ENHANCEMENT OF SWINE WASTE DIGESTION
THROUGH AMMONIA AND CARBON DIOXIDE REMOVAL

by

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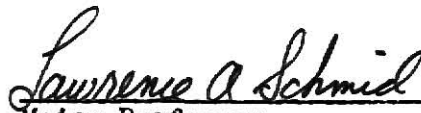
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INTRODUCTION

In 1968 investigations conducted at Kansas State University characterized properties of swine waste and explored the possibilities of digesting the waste anaerobically (25). Laboratory scale digestion studies showed digestion by conventional means would provide liquification of solids. Methane production was inhibited, however. Volatile acid concentrations were high but the pH of the digester contents remained near neutral rather than dropping. High ammonia concentrations observed were thought to be the cause of low methane production.

Research supported by the Kansas State Water Resources Research Institute has permitted examination of a method of carbon dioxide and ammonia removal from a full scale anaerobic digester located at the Kansas Pork Producers' Council Boar Testing Station, Manhattan, Kansas.

Construction of the digester was initiated in January, 1974, through the cooperation of the Departments of Animal Science and Industry, Agricultural Engineering and Civil Engineering of the Kansas State University, Manhattan, Kansas. Operation of the digester commenced in July of 1974, and continued until March of 1975.

The literature reviewed summarizes the investigations of ammonia toxicity by McCarty and McKinney in the early 1960's. The work of these investigators established the levels of ammonia concentration toxic to bacteria in anaerobic digesters. Literature published subsequent to this work supports these findings and indicates that anaerobic digestion of undiluted swine waste can be hampered by high ammonia concentrations.

The examples of swine waste digestion cited attest to the interest in anaerobic digestion on the part of agricultural producers concerned with animal waste management. A good deal of this interest stems from the attractiveness of recovering valuable energy in the form of methane gas; but, it should be remembered that the stabilization of a possible source of pollution is the primary objective of this as well as any other waste stabilization process.

Anaerobic digestion will occur readily where organic material is allowed to decompose in the absence of oxygen. The numerous small sized swine waste digesters used in Taiwan take advantage of this natural biological decomposition. Their simple construction, while suitable for that society, makes them inefficient. The problem then is to develop a system of swine waste digestion that is both highly efficient and reliable.

This study examined a method intended to intensively and efficiently digest waste from large confined swine feedlots. Recovery of the nitrogen and methane by-products of the waste stabilization process was sought. A discussion of the results of ten months of field research is presented. Recommendations for further research necessary are discussed.

LITERATURE REVIEW

Description of the Anaerobic Process

Anaerobic digestion is a fermentation process carried out by bacteria which utilize organic matter and many synthetic organic compounds as a growth substrate. The breaking down of this organic matter results in the formation of carbon dioxide and methane gases when the anaerobic process proceeds to completion. If the methane fermentation step does not take place, less stabilized, odorous compounds may result. These are partially oxidized end products such as mercaptans, amines and volatile acids (13).

In contrast to aerobic stabilization of waste, anaerobic digestion occurs in an oxygen free environment. Several species of either obligate anaerobic or facultative bacteria break down organic matter to volatile fatty acids, hydrogen and carbon dioxide. Lysis of proteins, amino acids and lipids also occurs.

Hobson (10) has concluded that facultative anaerobic Streptococci constitute about 50 percent of the bacteria found in swine waste. However, the Streptococci do not possess enzyme systems which can take part in the fundamental breakdown of polysaccharides and proteins. The Streptococci are instead thought to reduce the digester contents to an oxidation-reduction potential suitable for growth of strict anaerobes. Gram-negative non spore-forming anaerobes fermenting sugar are the most likely group responsible for the primary stage of anaerobic digestion. Shaw (26) analyzed digesters treating swine waste. Hydrolytic activity was attributed to the anaerobic bacteria rather than the facultative anaerobes.

Amylolytic activity was found to be carried out by several groups of bacteria; the major groups are gram-negative <u>Coccobacilli</u> and <u>Clostridium butyricum</u>. Cellulolytic bacteria are also heterogenous while hemicellulose-fermenting bacteria were predominantly <u>Bacteroids ruminicola</u>, a species prevalent in rumens. This bacterium and many others produce ammonia through deamination of amino acids. <u>Clostridia</u> were found to be the principal proteolytic bacteria.

Products associated with the breakdown of complex waste by bacteria such as those mentioned above include hydrogen gas, carbon dioxide, formic acid, acetic acid, propionic acid and butyric acid as well as other intermediates. The acids are collectively referred to as volatile acids. Their levels of concentration and effect upon pH are of considerable importance in operation of stable digestion. A clearer understanding of ammonia toxicity resulted from investigations of volatile acid toxicity by McCarty and McKinney (15,16).

The biological transformations discussed above are the first stage of the two stage anaerobic digestion process as conceived by McCarty (17), Pretorius (20) and McKinney (18). The second stage (both stages actually occur simultaneously) is referred to as the methane phase. Hobson (10) suggests that bacteria such as <u>Methanobacterium</u> ferment glucose producing hydrogen, acetate and ethanol among other products and yield hydrogen in sufficient amounts to form more acetate rather than ethanol. Acetic acid constitutes approximately 72 percent of the volatile acids present in anaerobic digesters (17,23). The high percentage of acetic acid has led investigators to theorize that this is the major precursor of methane production (10,17,18,20). Shaw (26) detected only acetic acid during balanced digestion of swine waste, although propionic, butyric and higher volatile

fatty acids were present during initiation of digestion. Hydrogen and carbon dioxide gases were initially present but methane and carbon dioxide were the only gases present during balanced digestion.

The importance of common volatile acid intermediates, formic, propionic, butyric, valeric, isovaleric and caproic acids has not been fully determined, although McCarty (23) attributes 13 percent of methane produced to propionate reduction. Methanogenesis has been demonstrated in pure cultures by gas flow techniques from the substrates hydrogen and carbon dioxide and formate (30). Pretorius (20) summarizes the present (1973) knowledge of methanogenesis well:

> "As acetate seems to play such an important role, one would expect that the most numerous methanogenic bacteria present in anaerobic digestion would be those able to grow on acetate as their sole energy source. Surprisingly the pure cultures of methanogenic bacteria thus far isolated and cultivated could only obtain their energy for growth from formate methanol and hydrogen-carbon mixtures. Acetate alone could not maintain the growth of methanogenic bacteria, unless it was supplemented with some other energy source such as formate. These findings seem to indicate that the formation of methane from complex substrates is not just a simple inter- or intracellular process but probably a combination of both."

Control of volatile acid synthesis is necessary to achieve adequate digestion of wastes and to prevent inhibition of methane production. Municipal digestion facilities achieve this control by limiting solids concentrations fed to digesters. Swine wastes contain volatile acids in higher concentrations than municipal waste systems, particularly when the swine waste is undiluted (24). In addition, ammonia nitrogen concentrations are higher in swine waste than municipal wastes. These high concentrations can cause problems peculiar to swine, chicken, highly concentrated municipal and industrial wastes. The section entitled Ammonia Toxicity examines these problems.

Ammonia Toxicity

McCarty and McKinney (15) undertook investigations in 1961 to resolve controversy surrounding volatile acid toxicity. In their words:

> "One group of investigators believes that high acid concentrations are the result of a low activity of the methane-producing organisms. They believe that volatile acids are toxic to these organisms only in an indirect manner through a reduction in pH, a condition which can be relieved by the addition of buffering materials such as lime.... The other group of investigators feels that a volatile acid concentration above about 2,000 mg/l causes a retardation of the methane-producers regardless of the pH maintained. Thus, they believe materials added to raise the pH are of no benefit and the toxic conditions can be relieved only through a reduction in the organic load or by dilution."

Laboratory scale digesters containing buffered waste sludge were fed sodium acetate in concentrations from 2,000 to 16,000 mg/l. Rate of acetate utilization was determined and found to decrease as the concentration of acetate fed was increased from 2,000 mg/l upward. The pH of the digesters was 7.40-7.50 initially and rose to 7.85-8.20. The high pH at the end of the runs was due to formation of sodium bicarbonate as the acetate was utilized. Similar results were obtained with slug feeding of sodium chloride, sodium carbonate and sodium sulfate. At concentrations of 4,000 mg/l and above, the various salts were highly toxic. Rate of acetate utilization for digesters fed the four different salts was essentially the same and six to ten times lower than that of the control. The four different anions showed little difference in effect and the main toxic effect was attributed to the sodium cation. Cation toxicity was thus felt to be a more appropriate description of toxicity associated with high volatile acids than was the phrase volatile acid toxicity.

McCarty and McKinney (16) next examined the effects of various cations upon methane bacteria utilizing acetate. Chloride and acetate salts of calcium, magnesium, sodium, potassium and ammonium were used in the study. Again slug feeding was employed to simulate a rapid increase in volatile acid concentrations and subsequent neutralization with alkaline materials.

The effect of the various chloride salts added in equivalent concentrations was different. Calcium and magnesium chlorides were least toxic. The two monovalent cations, sodium and potassium, were notably more toxic, whereas ammonium chloride was the most toxic.

Digesters fed equivalent concentrations of 9,000 mg/l of the acetate salts of the five cations produced the same results as the chloride salts. The ammonium salt was again the most toxic.

When 16,000 mg/l as acetate was fed, results differed. Ammonium acetate utilization was initially greater than sodium acetate or potassium acetate but when ammonium acetate utilization reached 3,000 mg/l acetate utilization ceased entirely in that unit. Acetate utilization continued in the other four digesters. Thus, a different type of toxicity occurred due to the ammonium cation than the calcium, magnesium, sodium or potassium cations. Again the results showed that toxicity of volatile acids was primarily due to the cation associated with either the chloride or acetate salts.

McCarty and McKinney then further investigated ammonia toxicity. Concentrations from 2,000 mg/l to 14,000 mg/l of ammonium acetate were added to five digesters. The digester containing 2,000 mg/l ammonium acetate was the control. Those digesters with higher ammonium acetate concentrations showed initial rates of acetate decomposition lower than

that of the control with the exception of the 5,000 mg/l fed digester. With time, however, all four of the digesters showed declining rates of acetate utilization. No acclimation to the toxic effect was exhibited. All activity ceased in the units after nine days. Acetate utilization resulted in ammonium bicarbonate formation and an increase in pH above the initial value of 7.00. Failure occurred at correspondingly lower pH's in the digesters fed higher concentrations of ammonium acetate.

Free ammonia (NH_3) is related to the ammonium ion (NH_4^+) and pH as follows:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \quad \text{- (1)}$$

The equilibrium constants for this equilibrium and water may be expressed as:

$$\frac{(NH_4^+)(OH^-)}{(NH_3)(H_2O)} = k_b \quad \text{- (2)}$$

$$\frac{(H^+)(OH^-)}{H_2O} = k_w \quad \text{- (3)}$$

k_b and k_w are the ionization constants of aqueous ammonia and water, respectively. Combining these equations yields:

$$(NH_3) = \frac{k_w}{k_b} \frac{(NH_4^+)}{(H^+)} \quad \text{- (4)}$$

The ratio k_w/k_b will be constant at constant temperatures. Equation four shows that at lower pH's higher ammonia concentrations are necessary to produce equal concentrations of free ammonia.

McCarty and McKinney calculated free ammonia concentrations from the ammonium acetate addition results. Death occurred at free ammonia concentrations in excess of 150 mg/l.

Similar trials with additions of ammonium acetate, ammonium chloride and ammonium bicarbonate also indicated that *free ammonia concentrations in excess of 150 mg/l caused digestion failure.*

The effect of pH and ammonia ion toxicity was investigated next. Three units were fed 10,000 mg/l ammonium acetate as acetic acid. The pH was held constant in one unit by adding an additional 4,000 mg/l of calcium acetate. The second unit was fed 4,000 mg/l of magnesium acetate while the third unit was fed nothing other than the 10,000 mg/l ammonium acetate.

The pH of the calcium fed unit remained near seven, due to precipitation of calcium carbonate in accordance with the equation:

$$1/2\ Ca\ (HCO_3)_2 \longrightarrow 1/2\ CaCO_3 + 1/2\ CO_2 + H_2O \text{ - - - - - - - - - } (5)$$
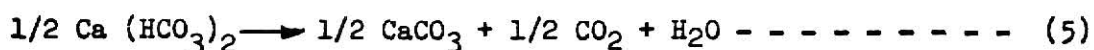
In the magnesium fed unit and the unit fed only ammonium acetate the pH rose. These two units quickly died.

Acetate utilization proceeded uniformly in the calcium fed unit until the calcium was driven from solution, the pH increased and the unit died. Death occurred at free ammonia concentrations above 130 mg/l. At this point McCarty and McKinney were able to state:

> "From these results it appears the *ammonium ion is toxic in two ways.* Initially, when added at a low pH of about 7.0 the ammonium ion produces a toxicity similar in nature to that produced by other ions in solution.... As the pH increases, however, the second effect comes into play and appears to be related to an increase of free ammonia in solution. This second effect is quite a toxic one and results in the complete stoppage of all activity."

A final trial was conducted to determine the effect of cations added to digesters over a period of time rather than on a slug basis. The results were generally the same except that higher concentrations were tolerated when the acetate salts were added gradually. Gas

production began to decline as free ammonia concentrations approached 140 mg/l. The ammonium acetate concentration was just over 4,000 mg/l.

At the same time that McCarty and McKinney were conducting their investigations, Albertson (1) examined the effect of high loading rates upon anaerobic digestion of municipal sludge. Four small scale digesters were loaded to failure with the following results:

1. The pH fluctuated between a low of 6.60 to a high value of 7.4.

2. The percent carbon dioxide fluctuated between 33 and 39.

3. Volatile acids increased from low values of 200 - 761 mg/l to high values of 2,160 - 6,750 mg/l.

4. Alkalinity increased from about 2,500 mg/l to 4,900 - 5,800 mg/l.

5. Ammonia nitrogen concentrations increased to 1,200 - 1,400 mg/l.

Ammonia nitrogen concentrations and pH increased simultaneously until just prior to failure when the pH dropped. Albertson then examined the effect of ammonium bicarbonate and ammonium chloride salt additions. The two digesters fed ammonium chloride failed at concentrations of 1,800 to 2,000 mg/l ammonia nitrogen. The two digesters fed ammonium bicarbonate showed rapid increases in volatile acids when the ammonia nitrogen concentration was about 1,350 mg/l and failure ensued. Albertson notes that failures in all trials, with the exception of the ammonium chloride trial, occurred at ammonia nitrogen concentrations between 1,200 to 1,400 mg/l.

