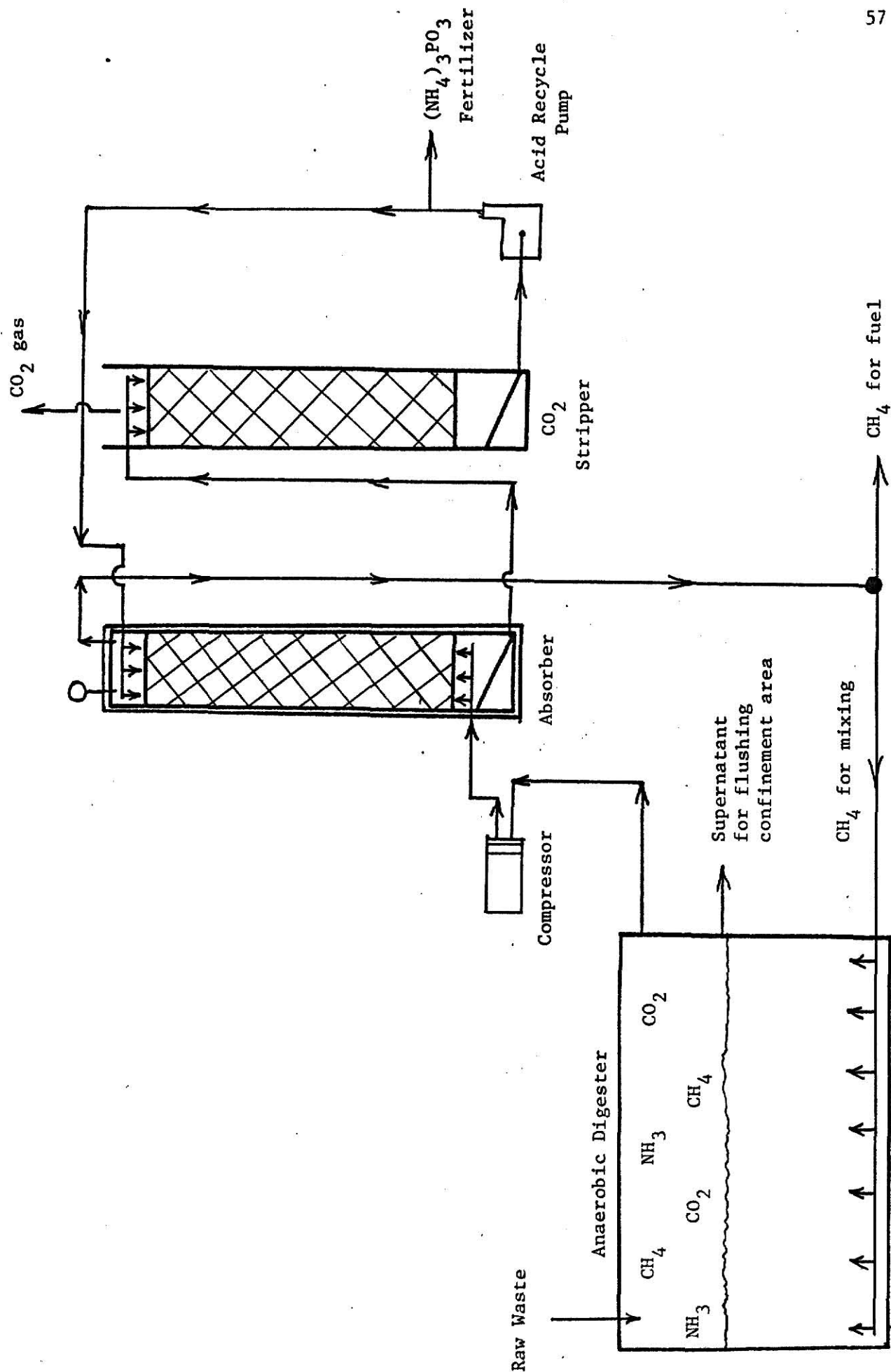


Fig. 17 - Proposed purification system for anaerobic digester gas

Digester

Computation of dimensions needed for a 2000 head swine feedlot. Assume average animal weight of 100 lbs.

Liquid volume per 100 lbs. of animal = 0.90 gal/day (3)

(2000 head) (0.90) = 1800 gal/day

Assume 15-day retention in digester: (1800) (15 days) = 27,000 gal.

27,000 gal. = 3610 cu. ft....assume 4000 cu. ft.

Check to see if volume is sufficient for volatile solids loading.

