

## DIVISION S-4—SOIL FERTILITY AND PLANT NUTRITION

### Ammonia Losses from Surface-Applied Nitrogen Fertilizer as Controlled by Soluble Calcium and Magnesium: General Theory<sup>1</sup>

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#### ABSTRACT

Ammonia volatilization from soils after surface application of urea or inorganic N was reduced by Ca and Mg nitrates or chlorides. Sulfates were only slightly effective. Suppression of  $\text{NH}_3$  loss was a result of two chemical reactions: (i) precipitation of  $\text{CO}_2$  by Ca, thus preventing permanent  $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$  (AC) formation, and (ii) Ca depression of soil pH by depression of the dissociation of the  $\text{CaCO}_3\text{-Ca(OH)}_2$  buffer system. Soil pH values as low as 6.5 were recorded in calcareous soil and 9.9 and 4.5 in the acid soils after addition of Ca. Soil pH values in the presence of Ca reached approximate neutrality in 24 hours even in acid soils. Soil pH without Ca but with AC increased to  $> 9.0$  in every soil. Addition of AC plus Ca reduced the pH of calcareous soil to 5.3 and raised it to 5.7 in acid soils. Calcium carbonate precipitation eventually occurred in acid soils, preventing high  $\text{NH}_3$  losses. Evidently,  $\text{CaCO}_3$  precipitated on the surface of acid soils after the pH reached a certain critical value and, as expected, the pH was maintained near that of the pure  $\text{CaCO}_3$  system.

*Additional Index Words:* urea,  $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$ ,  $\text{CaCO}_3$ , precipitation.

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EFFECTIVE USE of urea [ $\text{CO}(\text{NH}_2)_2$ ] on crops requiring surface fertilizer applications is limited by high ammonia ( $\text{NH}_3$ ) loss (2). In calcareous soils,  $(\text{NH}_4)_2\text{SO}_4$  (AS) and  $(\text{NH}_4)_2\text{HPO}_4$  (DAP) also lose equally large quantities of  $\text{NH}_3$  (5). If urea- and inorganic-N fertilizers are surface applied to calcareous soils, rapid soil incorporation is recommended (4, 9, 16). Unfortunately, this generally limits use of urea on non-row crops such as pastures or orchards, and of AS and DAP on calcareous soils. Previous research by Fenn and Miyamoto (7) suggests a reaction within the soil between extractable calcium and magnesium (Ca + Mg) and the carbonate ( $\text{CO}_2$ ) produced by hydrolyzed urea to form  $\text{CaCO}_3$ . This is significant, since precipitation of  $\text{CO}_2$  by this exchangeable Ca +

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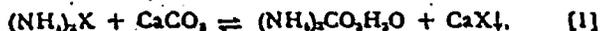
Mg should allow ammonium ( $\text{NH}_4$ ) to noncompetitively occupy cation exchange sites and be protected against  $\text{NH}_3$  loss by volatilization.

DuPlessis and Kroontje (3) found that retention of  $\text{NH}_4$  by soil increased with increasing amounts of  $\text{CO}_2$  present. They postulate that Ca precipitated as  $\text{CaCO}_3$ , thereby eliminating its potential as a replacement cation for exchangeable  $\text{NH}_4$ . Hydrolyzing urea produces its own  $\text{CO}_2$ ; therefore, it would logically be expected to precipitate exchangeable Ca. Fenn and Miyamoto (7) showed significantly less  $\text{NH}_3$  loss from urea than from AS banded in soil at all depths. Ammonium sulfate reacts strongly with solid phase  $\text{CaCO}_3$  as well as with adsorbed Ca. Since  $\text{CaSO}_4$  produced from  $\text{CaCO}_3$  is slightly soluble, the Ca can still act as a replacement cation for  $\text{NH}_4$ . Therefore, losses of  $\text{NH}_3$  with AS are explainably higher.

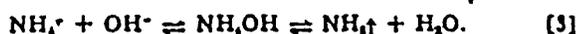
If Ca and Mg reactions with  $\text{CO}_2$  can be made to occur on the soil surface, a great improvement in N retention should result. Generally, soluble Ca on the soil surface in the vicinity of urea granules would be inadequate for quantitative precipitation of  $\text{CO}_2$ . If this quantity of soluble Ca existed, plants could not grow because of excess salinity. However, addition of soluble Ca with the urea would seem feasible and not contribute a general salt problem. This research was designed to determine if the use of soluble Ca and Mg salts with surface-applied urea and inorganic-N fertilizers would precipitate  $\text{CO}_2$  and reduce  $\text{NH}_3$  losses.