McCarty (17) summarized his own and Albertson's findings in 1964. The effect of ammonia nitrogen upon anaerobic treatment was tabluated. Ammonia nitrogen concentrations of 50 to 200 mg/l were considered beneficial, concentrations from 200 to 1,000 mg/l had no adverse effect, 1,500 to 3,000 mg/l were inhibitory at higher pH values and concentrations above 3,000 mg/l were considered toxic. McCarty explained:

"If the [ammonia nitrogen] concentration is between 1,500 and 3,000 mg/l and the pH is greater than 7.4 to 7.6, the ammonia gas concentration can become inhibitory. This condition is characterized by an increase in volatile acid concentration which tends to decrease the pH, temporarily relieving the inhibitory condition. The volatile acid concentration here will then remain quite high unless the pH is depressed by some other means, such as by adding hydrochloric acid to maintain the pH between 7.0 and 7.2.

"When the ammonia-nitrogen concentration exceeds 3,000 mg/l, then the ammonium ion itself becomes quite toxic regardless of pH and the process can be expected to fail. The best solution then is either dilution or removal of the source of ammonia-nitrogen from the waste itself."

McCarty also noted inhibitory concentrations may be found in some industrial waste streams and in highly concentrated municipal waste.

In 1968 Schmid and Lipper (24) conducted studies to characterize properties of swine waste and explored the possibilities of digesting the waste anaerobically. Laboratory scale digestion studies showed digestion by conventional means would provide liquification of solids. Methane production, however, was inhibited. The swine waste included urine as digester feed and was high in ammonia concentration. At solids loadings of 0.26 and 0.50 lb. total solids per cubic foot of digester capacity per day anaerobic mixed liquor ammonia nitrogen concentrations varied within a range of 1,800 to 2,500 mg/l. Volatile acid concentrations were above 15,000 mg/l and alkalinity concentrations varied from 10,000 to 15,000 mg/l. Both of these parameters are more highly concentrated than those observed in other studies. This is a result of collecting urine along with the feces and providing no water for dilution.

Poor methane production was attributed to ammonia nitrogen concentrations in the range McCarty (17) determined were inhibitory since the pH of the digesters remained near neutral rather than dropping as would be expected when volatile acid concentrations are high. Ammonia as

ammonium bicarbonate was also thought to contribute to the high alkalinity which tended to buffer the volatile acids. The facts that liquification of solids and production of volatile acids occurred but that methane production was poor led the investigator to conclude ammonia was toxic to the methane forming bacteria at the ammonia nitrogen concentrations observed.

Zablatzky and Peterson (31) reported two occurrences of failure in digesters treating combined municipal and industrial waste in 1968. The first event was found to be caused by washout of alkalinity and the ensuing drop in pH. Alkalinity washout was the indirect result of a decrease in solids loading to the treatment plant during an industrial and residential vacation period. Anaerobic decomposition occurred in the sewer system and thickeners at the treatment plant lost efficiency yielding a less concentrated, more voluminous sludge to the digesters. To correct this failure, sludge loadings to the four digesters were decreased. Thickened sludge was pumped from three digesters into the fourth digester. Sodium hydroxide, potassium hydroxide and calcium oxide were added to the digesters to hasten recovery with the result that digestion and sludge loadings returned to normal within thirty days.

In contrast to the first failure, the second one occurred as a consequence of increased solids loadings to the digesters. The end of a drought brought an increased wastewater flow to the plant with a corresponding increase in solids. Ammonium alkaline products accumulated in the more concentrated sludges. The pH, alkalinity and volatile acids rose as did the carbon dioxide content of the gas. Methane production dropped markedly. The increase in ammonium alkalinity was believed to

have a toxic effect on anaerobic microorganisms. Addition of water washed out the ammonium alkalinity and the digesters returned to normal operation in a short period of time.

In 1971 Melbinger and Donnellon (19) reported problems associated with high ammonia nitrogen concentrations in two high rate anaerobic digestion facilities located in New York City. The first plant at Tallman Island normally received an eleven percent solids loading to two digesters with a third digester receiving their overflow. One of the two primary digesters failed although both were receiving the same load. Failure was preceeded first by dilution of the digester contents due to leaking heater pumps. During this time solids loadings were decreased when sludge thickening was converted from modified aeration to step aeration. A return to modified aeration then increased solids concentrations and repairs halted dilution from the leaking heater pumps. Ammonia nitrogen concentrations of 1,900 mg/l were measured just after failure in the primary digester that failed. The second primary digester had an ammonium nitrogen concentration of 1,700 mg/l at this time. Prior to failure, solids, volatile acids and alkalinity had all increased above normal operating concentrations. Melbinger and Donnellon state that the ammonia concentrations "...agree with Albertson's work (1), which placed the threshold failure point in the 1,700 to 1,800 mg/l range." Albertson's reference cited does not specifically define this threshold failure point. As noted previously, Albertson simply noted that the two digesters fed ammonium chloride failed at ammonium nitrogen concentrations of 1,800 to 2,000 mg/l.

Correction of the failed digester was accomplished by halting feed to it and using the digester receiving overflow as a primary digester. Normal operation was established a month after failure.

The second event of digestion failure reported by Melbinger and Donnellon occurred at the Newtown Creek Pollution Control Plant receiving combined municipal and industrial wastes. When the first half of the plant was placed in operation the two primary digesters and one gas extractor were seeded with sludge from a nearby municipal digester. The combined industrial and municipal waste contained a higher ammonia nitrogen concentration than originally anticipated and as this concentration increased the two primary digesters failed within one week of each other. The ammonia nitrogen concentrations at failure were 1,740 and 2,000 mg/l. Volatile acids increased sharply to more than 5,000 mg/l and the alkalinity increased, but more slowly. The pH at this time, as it has been in the digesters over the two and a half year period discussed, was between 7.4 and 7.6.

At the time of this failure gas meters had not been installed. The feed schedule was based on the volatile acid to alkalinity ratio rather than gas production rates. The gas extractor was utilized as a primary digester to aid in recovery, which was complete in approximately two months. Feeding was limited initially to less than half the raw waste volume and increased to 100 percent over the two month period. The digesters then were operated for five months with ammonia concentrations greater than 2,300 mg/l and volatile solids destructions averaging 51 percent. The volatile solids destruction showed that effective anaerobic digestion was taking place in an ammonia nitrogen concentration range normally quite toxic. The authors attribute this situation to an acclimation of the methane forming organisms to the sludge which was fed slowly and at volatile acid to alkalinity ratios less than 0.75 and for the majority of the time at 0.55.

Total Kjeldahl nitrogen, organic nitrogen and ammonia nitrogen con-
centrations at two separate treatment plants were then analyzed with the
anticipation of predicting what concentrations would indicate problems.
High organic nitrogen concentrations in the thickeners were found to
increase the ammonia-nitrogen concentrations in the digesters as digestion
proceeded. The ammonia nitrogen was also found to account for approxi-
mately 23 percent of the alkalinity.

Further studies conducted with all six digesters in operation at the
Newtown Plant showed that digestion and gas production would take place
over an extended period of time at ammonia nitrogen concentrations above
2,500 mg/l and at pH values of 7.4 to 7.6. In addition, a 35 percent
recycling of digester effluent reduced ammonia nitrogen concentrations
to 1,800 - 1,900 mg/l and resulted in somewhat higher volatile solids
reduction. The authors concluded that if the rate of feeding raw waste
to the digesters is controlled using the volatile acid to alkalinity
ratio as the key parameter methane forming organisms will become acclimated
to the extent that ammonia nitrogen concentrations up to 2,700 mg/l will
not affect gas production or volatile matter destruction.

Ammonia toxicity in anaerobic digestion of swine waste is the
primary concern of the research presented in this thesis. The literature
review defines the problems encountered with high ammonia concentrations.
The next section describes the basis upon which the problem was approached.

Fundamental Considerations

Anaerobic digestion of swine waste has been attempted and been suc-
cessful in several instances. Chung Po (3,4) reports that Taiwan has a

large number of small simply constructed digesters that receive waste from ten to fifteen swine. The gases produced are drawn off intermittently at low pressure and used in small burners for domestic cooking purposes. L. John Fry (7) has built several digestion units out of steel drums and concrete tanks with sheet metal gas holders on a swine farm outside of Johannesburg, South Africa. He reports gas production of 8,000 cubic feet per day from the waste of an unspecified number of swine. Harold McCabe (14) has operated a digester on his swine farm near Mt. Pleasant, Iowa. Digestion stabilizes the waste and eliminates odors in a populated area. These examples of swine waste digestion as well as others (2) treating swine, chicken, beef, and vegetable waste emphasize the interest in anaerobic digestion on the part of agricultural producers coping with livestock waste management problems. Unfortunately, digestion facilities of this type are often crude improvisations. Little or no records are maintained and data defining their efficiency is nonexistent.

Two large scale studies of anaerobic digestion were reported in 1975 (12,21). The first one in Scotland consists of a 3,600 gallon digester operated at 35° Centigrade. Wastes were loaded at four percent total solids at retention times greater than ten days. Reductions in biochemical oxygen demand of 91 percent, total solids of 49 percent, volatile fatty acids of 92 percent and chemical oxygen demand of 50 percent were reported for a six month period of operation. Gas produced has contained 65 - 70 percent methane. The gas has been utilized to aid in fueling a heat exchanger.

The second study conducted at the University of Minnesota employs four 750 gallon digesters. Bench scales studies conducted at 32° C and 52° C, loading rates of 0.15 and 0.25 pounds volatile solids per cubic

foot per day and detention times of ten and fifteen days resulted in volatile solids destructions from 26 to 76 percent and gas production between 7.7 and 16.8 cubic feet per pound of volatile solids added. The methane content of the gas produced was 57 to 60 percent. The first month of full scale operation produced 2.7 to 4.2 cubic feet of gas per pound of volatile solids added.

Several laboratory studies (6,8,11,22,24,29) examining anaerobic decomposition of swine waste have been conducted in recent years. Digestion has not been sustained for an appreciable length of time in these laboratory studies. With the exception of the study conducted by Schmid and Lipper (24) waste fed to the digestion units has been subjected to some form of dilution. In some instances digestion has been enhanced by the addition of municipal anaerobic digestion sludge (11,22). With respect to dilution the study conducted by Taiganide, et al. (29) is significant. Solids loadings no greater than 3.6 percent were recommended primarily upon the basis that copper concentrations in waste fed at higher solids loadings would inhibit digestion processes. Hobson and Shaw (11) acknowledged observed digestion failures at solids concentrations of 4.0 to 4.5 percent and noted that copper concentrations at these loadings were below those of Taiganide's. Hobson and Shaw also reported no problems associated with ammonia nitrogen concentrations that occurred as high as 1,400 mg/l.

Difficulties encountered with highly concentrated wastes have been examined. Swine wastes, in particular, when undiluted exhibit high concentrations of total solids, volatile solids, volatile acids and ammonia nitrogen. Additions of these wastes to an anaerobic digester with a minimum of dilution would result in considerable savings of additional

water. However, this can lead to high solids concentrations with accompanying high volatile acid concentrations and high ammonia concentrations. McCarty (17) suggested dilution and removal of ammonia from the source as possible solutions to this problem. A third possibility is the reduction of the ammonia concentration within the digester itself.

As a solution to the problem of swine waste anaerobic digestion, the original proposal (25) was based upon removing ammonia from the waste and thereby eliminating ammonia toxicity and dilution requirements. An estimate of the amount of removal of ammonia possible may be made on the basis of the findings of Srinath (27) and Loehr (13,27). Ammonia exists in equilibrium with ammonium ion in water:

$$NH_4 + H_2O \rightleftharpoons NH_3 + H_2O + H^+ \quad \text{------------} \quad (6)$$

Undissociated ammonia (NH_3-N) is the only form that can come off as a gas. The ammonia available is described by the equation:

$$(NH_3\text{-}N) = (NH_4\text{-}N) \cdot \frac{10^{pH}}{\dfrac{k_b}{k_w} + 10^{pH}} \quad \text{----------------} \quad (7)$$

k_b and k_w are the ionization constants of aqueous ammonia and water, respectively. Equations (6) and (7) are equivalent to (1) and (4) in the section on Ammonia Toxicity.

The effect of temperature upon the ionization constants may be calculated from:

$$k_b/k_w = [-3.398 \ln (0.0241 \cdot \theta^\circ C)] \cdot 10^9 \quad \text{---------} \quad (8)$$

Equations (7) and (8) may be solved at a given ammonia (NH_4-N) concentration and various pH and temperature values to yield corresponding free ammonia (NH_3-N) concentrations. This has been done as shown in Table 1 for ammonia nitrogen concentrations up to 3,500 mg/l and

TABLE 1

Free Ammonia Concentrations for Selected Total Ammonia Concentrations

pH	7.0			7.5			8.0		
Temperature ($^{\circ}$C)	15	25	35	15	25	35	15	25	35
Total Ammonia Concentration (mg/l)									
2,000	5.8	11.5	34.0	18.1	36.1	10.4	56.2	110	292
2,500	7.2	14.4	12.5	22.7	45.0	130	70.3	137	369
3,000	8.7	17.3	51.0	27.2	54.1	156	84.3	165	442
3,500	10.1	20.2	59.5	31.7	63.1	181	98.3	192	516

temperatures from 25° C to 35° C. An operating temperature of 35° C is optimum for mesophilic bacteria (18). Temperatures lower than this may be encountered, particularly during colder seasons depending upon the efficiency of the heating system employed. Temperatures higher than 35° C will tend to sterilize digester contents until the optimum for thermophilic, 53° C to 57° C, is reached. Digestion occurs more rapidly in the thermophilic range but the maintenance of a stable, balanced digestion is critical in that small changes in loading and temperature will cause upsets (18). In addition, heating requirements will be greater. At this time operation in the thermophilic range has not been justified.

Returning to ammonia concentrations, Table 1 shows that operation at a pH of eight and a temperature of 35° C results in larger free ammonia concentrations. The pH of eight should not in itself be detrimental to the bacterial population. Clark and Speece (5) report no inhibition of digestion in anaerobic filters between pH values of seven and eight. Melbinger and Donnellon (19) reported satisfactory digestion at pH values up to 7.6. In the other studies that have been reviewed, high pH values were the result of and not the cause of failure.