A reasonable VSS loading on a digester is considered to be 250 lbs.

VSS/1000 cu. ft. digester volume (3).

VSS = 0.47 lbs/day/head (3)

Total VSS per day = (2000) (0.47) = 940 lbs/day

$\frac{940}{4000} = \frac{X}{1000}$ solving for X X = 235 lbs/1000 cu. ft.

Since this is fairly close to the theoretical value, a 4000 cu. ft.

digester will have sufficient capacity for VSS.

Assume a depth of 10 ft., thus dimensions will be 20 x 20 x 10 ft.

Ammonia Removal

There is a 15-day retention time in the digester and the methane gas is returned there to be used for mixing. A removal of about 95% of the ammonia that enters the absorber was assumed for each pass.

As much as 0.05 lb/day/head of ammonia could be in the methane stream (23).

(2000 head) (0.05) = 100 lb/day

Remove 95%: (0.95) (100) = 95 lbs/day = 43,100 grams/day

From the data of Appendix 1, 85,000 mg/l of ammonia was in the 20 liters of acid after 31 days.

(85,000) (20) = 1,700,000 mg of ammonia

$$\frac{1,700,000 \text{ mg}}{(31 \text{ days}) (1000 \text{ mg/gm})} = 54.8 \text{ gm/day removed from the gas}$$

This was approximately a 99% removal rate. Assuming the worst conditions, that is that the capacity of the acid for ammonia absorption had been reached, a 95% removal rate would have required removal of 52.1 gm/day. If the capacity of the acid was not reached (as is very likely) a higher actual removal rate than 95% would occur. However, assuming these conditions,

$$\text{Acid volume: } \frac{20 \text{ liters}}{52.1 \text{ gm/day}} = \frac{X \text{ liters}}{43,100 \text{ gm/day}} \dots\dots X = 16,500 \text{ l/day} \\ = 4300 \text{ gal/day}$$

Passes per day @ 5 minutes

$$(12/\text{hr}) (24 \text{ hr/day}) = 288 \text{ passes per day}$$

$$\frac{8600 \text{ gal/day}}{288/\text{day}} = 15.0 \text{ gal/pass are needed for desired removal}$$

CO₂ Removal

Since phosphoric acid is also being used to absorb CO₂, the amount of CO₂ to be removed may require more than 15.0 gal/pass. If this is true, this amount will determine the quantity of acid needed per 5 minute pass. First, methane production must be calculated:

$$1 \text{ lb BOD}_L \text{ will yield } 5.62 \text{ cu. ft. of pure methane (24)}$$

Through review of the available data, an average of 0.3 lbs. of BOD_L/day/head was used.

$$\text{Total BOD}_L = (0.3) (2000 \text{ head}) = 600 \text{ lbs/day}$$

$$\text{Methane production} = (600) (5.62) = 3370 \text{ cu. ft/day}$$

Assume only 80% conversion of BOD_L to methane.

$$(0.80) (3370) = 2700 \text{ cu. ft/day}$$

Assume 50% of gas volume produced is CO₂

$$\text{Total gas produced} = (2700) (2) = 5400 \text{ cu. ft/day}$$

Want to remove 85% of CO_2 from gas produced in digester

$$(0.85) (2700) = 2300 \text{ cu. ft./day}$$

$$\frac{(2300 \text{ cu. ft./day}) (28.3 \text{ l/cu. ft.})}{22.4 \text{ l/Mole}} = 2906 \text{ M/day} = 128,000 \text{ gm/day}$$

Since methane is used to mix the digester contents, large amounts of the gas drawn off the digester is CO_2 -free methane. This gas used for mixing is probably about 10-15% CO_2 and picks up only a small amount of CO_2 during mixing. So the gas drawn into the absorber would actually be only about 10% CO_2 or a little more. If the absorber pressure is 3 atm (gage), the partial pressure of CO_2 is then about (3.0) (0.10) or 0.3 atm. According to the plot of data in Appendix 2, for a total pressure of 3 atm and a CO_2 partial pressure of 0.3 atm, an uptake rate for CO_2 into H_3PO_4 would be about 0.08 mg CO_2 /gm H_3PO_4 . If want to remove 1.28×10^8 mg CO_2 /day,

$$\frac{1.28 \times 10^8 \text{ mg/day}}{288/\text{day}} = 4.44 \times 10^5 \text{ mg/pass @ 5 min.}$$

$$\frac{0.08 \text{ mg}}{1 \text{ gm}} = \frac{4.44 \times 10^5 \text{ mg}}{X \text{ gm}} \text{ solving for } X \dots X = 5.55 \times 10^6 \text{ gm/day}$$

$$\text{Specific gravity of } \text{H}_3\text{PO}_4 = 1.319 \text{ gm/ml}$$

$$\frac{5.55 \times 10^6 \text{ gm}}{1.319 \text{ gm/ml}} = 4.21 \times 10^6 \text{ ml/pass} = 149 \text{ gal/pass}$$

Since this acid requirement is larger than the one for ammonia removal, this quantity controls.