## THEORY

A previous paper contains the reaction mechanisms for the inorganic-N compounds with  $\text{CaCO}_3$  (5). Ammonium sulfate and DAP reacted with  $\text{CaCO}_3$  to form Ca reaction products of low solubility as follows:



where  $\text{X}=\text{SO}_4^{2-}$  or  $\text{HPO}_4^{2-}$

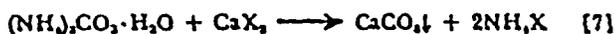
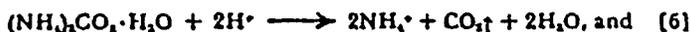
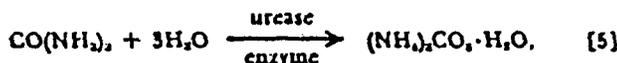


Inorganic-N compounds which did not produce insoluble Ca precipitates and result in lower  $\text{NH}_3$  losses were  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$  (AN), and  $\text{NH}_4\text{H}_2\text{PO}_4$  (MAP) and react as follows:



where  $\text{X}=\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{H}_2\text{PO}_4^-$ .

Since Ca salts of Eq. [4] did not precipitate, no driving force existed to form AC. Therefore, the equilibrium of the reaction is such that where AC exists, such as from hydrolysis of urea, the addition of Ca salt causes the rapid production of  $\text{CaCO}_3$  and  $\text{NH}_4\text{Cl}$  or AN as follows:



where  $\text{X}=\text{Cl}^-$  or  $\text{NO}_3^-$ .

In acid soils, initial pH values in the presence of Ca may be too low for  $\text{CaCO}_3$  precipitation. Initial urea hydrolysis, therefore, will occur in a strong acid environment with  $\text{CaCO}_3$  precipitating only if AC has increased the pH above 7.0. Protection against  $\text{NH}_3$  loss will not be necessary until the pH exceeds 7.0. Calcium, therefore, will be an effective  $\text{NH}_3$  loss-suppressing agent in acid soils (Eq. [6] and [7]).

Volatility of  $\text{NH}_3$  from urea, AS, and DAP in acid and calcareous soils can therefore be depressed by addition of soluble Ca salts (Eq. [7]). Calcium will convert  $\text{NH}_3$  from AC to more

stable products. Ammonium nitrate and  $\text{NH}_4\text{Cl}$  are acidic products; they also will neutralize some of the AC produced. This means that < 1 equivalent of Ca may be required to suppress  $\text{NH}_3$  volatilization for each equivalent of urea-N or inorganic-N compounds added.

Soluble Ca or Mg salts have an additional beneficial role. Calcium, before it has completely reacted with the  $\text{CO}_2$  from AC formed from urea, will reduce the pH of calcareous soils. The precise mechanism (1, 11) involves precipitation of  $\text{CaCO}_3$ , reduction of soil pH by Ca and Mg, plus formation of acidic products AN or  $\text{NH}_4\text{Cl}$ . All contribute to reducing the  $\text{NH}_3$  loss potential. Therefore, in a calcareous soil,  $\text{NH}_3$  losses can theoretically be reduced to much lower values than occurred with inorganic compounds such as  $\text{NH}_4\text{Cl}$ , AN, and MAP. Loss of  $\text{NH}_3$  from compounds like AN and  $\text{NH}_4\text{Cl}$  results from an inherently high pH of calcareous soils and is not due to an induced increase in pH. Reduction in  $\text{NH}_3$  loss below that found with AN will, by necessity, be a measure of the pH reductive effect of Ca and Mg.

## MATERIALS AND METHODS

A description of the physical arrangement for the  $\text{NH}_3$  collection apparatus can be found in a prior publication (5).