Ammonia stripping within a digester may be accomplished by recirculating digester gases. Gases may be recirculated many times through the proper selection of air flow rates which, together with adequate retention time, will provide high stripping gas volume to liquid volume ratios. Although ammonia removal would be greater at pH values higher than eight, a sufficiently high ratio could result in the removal of enough ammonia to maintain concentrations below the levels considered toxic. In addition, a high rate of gas recirculation should remove ammonia gas (NH_3^+) as it formed, leaving concentrations in the digester much lower than the

130 mg/1 McCarty and McKinney (16) found to be toxic.

Ammonia gas can be stripped from the gas recirculation stream by bubbling the gas through an acid solution. Phosphoric acid can serve this purpose. Ammonium phosphate, a valuable storable fertilizer, is formed during the stripping process.

In order to increase the pH of the digester to near eight, carbon dioxide can be stripped from the gas recirculation stream. Basic solutions of sodium hydroxide, potassium hydroxide or calcium hydroxide are all suitable chemically for this purpose. At pH values of about seven or eight most of the alkalinity present in the digester is in equilibrium as bicarbonate ion. Removal of carbon dioxide results in a decrease in hydrogen ion concentration due to a decrease in bicarbonate ion concentration in accordance with the following equilibrium:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \text{ - - - - - - - - - - - - - - } (9)$$
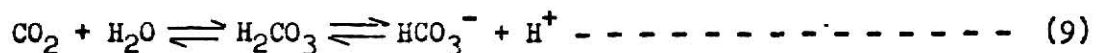
Removal of carbon dioxide will result in an excess methane gas of relatively high purity.

Based upon the concepts discussed above, research was initiated for the purposes enumerated in the next section.

RESEARCH OBJECTIVES

The field research presented in this thesis is an investigation of a method of anaerobic digestion of swine waste that has not been previously attempted. For this reason, several objectives were established to evaluate the potential value of the process.

The overall performance of the field scale unit may be determined through observation of the following phenomena:

1. The extent of ammonia removal necessary to achieve stable digestion,

2. The feasibility of controlling the pH of the digester by removing carbon dioxide from the digester gases,

3. The degree of waste stabilization possible under conditions somewhat removed from those peculiar to conventional anaerobic digesters, and,

4. The amount of methane gas produced.

If the overall performance proves workable, then design parameters may be devised for practical applications. Of particular interest in this respect are:

1. The energy requirements necessary to provide the desired mixing and stripping effect in excess of the energy required to operate conventional anaerobic digestion plants,

2. The material most economically suitable for use in the stripping units to produce the desired end products, and,

3. The development of cost estimates for a larger scale process based on final design considerations.

PROCEDURES

Description of Facilities

Existing Facilities and Waste Flow

The Kansas State University Boar Testing Station of the Kansas Swine Improvement Association is the site of the field research conducted to study the anaerobic digestion of swine waste. The station is located approximately one mile north of the Kansas State University, Manhattan, Kansas, Campus. Figure 1 is a schematic diagram of the facilities in existence at the beginning of the study.

Forty pens are enclosed in two sheds oriented so that the open face is toward the south. The floors are concrete sloping to six inch wide and twelve inch deep gutters just outside the pens. Feces and urine are scraped daily from the pens into the gutters. The gutters slope to a diversion box which combines waste flows from the two collection gutters. The waste may be directed into a four foot cubicle concrete sample pit or into an eight foot cubicle concrete tank used as a digester for the purposes of this study. The sample pit was not directly used for this study.

Six inch vitrified clay pipe delivers waste from the diversion box to the digester beneath the liquid level. The digestion tank extends seven feet into the ground. The liquid level is one foot from the fixed roof. This results in a liquid volume of 448 cubic feet or a capacity of 3,350 gallons.

Waste flows by gravity from the digester through six inch vitrified clay pipe that also extends below the digester liquid level. The waste
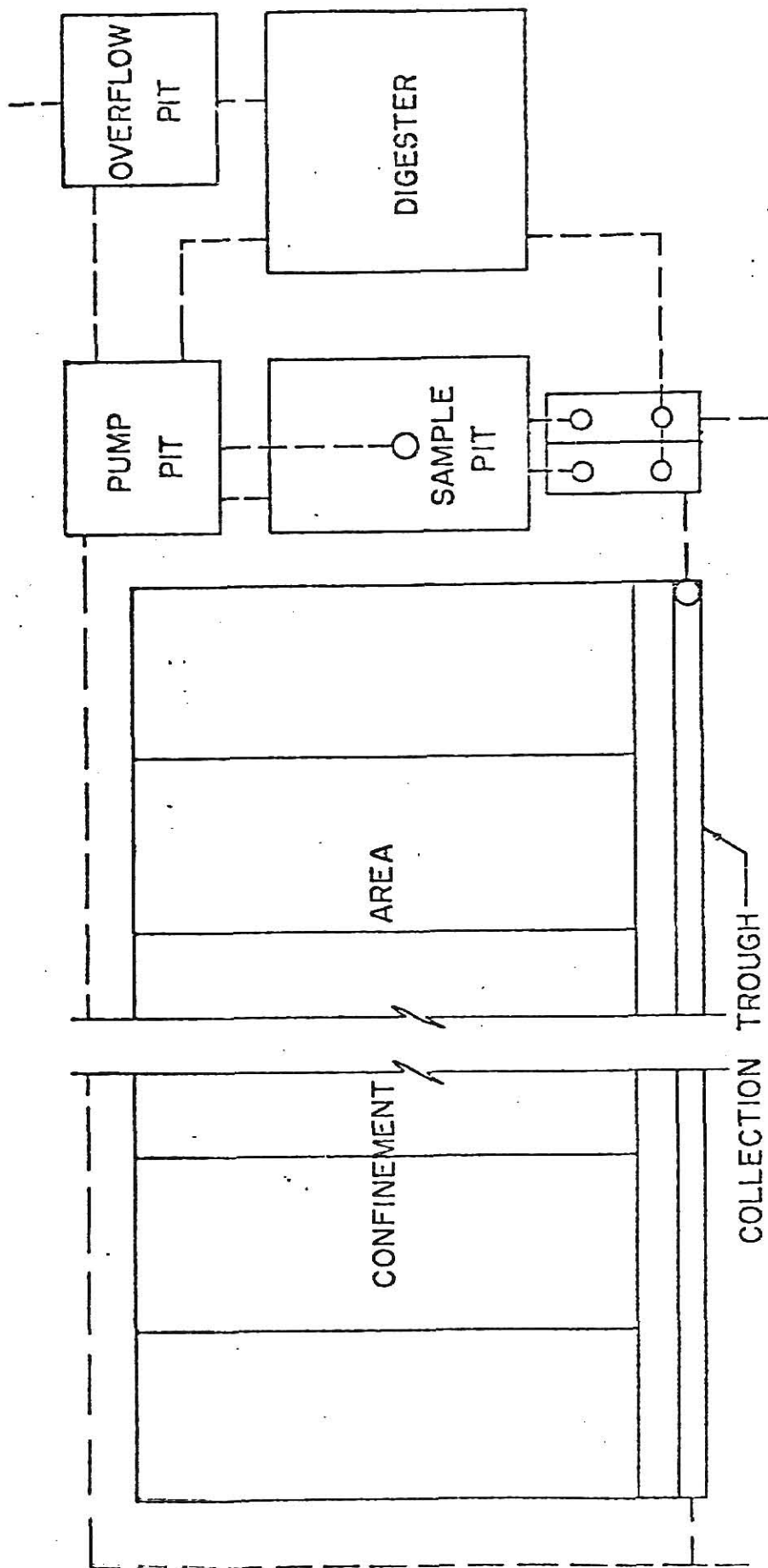
FIGURE 1. Schematic of Waste Collection Facilities

enters an overflow pit with a 1,200 gallon capacity. The liquid level of this pit controls the level in the digester. This control maintains a constant level in the digestion tank which is necessary to prevent air from entering.

Digested waste from the overflow pit is pumped to the elevated end of the gutters through two and one-half inch buried pipe. A one and one-half horsepower electric motor driving a centrifugal trash pump accomplishes this. Valves direct the pumped waste to either gutter through which gravity flushing and occasional scraping conveys the daily waste accumulation to the digester. Digester supernatent in excess of that used for flushing of gutters drains by gravity from the top of the overflow pit to a final storage pit. From this pit the waste is pumped into a liquid waste spreader periodically for ultimate disposal on nearby crop land.

Swine Handling

Area swine breeders deliver two purebred boars and a barrow from the same litter to the station for confined feeding tests conducted by the Kansas State University Animal Science Department. A total of 120 swine weighing between 40 and 60 pounds are delivered over a period of two weeks. The barrows are penned with the boars for approximately one month, at which time they are removed from the confined feeding pens and collectively housed in two pens removed from the waste collection system. The 80 boars are confined two to a pen until taken off ration at a weight of 220 pounds, attained in approximately five months.

The swine are self-fed a growing-finishing ration consisting of the ingredients shown in Table A1 of Appendix A. Table A1, as well as the other data included in this Appendix, was compiled by Schmid and Lipper (24) as a result of their study conducted at the station to characterize

properties of swine wastes. Figure A1 shows the total solids and COD production per animal vs. animal weight as observed by the investigators over a two month period. Table A2 lists the average strength parameters of the feces and urine collected in the sample pit and mixed to a slurry by changing the valving of the sludge recirculation pump. Dilution of the waste with water was minimal during these studies. Waste was scraped down the gutters by hand and flushing was not employed. Table A3 shows representative values of anaerobic mixed liquor observed during laboratory scale anaerobic digestion studies using the concentrated waste collected as feed.

Waste could not be collected during this study at the concentrations achieved by Schmid and Lipper due to unavoidable routine operating conditions. The swine have unlimited access to automatic float valve waterers. Considerable leaking occurred throughout the study as a result of faulty mechanisms. During summer months excess water was introduced from the overhead sprinkling systems supplying a cooling mist to the pens.

Bedding comprised of wood chips, although used sparingly and confined to a small area at the rear of the pens, was at times unavoidably included with the waste scrapings.

Anaerobic Digestion Unit

Extensive additions to the eight foot cubicle concrete tank were necessary to convert it to the type of anaerobic digester required for this study. The foot of concrete extending above ground and the roof were coated with plastic roofing coating to prevent loss of digester gases through the concrete. The exposed area was enclosed with one and

one-half inch styrofoam sheeting to provide insulation. A plywood floor was then laid on top of the styrofoam.

Figure 2 shows schematically the equipment housed in a six foot square shed placed on top of the digester. Two rotary lobe blowers in series driven by a three horsepower electric motor provided gas recirculation. Digester gases were drawn off the top of the digester at a pressure of 7 1/2 pounds per square inch and circulated at an estimated rate of 50 cubic feet per minute per 1,000 cubic feet of digester capacity. The gases first bubbled through an 85 percent solution of phosphoric acid. Forty gallons of acid were contained in an 80 gallon fiber glass tank rated at 75 pounds per square inch pressure capacity. The phosphoric acid stripped free ammonia from the gas stream.

The gases were next bubbled through a similar tank containing a base such as sodium hydroxide, potassium hydroxide or calcium hydroxide in solution. Solutions of these three chemicals were tried with calcium hydroxide proving the most satisfactory in that it is readily available and the least expensive of the three. The calcium hydroxide was obtained locally in the form of hydrated lime.

Several methods of continuously feeding and withdrawing the basic solution in the carbon dioxide stripping tank were attempted. The methods used and problems encountered will be examined in the section entitled Equipment Performance. Although the level of the solution in the carbon dioxide stripping tank varied, the volume was generally maintained at forty gallons.

Gases leaving the carbon dioxide stripper returned to the digester at a depth four feet below the level of the digester slurry. Schedule 80 one and one quarter inch polyvinylchloride pipe was used throughout
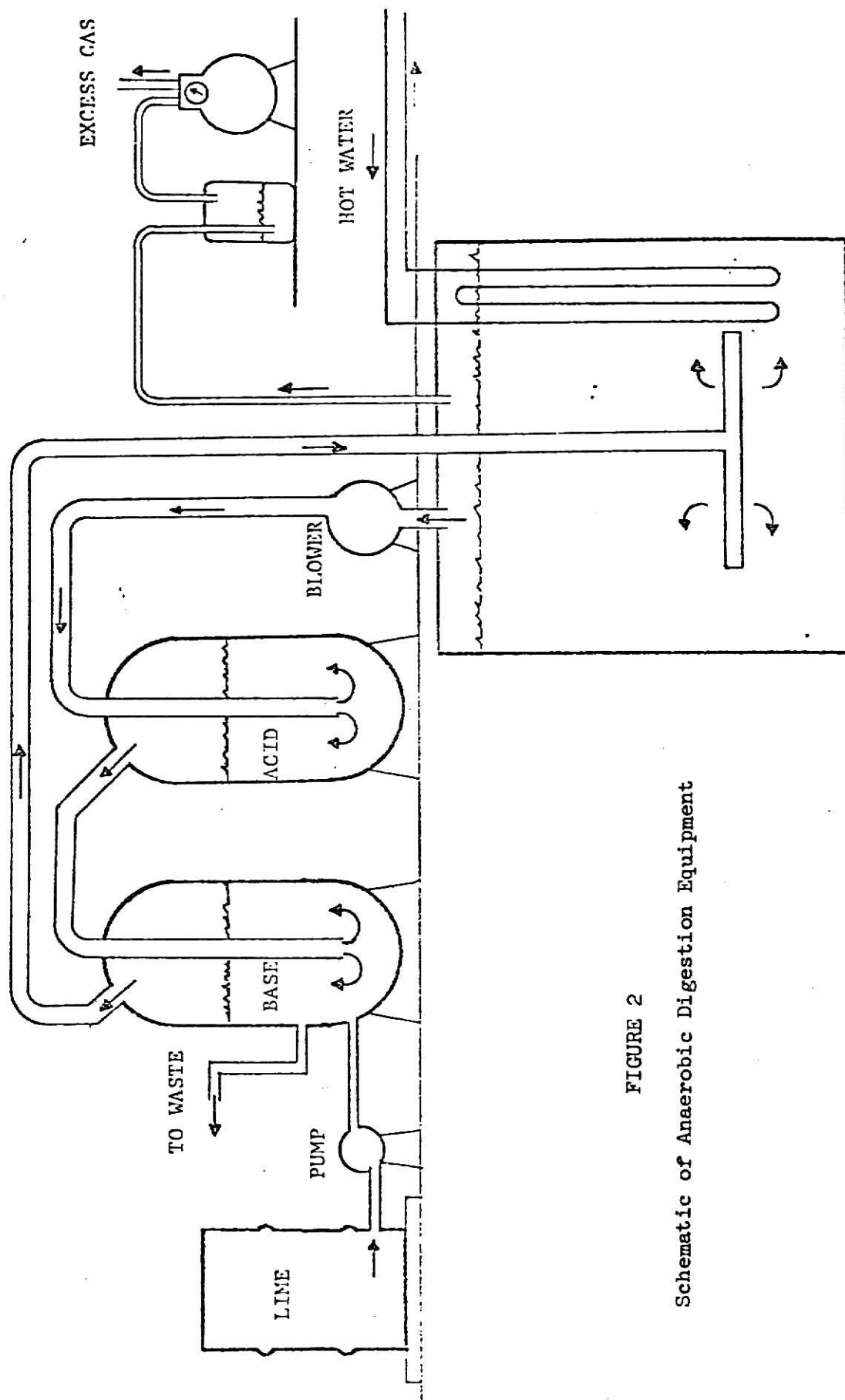
FIGURE 2

Schematic of Anaerobic Digestion Equipment

the system for gas conveyance. The diffuser in the digester was fabricated out of an eight foot section of this material and oriented horizontally and diagonally in the digester. Gases escape through holes drilled randomly in the length of pipe. Care was taken to ensure that no leakage of gas would occur throughout the system.

