COMPARISON OF LIME AND SODIUM HYDROXIDE FOR THE CONTROL OF GAS PRODUCTION FROM SEWAGE SLUDGES

by

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I am indebted to my parents and my brother who in more ways than I can mention here helped me throughout my period of study. This thesis is dedicated to the loving memories of my late brother Narendra Prasad.

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I. INTRODUCTION

The handling and disposal of wastewater sludge often requires dealing with odor problems. A large sludge pond at a chemical plant which is used for the disposal of both sewage sludge and flyash faced severe odor problems during the summer of 1989. The odors at this facility increased enormously during summer months and were most pronounced soon after a period of sustained heavy rainfall. Personnel from the chemical plant contacted members of the Virginia Tech Environmental Engineering faculty to see if a solution to this problem could be found. The results of the study which were initiated to evaluate the problem are reported in this thesis.

This research involved establishing a caustic chemical dose to arrest or slow gas production in the sludge pond, and to determine the role of calcium in influencing bioactivity.

Odor problems associated with anaerobic bioactivity have been widely reported. Lime stabilization remains a popular choice for odor control owing to its low cost and simplicity of operation. Studies in the past have suggested that addition of lime to raise the pH to 12.0 is needed to reduce odors and pathogens. No alkali other than lime is reported in the literature for odor control. In this study lime is compared to sodium hydroxide (NaOH) for odor control.

Metal cations are both toxic and stimulatory to anaerobic systems (1). Because caustic chemicals add cations, it was of interest to determine the relative effects of cations and pH on gas production. Therefore studies were performed to determine the combined effects of calcium and lime, and calcium and sodium hydroxide.

Specific objectives of this study are as follows:

1) Determine a lime dose that would permanently arrest gas production from the sludge being discharged to the sludge pond.

2) Determine a NaOH dose that would permanently arrest gas production from the sludge being discharged to the sludge pond.

3) Determine the combined effects of calcium and lime, and calcium and NaoH on gas production from the influent to the sludge pond.

4) Determine the gas production potential of sludge currently deposited in the sludge pond.

II. LITERATURE REVIEW

This chapter provides the background for chemical inhibitions in anaerobic treatment and a review of the literature which deals with chemical inhibition in anaerobic treatment and with lime stabilization.

Chemical Inhibition in Anaerobic Treatment :

Anaerobic degradation of organic matter to gaseous end products, the majority of which is methane, is a three step process. In the first phase of degradation, fermentative bacteria hydrolyze complex organics and ferment them to fatty acids, alcohols, and other soluble organics. In the second phase acetogenic bacteria degrade propionate and longer chain fatty acids to acetate, hydrogen and carbon dioxide. In the final phase methanogenic bacteria, which are strictly anaerobic, convert the volatile acids to methane and carbon dioxide, and convert carbon dioxide and hydrogen to methane.

Chemical inhibition can occur in any of the three phases discussed. The third phase of reactions involving methanogens has been reported as the rate limiting step (2). Methanogens are very sensitive to even minor fluctuations in pH, substrate concentration, and temperature, unlike the acetogenic bacteria which function over a wide range of environmental conditions. At solids retention times over 10 days and at a temperature of 35° C, the hydrolysis of organic solids (cellulose in particular) was found to be rate limiting in sewage sludges (3).

McCarty (4) reported that methanogens have an optimum pH range of 6.6 to 7.6. Similar results were reported by Heukalekian et.al. (5), and Barker (6). Beyond these pH limits, digestion has been reported to occur, but with less efficiency. Clark and Speece (7) reported in 1970, that bacteria are not necessarily killed by high and low pH levels, but their growth is merely slowed or stopped. At a pH below 6.2, the methanogens activity lags behind that of acid formers, which leads to further accumulation of acids. Under these conditions, the methanogens are further inhibited and the reactor fails. This problem could be cured by increasing the reactor pH and buffering capacity by the addition of sodium bicarbonate (8).

McCarty and McKinney (2) suggested pH control by any alkaline material, as long as the cation associated with the alkaline material did not cause toxicity. They reported Ca^{++} and Mg^{++} as non toxic, and Na^+, K^+, and ammonium (NH_4^+ as toxic.

The major cause of sludge odors is the presence of gaseous sulfur compounds such as hydrogen sulfide (H_2S), methyl mercaptan, ethyl mercaptan, and other meracptans. Amino compounds such as ethylamine, butylamine, and hexylamine are also reported to cause sludge odors. The H_2S content of the gas varies with chemical composition of the sludge (9). Industrial wastes with high sulfur contents increase H_2S levels in sludge gas. The H_2S content can be reduced by the presence of metal ions which form insoluble metal sulfides (10). pH is an important factor in the control of H_2S in the gas as it governs the hydrogen sulfide - sulfide equilibrium. The fraction of total sulfide in the H_2S form at pH 7 is about 50% and at pH 9 is near to zero. So little H_2S odor would be expected above pH 9.

Lime Stabilization :

The main objectives of lime stabilization of sewage sludge are to prevent odors and reduce pathogen levels. Its principal advantages over other stabilization processes are low cost and simplicity of operation. Nitrogen and sulfur containing gases evolved during anaerobic degradation of sludges are the chief causes of odors. Lime addition to sludges creates a high pH environment hostile to bioactivity. Hence the microorganisms involved are either inhibited or killed.

Most work on lime stabilization was based on twenty-four hours of storage after lime addition. Paulsrud and Eikum (11) monitored the stability of lime added sludges for four weeks. They found that lime dosages in excess of those required to raise the pH of the sludges to 12.0 were required to prevent a pH decline and return of odor production during storage. Counts and Shuckrow (12) reported odor prevention by lime stabilization at pH's greater than 12.0. Similar results were reported by

Kampelmacher and Jansen (13). Paulsrud and Eikum (11) also reported that no reduction of the odor intensity index occurred due to lime stabilization, but rather, the type of odor changed. They explained that the lime added to the sludge transformed the rotten offensive smell usually associated with the raw sludge to a less objectionable but equally strong ammonia odor.

Lime stabilization also improves sludge dewatering and settling characteristics. Sontheimer (14) reported improved sludge dewatering by lime addition. A study conducted by the USEPA in 1975 (12) reported enhanced settling in lime stabilized sludges. The EPA study also investigated the effect of lime addition on nutrients in the sludge. This study also reported that lime stabilized sludges had lower concentrations of soluble phosphate, ammonia nitrogen, and total Kjeldahl nitrogen than anaerobically digested sludge from the same plant. This facilitated higher sludge loadings rates per unit area when nitrogen limited the rate at which sludge had to be land applied.

III. METHODS AND MATERIALS

The research conducted to accomplish the objectives of this study was divided in to four phases. Experiments in the first phase were conducted using the solids obtained from different sites in the sludge pond. The sludge pond serves as a storage system for the wastewater treatment plants primary and secondary waste sludge, and flyash from the power house. The treatment plant treats both domestic waste and industrial waste from the chemical plant.

Phase I experiments were performed on the sludge pond solids. Experiments in phases II, III, and IV were conducted using the influent sludge to the sludge pond. Specific procedure followed in each phase of the study were as described below:

PHASE - I :

Experiments were performed in this phase to estimate pH and calcium effects on gas production from solids obtained from the sediments in the sludge pond. Samples tested in this phase were obtained from specific sites in the sludge pond represented by their location grid number and depth. The pH of all these samples was adjusted to seven prior to incubation and gas collection. Sample 6-18 2B was elutriated in this phase to estimate solution phase toxicity of calcium to anaerobic microorganisms. Elutriation of the sludge was accomplished by successive replacement of the supernatant with tap water by settling, decanting, and replacing the supernatant with tap water till the supernatant was clear.

PHASE - II :

Lime effects on gas production from the influent sludge to the sludge pond were studied in this phase. The sludge pond influent sludge was initially titrated with lime to determine the approximate lime doses required to elevate it to different pH levels. These lime doses were added to reactors with the sludge pond influent sludge. The initial pH of each reactor was recorded immediately after lime addition. Another set of pH observations were made 24 hours after lime addition. These pH readings are denoted in this report as 24-hour pH values.

Gas production from these reactors was monitored for a maximum of 80 days. The pH was recorded every ten days for the first 40 days. The pH of all reactors except the control was adjusted with concentrated sulfuric acid to between pH 6.5 and 7.0 on the 50th day.

PHASE - III :

The calcium effects on gas production at seven lime doses were studied in this phase. The experimental procedure was same as in phase - II. Quick lime - CaO, and

Ca^{++} as anhydrous calcium chloride ($CaCl_2$) were simultaneously added to the sludge pond influent sludge. Initial pH observations were made immediately after chemical addition and thorough mixing. The reactors were then capped with a rubber stopper for 24 hours and then a second set of pH measurements was made.

Gas production from these reactors was monitored for a maximum of 166 days. Measurements of pH were made every 25 days till all the reactors, except the controls, were elutriated with distilled water on the 125th day.

PHASE - IV :

The Ca^{++} effects on gas production at different pH's elevated by NaOH were observed in this phase. The sludge pond influent sludge was initially titrated with 1N. NaOH to determine the doses of NaOH required to elevate its pH to various levels. Ca^{++} was added as anhydrous $CaCl_2$. The experimental procedure was same as in phase - III. The reactors were monitored for a maximum of 171 days. The pH of the reactors was recorded every 25 days till the 125th day. All the reactors, except the controls, were elutriated with distilled water on the 125th day.

Experimental Set-up :

In designing the experimental set-up it was assumed that the gas production in an anaerobic reactor is a direct measure of its bioactivity. The experimental set-up used is shown in Figure 1. Chemicals were weighed and mixed thoroughly with two hundred milliliters (ml) of sludge in a 300 ml Erlenmeyer flask. The initial pH reading was recorded when the pH meter exhibited a constant reading for three minutes. The flask was immediately capped with a rubber stopper. Twenty four hours later a second pH reading was made. One end of a bent Pyrex glass tube (2mm - internal diameter) as shown in Figure 1 was then driven through the rubber stopper. Its other end was covered with an inverted graduated cylinder (300 ml) filled with acidified water, immersed in a 600 ml Kimax beaker half filled with acidified water. Adhesive tape was used to keep the graduated cylinder perpendicular to the base of the beaker.

The gas produced from the sludge escaped through the glass tube into the graduated cylinder and displaced an equivalent volume of water. The volume of gas produced was monitored.

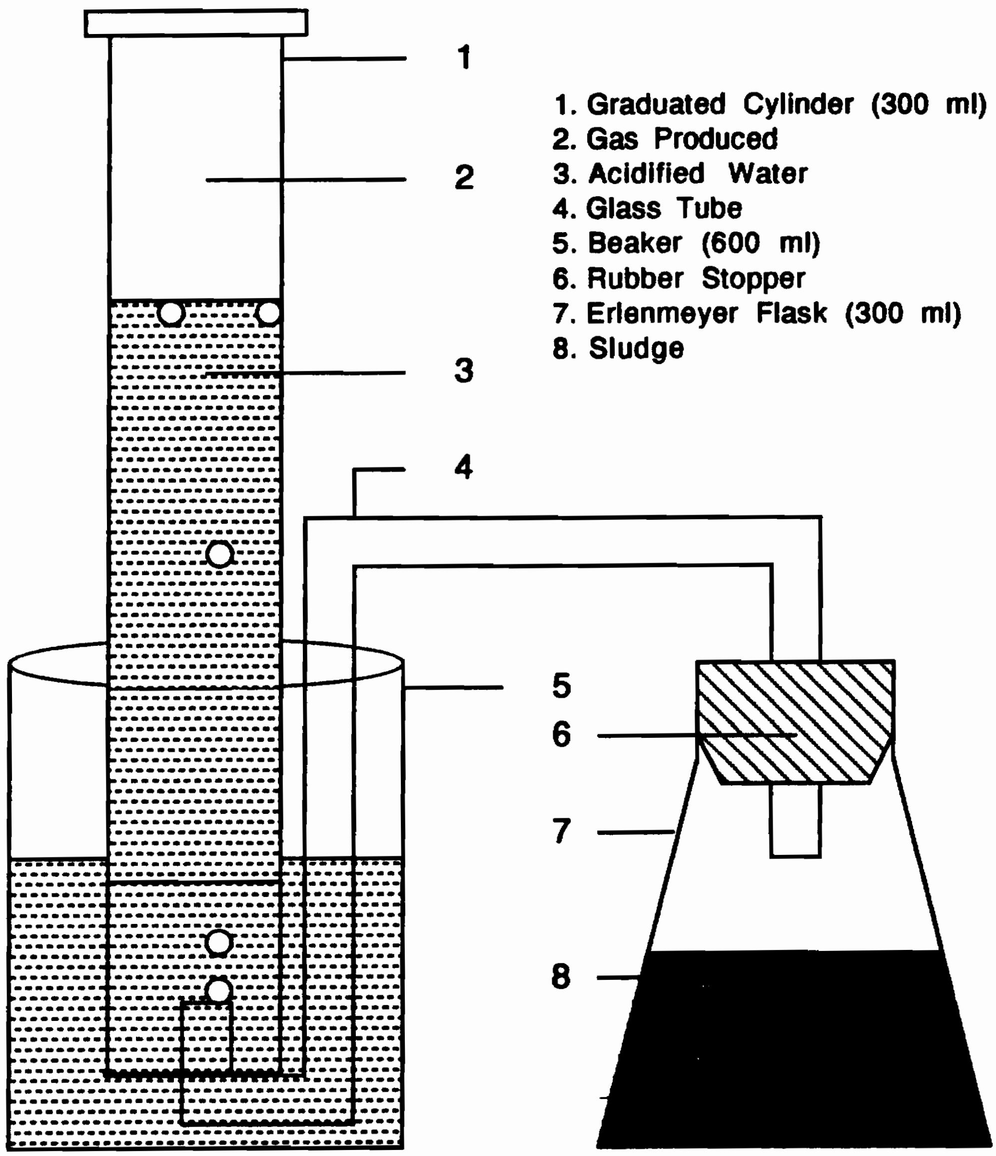

Figure 1. Experimental set up.