A series of experiments was conducted to determine  $\text{NH}_3$  loss and chemical reaction mechanisms under various conditions. Urea, AS, and AN were surface applied in all cases (at 550-kg  $\text{NH}_3$ -N/ha and 32°C) to Harkey s1cl (6), Beaumont c (8), and Darco fs (9). Native soil pH values are shown in Table 1. All < 1-mm soils were oven-dried, 1.0% organic matter was added (bluegrass clippings), pH was determined, and samples were placed 2.5-cm deep (250 g) on a leached sand saturated with distilled water. Calcium carbonate was adjusted to 15% by weight in Harkey s1cl; Darco fs and Beaumont c soils were not limed.

The main study consisted of adding  $\text{CO}(\text{NH}_2)_2$ -N or  $\text{NH}_3$ -N alone to the surface of the three soils and with Ca or Mg salts at a chemically equivalent ratio. The Ca-N fertilizer mixture was surface applied to each soil as a liquid (9%  $\text{NH}_3$ -N or  $\text{NH}_4$ -N by weight). The Ca and Mg sources were  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{CaCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{MgCl}_2$ ,  $\text{Mg}(\text{NO}_3)_2$ , and  $\text{MgSO}_4$ . Dry  $\text{CaSO}_4$  was used because of its low aqueous solubility. Ammonia collection was continued until the  $\text{NH}_3$ -N collected was < 1%/day of the applied N.

In another experiment, the effect of Ca and AC on soil pH was measured on Harkey s1cl, Darco fs, and Beaumont c. A fixed amount of Ca salt was added to 26.6 g of soil, and its pH was measured. A chemically equivalent amount of AC was

Table 1—Surface soil pH values as affected by 1.96 g of  $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$  and an equivalent amount of Ca added to 26.6 g of soil.

Soil	Salt	$(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$	Initial pH	Soil pH after time		
				4	24	72
— hours —						
<b>Harkey s1cl</b>						
Soil	-	-	7.7			
Soil	-	+	8.4	8.8	9.1	9.2
Soil + CaCl <sub>2</sub>	2.66	-	6.6			
Soil + CaCl <sub>2</sub>	2.66	+	6.3	6.7	6.0	6.3
Soil + Ca(NO <sub>3</sub> ) <sub>2</sub>	2.81	-	6.8			
Soil + Ca(NO <sub>3</sub> ) <sub>2</sub>	2.81	+	6.8	6.8	7.6	8.0
Soil + CaSO <sub>4</sub>	3.00	-	7.7			
Soil + CaSO <sub>4</sub>	3.00	+	7.0		7.1	
<b>Darco fs</b>						
Soil	-	-	6.8			
Soil	-	+	8.6		9.1	
Soil + CaCl <sub>2</sub>	2.66	-	4.8			
Soil + CaCl <sub>2</sub>	2.66	+	6.8		7.2	6.9
Soil + Ca(NO <sub>3</sub> ) <sub>2</sub>	2.81	-	4.6			
Soil + Ca(NO <sub>3</sub> ) <sub>2</sub>	2.81	+	6.6		7.8	7.7
<b>Beaumont c</b>						
Soil	-	-	4.8	6.0	6.0	4.9
Soil	-	+	8.6			8.8
Soil + CaCl <sub>2</sub>	2.66	-	3.9			
Soil + CaCl <sub>2</sub>	2.66	+	6.7	6.6	6.8	6.0
Soil + Ca(NO <sub>3</sub> ) <sub>2</sub>	2.81	-	3.9			
Soil + Ca(NO <sub>3</sub> ) <sub>2</sub>	2.81	+	6.3	6.3	6.6	6.9

added to each soil, and pH values were again measured with time up to 72 hours. Ammonium carbonate was used instead of urea since urea will hydrolyze only over a 3- to 5-day period.

Carbon dioxide evolution from Darco fs originally fertilized with urea was examined to determine the presence of residual  $\text{CaCO}_3$ , by placing a sample in an Erlenmeyer flask, adding 30 ml of 3N HCl, and measuring weight loss. A laboratory analysis of  $\text{CaCO}_3$  precipitation was also attempted using a pure chemical system of AC and each Ca salt. Each mixture was allowed to stand overnight and filtered. Precipitate and filter paper were dried in the oven at 82°C, added to the Erlenmeyer flask, and weighed. Acid was added to the Erlenmeyer flask containing the filter paper and  $\text{CaCO}_3$ . The  $\text{CaCO}_3$  content was determined by  $\text{CO}_2$  weight loss.