Check valves were installed in the gas lines between the blowers and the ammonia stripping tank and between the ammonia stripping tank and the carbon dioxide stripping tank. The valves prevented transport of tank liquids backward through the lines due to pressure present in the tanks when the blowers were shut off.

The digester was heated with hot water supplied from a 30 gallon gas water heater located in the shed. Hot water was pumped by a centrifugal pump through one-half inch rigid wall copper tubing soldered in the shape shown in Figure 2. The fifty foot length in the digester adequately maintained the digester contents at a temperature of 35° C, although the water heater burned almost continuously when ambient temperatures were near or below freezing. The hot water heater was fueled by propane gas rather than gases produced by the digester. Excess gases were produced too intermittently and at too low a pressure to serve as a reliable source of fuel during this field study.

Excess gases produced during digestion were drawn off the top of the digester through one-half inch tygon tubing. The gas bubbled through a solution of water and anti-freeze before passing through a Sprague gas meter. Initial carbon dioxide removal resulted in a decrease in the partial pressure of gases in the digester which created a vacuum. The water-antifreeze solution prevented air from entering in this instance. The gas meter is calibrated in cubic feet. Estimates of gas production

may be made to the nearest ten cubic feet.

Anaerobic digestion of waste employing the type of unit discussed has not been attempted previously. Guidelines were not available to aid in selection of equipment. Many modifications and replacements were required as the study proceeded. The system described is the one which ultimately produced significant results. The section examining equipment performance will review problems encountered with inadequate equipment and the subsequent changes.

Sampling Procedures

During periods of operation, which were much shorter than desired, samples were collected every third day. Operational difficulties permitted only salutory adherence to this schedule. All samples collected were conveyed to the sanitary engineering laboratories for analysis since space was not available for analytical equipment at the boar testing station.

One liter grab samples of the digester contents were collected through a sampling hole in the top of the digester. A six inch cast iron pipe extending vertically five feet into the digester provided a water seal preventing air from entering and mixing with digester gases. A plastic sample bottle taped to the end of a pole was used to retrieve the sample. The pole was short enough to prevent sampling at a depth where solids may have settled and accumulated. The parameters measured were temperature, pH, total solids, alkalinity, volatile acid concentration, chemical oxygen demand, and ammonia nitrogen concentrations. The temperature was measured at the time of sampling.

Two hundred milliliter phosphoric acid samples were drained from the ammonia stripping tank through a faucet valve. The valve was located so that samples were drawn from a depth approximately two thirds of the distance from the top of the phosphoric acid solution. The temperature was recorded immediately. The pH and ammonia nitrogen concentrations were measured at the laboratory.

The contents of the carbon dioxide stripping tank were sampled in the same manner as the phosphoric acid. The sample temperature and pH were measured.

Gas samples were collected from three locations in the gas recirculation line. Valves and stopcock hose connectors were fitted immediately after the blowers, between the ammonia stripper and the carbon dioxide stripper and between the carbon dioxide stripper and the digester. These valves thus permitted sampling of gases as they left the digester, ammonia stripper and carbon dioxide stripper respectively. The two vessels devised to collect the gases are shown in Figure 3. The first apparatus consists of a balloon fitted into a five hundred milliliter filtering Erlenmeyer flask. A vacuum pump attached to the rubber hose evacuated the air in the flask causing the balloon to be expanded to the inside surface of the flask. The vacuum was maintained until the hose collapsed upon itself. A pinch clamp was then applied to the loose end of the hose maintaining the vacuum in the flask until time for sampling.

At the digester the sampling valve in the gas line was first opened with the blowers operating. This ensured gas was flowing before the hose was attached to the stopcock hose connector. The pinch clamp was removed after the hose had been attached. Gases entered the flask, forcing the balloon through the top and expanding it to a diameter of

Flushing position

Rubber hose

Expanded Balloon

(Gas collected)

Rubber hose

Balloon collapsing during gas intake

7 inch Distillation Tube

500 ml Filtering Flask
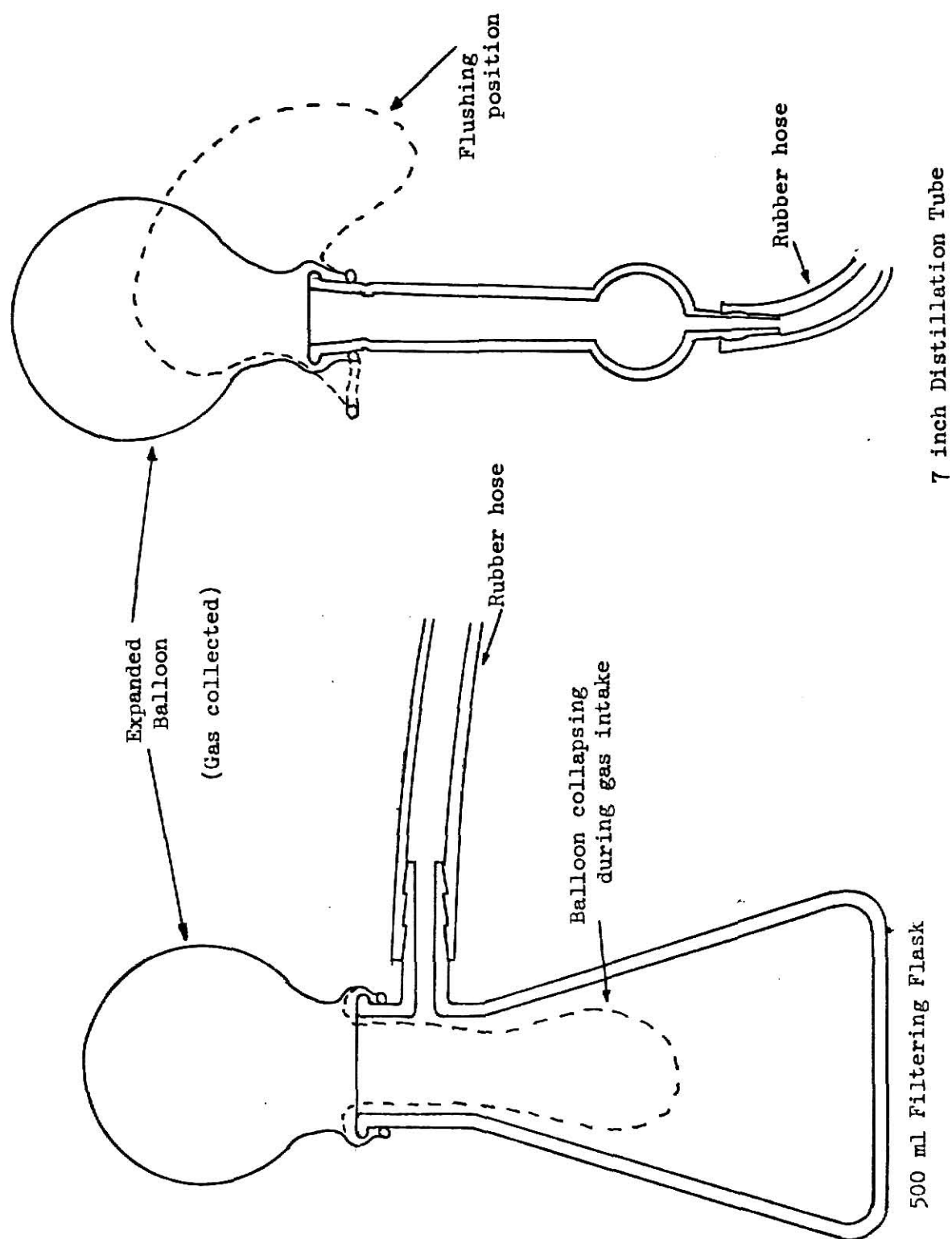
FIGURE 3. Gas Collection Apparatus

approximately eight inches. The pinch clamp was then reapplied and the hose removed from the connector. Finally, the valve was closed.

The second apparatus is a distillation tube fitted with a balloon on the wide end and a rubber hose on the other. This method of sampling eliminated the need for preliminary preparations involving the vacuum pump. The results where the same as those achieved by the first method. The hose was attached to a connector in the gas line at the digester. The valve was opened and the air in the distillation tube and balloon flushed out. Flushing was accomplished by allowing the balloon to expand and then raising the lip of the balloon to allow gases to escape. After this procedure had been performed six or seven times, the balloon was permitted to expand to a diameter of about eight inches. The hose was clamped and then removed from the valve. The gas flow was then turned off.

As previously described, gases were sampled from three different locations to determine how the stripping units individually affected gas composition. No effect was observed in samples acquired at the same time. The flow rate was high enough that stripping occurred in many passes through the stripping units in a relatively short time. The net effect was no discernable difference in gas composition between the samples. The gross effect is noted in the discussion and results section of this thesis. The three individual daily samples have been averaged and presented as one value for further purposes of discussion.

Analytical Procedures

pH

The pH of the digester contents, phosphoric acid and basic solutions was measured on a Fisher Accumet Model 320 pH meter with expanded scale capabilities. The normal meter scale with one tenth pH unit graduations was used for this study. Accuracy of the meter is within ± 0.05 pH units on the normal scale.

The pH was standardized with buffers of known pH (4.0, 7.0, 10.0). The electrodes were rinsed with demineralized water prior to and between each pH measurement. The pH of the phosphoric acid was so low throughout the majority of the study that the electrodes used could not accurately measure the hydrogen ion activity. The pH of the phosphoric acid was monitored simply to indicate when the ammonia uptake had been great enough to deplete the free hydrogen ion concentration. This did not occur and for the majority of the time a pH value of zero was recorded, indicating no significant change in pH.

Alkalinity

The total alkalinity of the digester contents was determined in accordance with the procedures described in the 13th edition of Standard Methods for the Examination of Water and Wastewater (28). Measurements were made by potentiometric titration with 0.05 N (0.05 normal) sulfuric acid (H_2SO_4) to an endpoint pH of 3.7. The Fisher pH meter was used to observe the endpoint. Figure 4 shows a typical pH-alkalinity relationship observed during analyses.

Samples were diluted to one-tenth full strength. Fifty milliliters of the diluted waste were used for titration. The results are expressed
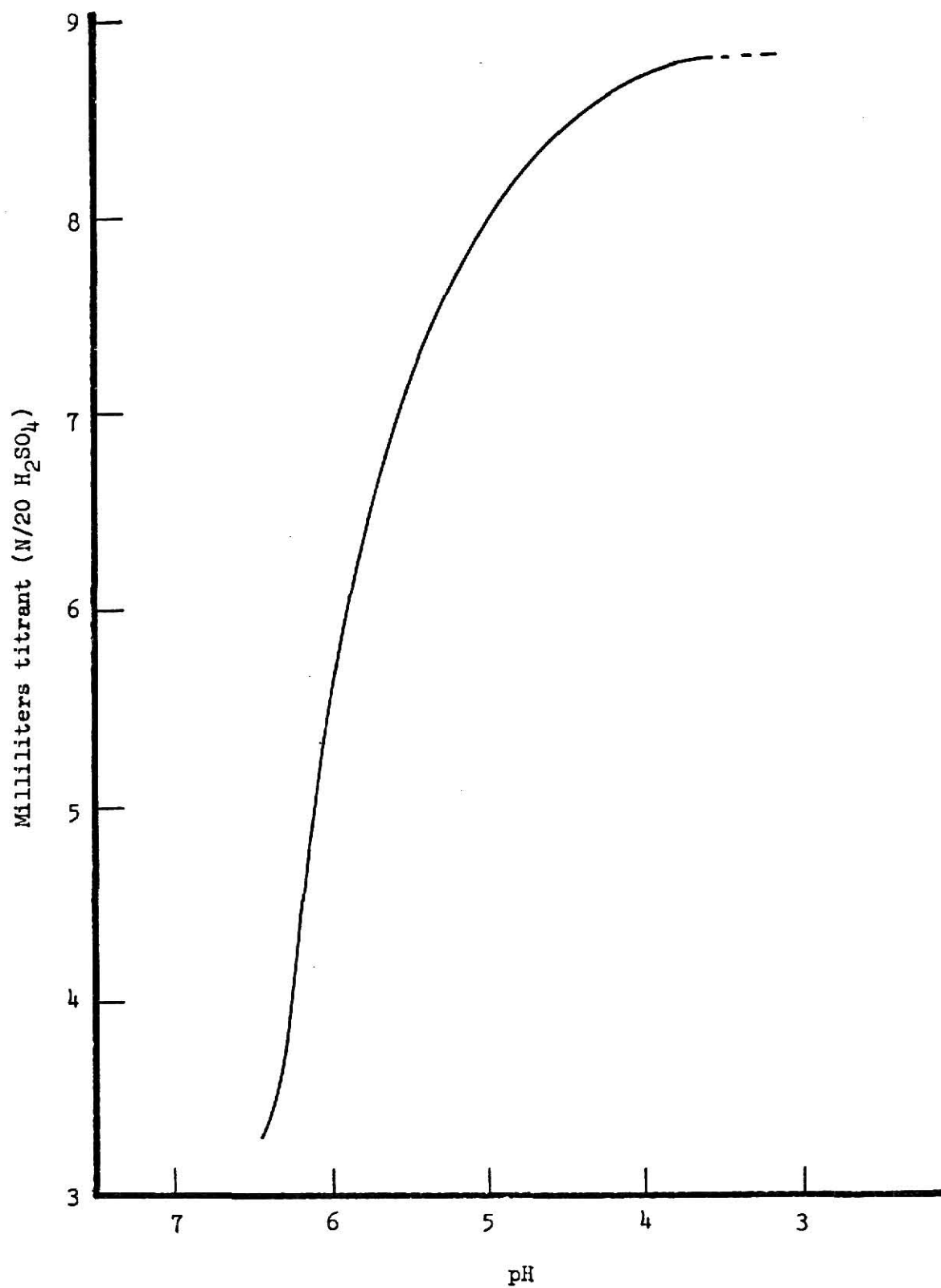
FIGURE 4. Alkalinity Determination – Typical
pH Response to Titrant Addition

in milligrams per liter as calcium carbonate ($CaCO_3$). The equation used to calculate alkalinity concentration is:

$$\text{Alkalinity (mg/l as } CaCO_3\text{)} = \text{ml } 0.05 \text{ N } H_2SO_4 \times 2.5 \times \frac{1,000}{\text{sample size, ml}} \times 10$$

$$\text{or} = (\text{ml N/20 } H_2SO_4)\,(500) \text{ - - - - - - - - - - - } (10)$$

Each milliliter of N/20 H_2SO_4 is volumetrically equivalent to 2.5 mg/l of calcium carbonate. The factor (1,000/sample size, ml) is the correction for sample size. The multiplier, 10, is the dilution factor.