IV. RESULTS AND DISCUSSION

The laboratory data obtained in this study are presented in this chapter and discussed. Two major parameters measured in the study were volume of gas produced and pH. The main emphasis of the study was on evaluating the effects of lime, NaOH, and calcium on gas production from sewage sludges.

PHASE - I

pH and Cation Effects on Gas Production:

In this phase of the study, pH and cation effects on gas production from solid sediments in the sludge pond were determined. Each sample in this phase was taken from a different site in the sludge pond and is represented by its location grid number and depth. Some of the data obtained in this phase are presented in Figures 2, 3, and 4. The pH of these samples was adjusted to 7.0 prior to incubation and gas collection.

Figure 2 shows the volume of gas produced as a function of pH of the sample when it was removed from the pond (sample location 2B). Gas production from these reactors was monitored for a maximum of 200 days. A sharp increase in gas

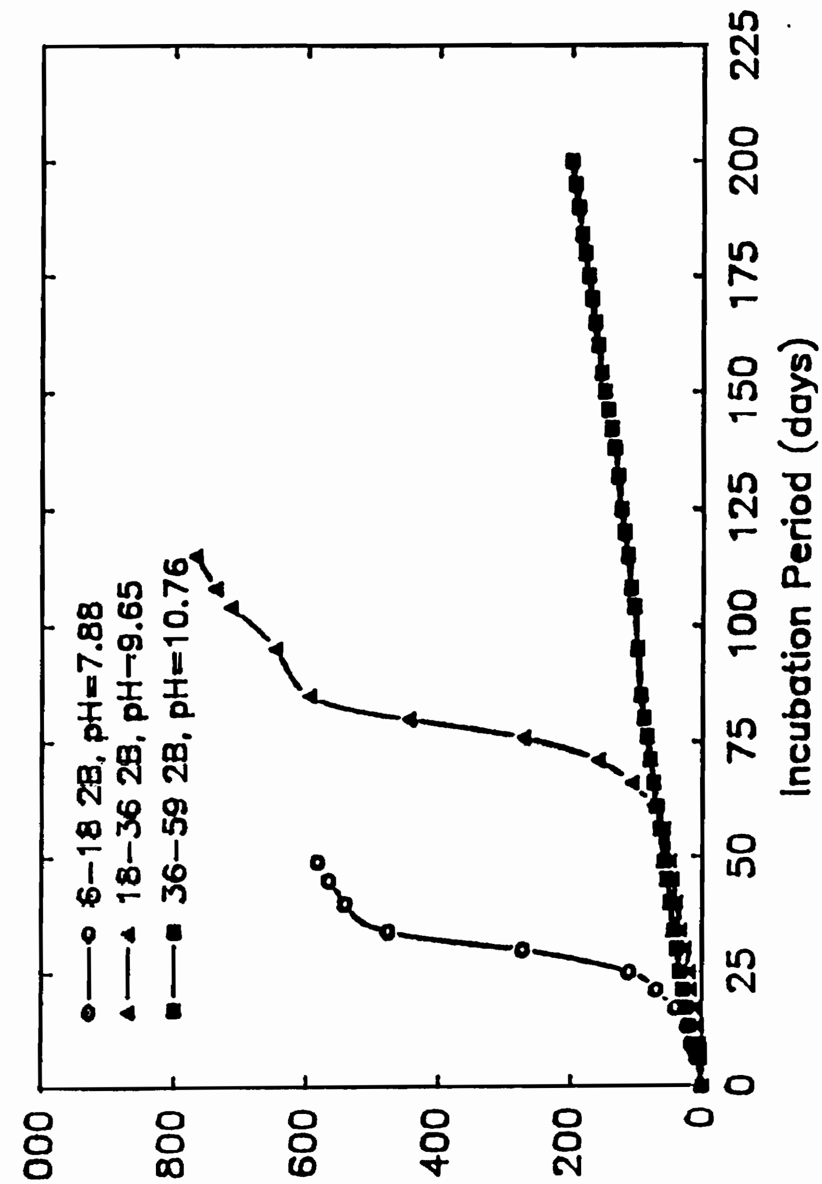

Figure 2. Gas production at different depths from sample location 2B.

production from sample 6-18 2B was observed on the 20th day, whereas substantial gas production from sample 18-36 2B was not observed until the 60th day. Sample 36-59 2B produced very small amounts of gas till the 40th day, after which it completely stopped producing gas.

It can be observed from these data that the pH of the sample increased with depth. This might have been due to the accumulation of excess lime, and the presence of older sludge and less active microorganisms at greater depths. It can also be observed from these data that the time required for initiation of high gas production rates increased with an increase in initial pH; this indicates that methanogens take longer to recover from higher pH values.

Figure 3 shows the gas production from three reactors with sample 6-18 2B. Cations were added to two of the reactors, while the third was used as a control (no cation addition). It can be clearly seen from these data that cations reduced gas production. This indicates that cations inhibit gas production from anaerobic microorganisms. Ca^{++} was found to be more inhibitory to anaerobes than Na^{+}.

A greater number of odor-related complaints were received from the neighborhood near the sludge pond after a heavy rainfall. This indicated that gas production increased with sludge washing. Therefore sample 36-42 6BC was monitored to study the effect of elutriation on gas production (see Figure 4).

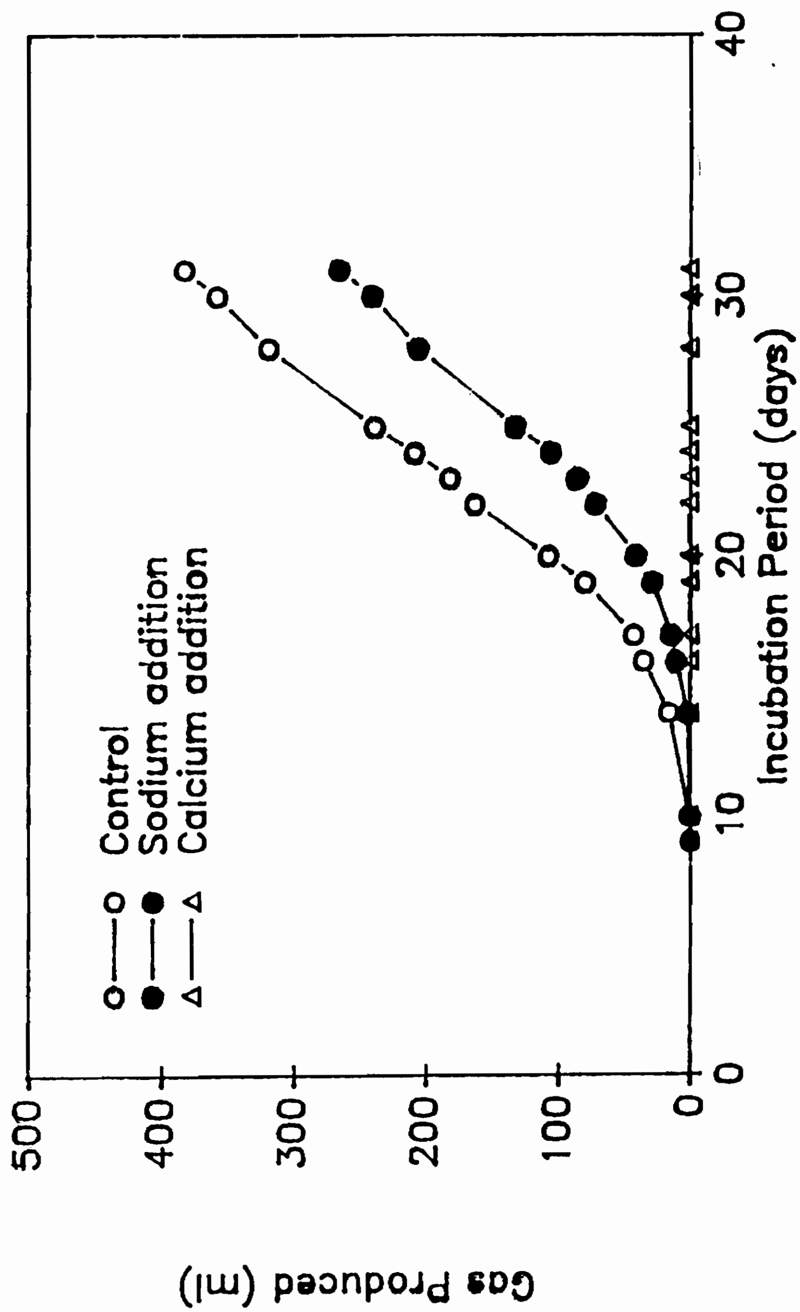

Figure 3. Effect of cation addition on gas production.

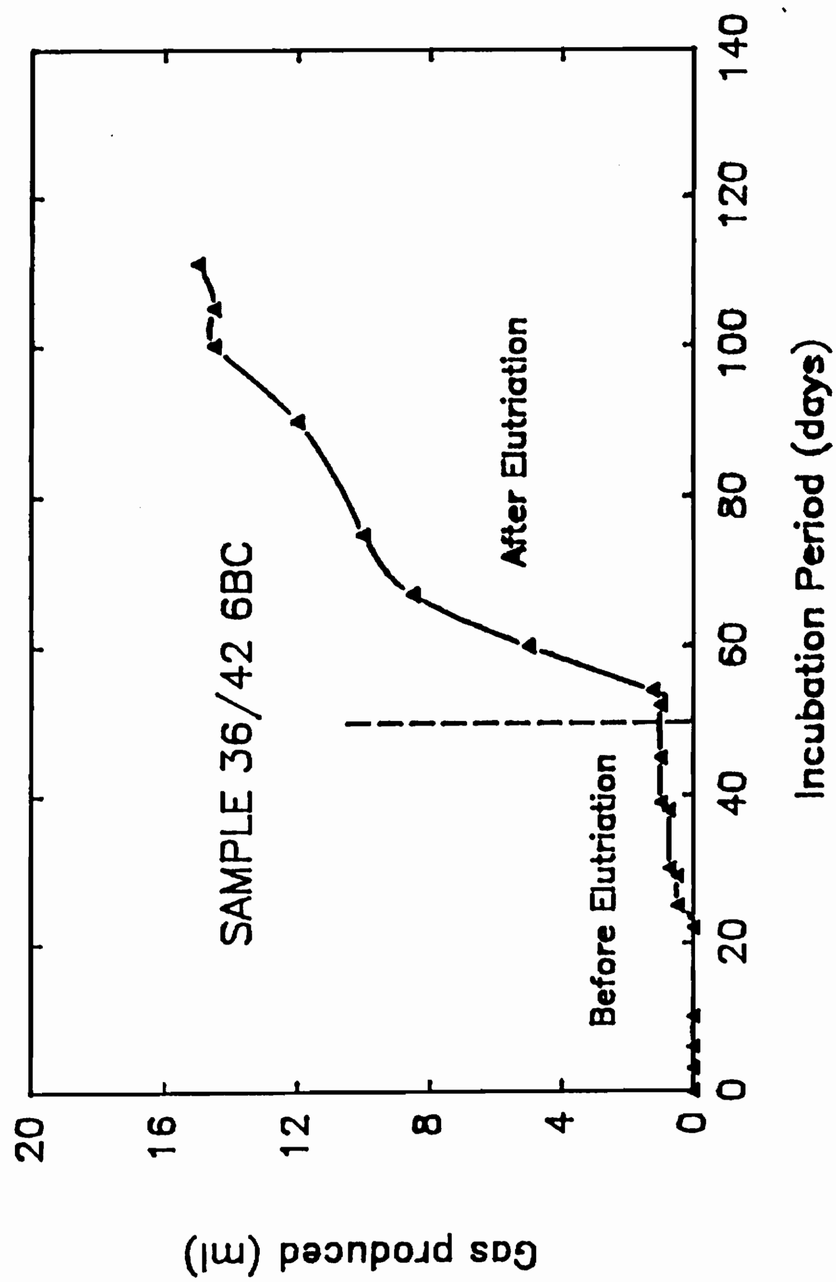

Figure 4. Effect of sludge washing on gas production.