Disappearance of soluble and adsorbed Ca and Mg from Harkey sicl was also determined. Dry soil (250 g) was added to four columns containing sand which was saturated with distilled  $\text{H}_2\text{O}$ . Urea alone or combined with a chemically equivalent amount of  $\text{CaCl}_2$  was added to the surface of the soil. Ammonia was collected for 14 days, the soil was extracted with 500 ml of 2N KCl, and extractable Ca and Mg determined by titration with 0.01N EDTA. Decrease in extractable Ca and Mg was related as the difference between nontreated and urea-plus-Ca treated samples.

RESULTS

Results in Fig. 1, 2, and 3 show reductive effects of added Ca and Mg on  $\text{NH}_3$  loss from urea. Losses for

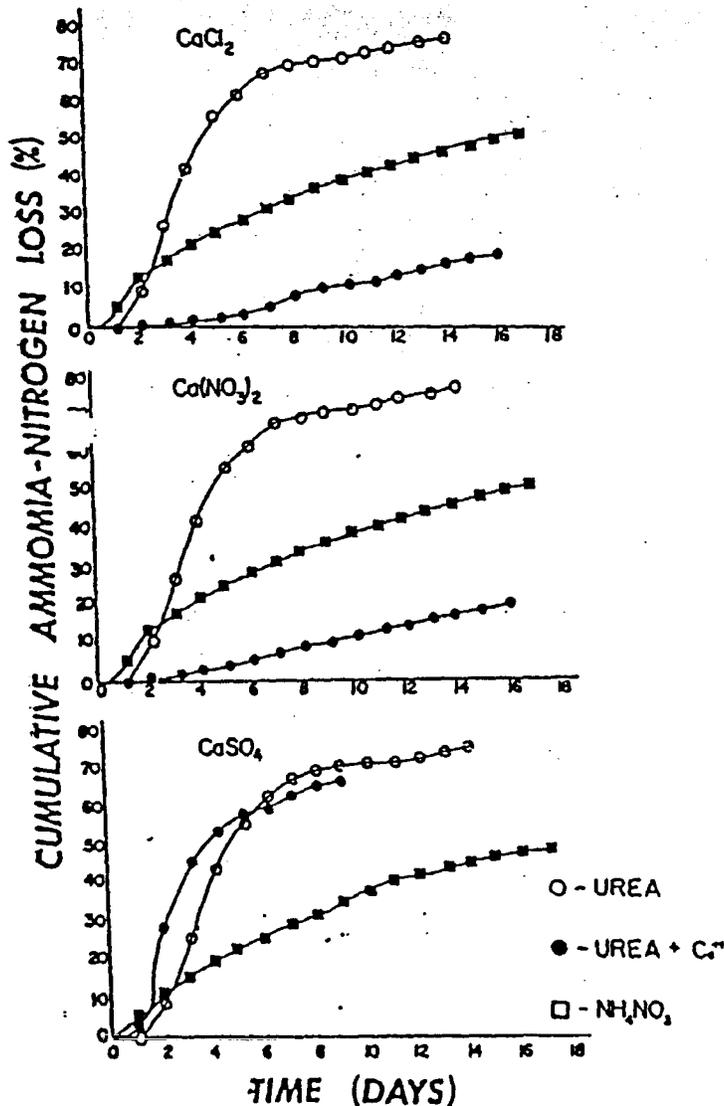


Fig. 1—Ammonia loss from surface-applied urea to calcareous Harkey sicl as affected by three Ca salts.

$\text{MgCl}_2$  (not shown) were identical to those from  $\text{CaCl}_2$ . Urea applied alone resulted in a maximum  $\text{NH}_3$ -N loss of 76% from Harkey sicl (Fig. 1) and 50 to 60% from other soils (Fig. 2, 3). No differences were found in  $\text{NH}_3$  loss between  $\text{CaCl}_2$  and  $\text{Ca}(\text{NO}_3)_2$ . Use of  $\text{CaSO}_4$  resulted in  $\text{NH}_3$ -N losses of 71% of applied N, not significantly less than the 76% loss found with urea alone (Fig. 1).