Volatile Acids

Total volatile acid determinations of the digester contents were made by the column partition chromatography method as presented in Standard Methods (28). This test measures nearly 100 percent of the volatile acids present. The analysis is used as a control to determine if the digester is in balance (17).

Samples were first centrifuged 30 minutes to remove excessive solids. The residue was discarded and the supernatant acidified with concentrated sulfuric acid to a pH of 1.2. The pH meter previously described was used to ensure the proper acidification rather than thymol blue indicator solution since considerable turbidity remained after centrifuging.

Five milliliters of the acidified sample were drawn through the silicic acid column followed by the chloroform-butanol reagent. The eluate was titrated with 0.02 N sodium hydroxide (NaOH) in methanol. Two five milliliter acidified demineralized water blanks were titrated in the same manner. The sodium hydroxide titrant was standardized each time an analysis was performed. Twenty-five milliliters of the 0.02 N sodium hydroxide was titrated against 0.02 N sulfuric acid to the methyl red endpoint.

Results are presented in milligrams per liter as acetic acid. The equation used to calculate the concentration of volatile acids is:

$$\frac{mg/l}{(as\ acetic\ acid)} = \frac{60 \times 1,000 \times N \times (A-B)}{5}$$

$$or \qquad = 12,000 \times N \times (A-B) - - - - - - - - - - - - \quad (11)$$

The factor 60 is the equivalent weight of acetic acid in milligrams per milliliter. One thousand converts milliliters to liters. Five is the sample size in milliliters used throughout the study. N is the normality of the sodium hydroxide titrant. A is the volume in milliliters of 0.02 N sodium hydroxide required to titrate the sample. B is the volume required to titrate the blank.

Chemical Oxygen Demand

The chemical oxygen demand (COD) test was used to monitor the strength of the waste in the digester. The procedure followed is that described in Standard Methods (28). The test measures the total quantity of oxygen required for oxidation of a given waste to carbon dioxide and water. Potassium dichromate, a strong oxidizing agent, is capable of almost completely oxidizing a wide variety of organic substances under acidified conditions.

Twenty-five milliliters of waste were first diluted to 500 milliliters. Ten milliliters of the diluted waste were then pipetted into 250 ml Erlenmeyer flasks. Glass beads were added to distribute heat evenly during boiling. Approximately 0.2 grams mercuric sulfate was added to complex chlorides which might be present. Five milliliters of 0.25 N standard potassium dichromate were added, followed by 15 milliliters of concentrated sulfuric acid with silver sulfate which is a catalyst that aids in oxidizing straight chain compounds.

After the addition of sulfuric acid, the flasks were immediately placed on reflux condensers along with a blank. The blank contained all the reagents and ten milliliters of demineralized water rather than ten milliliters of diluted waste. The flasks were boiled for two hours. Prior to titration, the condensers were washed down with demineralized water and allowed to cool to room temperature.

The samples were titrated with 0.05 N ferrous ammonium sulfate using ferroin as an indicator. The exact normality of the ferrous ammonium sulfate was determined by titration against standard 0.25 N potassium dichromate immediately before titration of unknowns. The equation for calculating COD is:

$$\text{COD, mg/l} = (a-b) \times N \times 8 \times \frac{1,000}{\text{sample size, ml}} \times \text{D.F.} \quad - - - - - - (12)$$

where:

a = ml $Fe(NH_4)_2(SO_4)_2$ used for the blank

b = ml $Fe(NH_4)_2(SO_4)_2$ used for the sample

N = normality of $Fe(NH_4)_2(SO_4)_2$

D.F. = the dilution factor

Eight is the atomic weight of oxygen. For a sample size of ten milliliters the equation reduces to:

$$\text{COD, mg/l} = (a-b) \times N \times \text{D.F.} \times 800 \quad - - - - - - - - - - - - - - (12\text{-}1)$$

Total Solids

The total solids analysis serves to indicate gross changes in loading and when used on a comparative basis aids in the monitoring of the digester. The solids measured are the matter remaining as residue after a sample of waste has been evaporated and dried at a temperature of 103° C.

A 100 milliliter sample of undiluted waste was pipetted into a preweighed evaporating dish and allowed to dry for 24 to 48 hours in an oven at 103° C. Prior to making weight measurements, the dishes were cooled in a dessicator. All weight measurements were made on a Mettler Model H6 digital analytical balance. The balance is accurate to $\pm$ 0.05 mg.

The concentration of total solids is expressed in milligrams per liter and may be calculated by dividing the milligrams solids recorded by the sample size in liters.

Gas Composition

Samples of gas collected were analyzed on the Fisher/Hamilton Model 29 Gas Partitioner capable of separating carbon dioxide, oxygen, nitrogen, methane and carbon monoxide. No carbon monoxide was indicated in samples analyzed. Relative percentages of these gases were recorded graphically on a Fisher laboratory recorder.

Samples were introduced into the analyzer through an integral sampling valve to a sample loop which admitted 0.25 milliliters of gas at atmospheric pressure.

Ammonia Nitrogen

Ammonia nitrogen concentrations were determined for the digester contents and the phosphoric acid used in the ammonia stripping unit. Analyses were made by the direct Nesslerization method as presented in Standard Methods (28). The Coleman Model C6 Spectrophotometer set at a wavelength of 410 millimicrons was used for colorimetric analysis. The standard curve shown in Figure 5 was prepared for use in determining ammonia nitrogen concentrations. Samples were clarified by centrifuging and treated for solids removal as specified in Standard Methods (28).
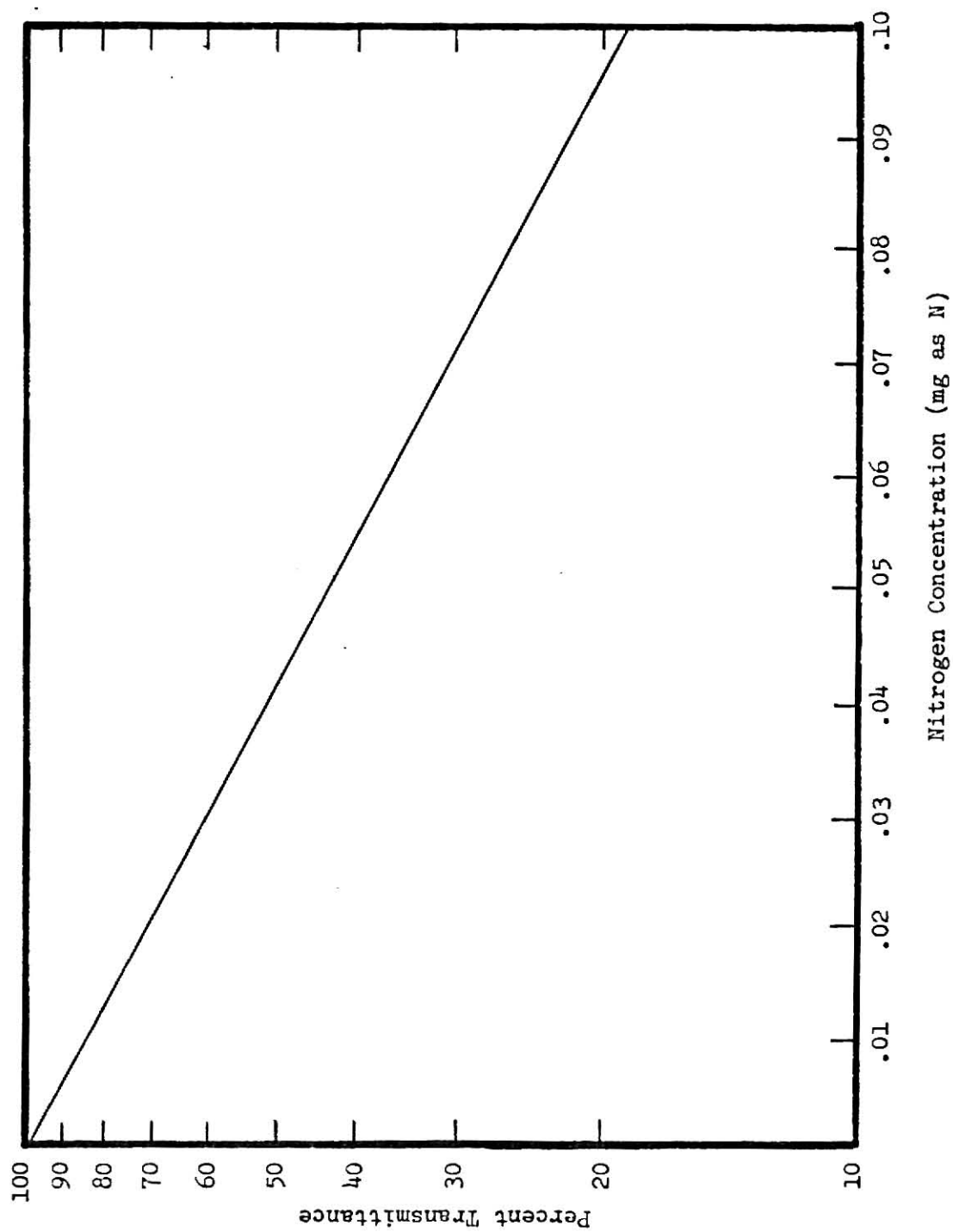
FIGURE 5. Calibration Curve for Ammonia Nitrogen Determination
(Model 6C, Coleman, Wavelength = 410 millimicrons)

DISCUSSION AND RESULTS

Overall Performance

Field research investigating the anaerobic decomposition of swine waste was initiated in June of 1974. Several months were required prior to June to set up equipment at the Kansas State Boar Testing Station. Correction of equipment inadequacies during June and July permitted only intermittent operation of the digester. Throughout the rest of the period of operation, which concluded March 24, 1975, mandatory equipment alterations prohibited lengthy operation of the digester. The longest period of operation, 30 days, was achieved in September. The time between runs was spent modifying and repairing the various components. Since the facilities were designed without previous guidelines, the performance of the equipment is discussed for the purpose of aiding further investigators in the selection of material.

Waste characteristics observed on site and waste handling peculiarities are included with equipment performance. Concentration of waste fed to the digester was lower than that originally anticipated. The type of collection system available did not permit collection of waste in the high concentrations desired. Ammonia nitrogen concentrations did not reach levels generally considered to be toxic, even during the period when ammonia was not being removed. Nevertheless, data generated was sufficient to produce significant conclusions defining ammonia nitrogen removal parameters.

The field research is divided into three separate periods. The first period commenced June 1, 1974, and extended to August 24, 1974,

when the swine confined feeding tests initiated in March, 1974, were
concluded and the boars removed from the station. The second period was
from August 25, 1974, to October 15, 1974. During this time no swine
were confined at the station. The digester was fed only the waste scraped
from pens being cleaned in preparation for the next confined feeding test
period.

The third and final period was from October 16, 1974 to March 24,
1975. One complete confined feeding test period was conducted during
this time. The three periods of operation are designated Phase I, Phase
II and Phase III, respectively.

Data from all three phases is useful in characterizing the digestion
process. Phase II is significant since the carbon dioxide stripper was
not used during this phase. Phase III includes a period of successful
ammonia and carbon dioxide removal.

Data obtained during the study is presented in Appendix B. The
information necessary for characterizing solids loadings, organic loadings,
retention time and digestion efficiency was not sought. Schmid and
Lipper (27) defined these characteristics in previous investigations at
the Boar Testing Station.

An economic analysis of the system has not been undertaken. The
system existing at the conclusion of the field tests, despite the many
modifications, was far from reliable. The method used for removing carbon
dioxide is considered unsuitable for the reasons explained in the section
on Carbon Dioxide Stripping. In addition, methods of recovery of ammonium
phosphate from a phosphoric acid solution remain to be determined.

Gas Recirculation System

The blowers and electric motor described in the Anaerobic Digestion Unit section were used throughout the study. The blowers are not designed for gas tight operation and a special manifold constructed out of copper tubing was devised to prevent intake of air or expulsion of recirculated gases through the rotary lobe housing vents.

The blowers required repair once. The first time the blowers were shut off, phosphoric acid under pressure backed up through the gas recirculation lines and entered the blowers. The most seriously damaged blower required extensive refinishing of machine surfaces before it could be placed back in operation. Check valves were installed in the gas recirculation lines to prevent phosphoric acid that backed up from reaching the blowers during subsequent shutdowns.

The blowers are rated at a maximum discharge temperature of 135° C. Temperatures this high were not encountered. The highest temperature in the ammonia stripping unit which immediately followed the blowers was 49° C. Clogging of the carbon dioxide stripper, however, caused an excessive pressure head that increased the temperature of the blowers. The excessive heat caused the polyvinylchloride (PVC) pipe used between the blowers and the ammonia stripper to deform and leak at threaded joints. Preventing clogging of the carbon dioxide stripper would have eliminated this problem. The unit clogged throughout the study, however. A portion of the PVC pipe was replaced with flexible vinyl hose that also deformed at high temperature but could be replaced more easily.