Elutriation was performed by successive replacement of supernatant till the supernatant was clear. By this process, the chemicals in the sludge liquor were almost all removed. Thus, an attempt was made to understand the significance of cations in anaerobic systems by comparing the gas production from this sample, before and after elutriation. No gas production from this reactor was observed prior to elutriation. A small quantity of gas was produced after elutriation. This might have been either due to the reduction in pH and/or the reduction in cations or the reduction in some other inhibitor.

With the observations made in this phase, the next three phases of experiments were carefully designed to evaluate in more detail the effects of lime, NaOH, and calcium on gas production from sewage sludges.

PHASE - II

Lime Effects on Gas Production :

In this phase the lime effects on gas production from the influent sludge to the sludge pond were monitored. The data obtained from these reactors are presented in Figure 5 and Table I. The pH values presented in Figure 5 and Table I are the pH readings obtained 24 hours after chemical addition. "RCT" is used as a short form for reactor in all the figures presented in this thesis.

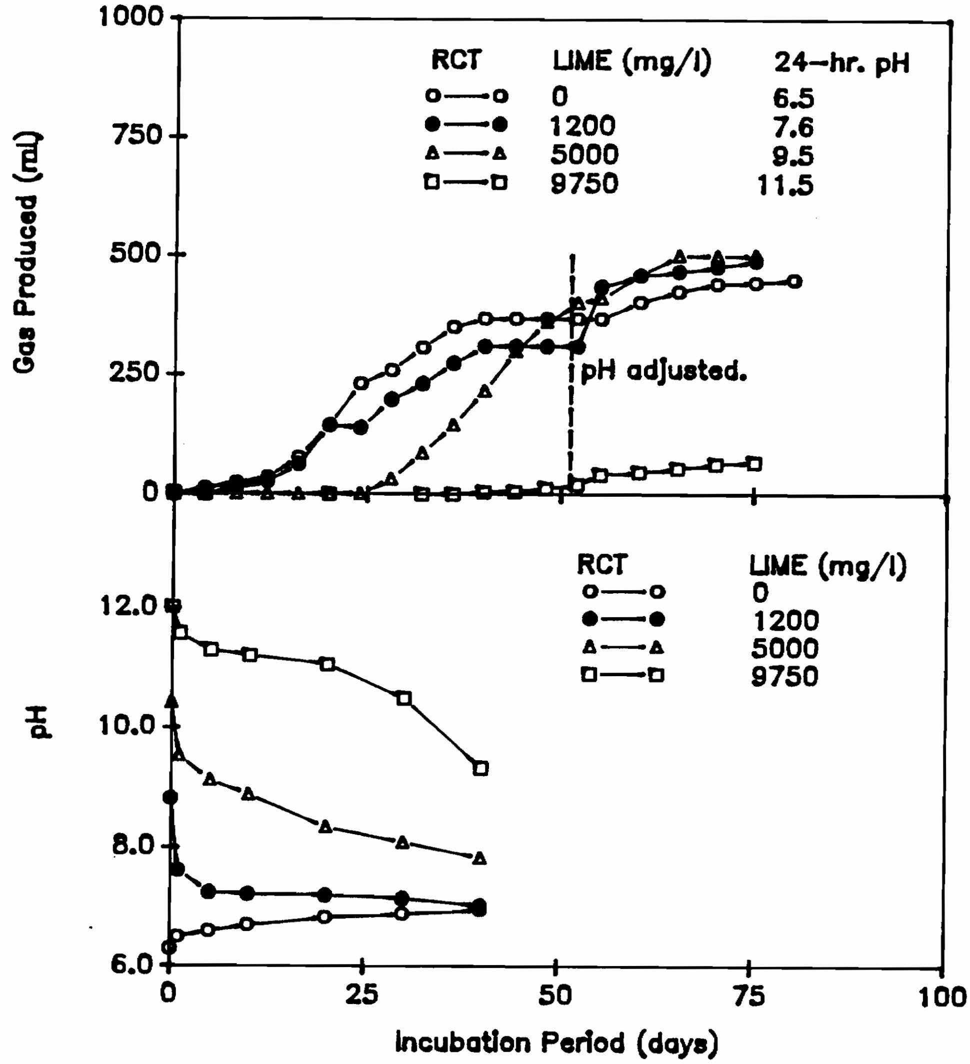

Figure 5. Effect of lime on gas production and pH.

A plot of gas production over time at different lime doses shows the inhibition of gas production for longer times at higher pH values (see Figure 5). The first day of gas production at different pH values is presented in Table I. The first day of gas production was defined in this study as the first day on which a cumulative gas production of 25 ml was observed. The first day of gas production was 8 days for the control, 12 days at pH 7.6, 28 days at pH 9.5, and 56 days at pH 11.5. It is evident from these data that an increase in pH resulting from lime addition slows the onset of bioactivity. This property of lime makes it a very popular choice for temporary control of odor problems. The change in pH with incubation time in all the four reactors is also presented in Figure 5. A decline in pH with incubation time was observed in all the lime dosed reactors. A final pH of less than 8.0 was observed in all reactors except the reactor with a 24-hour pH of 11.5. Also, the total volume of gas produced was nearly equal in all reactors except the reactor with a 24-hour pH of 11.5. It seems evident from these data that a pH between 7.0 to 8.0 is most conducive to gas production. This is supported by the fact that the gas production in the reactor with a lime dose of 5000 mg/l started only after the pH decreased to less than 8.0 on the 25th day. It also seems evident from these data that the methanogens were very active at pH values below 8.0 and were inhibited at a pH greater than 8.0. The acid formers were active even at pH 11.5, which is clearly shown in Figure 5 by the decrease in pH of the reactor with 9750 mg/l of lime.

Table I

First day of gas production in the lime dosed reactors

24-hour pH	Day
6.5	8
7.6	12
9.5	28
11.5	56

Sulfuric acid was added to all reactors except the control on the 50th day to decrease the pH of the reactors to between 7.0 and 6.5. A slight increase in gas production was observed in all the reactors after this adjustment. This observation might have been due to the initiation of mehtnaogenic activity at these reduced pH levels. A steady decline in pH was also observed in all the reactors. This indicated that acid formers were active throughout the period of study. None of the lime doses tested in this phase completely arrested gas production. Therefore, it is evident from these data that lime doses greater than those applied are required for permanent prevention of gas production.

PHASE - III

Combined Effects of Lime and Calcium on Gas Production:

Caustic chemicals used to elevate the pH of anaerobic systems add cations to the systems. Since metal cations can be both toxic and stimulatory in anaerobic systems, it was of importance to study the impact of these cations on gas production. This phase of the study was conducted to assess the impact of Ca^{++} present in anaerobic systems being treated with lime.

In this phase, the effects of Ca^{++} on gas production at seven lime doses were studied. Three reactors with different Ca^{++} concentrations, and a reactor without Ca^{++}

were also established at each lime dose to serve as controls. Ca^{++} was added as anhydrous calcium chloride. A slight decrease in pH with calcium chloride addition was observed in all the reactors. Figures 6 through 16 and Table II present the data obtained in this phase.

A plot of gas production over incubation period at different Ca^{++} doses without lime addition is presented in Figure 6. Data presented in this figure show that the first day of gas production did not vary significantly with calcium chloride addition. However, a decrease in total gas production was observed. In contrast, with lime addition, the first day of gas production increased with the lime dose, without significant change in the final volume of gas produced, as long as the pH remained below 8.0. These results indicate that lime addition temporarily inactivated microorganisms, whereas Ca^{++} permanently affected the metabolism of the microorganisms. The reduction in total gas production with Ca^{++} addition may have been due to permanent inactivation of some of the enzymes responsible for gas production. The change of pH with time in these reactors is also presented in Figure 6.

Gas production at a constant lime dose of 1200 mg/l and varying Ca^{++} doses is presented in Figure 7. These data show slightly higher first day of gas production values due to lime addition. The total gas production decreased with increasing Ca^{++} dose. The total gas production values were similar to those in Figure 6 (reactors

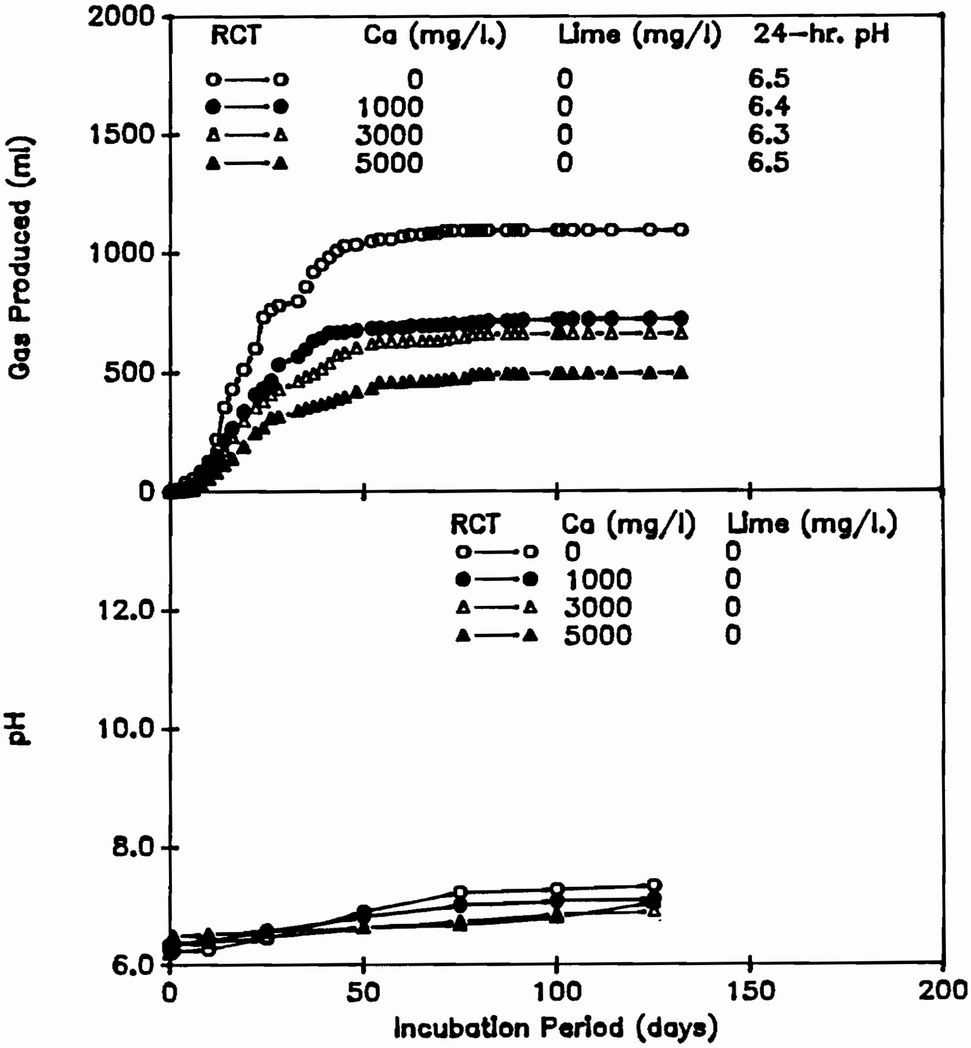

Figure 6. Effect of calcium on gas production and pH.