Purification of the 5400 cu. ft./day of gas (2700 cu. ft. of which is pure methane) produced by the anaerobic digestion of the waste from 2000 swine could be accomplished in a treatment scheme like the one described here. Besides the products usable directly from the digester--

supernatant and stabilized solids--a purified methane gas stream and an ammonium phosphate fertilizer can be produced. By using the phosphoric acid solution already present for ammonia removal as a physical absorption medium for CO_2 , approximately 85% of the CO_2 can be removed from the methane stream, thus improving its fuel value greatly. In order to achieve this level of CO_2 removal, approximately 150 gallons of acid solution is needed for a five minute retention time in a packed tower. This is far greater than the 15.0 gallons needed to remove 100% of the ammonia present in the same five minute pass through a packed tower. The liquid ammonium phosphate fertilizer produced could be applied directly to croplands once its pH has been raised to near neutrality. As the concentration of ammonia in the acid approaches 70-80,000 mg/l, precipitation of ammonium orthophosphate will probably occur. There is the possibility of removing this precipitate to allow for more ammonia absorption. The precipitate itself may be useful as a fertilizer, either in the solid form or in aqueous solution.

CONCLUSIONS

1. The use of phosphoric acid in a packed tower to absorb ammonia from a gas stream will produce a solution of ammonium phosphate and will result in significant removal of ammonia from the gas stream.
2. Formation of ammonium orthophosphate crystals (probably $(\text{NH}_4)_3\text{PO}_4$) occurs when ammonia nitrogen concentrations approach 70,000 to 80,000 mg/l. These crystals could cause difficulties like the clogging of pipes and valves.
3. The physical characteristics of phosphoric acid which were investigated did not change significantly because of ammonia absorption, in the studied concentration range.
4. Carbon dioxide can be removed from a gas stream by physical absorption into phosphoric acid under pressure. The amount of removal is dependent upon the operating pressure. The CO_2 will then be released when the acid solution is returned to atmospheric pressure.
5. Under conditions found to be conducive to physical absorption of CO_2 , no significant amounts of methane were absorbed into the acid. Thus, the loss of methane by this route would only be in trace amounts, if at all.

RECOMMENDATIONS

1. A determination of whether the maximum concentration of ammonia allowable in the acid solution is controlled by a) the neutralization concentration of ammonia in H_3PO_4 or, b) by the saturation concentration of ammonium orthophosphate in solution should be made. If the acid becomes saturated and begins to precipitate ammonium orthophosphate, dilution of the acid may be necessary to permit ammonia concentrations to increase enough to neutralize H_3PO_4 . A much more careful measurement of the ammonia into and out of the acid solution would have to be carried out than was used in this study.
2. A numerical value should be obtained for neutralization concentration of ammonia in phosphoric acid. This could be used to determine how long it would take to obtain enough ammonium phosphate fertilizer to be useful for application to croplands.
3. Further investigations could be conducted to study the possibility of recovery of ammonia as ammonium orthophosphate crystal, rather than the liquid, for use as fertilizer. A determination of the fertilizer value of the crystal would have to be made. This would still provide a useful by-product in the event saturation of the acid is reached before neutralization occurs.