Solid matter collecting in the effluent pipe of the digester occasionally prevented gravity discharge of the waste to the overflow pit. This caused a rise in the liquid level to the roof of the digester. The

digester liquid was then drawn through the blowers and forced into the ammonia stripper. The inside surfaces of the blowers became coated with a rosin-like film, but this did not hinder lobe rotation. A cleanout apparatus consisting of a weighted cord was suspended in the effluent pipe and raised and lowered periodically to prevent solids buildup.

Line pressure was initially monitored by a gauge on the discharge side of the blowers. The blowers normally operated at pressures near seven pounds per square inch gauge. Carbon dioxide stripper clogging was indicated by higher pressures. After two gauges were destroyed by vibration, a mercury manometer was used to monitor pressure. Flexible tubing was used to attach the manometer to the gas sampling stopcock hose connectors. The pressure drop in the carbon dioxide stripper could be directly measured. The manometer proved much more satisfactory than the single pressure gauge.

Despite the difficulties encountered, the blowers provided excellent mixing of digester contents. Twelve to 14 inches of solids accumulated above the liquid in the digester during quiescent periods. This material was readily broken up when the blowers were started. Gas mixing appears to be as satisfactory and perhaps better than mechanical mixing. The blowers operated a total of 121 days.

The gases that may potentially escape from the blowers are flammable and potentially explosive. A five to 15 percent methane volume in air is explosive (9). For this reason, blowers with effective gas seals are recommended in further installations of this type.

The PVC pipe used throughout the gas recirculation system proved a good choice. It is easily assembled and readily repaired. Glued joints are better than threaded joints, which tend to loosen when subjected to prolonged vibrations. The diffuser in the digester caused no problems.

Carbon Dioxide Removal

The unit designed to remove carbon dioxide presented the most problems throughout the field research. A satisfactory method of feeding basic solutions (primarily lime) and withdrawing the carbonate sludges formed was not achieved. Since the gas recirculation system was under constant pressure and it was undesirable to shut the system down daily or admit air into the digester, the basic solution could not be replaced on a batch basis.

Different methods of continuously feeding the basic solution were tried and failed. The carbonate sludges formed within the fiber glass tank could not be readily removed. The accumulation of the sludge plugged the PVC diffuser. When this occurred, the blowers overloaded and the circuit fuse blew. Attempts were made to withdraw the sludge from the bottom of the stripper. Constant recirculation of the lime solution between the stripper and settling tanks, pumping of the sludge directly to waste and dilution of the stripping solution with constant withdrawal of sludge did not prevent sludge buildup and diffuser clogging.

Despite these difficulties, carbon dioxide removal was achieved for short durations. Initial removal occurred readily after oxygen and nitrogen had been flushed from the digester. Pressure in the digester fell below atmospheric pressure for a few hours since the partial pressure contributed by the carbon dioxide was removed. Subsequent methane production would raise the pressure with time and excess gas production was then observed.

Sodium hydroxide (NaOH), potassium hydroxide (KOH) and calcium hydroxide (Ca(OH)$_2$) in ten to 15 percent solution were the bases used in

the stripping unit. These chemicals react with carbon dioxide in the following manner: ·

$$2 \text{ NaOH} \quad + \quad \text{CO}_2 \longrightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \text{ - - - - - - - - - - - (13)}$$
$$\text{(40 g/mole)} \quad \text{(44 g/mole)}$$

$$2 \text{ KOH} \quad + \text{CO}_2 \longrightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O} \text{ - - - - - - - - - - - - - (14)}$$
$$\text{(56 g/mole)}$$

$$\text{Ca(OH)}_2 \quad + \text{CO}_2 \longrightarrow \text{CaCO}_3 + \text{H}_2\text{O} \text{ - - - - - - - - - - - - - - (15)}$$
$$\text{(74 g/mole)}$$
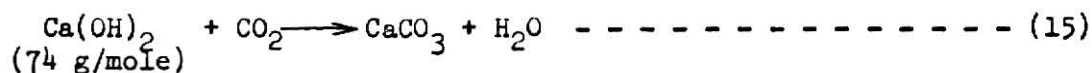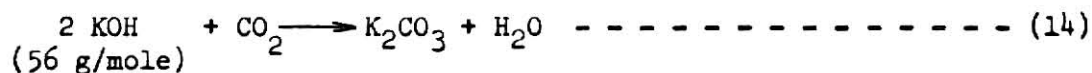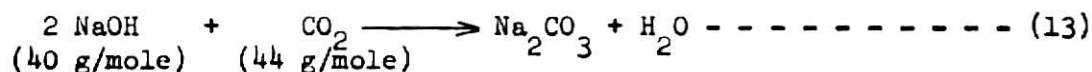
Assuming that 5.62 cubic feet of methane is produced from one pound of chemical oxygen demand stabilized and that 90 percent of the chemical oxygen demand fed the digester is stabilized, an estimate of the methane produced per day may be calculated (17). Using an average COD of 0.52 pounds per day per 100 pounds live weight (25, see Appendix A) contributed by 80 swine, the amount of methane produced could be 210 cubic feet per day.

The carbon dioxide content of the digester gas would be nearly 40 percent if the methane content is near 60 percent. The amount of carbon dioxide produced per day is then 140 cubic feet. One hundred forty cubic feet of carbon dioxide is equivalent to 177 moles. Equations (13), (14) and (15) show that one mole of carbon dioxide will react with two moles of NaOH or KOH or one mole of Ca(OH)_2. Thus, to remove 140 cubic feet of carbon dioxide per day, approximately 31 pounds of NaOH per day, 44 pounds of KOH per day or 28 pounds of Ca(OH)_2 per day would be required.

Ca(OH)_2 is readily available in the form of hydrated lime. This was purchased at a price of $5.00 per 100 pounds for this research. Potassium hydroxide (KOH) cost $47.00 per 100 pounds. Sodium hydroxide (NaOH) is nearly as expensive as KOH. Even if these chemicals were purchased in bulk quantities, it is apparent both on a weight and monetary

basis that calcium hydroxide ($Ca(OH)_2$) is the preferred chemical.
Solutions of each of these three chemicals were tried. Each removed
carbon dioxide as expected. $Ca(OH)_2$ was used most extensively, however.

The percentages of gases measured throughout the study are shown in
Appendix B. Carbon dioxide removal was accomplished for very short time
periods in June, July, August and February. Sludges formed at these
times disrupted operation. During March, carbon dioxide removal occurred
but the oxygen and the nitrogen content of the gas remained high. This
was the final attempt to remove carbon dioxide. The boars were being
removed from the station and feed to the digester was decreasing quickly.
The method of feeding lime at this time was, in essence, a batch type
operation. Air entered during the daily removal of sludge. In addition,
a vacuum was present in the digester from March 10th onward. No excess
gas was produced and the oxygen and nitrogen could not be flushed out.

The reason for removing carbon dioxide, as stated in the Fundamental
Considerations Section, is to raise digester pH so that free ammonia con-
centrations will increase within the digester. Carbon dioxide removal
from January 5th to January 19th during Phase III showed that this can
be accomplished. The percentage of carbon dioxide was reduced to nearly
zero by January 7th. Flushing of oxygen and nitrogen also occurred.
The pH of the digester rose from 7.20 to 7.55 between January 5th and
January 7th. By January 9th the pH had increased to 8.1. Freezing lines
prevented further addition of lime. Carbon dioxide percentage immediately
began increasing with a resultant decrease in pH, further confirming
digester pH response to carbon dioxide removal. By January 9th, the pH
had dropped from 8.1 to 7.6. With no significant carbon dioxide removal
accomplished by February 10th, the pH had dropped to 6.8.

Operating problems prevented determining how high the pH might be increased. As the pH increases and ammonia is removed from the digester liquid, the bicarbonate alkalinity present may be reduced. Under this condition, the digester may be more sensitive to volatile acid concentration increases. The short duration of the test runs did not permit the investigation of this possibility.

Finally, the basic solutions quickly corroded an aluminum container used for mixing the stripping solutions. This container was replaced by a steel drum which held up well. The fiber glass stripping tank showed no adverse effects after containing basic solutions for ten months. PVC pipe was used for conveying basic solutions and sludge for part of the study. This material also showed no deterioration, with one exception. A diffuser made by drilling one-quarter inch holes in a one and one-quarter inch PVC pipe cap delivered the recirculated gases into the lime solution. After about two months use, the holes had deformed and enlarged. This was probably due to some carry-over of phosphoric acid from the ammonia stripping unit. When the acid contacts the lime solution, heat is generated in quantities large enough to melt the PVC. This appeared to be the cause since PVC in other areas of the unit showed no similar deterioration.

The method of removing carbon dioxide was not satisfactory. The sludges formed are difficult to remove. Air cannot be allowed to enter during removal of sludges. This problem might have been averted by bypassing the carbon dioxide stripper for the amount of time required to remove sludge. The time required for handling, storing, feeding and removing chemicals can be prohibitive if little automation is employed. The cost of chemicals also makes this method undesirable.

Ammonia Stripping

The ammonia stripping unit presented no difficulties throughout the study once the check valves had been installed in the lines to prevent backup of acid when the blowers were shut off. The unit was used for ten months without need for modification. Moisture traps installed between the ammonia stripper and carbon dioxide stripper would have been helpful in capturing the small amount of phosphoric acid carried by the gas stream into the carbon dioxide stripper. The fiber glass tank showed no deterioration from the phosphoric acid. PVC pipe in contact with phosphoric acid performed well also.

Srinath and Loehr (27) examined ammonia desorption from wastewater and published their findings in 1974. This timely article comprehensively discusses ammonia removal and with minor modifications provides the basis for the following calculations. The nomenclature adopted by Srinath and Loehr is retained.

As equation (6) shows, ammonium ion (NH_4^+) exists in equilibrium with ammonia gas (NH_3) in water. Ammonium ion is highly soluble, whereas gaseous ammonia is readily removed by desorption. Ammonia at the pH values normally present in anaerobic digester liquid (pH 6.8-7.2) is primarily in the ionized highly soluble form. In order to desorb this ammonia, it is necessary to bring the liquid into contact with a gas. Ammonia may then pass through the liquid to the gas in a mass transfer process. Resistance to this transfer occurs at the films or layers present where the liquid phase and gas phase make contact. The greatest resistance to mass transfer occurs when ammonia is to be transferred from the liquid to the gas phase. This resistance is a result of the high solubility

and ionization of ammonia in water. Undissociated ammonia (expressed as NH_3-N) in solution will tend to approach equilibrium with gas in contact with the liquid. At equilibrium, the partial pressures of ammonia in solution and in the gas phase will be equal. When the gas phase is not saturated with ammonia, the following relationship is valid:

$$-\Delta C = k \cdot A_i \cdot C \cdot F \cdot \Delta t \; - - - - - - - - - - - - - - - - - \; (16)$$

where:

ΔC = the quantity of ammonia removed

k = a coefficient of mass transfer

A_i = interfacial area of exposure

$C \cdot F$ = the concentration of undissociated ammonia

Δt = the time of exposure

Increasing the time of exposure, the interfacial area of exposure or the undissociated ammonia in the liquid will result in greater quantities of ammonia removal.

The system devised at the Boar Testing Station was constructed to take advantage of these three parameters. Rapid gas recirculation provided a high exposure time. A high area of gas to liquid exposure was provided by forcing recirculated gas through the many holes drilled in the PVC diffuser installed in the digester. The removal of carbon dioxide increased digester pH which increased the concentration of undissociated ammonia in the liquid. The undissociated ammonia transferred from the liquid phase to the gas phase was then stripped from the gas in the phosphoric acid solution. Gases returned to the digester after passing through the phosphoric acid should have had an ammonia partial pressure lower than the partial pressure of ammonia in the digester. Thus, further stripping of ammonia from the digester could be achieved.

For a continuous flow system equation (16) is expressed as:

$$(C_1 - C_2) \ Q = K_D \cdot F \cdot C_2 \cdot V \text{ - - - - - - - - - - - - - - -} \quad (17)$$

where:

C_1 = influent total ammoniacal nitrogen

C_2 = effluent total ammoniacal nitrogen

Q = flow through rate

V = volume of the digestion unit

F = ratio of undissociated ammonia concentration to total ammoniacal

   nitrogen as determined from equation (7)

K_D = a system specific desorption coefficient

V/Q is the average liquid retention time of the digestion unit also representing the average time of desorption. In terms of hydraulic retention time $t_{(HR)}$ equation (17) may be written as:

$$\frac{C_1 - C_2}{C_2} = K_D \cdot F \cdot t_{HR} \text{ - - - - - - - - - - - - - - - - - -} \quad (18)$$

Influent and effluent ammonia nitrogen concentrations were not obtained during this study but may be determined from daily ammonia uptake in the phosphoric acid solution in conjunction with the ammonia nitrogen concentrations observed in the digester. On this daily basis t_{HR} is 24 hours.