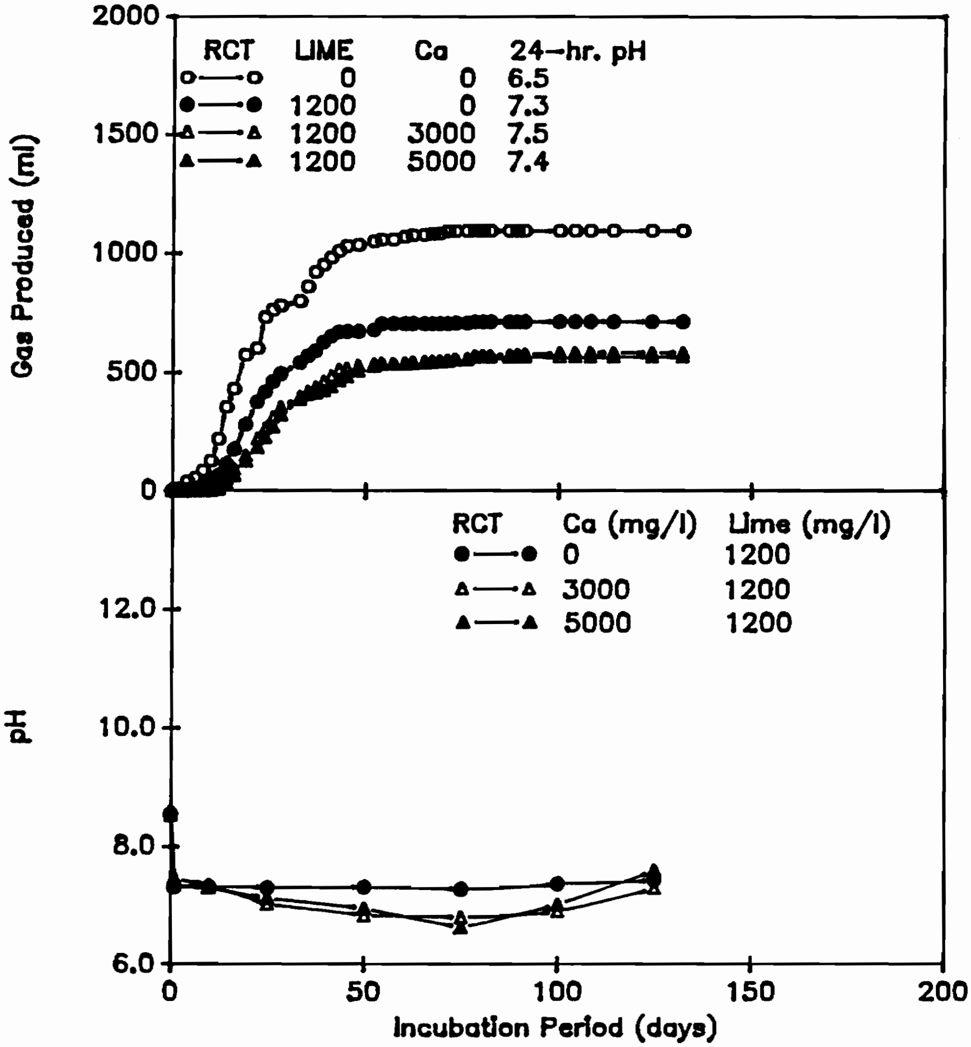

Figure 7. Effect of calcium on gas production and pH at 1200 mg/l of lime.

without lime addition). Most of the decline in pH occurred in the first 24 hours and it then remained essentially at pH 7.0 for the remainder of the test period (see Figure 7).

Figure 8 shows the gas production from the reactors with a constant lime dose of 1750 mg/l and varying Ca^{++} doses. Total gas production values approximately equal to that of the control were observed at this lime dose. The pH drop over time in these reactors is also presented in Figure 8. A rapid decrease in pH in the first 24 hours, and a gradual decrease up to the 75th day, followed by a final constant pH value was observed in all reactors. The final pH values decreased with increase in Ca^{++} concentrations. However, the difference was not significant.

Reactors with a lime dose of 2500 mg/l showed similar gas production results as obtained with a lime dose of 1750 mg/l (see Figure 9). The pH decline patterns were also similar at both lime doses. Figures 8 and 9 indicate that the inhibition by calcium was alleviated at pH values greater than 7.5. The maximum rate of gas production at lime doses of 1750 mg/l and 2500 mg/l was observed when the reactors were at pH values between 7.5 and 8.0. It can be seen from the Ca^{++} solubility plot (Figure 10) that the solubility of Ca^{++} is very low above pH 7.5. At these pH values, excess Ca^{++} is precipitated as calcium carbonate ($CaCO_3$) and the soluble Ca++ available to anaerobic microorganisms is very low. Therefore, Ca^{++} toxicity would not be expected at lime doses of 1750 mg/l and 2500 mg/l.

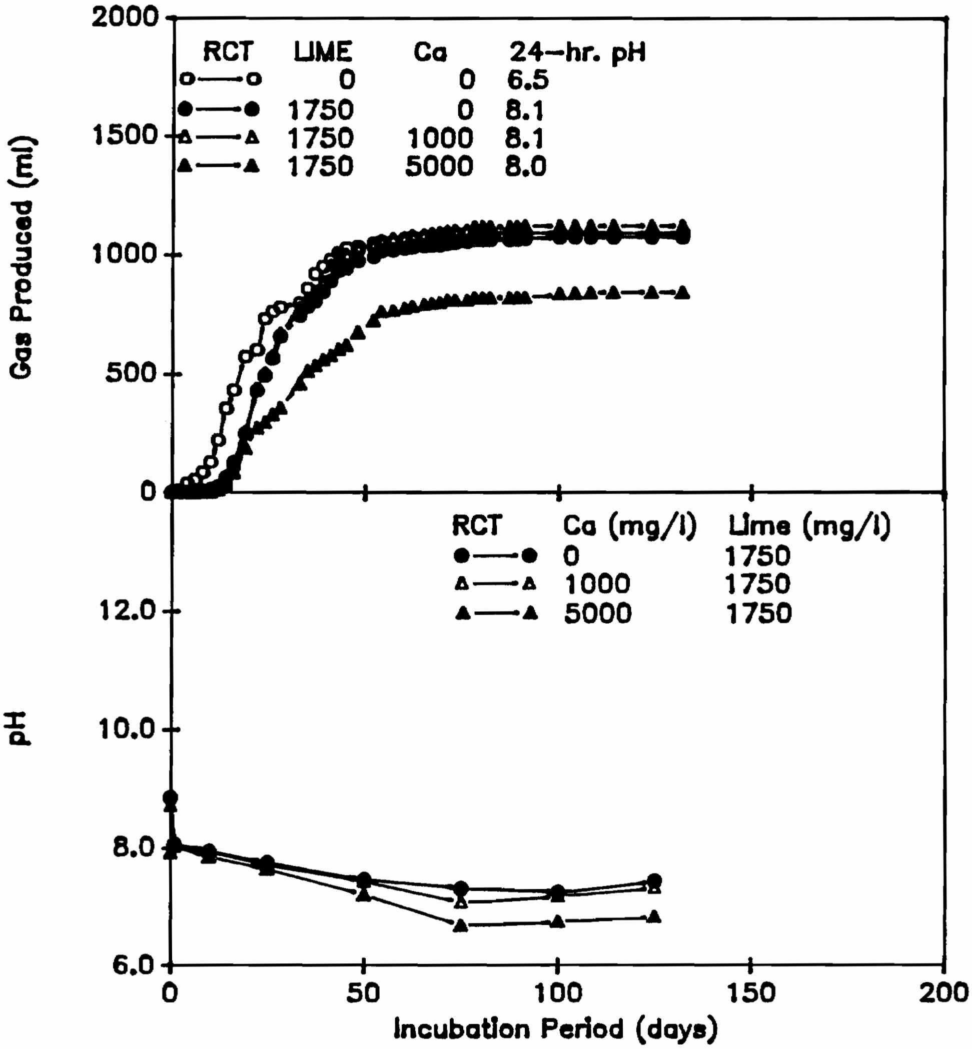

Figure 8. Effect of calcium on gas production and pH at 1750 mg/l of lime.

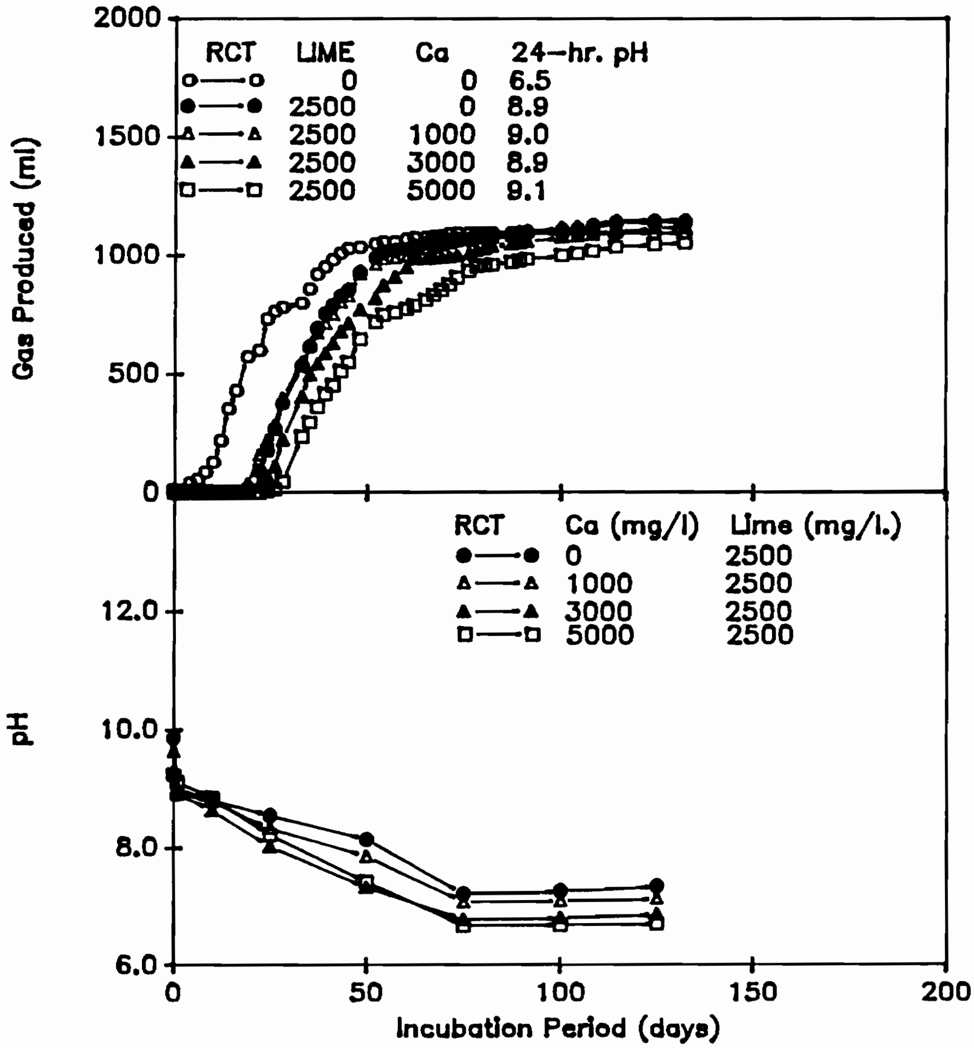

Figure 9. Effect of calcium on gas production and pH at 2500 mg/l of lime.

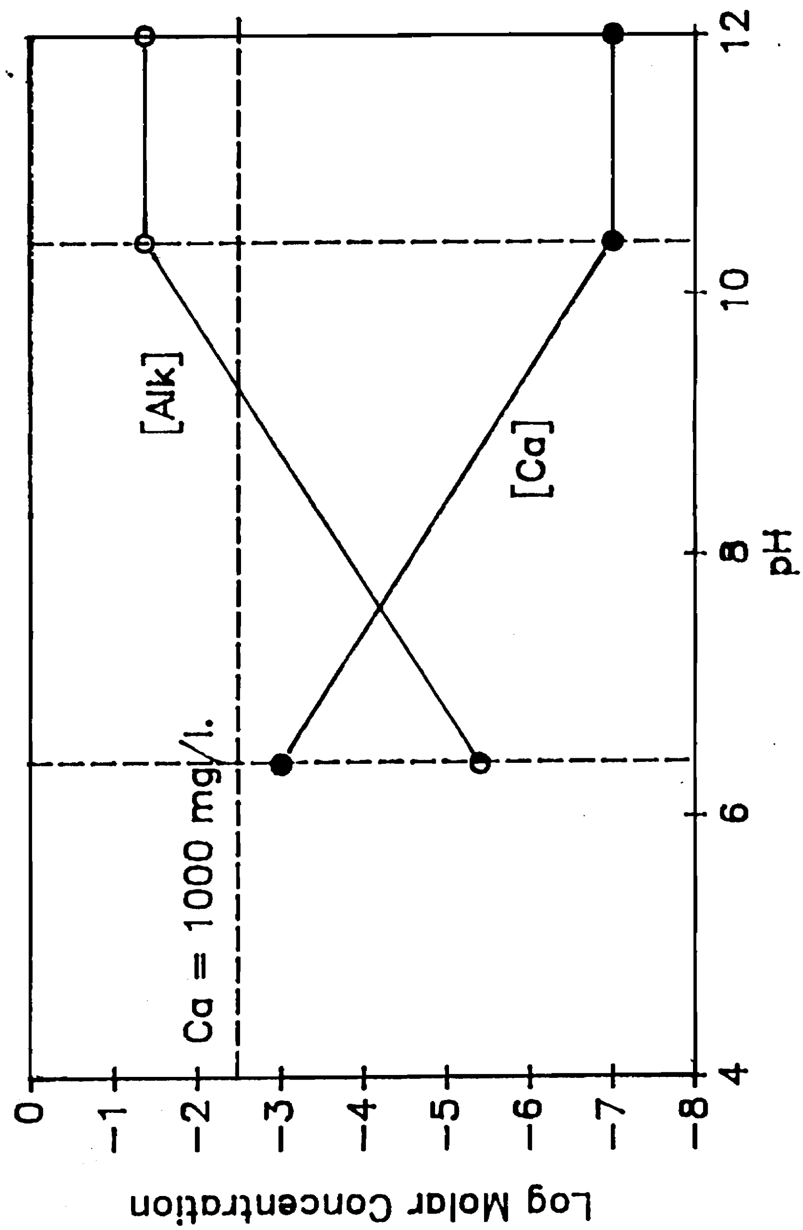

Figure 10. Calcium Solubility.