Ammonia loss from Darco fs occurred very rapidly

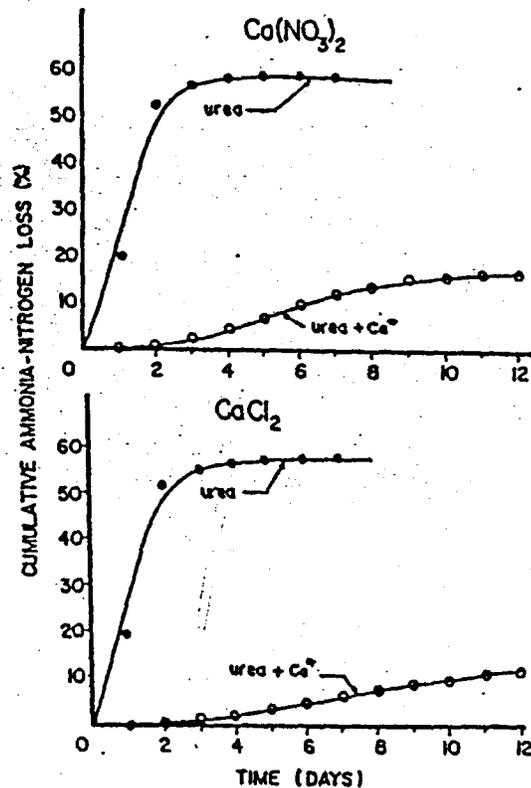


Fig. 2—Ammonia loss from surface-applied urea to acidic Darco fs as affected by two Ca salts.

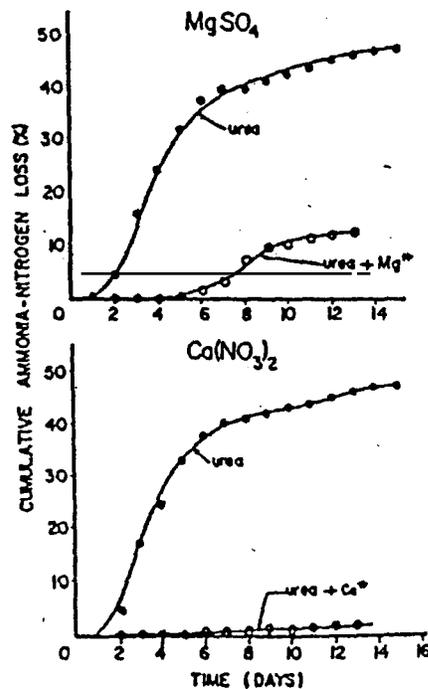


Fig. 3—Ammonia loss from surface-applied urea to acidic Beaumont clay as affected by Ca and Mg salts.

Table 2—Solution pH and CaCO<sub>3</sub> precipitated in solution reaction between (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>·H<sub>2</sub>O and CaCl<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, or CaSO<sub>4</sub>.

Salt	Initial solution pH	CaCO <sub>3</sub> measured %
CaCl <sub>2</sub>	5.9	96.7
Ca(NO <sub>3</sub> ) <sub>2</sub>	6.8	98.6
CaSO <sub>4</sub>	8.6	85.3
	7.3†	

† Stirring < 1 min reduced solution pH from 8.6 to 7.3, the pH of pure CaSO<sub>4</sub> solution.

and was 59% of the applied N (Fig. 2). Addition of a chemically equivalent amount of Ca reduced losses to 10 to 15% and resulted in much slower loss. The Beaumont c exhibited a maximum NH<sub>3</sub>-N loss of 46% of applied N (Fig. 3), but addition of Ca reduced NH<sub>3</sub> loss to < 3%.

Laboratory solution data (Table 2) indicate that the stoichiometric reaction between AC and Ca(NO<sub>3</sub>)<sub>2</sub> or CaCl<sub>2</sub> was approximately 97 to 99% complete. Reaction between CaSO<sub>4</sub> and AC was slightly lower with 83% of the CO<sub>2</sub> precipitated as CaCO<sub>3</sub>. The reaction of CaCl<sub>2</sub> and Ca(NO<sub>3</sub>)<sub>2</sub> with AC resulted in initial solution pH values of 5.89 and 6.77. The solution pH of CaSO<sub>4</sub> with AC, however, increased to 8.60, but surprisingly, slight agitation reduced it to 7.30, identical to the pH of pure CaSO<sub>4</sub> solution. Concurrent with a drop in solution pH was a strong NH<sub>3</sub> odor.