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A P P E N D I X A

Ammonia Stripper Data

Ammonia Stripper Data

Day No.	NH ₃ Add. Rate (ml/min)	NH ₃ Conc. in Column (mg/l)	Cummulative NH ₃ Added (x10 ⁵ mg)	Cummulative NH ₃ Out (x10 ³ mg)	Per Cent Removal
1	---	640	0	0	---
	395	1250	0.24	0.61	97.4
2	365	1250	1.13	0.61	99.5
3	310	2200	6.33	1.16	99.8
	310	2450	6.59	1.16	99.8
4	480	2700	7.22	1.16	99.8
	455	3000	9.20	1.16	99.9
5	430	3500	12.3	2.03	99.8
	415	3850	12.3	2.03	99.8
6	430	4200	13.7	2.33	99.8
7	340	4600	14.6	2.33	99.8
8	---	11,500 ¹	16.1	2.33	99.9
	440	12,000	16.3	6.45	99.6
9	400	13,300	16.4	7.57	99.5
	585	14,000	16.5	7.57	99.6
10	---	8500 ²	16.5	7.57	---
	120	10,500	16.7	9.22	99.5
11	130	8000	16.9	9.92	99.4
	185	7200	16.9	9.92	99.4
12	255	7500	17.2	9.92	99.4
13	285	6600	17.3	11.4	99.3
14	395	6500 ³	17.3	11.7	99.3
	470	8000	17.3	11.7	99.3
	470	7200	17.3	12.1	99.3
15	570	7200 ⁴	17.4	12.1	99.3
16	470	8800	22.2	41.5	98.1
17	615	16,000	44.9	42.1	99.1
18	710	45,000	57.7	43.2	99.2
19	525	45,000 ⁵	57.7	43.2	99.2
	---	45,000	57.7	43.2	99.2
	215	45,000 ⁵	57.7	43.2	99.2

Ammonia Stripper Data

Day No.	NH ₃ Add. Rate (ml/min)	NH ₃ Conc. in Column (mg/l)	Cummulative NH ₃ Added (x10 ⁵ mg)	Cummulative NH ₃ Out (x10 ³ mg)	Per Cent Removal
20	455	45,000	58.1	43.8	99.2
21	400	45,000	58.1	43.8	99.2
	525	45,000	65.7	43.8	99.3
	565	45,000 ⁶	65.7	43.8	99.3
22	340	60,000	66.7	44.4	99.3
23	375	90,000	73.6	44.6	99.4
24	400	70,000	73.9	44.6	99.4
25	585	70,000	88.6	49.7	99.4
26	460	70,000 ⁶	88.6	49.7	99.4
	185	70,000	91.3	50.3	99.4
27	335	70,000	95.4	50.8	99.5
	385	80,000	104	50.8	99.9
28	470	80,000	104	50.8	99.9
	575	70,000	104	54.1	99.5
29	575	40,000	104	55.8	99.5
	475	60,000	107	55.8	99.5
30	490	60,000	107	55.8	99.5
	510	45,000 ⁷	107	57.1	99.5
31	520	85,000 ⁸	116	79.9	99.3

¹ Added 1 liter of 5N NH₄Cl solution to speed up neutralization

² Removed some column acid and replaced with distilled water

³ Replaced NH₄OH bottle with new one

⁴ Replaced open graduated cylinders with sealed sample flasks

⁵ Add NaOH pellets to NH₄OH to raise pH back to 14

⁶ Replaced NH₄OH bottle with new one

⁷ Sample from top of column at same time was 85,000 mg/l

⁸ Sample from top of column

A P P E N D I X B

Data for CO_2 Uptake into H_3PO_4 Solution

APPENDIX B

Data for CO₂ Uptake into H₃PO₄ Solution

Total pressure = 1 atm

Trial (agitation time, min.)	% Sample Vol. as Gas				CO ₂ Uptake Rate (mg CO ₂ per gm H ₃ PO ₄)		
	100/1.0 ¹	50/0.5	10/0.1	0/0.0	100/1.0	50/0.5	10/0.1
I (10)	7.41	6.35	6.38	7.69 ²	---	---	---
II (10)	5.56	9.09	7.02	7.14 ²	0.184	0.180	0.011
III (10)	12.3	8.62	5.08	***	0.406	0.162	0
III (20)	9.26	***	***	***	0.307	***	***

¹Per cent CO₂ (by volume) originally present/CO₂ partial pressure (atm)²The average of these numbers (7.42%) was used as the helium uptake rate at 1.0 atm

--- Acid volumes were not recorded for these trials, thus no uptake rate could be computed

*** No test conducted

APPENDIX B (continued)

Data for CO₂ Uptake into H₃PO₄ Solution

Total pressure = 2 atm

Trial (agitation time, min.)	% Sample Vol. as Gas				CO ₂ Uptake Rate (mg CO ₂ per gm H ₃ PO ₄)		
	100/2.0 ¹	50/1.0	10/0.2	0/0.0	100/2.0	50/1.0	10/0.2
I (10)	21.7	15.1	7.14	7.41 ²	---	---	---
II (10)	26.8	14.8	8.62	7.55 ²	0.886	0.366	0.063
III (10)	30.4	10.7	6.90	***	1.004	0.230	0.006
III (20)	34.5	***	***	***	1.141	***	***

¹Per cent CO₂ (by volume) originally present/CO₂ partial pressure (atm)²The average of these numbers (7.48%) was used as the helium uptake rate at 2 atm.