The gas production patterns observed at lime doses of 3050 mg/l and 3500 mg/l (see Figures 11 & 12) were similar to those observed at 1750 mg/l and 2500 mg/l, except that the onset of gas production was delayed for longer times with increasing doses of lime. The maximum rate of gas production in the reactors with 3050 mg/l was observed between the 50th and the 75th day, when the pH was between 7.0 and 8.0 (see Figure 11). Similar relationships between pH and gas production were observed in the reactors with 3500 mg/l of lime (see Figure 12). Some of the effects of extra calcium addition may be due to impacts which occurred during the first day following $CaCl_2$ addition. The precipitation of calcium carbonate occurs over hours to days, so some of the Ca^{++} could have passed through the cell wall and ruptured the enzyme systems for the methanogenic organisms.

Figure 13 shows that gas production was arrested throughout the period of study at a lime dose of 7000 mg/l. No decline in pH was observed in any of the reactors at this lime dose. It can also be seen from Figure 13 that the final pH slightly decreased with increase in Ca^{++} dose, as observed at other lime doses.

From the data in Figure 13, it seems that both methanogens and acid formers were totally inhibited at about a pH of 12. The complete inhibition of acid formers was evidenced by the unchanging pH in all reactors with a lime dose of 7000 mg/l. Therefore, a pH of 12.0, which permanently arrested gas production, was observed in all these reactors throughout the period of study.

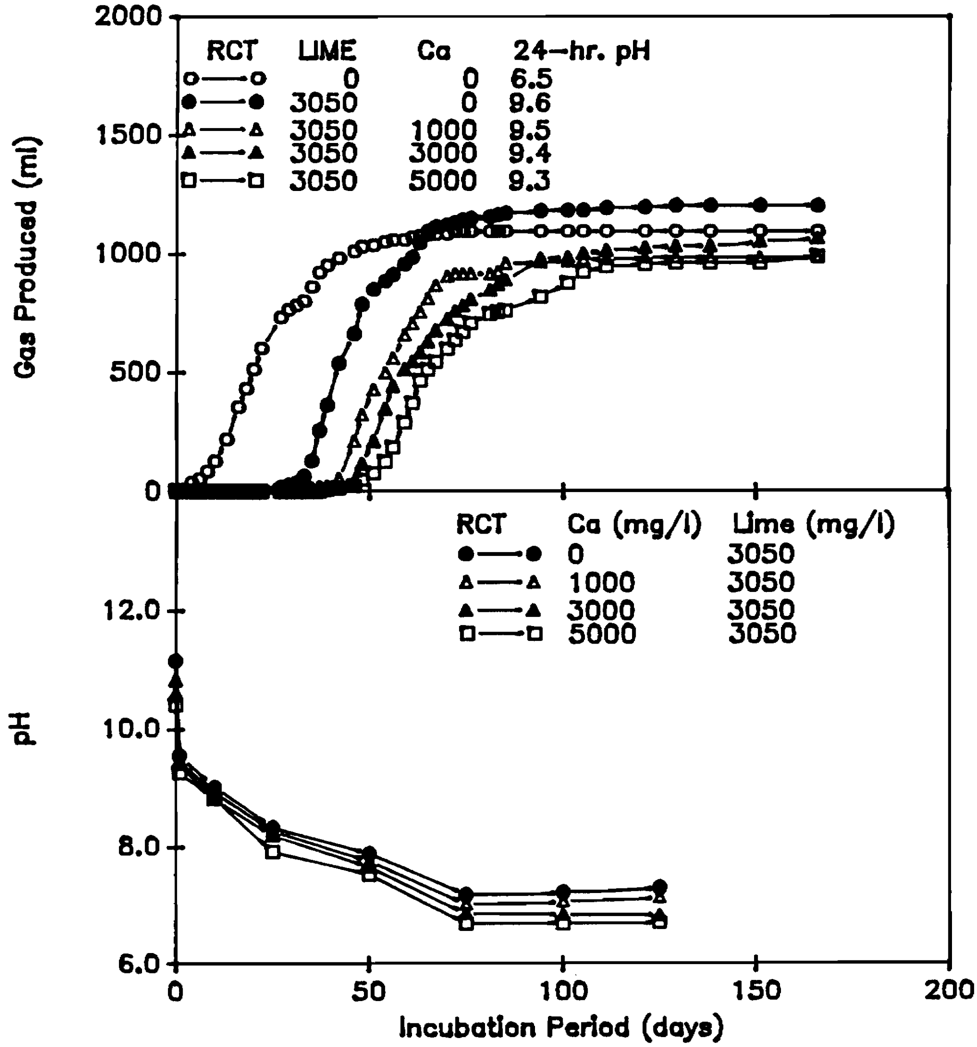

Figure 11. Effect of calcium on gas production and pH at 3050 mg/l of lime.

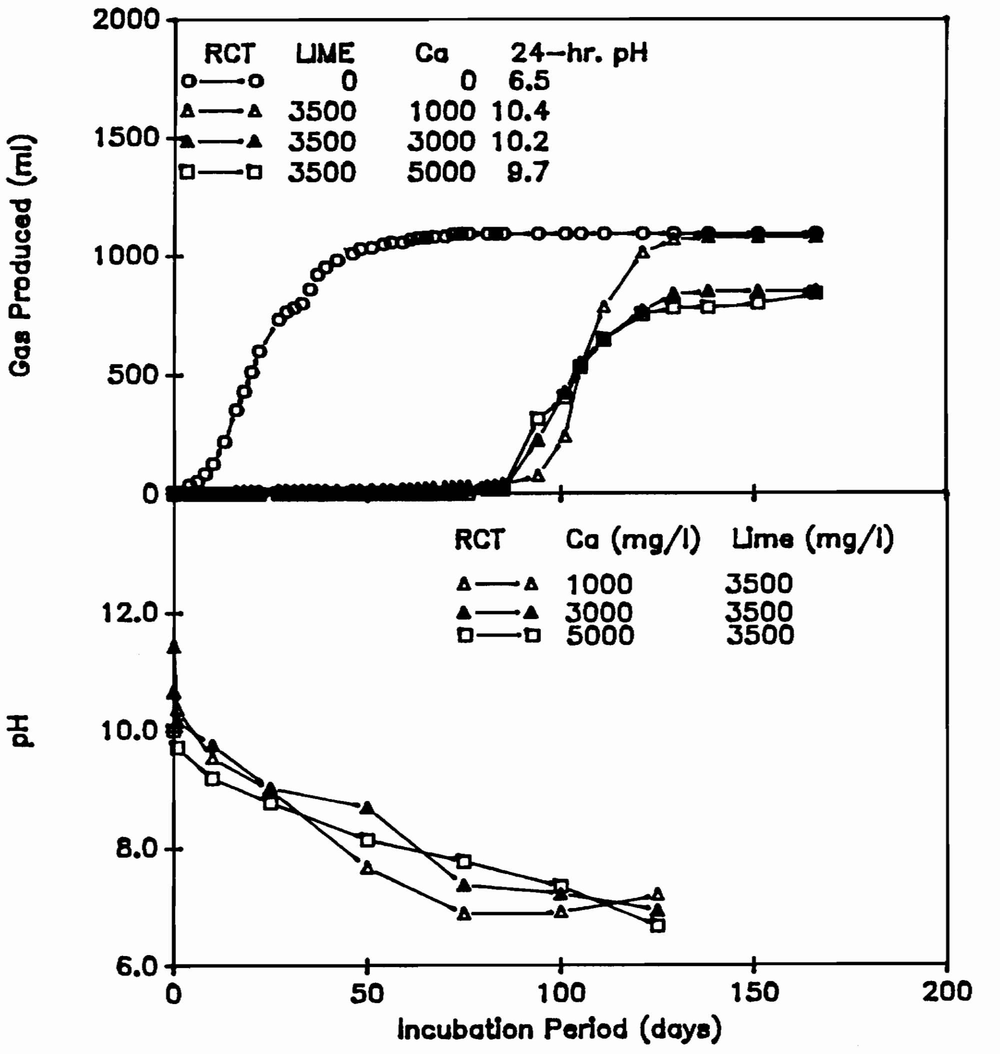

Figure 12. Effect of calcium of gas production and pH at 3500 mg/l of lime.

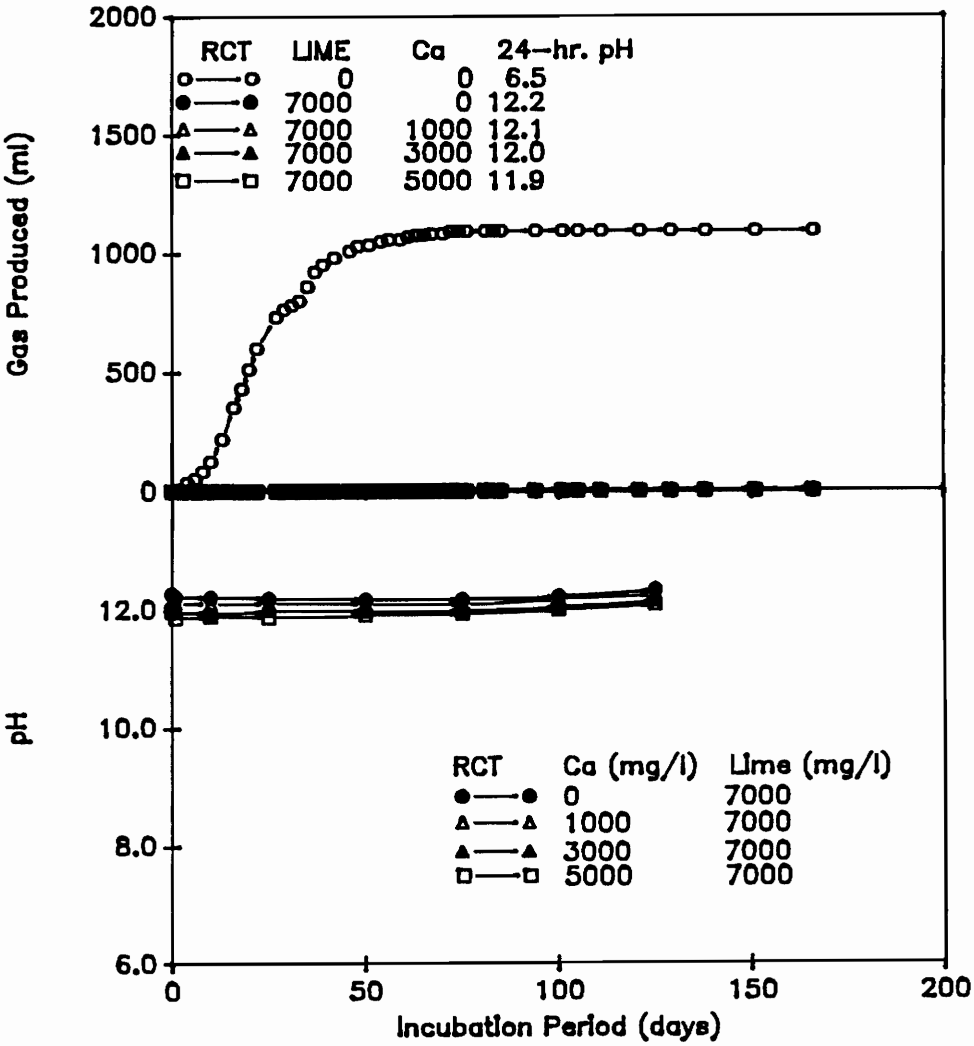

Figure 13. Effect of calcium on gas production and pH at 7000 mg/l of lime.

All the reactors in this phase were elutriated on the 125th day. Elutriation was achieved by repeated replacement of the supernatant with distilled water. The supernatant was replaced till clear. Elutriation did not have a significant effect on any of the reactors over the study period (an additional 41 days of incubation). The effects of elutriation would have been apparent if it were performed prior to gas production or during active gas production. As elutriation was performed in these reactors after complete gas production, no significant changes were observed after elutriation. However, no gas production was observed in the reactors with 7000 mg/l of lime even after elutriation and reduction of pH. This seems to indicate that all the microorganisms (both methanogens and acid formers) were killed at this lime dose.

The first day of gas production at different lime and Ca^{++} doses is presented in Table II and Figure 14. The maximum volume of gas produced in each of the reactors studied in this phase is also illustrated in Figure 14. It can be seen from these data that the first day of gas production varied significantly with the lime dose but was relatively unaffected by the Ca^{++} dose at pH values less than 9.0. But, at pH values greater than 9.0, higher calcium doses inhibited gas production for longer times. This might have been due to the impact of higher calcium concentrations that occurred during the first day following $CaCl_2$ addition. Reactors with a 24 hour pH between 8.0 and 9.0 exhibited maximum gas production. The time of inhibition gradually increased with pH up to a pH of 9.0, after which it markedly increased with even a slight increase in pH. Bioactivity was present up to a pH of 11.8 but was not observed at higher pH values.

Table II

First day of gas production at different Calcium Concentrations with lime added to elevate pH.