Meaningful results were obtained over short periods of time during Phase II and Phase III. The data for these two periods selected from Appendix B are shown in Table 2. During Phase I the carbon dioxide stripper was not in use. The pH of the digester was near seven and the ratio of undissociated ammonia to total ammonia would be expected to be low. Figure 6 shows the relative increase in this ratio for a pH range of 7.0 to 8.0. The figure was constructed from the data presented in

TABLE 2

Results of Field Tests to Remove Ammonia

	Digester			Waste Gas		NH$_4$ Stripper	CO$_2$ Stripper
Date	Temp., °C	pH	NH$_4$-N mg/l	% CH$_4$	%CO$_2$	NH$_4$-N mg/l	pH
Phase II							
9/12/74	26.0	7.25	1,360	46	45	1,156	*
9/16/74	26.0	7.15		46	48		*
9/20/74	27.0	7.05	715	48	45	1,645	*
9/24/74	27.0	7.15	795			1,825	*
9/26/74	26.0	7.15	750	49	41	1,740	*
9/30/74	24.5	7.15	760			1,925	*
Phase III							
1/ 6/75	28.5	7.55	1,290	86	1	6,000	11.2
1/ 9/75	32.0	8.08	1,400	87	0.3	8,450	12.6
1/19/75	27.0	7.63	1,325	58	32	9,390	9.0

* CO$_2$ stripper not in use during this period
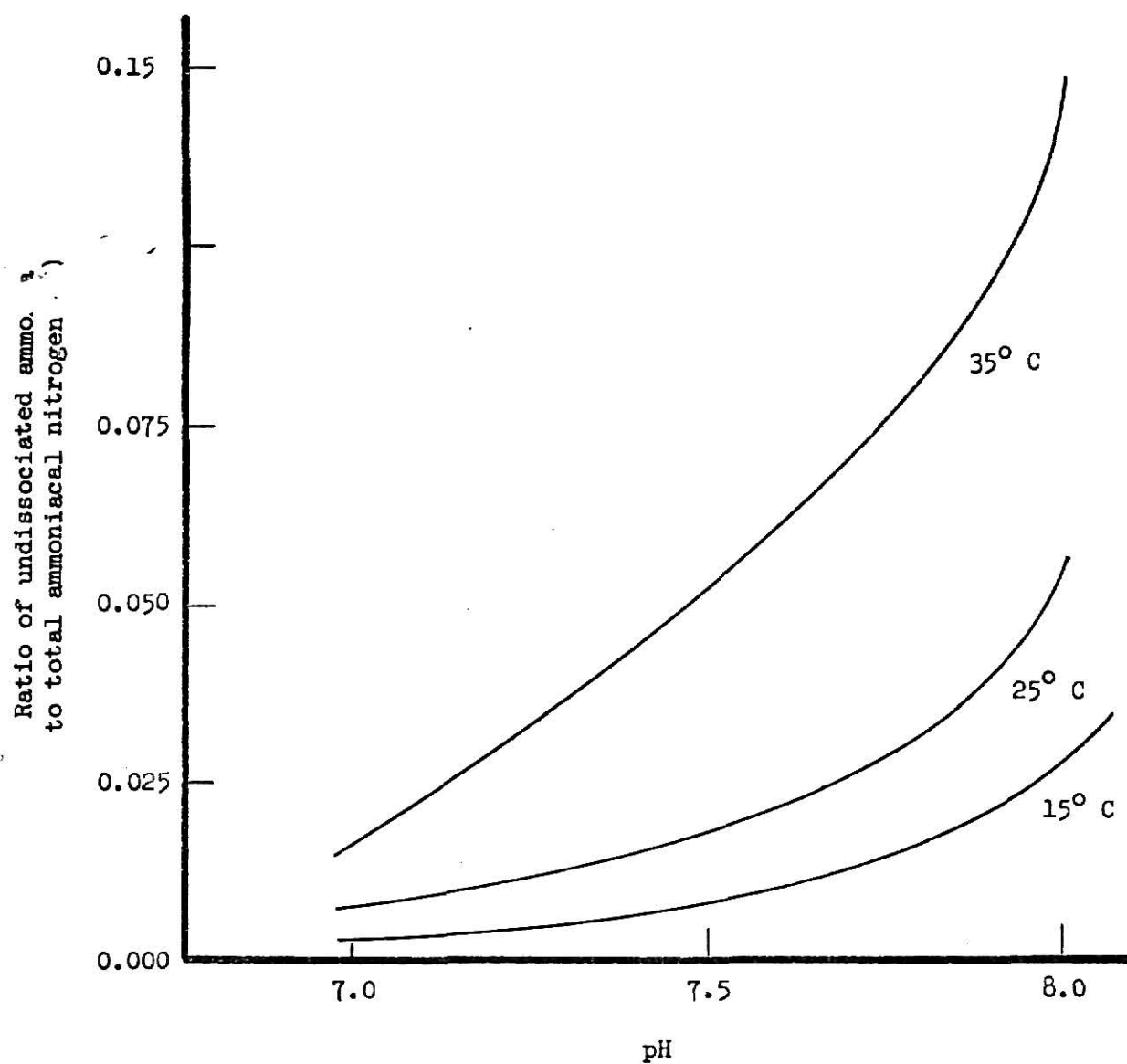
FIGURE 6. Effect of pH and Temperature
on Fraction of Undissociated Ammonia

Table 1. The uptake of ammonia in the 40 gallons (151 liters) of phosphoric acid during Phase II was 6.5 grams per day:

$$\frac{(1,925 \text{ mg/l} - 1,156 \text{ mg/l})(151 \text{ liters})}{(18 \text{ days})(1,000 \text{ mg/g})} = 6.5 \text{ g/day}$$

This represents a removal of ammonia from the 450 gallon (12,700 liter) digester per day of:

$$\frac{6,500 \text{ mg/day}}{12,700 \text{ liters}} = 0.5 \text{ mg/l/day}$$

The average ammonia concentration in the digester was 755 mg/l during this phase. The difference in effluent and influent ammonia nitrogen concentrations in the digester may be assumed to be 0.5 mg/l. This value divided by 755 mg/l may be used to evaluate the left hand portion of equation (18). The value of F, 0.00786 may be calculated from equations (7) and (8) or estimated from curves such as Figure 6. For a pH of 7.1 and an average temperature of 26° C solution of equation (18) yields a K_D value of 3.59×10^{-3}/hour.

K_D may be corrected to other temperatures by the following equation:

$$K_{D2} = K_{D1} \cdot 1.063^{(^{\circ}C_1 - ^{\circ}C_2)} \quad - - - - - - - - - - - - - - - - - (19)$$

At 35° C the calculated K_D value is 6.22×10^{-3}/hour.

The same procedure is followed to determine a K_D value for the results obtained for the period from January 6th to January 9th during Phase III. Carbon dioxide removal was accomplished during this period and the pH of the digester rose to nearly 8.1. As a consequence, ammonia uptake in the phosphoric acid was greater. Based upon the ammonia nitrogen concentrations for Phase III of 6,000 mg/l and 8,450 mg/l, an ammonia uptake rate of 123 grams per day can be calculated. This is equivalent to removing 0.7 mg/l/day from the digester. The average ammonia nitrogen

concentration in the digester for this period was 1,345 mg/l. Again, the latter two values may be used to calculate the left hand portion of equation (18). At a pH of 7.8 and a temperature of 30° C the F value calculated is 0.0984. Solution of equation (18) using these values results in a K_D of 5.55 x 10^{-3}/hour. The coefficient corrected to 35° C is 7.53 x 10^{-3}/hour.

Henry's Law may also be used to estimate K_D, provided the solubility coefficient of ammonia (H) can be determined. The partial pressure of ammonia (p) in a gas is related to the free ammonia concentration of the liquid (C · F) and the solubility coefficient of ammonia gas in the following manner:

$$p = \frac{C \cdot F}{H} \quad \text{---------------------------} \quad (20)$$

The quantity of ammonia removed from a liquid will equal the ammonia in the gas diffused through the liquid since the concentration of ammonia in the gas is at saturation and in equilibrium with the concentration of ammonia in the liquid. The following relation then exists:

$$V \cdot \Delta C = A \cdot \Delta t \cdot p \cdot \rho \quad \text{------------------} \quad (21)$$

where:

   V = the volume of the liquid

   ΔC = the change in NH_4-N concentration in the liquid that occurred
        by desorption in time t.

   p = the partial pressure of ammonia in the gas

   ρ = the density of ammonia

   A = the gas flow rate

Equation (21) may be rewritten as:

$$V \cdot C = A \cdot t \cdot \frac{C \cdot F}{H} \cdot \rho \quad \text{-----------------} \quad (22)$$

and combining (20) and (21),

$$\ln \frac{c_1}{c_2} = (\frac{A \cdot \rho}{V \cdot H}) \cdot F \cdot (t_2 - t_1) \text{ - - - - - - - - - - - - - - - } (23)$$

The factors in parentheses are equivalent to K_D upon inspection of equation (18).

Srinath and Loehr (27) confirmed the following relationship between the solubility coefficient (H) and temperature:

$$H \text{ (mg/l-atm)} = 3.564 \times 10^6 \cdot e^{[-0.0525 \cdot °C]} \text{ - - - - - - - - - - } (24)$$

A value for K_D may be calculated from equations (23) and (24). At a temperature of $35°$ C, H is 5×10^6. The density of ammonia at one atmosphere pressure and $35°$ C is 672 mg/l (17,000 mg/mole per 25.3 moles/liter). For a gas flow rate of 50 cubic feet per minute per 1,000 cubic feet of digester capacity, K_D calculated is 4.03×10^{-3}/hour.

Since K_D is directly related to A/V, a K_D value may be obtained from the experimental data of Srinath and Loehr. Multiplying their K_D value by the inverse of the flow rates yields:

$$0.52/\text{hr} \cdot \frac{50 \text{ cfm/1,000 cf}}{5,660 \text{ cfm/1,000 cf}} = 4.59 \times 10^{-3}/\text{hr}$$

Table 3 shows the four values of K_D calculated.

TABLE 3

Values of K_D for a Gas Flow Rate of
50 cfm/1,000 cf of Digester Capacity at $35°$ C

Source	K_D/hour
KSU, Phase II, pH 7.1	6.22×10^{-3}
KSU, Phase III, pH 7.8	7.53×10^{-3}
Calculated from Henry's Law	4.03×10^{-3}
Calculated from data of Srinath and Loehr (27)	4.59×10^{-3}

The average value of $K_D = 5.6 \times 10^{-3}$ may be used to calculate percentages of ammonia removal for an air flow rate of 50 cubic feet per minute per 1,000 cubic feet of digester capacity. Table 4 shows the percentage of ammonia removal which may be expected for various flow rates. K_D is proportionately increased for flow rates higher than 50 cubic feet per minute and adjusted by equation (19) for temperatures other than 35° C. Equation (18) was used to determine percent removals.

Table 4 shows that for a digester with a 15 day retention time, ammonia removals greater than 50 percent will require air flow rates of 200 cubic feet per minute per 1,000 cubic feet of digester capacity or greater.

One hundred percent removal of ammonia is not necessary. The literature reviewed indicates that reductions of ammonia to levels below 1,000 to 1,500 mg/l should be sufficient to eliminate the toxic effects attributed to ammonia.

Ammonia capture in the phosphoric acid solution was too small to indicate what final form would be present when saturation is reached. Ammonium phosphate will be formed during absorption. This chemical is widely utilized as a crop fertilizer and its recovery would be an asset. Laboratory studies conducted by another investigator in conjunction with this field research were aimed at determining how much ammonia can be absorbed by concentrated phosphoric acid. Ammonia uptake declined before the pH of the phosphoric acid reached a safe level for direct land application. Dilution before land treatment might solve this problem.

TABLE 4

Percentage of Ammonia Removal for a 15-day Digester Retention Time

Temp., °C	pH	% Removal 50 cfm/1,000 cf	% Removal 100 cfm/1,000 cf	% Removal 200 cfm/1,000 cf	% Removal 400 cfm/1,000 cf
15° C	7.0	0.5	1.1	2.3	4.4
15° C	8.0	5	10	18	31
25° C	7.0	1.1	2.2	4.4	8.5
25° C	8.0	10	18	31	47
35° C	7.0	3.3	6.4	13	22
35° C	8.0	23	37	54	70

CONCLUSIONS

1. Carbon dioxide removal from an anaerobic digester can be accomplished by high rate recirculation of digester gas through caustic stripping solutions. The stripping of carbon dioxide from the gas stream will result in an increase in digester pH to at least 8.0.

2. Ammonia can be removed from an anaerobic digester. Stripping of ammonia from the recirculated gas stream can be accomplished with phosphoric acid. Higher ammonia removals occur at a pH of eight.

3. A tentative system specific desorption coefficient has been determined for the swine waste anaerobic digester used during this study.

4. Removal of carbon dioxide for digester pH control can result in a digester excess gas composed of nearly 100 percent methane.

5. Gas recirculation provides a high degree of mixing of digester contents. Liquid surface scum accumulation is prevented.

RECOMMENDATIONS FOR FURTHER RESEARCH

The system devised for the separation of nutrients to enhance anaerobic digestion of swine waste has been shown to work as predicted. Further studies are necessary to verify the results obtained for the short periods of successful operation at the Boar Testing Station. These studies could be conducted best on a laboratory scale. Results obtained in laboratory scale anaerobic digestion studies may be applied directly to large scale facilities. Conditions can be controlled much more easily in the laboratory. The rate of feeding waste can be held constant. The climate will not present problems as it did, particularly during colder periods. The amount of chemicals required to obtain the same results will be a fraction of those required for full scale operation. No opportunity was provided to change gas flow rates at the Boar Testing Station. This can be easily accomplished in the laboratory. A number of digesters can be set up to operate under various conditions.

Stable digestion was not achieved during field research. The reasons for this have already been discussed. It is desirable to achieve stable digestion and maintain it for a significant length of time. If the system is to work, the primary objective of breaking down the waste as thoroughly as possible must be met.

Laboratory studies should be conducted to more accurately characterize the desorption coefficient, K_D. Flow rates should be varied and their relationship with K_D established for swine waste at ammonia concentrations found in undiluted waste.

The extent of pH elevation as a result of carbon dioxide removal was not determined. It is possible that the pH can rise above 8.0. The optimum pH for anaerobic digestion and simultaneous ammonia removal should be investigated. It may also be possible to raise the pH sufficiently for ammonia removal to proceed without removing all the carbon dioxide. The digester contents may become more sensitive to volatile acids as the pH is raised and some of the alkalinity is destroyed.

Influent and effluent ammonia nitrogen concentrations should be observed and the difference in these values compared to the uptake of ammonia nitrogen in the phosphoric acid. The ammonia levels should be in the range considered toxic (2,000-2,500 mg/l) to confirm that these levels can be reduced to non-toxic ones. The waste at the Boar Testing Station was too dilute to obtain high initial concentrations. Waste can be collected and conveyed to the lab in much higher concentrations.

A nitrogen balance for the entire system should be conducted. The recovery of nitrogen in forms which maximize its fertilizer value is desirable.

High loading rates should be investigated. Loading rates determine the size of digester required for a given size feedlot. Size will dictate initial capital costs. Loading rates are closely associated with influent concentrations. High loading rates and influent concentrations reduce hydraulic volume, water use and liquid handling throughout a system.

Running three to four digesters simultaneously in the lab would be desirable. One digester should be reserved to attempt to acclimatize anaerobic bacteria to high concentrations of ammonia. Stable digestion and gas production should be established at low concentrations. Loading

rates should then be increased gradually over a period of several months to determine if solids destruction and gas production will proceed favorably at high ammonia concentrations.