--- Acid volumes were not recorded for these trials, thus no uptake rate could be computed

*** No test conducted

APPENDIX B (continued)

Data for CO₂ Uptake into H₃PO₄ Solution

Total pressure = 3 atm

Trial (agitation time, min.)	% Sample Vol. as Gas				CO ₂ Uptake Rate (mg CO ₂ per gm H ₃ PO ₄)		
	100/3.0 ¹	50/1.5	10/0.3	0/0.0	100/3.0	50/1.5	10/0.3
I (10)	36.5	***	9.30	9.43 ²	---	***	---
II (10)	52.7	22.7	10.9	9.26 ²	1.746	0.597	0.082
III (10)	50.0	25.3	8.47	***	1.655	0.559	0.002
III (20)	52.6	***	***	***	1.740	***	***

¹Per cent CO₂ (by volume) originally present/CO₂ partial pressure (atm)²The average of these numbers (9.34%) was used as the helium uptake rate at 3 atm

--- Acid volumes were not recorded for these trials, thus no uptake rate could be computed

*** No test conducted

APPENDIX B (continued)

Sample Calculations

Trial II (10): 100% CO₂ at 2 atm and 490 ml acid present

5.56% of the sample volume was gas (assumed to be 100% CO₂)

Thus, assume that H₃PO₄ contained 5.56% CO₂ by volume.

$$(0.0556) (490) = 0.0272 \text{ liters}$$

As moles of CO₂:

$$\frac{22.4 \text{ liters}}{1 \text{ mole}} = \frac{0.0272 \text{ l}}{X \text{ moles}} \quad \text{Solving for X} \dots X = 0.0012 \text{ mole CO}_2$$

As weight of CO₂ (MW = 44 gm/mole):

$$0.0012 \text{ mole} = 0.0534 \text{ gm CO}_2 = 53.4 \text{ mg CO}_2$$

Assume specific gravity of H₃PO₄ = 1.319

Therefore, acid weighs 1.319 gm/ml

Only 45% (by volume) of solution is H₃PO₄

$$\text{Acid weight} = (0.45) (490 \text{ ml}) (1.319) = 291 \text{ gms}$$

CO₂ Uptake:

$$\frac{\text{mg CO}_2}{\text{mg H}_3\text{PO}_4} = \frac{53.4}{291} = 0.184 \text{ mg CO}_2/\text{gm acid}$$

Note: For trials of less than 100% CO₂, like II (10) @ 1 atm,

9.09% of sample volume was gas

$$9.09 - 0.5(7.42) = 5.38\% \text{ CO}_2$$

Then

$$(0.0538) (0.485 \text{ liters}) = 0.0261 \text{ liters}$$

CARBON DIOXIDE AND AMMONIA REMOVAL
FROM ANAEROBIC DIGESTION GAS

by

JAMES V. DABER

B.S., University of Wisconsin - Platteville, 1973

AN ABSTRACT OF A MASTER'S THESIS

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MASTER OF SCIENCE

Department of Civil Engineering

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ABSTRACT

The trend toward feedlot confinement for the raising of livestock is growing rapidly in the United States. The wastes are in larger and more concentrated quantities than have been previously encountered. Among the processes which have been investigated for the disposal of such wastes is anaerobic digestion, which will produce stabilized solids and methane gas.

The methane gas produced from the anaerobic digestion of animal wastes generally contain large amounts of carbon dioxide. In addition, ammonia is present in levels which may be toxic to anaerobic organisms. Thus, the removal or reduction of CO_2 and ammonia is desirable to improve methane quality as a fuel and to reach optimum production levels.

There are several available processes for ammonia removal from a gas stream, all of which involve stripping with acid. The use of phosphoric acid (H_3PO_4) which produces a liquid fertilizer, ammonium phosphate, was investigated.

Physical absorption of CO_2 into a solution of H_3PO_4 under moderate pressures is feasible. Upon return to atmospheric pressure, the CO_2 is released from solution as a gas. Methane losses due to physical absorption are not significant.

Combination of acid stripping of ammonia and physical absorption of CO_2 in the same acid solution appears to be possible. This could be accomplished in single pressurized, packed tower, followed by another packed tower open to the atmosphere where CO_2 release would occur.