Without Ca^{++}		With Ca^{++} = 1000 mg/l	
pH	Day	pH	Day
6.47	4	6.36	6
7.30	9	8.10	13
8.10	12	9.00	19
8.90	20	9.50	41
9.60	29	10.40	67
12.20	--	12.10	--
With Ca^{++} = 3000 mg/l		**With Ca^{++} = 5000 mg/l**	
pH	Day	pH	Day
6.34	7	6.49	8
7.50	13	7.40	14
8.90	22	8.00	14
9.40	45	9.10	27
10.20	88	9.30	47
12.00	--	9.70	90
		11.90	--

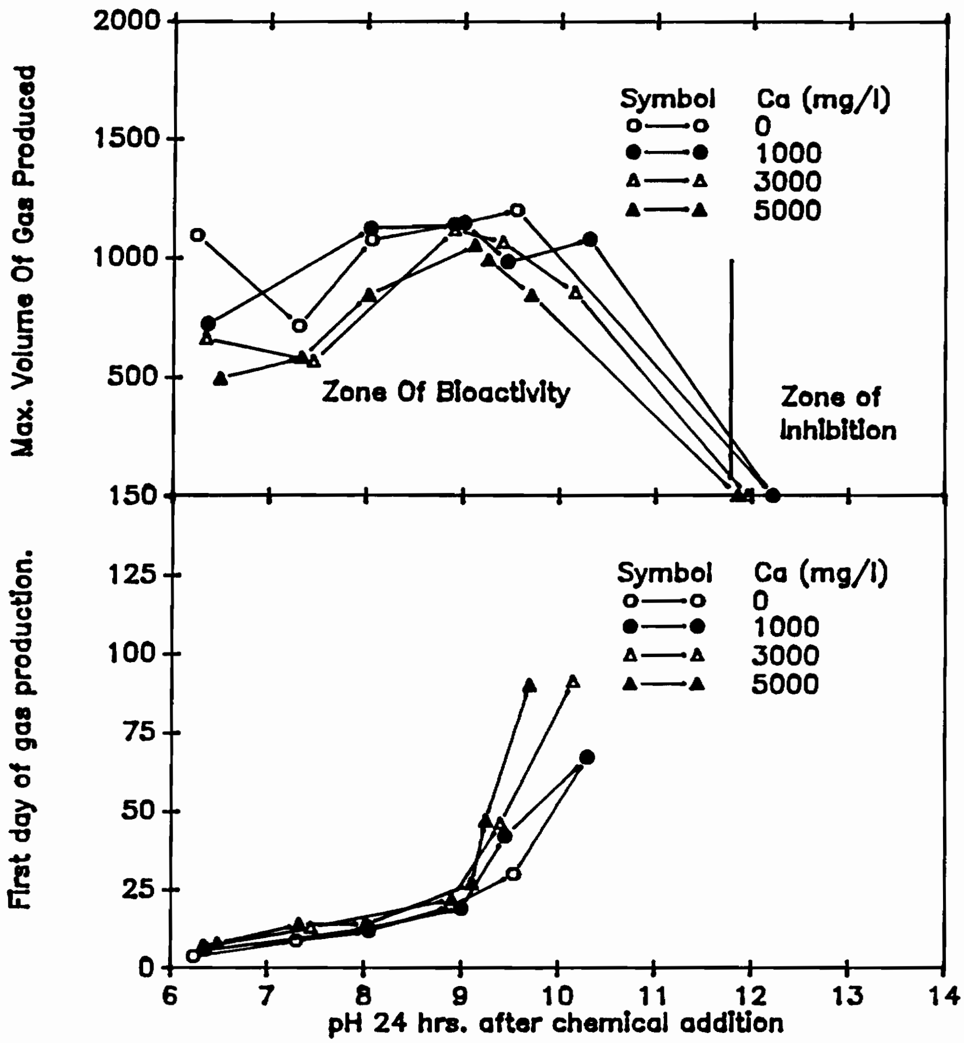

Figure 14. Effect of pH and calcium on gas production with lime as the alkali.

Figure 15 shows the total gas produced in the reactors as a percent of the total gas produced in the control. Total gas production decreased with increasing Ca^{++}. Maximum gas production was observed in the reactors with a 24 hour pH between 8.0 and 9.0. Ca^{++} inhibition was not significant at higher pH values due to the decrease in Ca^{++} solubility at these pH values. This effect is more clearly illustrated in Figure 16.

The general trends observed in this phase of the study are :

1) The first day of gas production increased significantly with an increase in pH, but did not vary much with Ca^{++} dose.

2) In all lime-dosed reactors, except in reactors with pH greater than 12, a rapid decrease in pH was observed over the first 24 hours, followed by a gradual decrease before attaining a constant pH. This indicates that the acid forming bacteria were active even up to a pH of 12.0.

3) The maximum rate of gas production was observed when the pH was decreased to between 7.0 and 8.0. This indicates that the methanogens were inhibited at a pH greater than 8.0.

4) The effect of Ca^{++} on total gas production was not significant at higher pH values due to low solubility of Ca^{++} at these pH values.

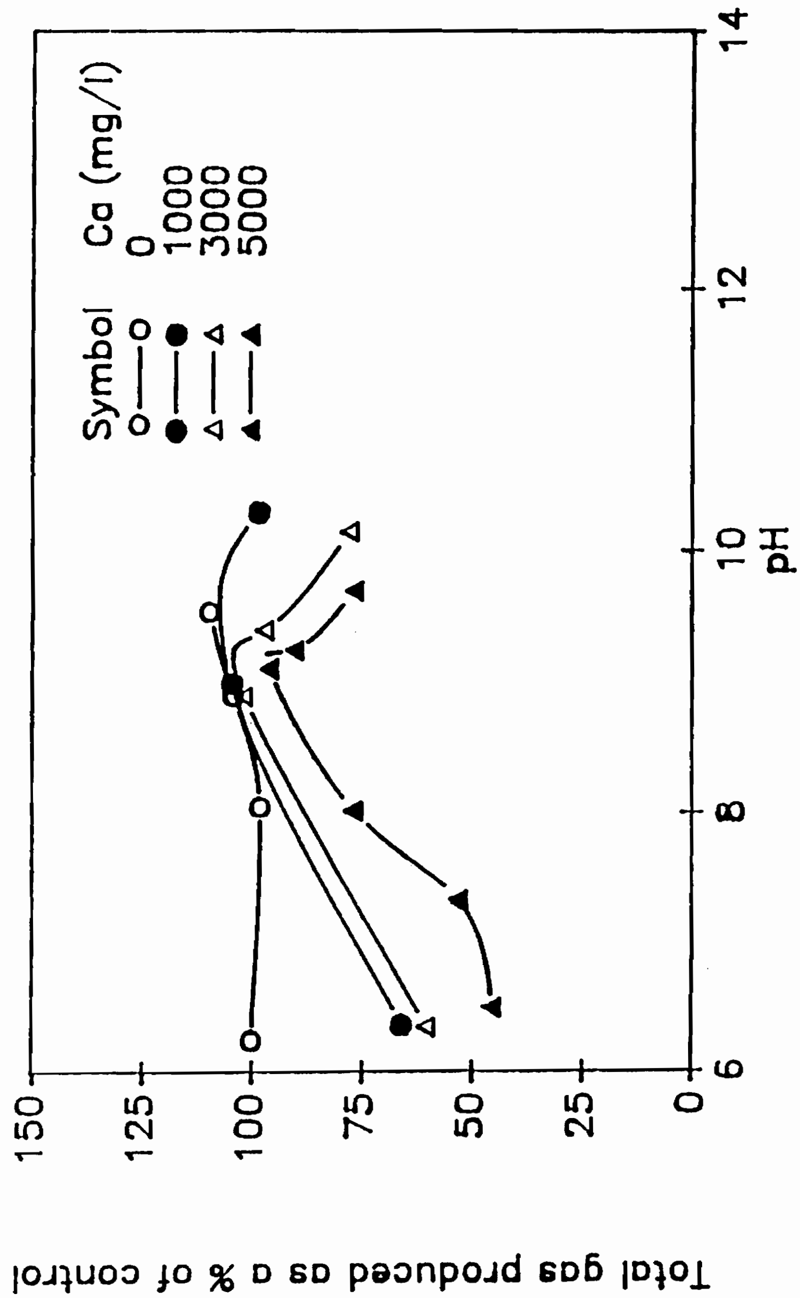

Figure 15. A comparison of total gas production at different calcium concentrations.

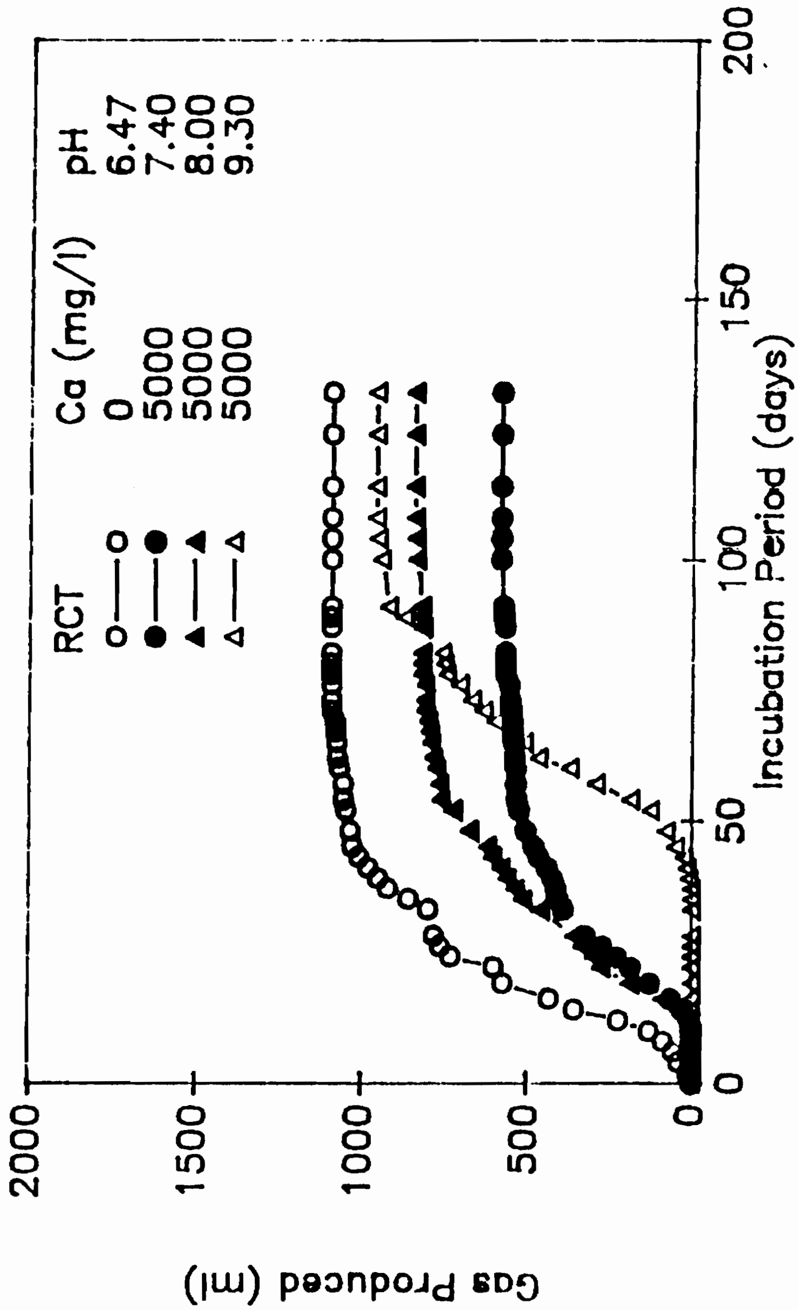

Figure 16. Effect of calcium on gas production with changing pH.

5) A pH of about 12.0 was required to permanently prevent pH decline and gas production throughout the period of study.

PHASE - IV

Combined effects of Calcium and Sodium Hydroxide on Gas Production:

In this phase of the study, NaOH was tested as an odor control compound in combination with Ca^{++}. Figures 17 to 21 and Table III show the results obtained in this phase of the study. The NaOH doses shown in these figures are in units of mg/l of 1N NaOH per liter of sludge. Ca^{++} was added as anhydrous calcium chloride. Ca^{++} concentrations of 0 mg/l, 1000 mg/l, 3000 mg/l, and 5000 mg/l were tested at four NaOH concentrations. All the reactors, except the control, were elutriated on the 125th day. Elutriation was performed by successive replacement of the supernatant with distilled water till the supernatant was clear.

Gas production from the reactors with an NaOH dose of 65 ml/l is presented in Figure 17. A significant decrease in pH was observed in all reactors with the addition of $CaCl_2$. The decrease in pH was greater at higher $CaCl_2$ doses. This is thought to be due to calcium precipitation, probably as $CaCO_3$ but also some $Ca(OH)_2$ at higher pH values.