A second digester can be operated at high initial loading rates. Nutrient separation may be accomplished by the method used for the field research. The chemicals will work. The problems encountered in the field would be much easier to cope with in the lab.

Other methods of ammonia and carbon dioxide removal can be examined with additional digesters.

The digesters should be analyzed for total Kjeldahl nitrogen and ammonia nitrogen. The organic nitrogen can be obtained by the difference. Influent and effluent nitrogen concentrations should be determined, as well as nitrogen concentrations in the digester and ammonia removing unit. The nitrogen balance may then be defined with these values.

Influent and effluent chemical oxygen demand analyses will indicate the degree of stabilization of the waste. Volatile solids destruction and gas production should be determined for this purpose also.

The relationship between alkalinity and volatile acids with respect to pH should be closely observed. Proper ratios may serve as indicators of stable operating conditions as Melbinger and Donnellon (19) indicate.

Finally, gas composition should be examined and the heating value determined for comparison with other fuels.

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APPENDIX A

DATA FROM SCHMID AND LIPPER (25)
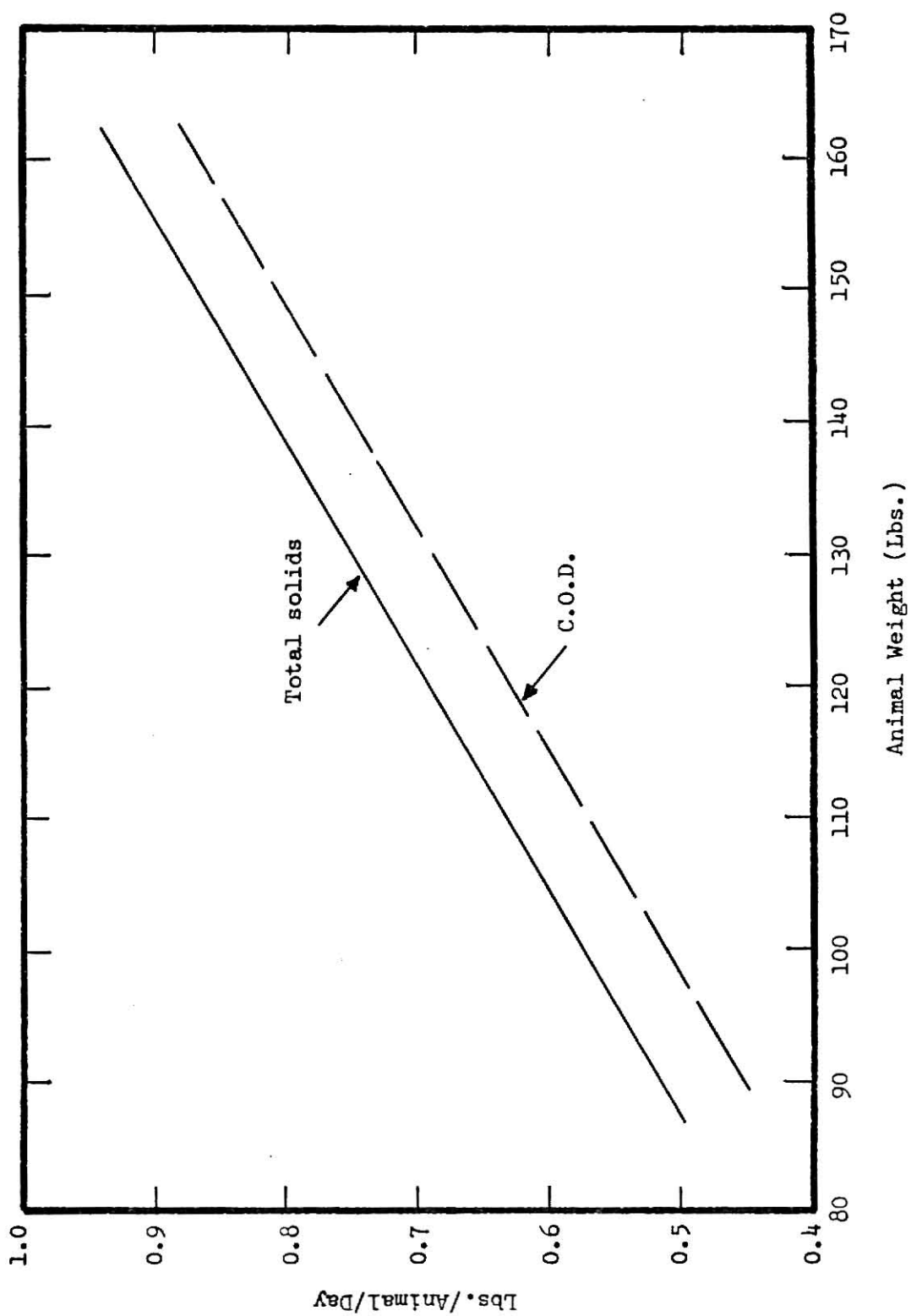
FIGURE A1. Total Solids and COD Production per Animal vs. Animal Weight

TABLE A1

Feed Ingredients for Finish Ration

Ingredients	Amount/500 lbs.
Bulk (pounds)	
Soybean oil meal	100
Ground sorghum grain	369.5
Dehydrated alfalfa (17%)	12.5
Premix A (pounds)	
Ground limestone	5.0
Dicalcium phosphate	5.0
Salt	0.5
Trace minerals (5% Zn)	0.5
Premix B (grams)	
Vitamin D (15,000)	5.0
Vitamin A (10,000)	75.0
B-complex (Merck 1233)	75.0
Vitamin B_{12} (Proferm 20)	57.0
Tylosin (10)	227.0
Ground sorghum grain	1,831.0

TABLE A2

Average Strength Parameters
units/day/100 lb.
Live Weight

Parameter	Average
Gallons	0.90
Cubic feet	0.12
Total solids, lb.	0.59
Volatile solids, lb.	0.47
Suspended solids, lb.	0.47
COD, lb.	0.52
BOD, ultimate, lb.	0.20

TABLE A3

Representative Values of Anaerobic Mixed Liquor

Unit	Loading lb. TS/cf/day	pH	Volatile Acids mg/l	Alkalinity mg/l as $CaCO_3$	NH_3-N mg/l	Off Gases % CH_4	Total Gas per lb. vs. added/cu. ft.
Temperature 35° C							
#1	0.26	6.65	16,500	10,700	1,800	18	1.00
#2	0.52	6.75	19,000	11,800	1,800	16	0.92
Temperature 20° C							
#1	0.25	6.80	16,800	15,000	2,200	15	0.30
#2	0.50	6.90	17,500	15,000	2,500		

TABLE A4

Solids Loadings and Solids Destruction at 20° C

| | Digester Loading, lb/cf/day | | | % Reduction | | |
Unit	Total Solids	Total Volatile Solids	Suspended Solids	Total Solids	Total Volatile Solids	Suspended Solids
#1	0.25	0.20	0.20	33	31	31
#2	0.50	0.40	0.40	23	20	37

APPENDIX B

OPERATIONAL DATA, PHASE I, II AND III

TABLE B1

General Operational Data

Date	Temperature (°C) Dig.	NH3 Stripper	CO2 Stripper	pH Dig.	NH3 Stripper	CO2 Stripper	Volatile Acids mg/l	Alkalinity mg/l	COD mg/l	Total Solids mg/l
Phase I										
Jun 12	29.0			5.90	1.30		2,250			
Jul 21	25.5			6.95			2,760		26,570	24,630
Jul 30	27.5			7.40	1.00	10.25				
Aug 14	23.3	26.0		7.40	1.00		952	5,600	13,500	9,340
Aug 16	30.5			7.25	1.58			8,750	38,700	45,800
Aug 23	23.5	40.5		7.10	1.70		1,816	2,330	6,340	4,865
Aug 24	27.5	41.5		7.58	1.70		932	2,690	6,220	5,035
Phase II										
Sep 5	25.0	38.0		7.40	1.53		470		5,180	4,340
Sep 9	27.0	43.0		7.50	0.70		230		4,770	4,610
Sep 12	26.0	38.5		7.25	0.60		175	2,900	5,110	4,430
Sep 16	26.0	36.0		7.15	0.90		100	3,280	6,510	5,970
Sep 20	27.0	43.0		7.05	0.25		90	2,900	5,060	4,575
Sep 24	27.0	41.0		7.15	0.15		60	2,725	4,460	5,590
Sep 30	24.5	37.0		7.15	0.00		150	2,575	3,820	4,830
Phase III										
Oct 18	36.0	49.0	36.0	7.20	0.00	8.20		2,625		
Oct 21	34.0	42.0								
Oct 29	33.0	42.0	36.0	7.20	0.00	6.80	200	3,175	4,480	6,140
Nov 4	24.0	43.0	23.5	7.25	0.00	8.47	300	3,575	2,950	
Nov 10	22.5	32.0	27.0	7.33	0.00	8.86		3,550	4,950	
Dec 17	12.0	29.5	25.5	7.25	0.00	12.65	600		3,700	4,330
Jan 6	28.5	40.0	31.7	7.55	0.00	11.25	200	7,625	11,200	13,050
Jan 9	32.0	45.5	29.5	8.08	0.00	12.60	640	5,050	4,813	6,340
Jan 14	27.0	41.5	31.0	7.63	0.00	9.00	450	4,375	2,435	4,250

Table B1 - General Operational Data (Continued)

| Date | Temperature (°C) | | | pH | | | Volatile Acids mg/l | Alkalinity mg/l | COD mg/l | Total Solids mg/l |
	Dig.	NH₃ Stripper	CO₂ Stripper	Dig.	NH₃ Stripper	CO₂ Stripper				
Phase III (Continued)										
Feb 10	22.5	30.0	9.0	6.80	0.00	5.82	900	3,300	2,700	3,800
Feb 13	22.0	26.0		6.90	0.00		1,170	3,375	4,990	4,430
Feb 18	14.0	26.0	14.0	6.95	0.00	7.43	980	2,950	3,920	3,240
Feb 20	15.0	28.0	20.0	7.10	0.00	7.22	1,020	2,875	3,700	3,320
Feb 26	9.5	21.0	15.0	6.95	0.00	8.03	730	2,550	2,690	2,850
Feb 28	17.5	32.0	23.5	6.99	0.00	7.35	540	1,850	2,920	2,625
Mar 2	22.0	27.0	17.0	6.97	0.00	7.56	550	2,300	2,900	2,660
Mar 4	27.0	33.0	23.5	6.85	0.00	4.00	140	2,150	1,580	2,500
Mar 6	33.5	39.0	24.0	6.88	0.00	10.95	440	2,050	1,230	2,130
Mar 10	40.0	40.5	39.0	7.04	0.45	7.60	625	2,000	1,800	2,340
Mar 12	42.0	38.0	25.0	7.06	0.35	3.30	670	1,850	1,835	2,080
Mar 14	32.0	30.5	12.0	7.05	0.90	12.60	640	1,800	1,875	2,050
Mar 16	35.0	39.0	33.0	7.20	0.75	7.10	440	1,850	2,043	2,100

TABLE B2

Ammonium Nitrogen Concentrations

Date	Digester NH₄-N mg/l	Ammonia Stripper NH₄-N mg/l	Date	Digester NH₄-N mg/l	Ammonia Stripper NH₄-N mg/l
Phase II			**Phase III**		
Sep 5	612	1,700	Feb 10	815	1,920
Sep 9	612	2,470	Feb 13	800	1,915
Sep 12	1,360	1,156	Feb 18	960	1,675
Sep 16	1,230	1,620	Feb 20	460	1,280
Sep 20	715	1,645	Feb 26	600	2,290
Sep 24	795	1,825	Feb 28	605	1,930
Sep 26	750	1,740	Mar 2	635	1,805
Sep 30	650	1,925	Mar 4	575	1,745
			Mar 6	605	1,795
Phase III			Mar 10	855	950
Oct 18	555	1,955	Mar 12	465	1,355
Oct 29	710	1,755	Mar 14	265	1,450
Nov 4	650	2,040	Mar 16	600	775
Nov 10	950	1,850			
Dec 17	870	2,625			
Jan 6	1,290	6,000			
Jan 9	1,400	8,450			
Jan 14	1,325	9,390			

TABLE B3

Percent Composition of Digester Gases

Date	CO_2	O_2	N_2	CH_4	Date	CO_2	O_2	N_2	CH_4
Phase I					Phase III				
Jun 12	11	20	58	11	Jan 7	1	1	12	86
Jul 30	9	5	59	27	Jan 9	0.3	4	9	86.7
Aug 15	37	4	24	35	Jan 14	32	1	9	58
Aug 16	44	5	18	33	Feb 10	41	2	7	50
Aug 24	17	4	38	41	Feb 13	39	3	4	54
					Feb 19	16	1	18	65
Phase II					Feb 21	20	0	9	71
Sep 6	23	4	35	38	Feb 27	2	5	78	15
Sep 9	24	4	47	25	Feb 28	9	3	42	46
Sep 12	45	1	8	46	Mar 2	29	2	5	64
Sep 16	48	2	4	46	Mar 4	39	1	4	56
Sep 19	45	2	5	48	Mar 6	40	0	4	56
Sep 26	41	1	9	49	Mar 10	60	1	2	37
Sep 30	8	12	26	54	Mar 12	49	3	14	34
					Mar 14	12	3	68	17
Phase III					Mar 16	12	3	46	39
Oct 18	25	2	49	24	Mar 18	18	4	30	48
Oct 29	48	1	2	49	Mar 20	1	4	38	56
Nov 4	43	1	2	54	Mar 21	5	6	31	58
Nov 10	44	1	9	46					
Dec 17	4	2	64	30					

ENHANCEMENT OF SWINE WASTE DIGESTION
THROUGH AMMONIA AND CARBON DIOXIDE REMOVAL

by

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AN ABSTRACT OF A MASTER'S THESIS

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ABSTRACT

A swine waste anaerobic digester receiving the waste from 80 boars was operated for a period of ten months. Digester mixing and nutrient removal were accomplished by the recirculation of digester gases through two stripping units. Phosphoric acid was used to strip ammonia from the recirculated gas stream. Caustic solutions, primarily lime, were used to strip carbon dioxide.

The removal of carbon dioxide resulted in an elevation of digester pH to 8.0. At the elevated pH ammonia was more readily stripped.

A system specific ammonia desorption coefficient was determined which may be used for selecting gas flow rates. The selection of the proper gas flow rate can provide the required degree of ammonia removal to reduce ammonia concentrations to levels non-toxic to anaerobic bacteria.