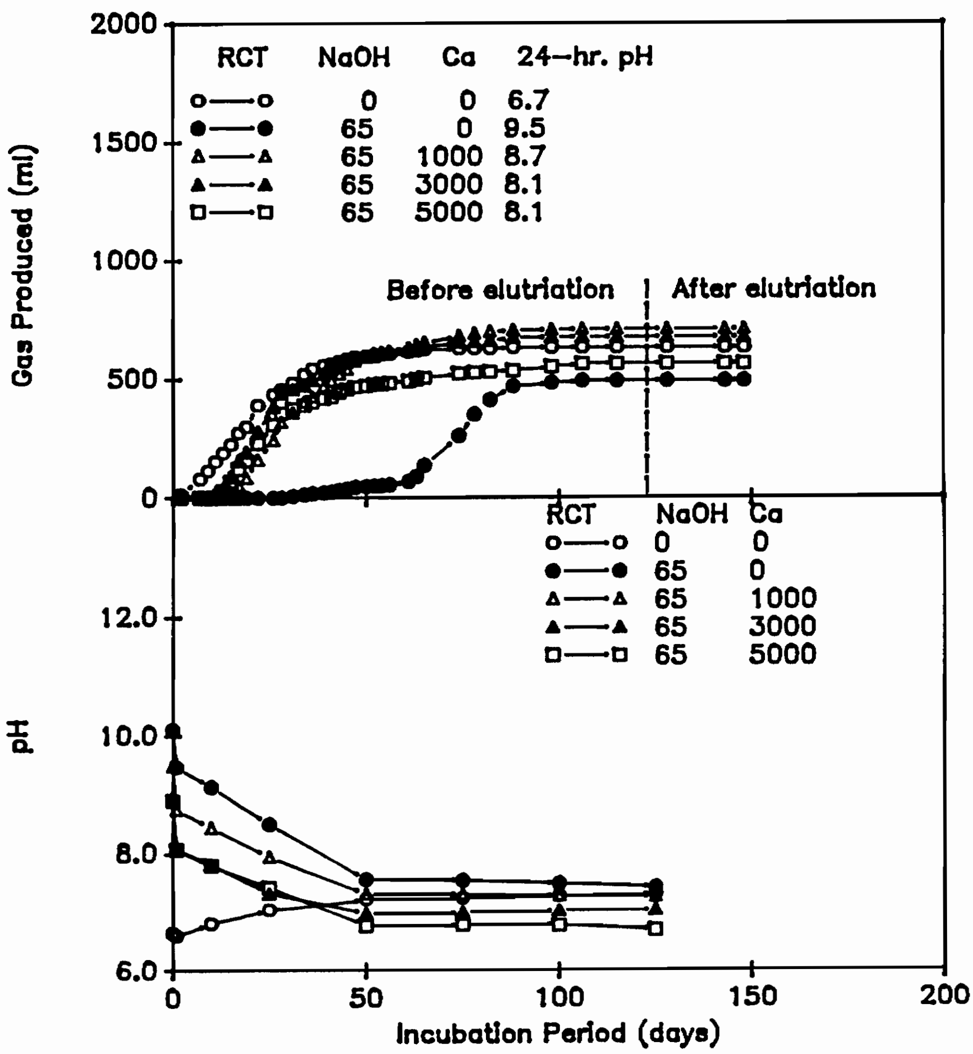

Figure 17. Effect of calcium on gas production and pH at 65 ml/l of 1N NaOH.

The precipitation of $CaCO_3$ and $Ca(OH)_2$ in these systems is a three step process as described below:

1) NaOH dissociation:

$NaOH$ <--------> $Na^+ + OH^-$

As NaOH is a strong base, it almost completely dissociates to form Na^+ and OH^-. The rate of the forward reaction is much greater than the rate of the backward reaction.

2) Calcium chloride dissociation:

CaCl2 <--------> $Ca^{++} + 2Cl^-$

When calcium chloride is added to these systems, it dissociates to form Ca^{++} and Cl^-.

3) Calcium carbonate and calcium hydroxide precipitation:

Ca^{++} + $CO_{3\text{-}2}$ <--------> $CaCO_3$ (S)

Ca^{++} + $2(OH)^-$ <--------> Ca(OH)2 (S)

When both the reactions occur simultaneously in these systems, Ca^{++} removes both carbonate and hydroxyl alkalinities as insoluble precipitates. Therefore, both the Ca^{++} concentration, and the pH of the system will be reduced simultaneously.

In the plot of gas production over incubation time at a NaOH dose of 65 ml/l, total gas production greater than the control was observed in the reactors with pH values of 8.7 and 8.1 (see Figure 17). Similar results were observed in the lime-dosed reactors with pH values between 8.0 and 9.0 (see Figures 8 and 9). The initial and final pH's at an NaOH dose of 65 ml/l were similar to those observed in Figure 9 at a lime dose of 2500 mg/l. However, the pH decline in the first 24 hours was greater with NaOH than with lime. A gradual decrease in pH following lime addition was observed till the 75th day, whereas the pH decline subsequent to NaOH addition was complete in 50 days. As in the lime dosed reactors, the NaOH dosed reactors exhibited a minor decrease in final pH values with increasing Ca^{++} concentrations.

A large difference in the first day of gas production values at equal NaOH doses can be seen in Figure 17. Unlike in lime-dosed reactors, the first day of gas production values varied significantly at equal NaOH doses. This variation is due to the reduction in pH subsequent to calcium chloride addition. From the results in Figures 17, 18, 19, and Table III it is obvious that the pH of the sludge was the most important factor influencing the first day of gas production.

The effect of elutriation can be clearly seen from the gas production in the reactor with 1000 mg/l of Ca^{++}, and 95 ml/l of NaOH (see Figure 18). The pH of this reactor was greater than 9.0 on day 125 (see Figure 18), when the reactors were elutriated. Therefore, no gas production was observed till day 125. After elutriation, the pH of the reactor with 1000 mg/l Ca decreased to below 8.0 and as a result, gas production started. These data correspond very well with the situation that existed in the sludge pond immediately after a heavy rainfall. Heavy rains might have washed

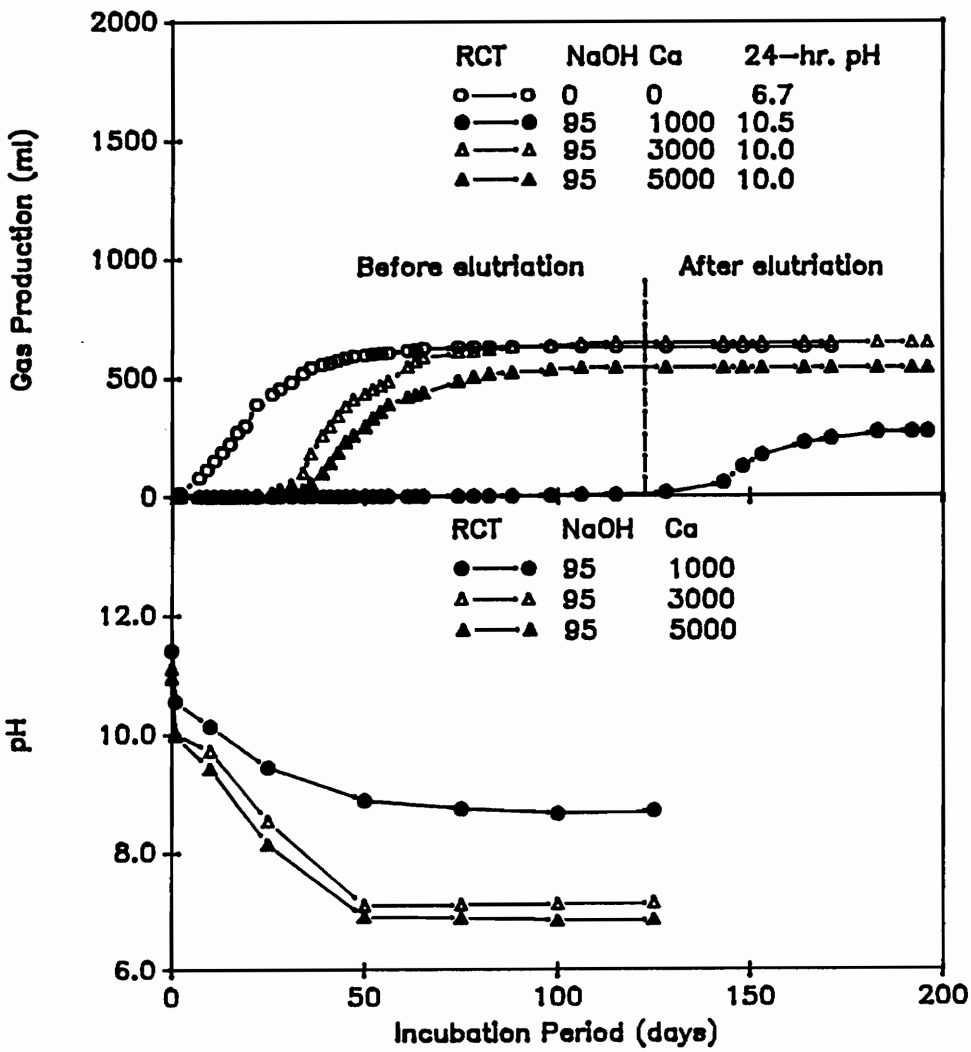

Figure 18. Effect of calcium on gas production and pH at 95 ml/l of 1N NaOH.

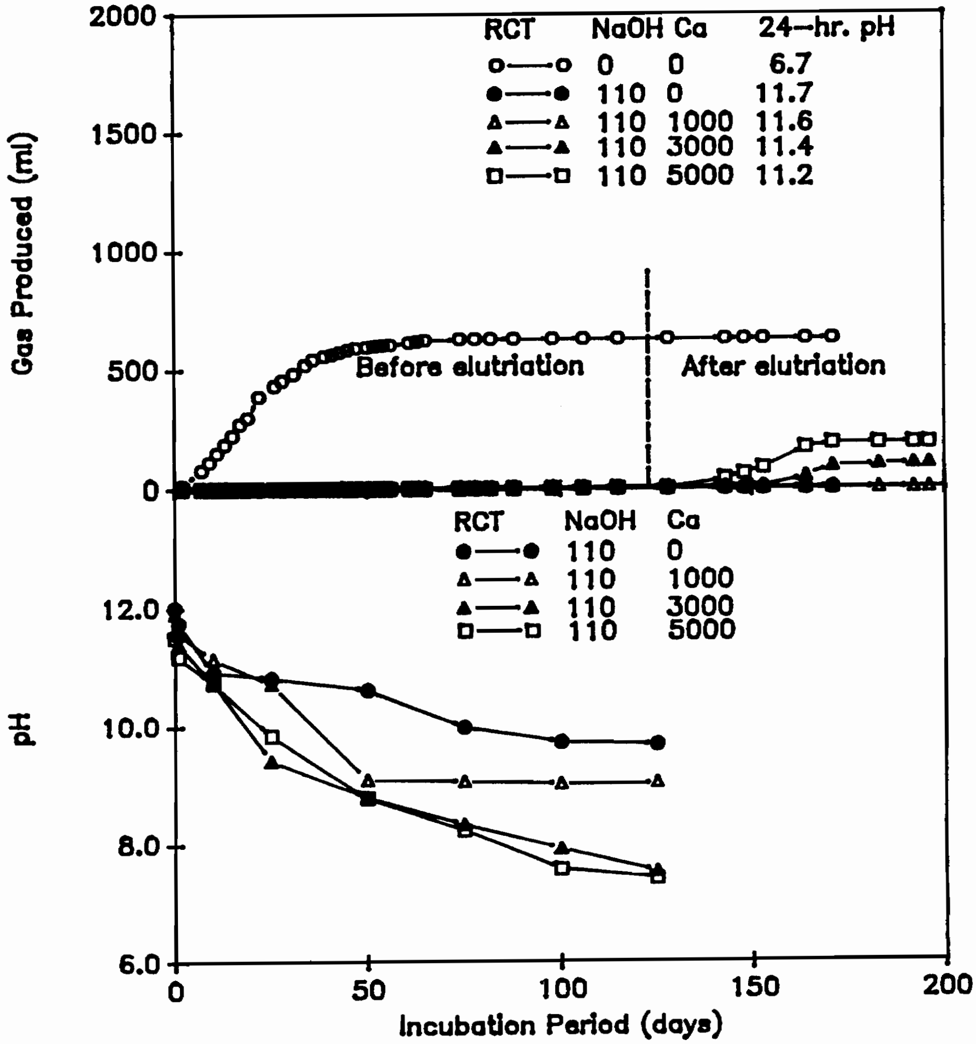

Figure 19. Effect of calcium on gas production and pH at 110 ml/l of 1N NaoH.

Table III

First day of gas production at different Calcium concentrations with sodium hydroxide added to elevate the pH.

Without Ca^{++}		With Ca^{++} = 1000 mg/l	
pH	Day	pH	Day
6.66	4	8.74	16
9.46	41	10.54	143
11.74	--	11.56	--
12.52	--	12.50	--
With Ca^{++} = 3000 mg/l		With Ca^{++} = 5000 mg/l	
pH	Day	pH	Day
8.07	10	8.06	13
10.00	28	9.97	34
11.38	--	11.17	--
12.40	--	12.29	--

the chemicals from the sludge, thus reducing the pH to favorable levels for increased gas production.

The first day of gas production values in this phase of the study are presented in Table III. It can be clearly seen from this table that the first day of gas production values were a function of pH. A comparison with the lime data presented in Table II shows similar trends to the lime and calcium results.

No gas was produced in any of the reactors with an NaOH dose of 110 ml/l before elutriation (see Figure 19). A small amount of gas was produced after elutriation in the reactors with pH values of 11.4 and 11.2. But no gas production was observed in the reactors with pH values greater than 11.5. These high pH levels might have killed the microorganisms, due to which no gas production was observed in these reactors throughout the period of study.

Figure 20 illustrates the data obtained at an NaOH dose of 180 ml/l. Neither gas production nor pH decline were observed in any of the reactors at this NaOH dose. The high pH values produced at this dose might have permanently destroyed the microorganisms. Lack of gas production, even after elutriation, supports the claim that the microorganisms in these reactors were killed. It can also be seen from these data that the decrease in pH subsequent to $CaCl_2$ addition was least at this NaOH

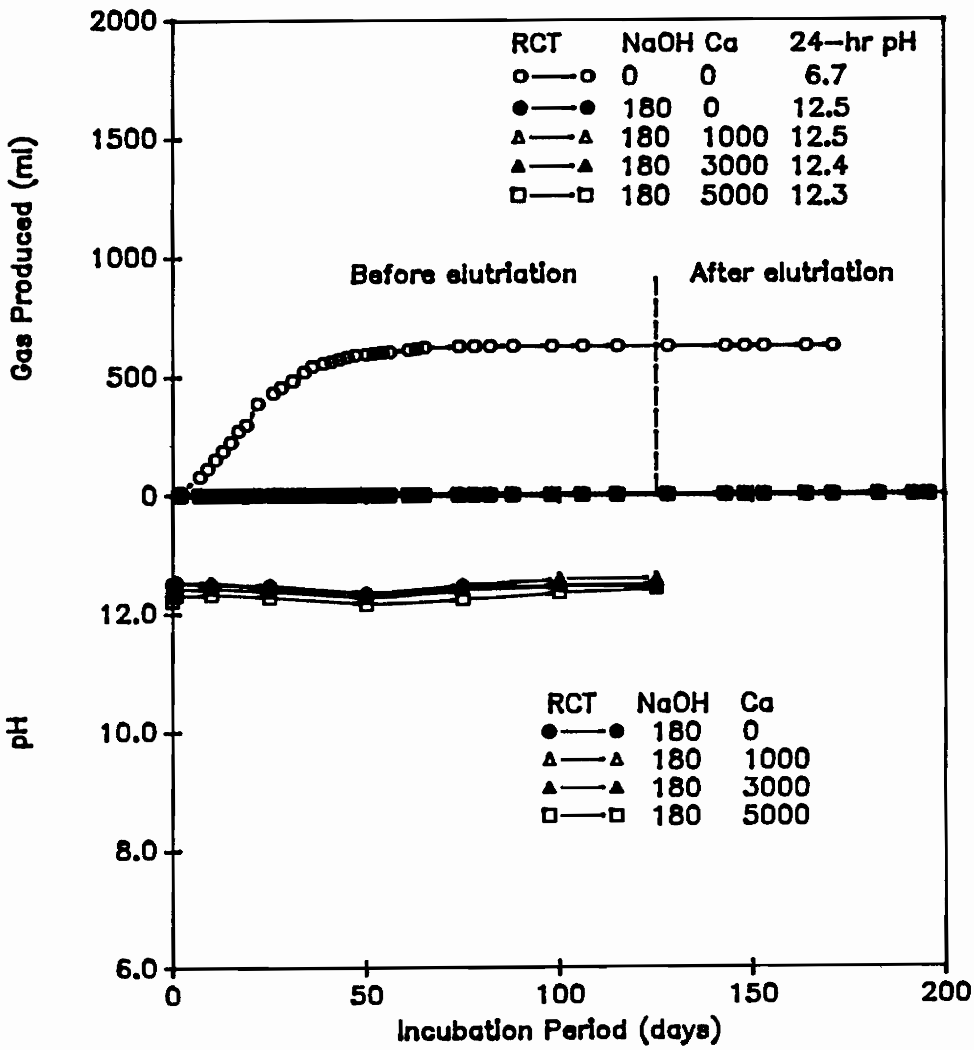

Figure 20. Effect of calcium on gas production and pH at 180 ml/l of 1N NaOH.

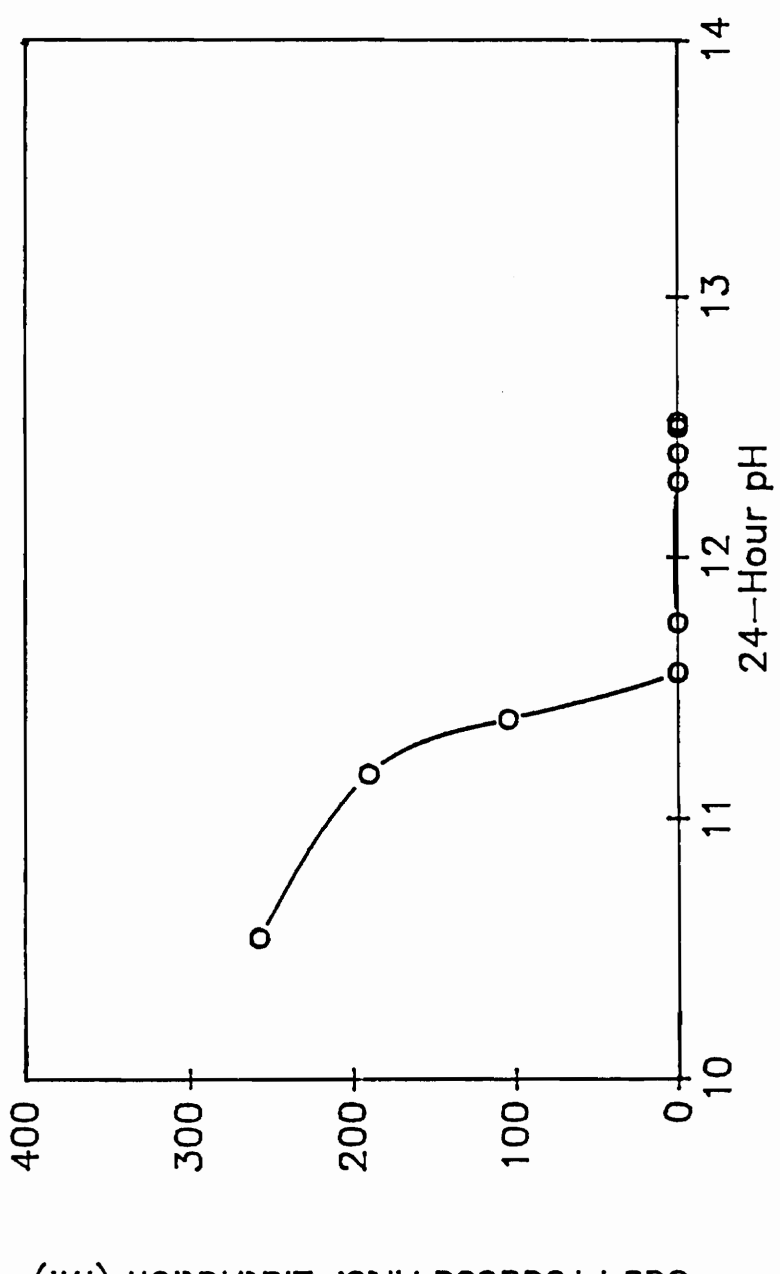

Figure 21. Gas production after elutriation.

dose. Excess NaOH present in these systems might have provided sufficient hydroxyl ions to prevent any decrease in pH due to $CaCl_2$ addition.

The amount of gas produced after elutriation in these reactors, is presented as a function of their 24-hour pH in Figure 21. The gas production after elutriation decreased with increase in 24-hour pH. From these results, it seems likely that the gas production from the sludge pond after a heavy rainfall can be reduced by subjecting the sludge pond sludge to higher pH values.

The general trends observed in this phase of the study are:

1) In reactors with equal doses of NaOH, the pH decreased with increasing doses of calcium.

2) The first day of gas production was a function of pH.

3) Doses of NaOH that elevated the pH to higher than 12.5 were required to permanently stop gas production and pH reduction.

4) The volume of gas produced after elutriation decreased with an increase in the initial pH.

Comparison of Lime and Sodium Hydroxide:

The capacities of lime and NaOH to inhibit gas production at varying Ca^{++} doses are presented Tables IV and V. The dry solids percentage of the sluge is 1.98. From Table IV it can be seen that 0.36 lb of quick lime for every lb of dry solids permanently arrested gas production, whereas 0.29 lb of 19N NaOH was required for every lb of dry solids to achieve an equivalent level of inhibition. Because lime is both less expensive and easier to handle, it is the recommended choice for odor control.

Significance of Lime and NaOH Results to the Sludge Deposited in the Sludge Pond:

It was observed from the lime and NaOH results that the gas production was permanently stopped only when the pH of the sludge was elevated to greater than 12.0. However, the pH of some of the sludge pond sludge samples were measured at pH values of about 8.5 to 9.0. At this pH range the gas production is just inhibited, and any slight decline in this can result in large amounts of gas production. Therefore, lime should be continuously added to maintain the sludge at a pH in excess of 12.0.

TABLE - IV

Lime Doses

LIME in (lb/lb of Dry Solids)	First Day of Gas Production at Different Ca^{++} Concentrations. (lb/lb of Dry Solids)			
	0	0.05	0.15	0.25
0	4	6	7	8
0.06	9	ERROR	13	14
0.09	12	13	ERROR	14
0.13	20	19	22	27
0.16	29	41	45	47
0.18	ERROR	67	88	90
0.36	No Gas	No Gas	No Gas	No Gas

TABLE - V

NaOH Doses

19N. NaOH (lb/lb of Dry Solids)	First Day of Gas Production at Different Ca^{++} Concentrations. (lb/lb of Dry Solids)			
	0	0.05	0.15	0.25
0.17	41	16	10	13
0.25	ERROR	143	28	34
0.29	No Gas	No Gas	No Gas	No Gas
0.48	No Gas	No Gas	No Gas	No Gas

Role of Calcium in the Control of Gas Production:

From the results obtained with calcium, it is clear that calcium alone is not capable of arresting gas production. However, it can be used to reduce the quantity of gas production at pH values less than 7.5. Gas production can be inhibited by elevating the pH to greater than 8.0. However, at these pH levels, the solubility of calcium is very low. Hence, its role in odor control is not very significant.

V. CONCLUSIONS

The following conclusions may be drawn based on the experimental results of the study:

1. pH was found to be the most important factor controlling gas production in sewage sludges. Longer periods of inhibition were observed with increasing pH values.

2) A decrease in pH was observed in all the reactors with an initial pH less than 12.0, and pH values greater than 12.0 were required to permanently prevent gas production.

3) A quick lime dose of 0.36 lb/lb of dry solids was required to permanently arrest gas production.

4) A 19N NaOH dose of 0.29 lb/lb of dry solids was required to permanently arrest gas production.

5) Lime, when compared with NaOH, was found to be the better odor control compound owing to its low cost and ease of handling.

6) Calcium alone did not inhibit gas production, but affected the total volume of gas produced.

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VITA

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COMPARISON OF LIME AND SODIUM HYDROXIDE FOR THE CONTROL OF GAS PRODUCTION FROM SEWAGE SLUDGES

by

Ravi Meher Thota.

(ABSTRACT)

The effects of lime and sodium hydroxide on gas production from stored sewage sludge were examined. The impact of calcium on gas production was also investigated. The rate and volume of gas production and change in pH over time were monitored in all the reactors in an effort to study the relationship between chemical dose, pH, and gas production.

The duration of inhibition of gas production increased with the lime dose. Gas production was initiated only after the pH in the reactors decreased to near 8.0. A decrease in pH was observed in all the lime dosed reactors with an initial pH less than 12.0. An initial pH greater than 12.0 was required to completely arrest organic acid and gas production. For the sludge used in this study, a quick lime dose of 0.36 lb/lb of dry solids, which elevated the pH to higher than 12.0, was required for complete inhibition of gas production.

Gas production and pH patterns observed in sodium hydroxide dosed reactors were similar to those in lime dosed reactors. A decrease in pH by nearly 2 pH units was observed in these reactors after calcium chloride addition. This was thought to be primarily due to the precipitation of calcium carbonate. Gas production after elutriation was observed in all the reactors with an initial pH less than 11.5. The

volume of gas produced after elutriation decreased with increase in initial pH. An NaOH (19N) dose of 0.29 lb/lb of dry solids was required for permanent prevention of gas production.

Calcium alone was not capable of arresting gas production but it reduced the total gas production in the reactors with a pH less than 7.5. At pH values greater than 7.5, calcium had little effect on gas production.