Use of CaSO<sub>4</sub> with AC did not reduce initial solution pH substantially, even though 83% of the CO<sub>2</sub> was precipitated. Ammonia volatilization from urea on Harkey sicl in the presence of CaSO<sub>4</sub> reduced NH<sub>3</sub>

losses very little (Fig. 1). Magnesium sulfate, however, with urea on a Beaumont c was almost as effective as either the CaCl<sub>2</sub> or Ca(NO<sub>3</sub>)<sub>2</sub>.

Presence of soil CaCO<sub>3</sub> from the reaction of hydrolyzed urea and Ca was examined in the acidic Darco fs. Slow evolution of CO<sub>2</sub> over a 24-hour period accounted for 11% of the potential CaCO<sub>3</sub> content. On the other hand, urea surface-applied with CaCl<sub>2</sub> to calcareous Harkey sicl decreased extractable Ca and Mg by 0.27 to 1.00 equivalent (27%) of urea added.

In calcareous Harkey sicl (Table 1), Ca from CaCl<sub>2</sub> and Ca(NO<sub>3</sub>)<sub>2</sub> reduced soil pH by > 1 unit from the soil pH of 7.70. The soil pH value with CaSO<sub>4</sub> was identical to that of the native soil. Maximum pH depressions after CaSO<sub>4</sub> and AC application was < 0.8 unit. Formation of NH<sub>4</sub>Cl and AN after addition of AC to soil containing CaCl<sub>2</sub> or Ca(NO<sub>3</sub>)<sub>2</sub> reduced soil pH as low as 5.3 after 4 hours. Soil pH values increased within 72 hours to 8.0 with Ca(NO<sub>3</sub>)<sub>2</sub> and 6.3 with CaCl<sub>2</sub>.

Addition of Ca to acid Darco fs also significantly reduced the soil pH to 4.60 and 4.48 with CaCl<sub>2</sub> and Ca(NO<sub>3</sub>)<sub>2</sub>, respectively, from the native soil pH of 5.84. However, addition of AC in presence of Ca raised soil pH to 6.85 and 7.67, respectively, with CaCl<sub>2</sub> and Ca(NO<sub>3</sub>)<sub>2</sub>. Soil pH with AC alone was 9.13 within 24 hours. Ammonium carbonate applied to Ca-treated Beaumont c resulted in much lower final soil pH values, consistent with a highly acidic native pH of 4.84. As with Darco soil, AC added to Beaumont clay raised the pH to 8.97. Again, addition of Ca reduced soil pH values in the absence of AC to 3.90 and 3.86, respectively, for CaCl<sub>2</sub> and Ca(NO<sub>3</sub>)<sub>2</sub>. However, addition of AC with Ca resulted in much lower pH values than in Darco or in calcareous Harkey. These pH values after 72 hours were 5.99 and 6.85, respectively, for CaCl<sub>2</sub> and Ca(NO<sub>3</sub>)<sub>2</sub>.

### Inorganic Nitrogen Fertilizers

Loss of NH<sub>3</sub> from surface-applied AS on Harkey sicl (Fig. 4) was identical to that of urea. Addition of a chemically equivalent amount of CaCl<sub>2</sub> reduced NH<sub>3</sub> losses from 72 to 31%.

Total loss of NH<sub>3</sub> from AN-surface applied to Harkey sicl was 33% (Fig. 4). Calcium added as CaCl<sub>2</sub> reduced NH<sub>3</sub> loss to 18%.

## DISCUSSION

### Urea

Addition of Ca from CaCl<sub>2</sub> or Ca(NO<sub>3</sub>)<sub>2</sub> to soils produced a lower soil pH. Calcium sulfate, because of its low solubility, resulted in no soil pH reductions in Harkey sicl. The apparent reaction of Ca or Mg with AC, produced from urea, resulted in significant reductions in NH<sub>3</sub> loss. The reduction in NH<sub>3</sub> loss occurred from the precipitation of CO<sub>2</sub> as CaCO<sub>3</sub> at pH values > 7.0 or from H<sub>2</sub>CO<sub>3</sub> decomposition in the acid soils, or from both (Eq. [6] and [7]). Removal of CO<sub>2</sub> results in the formation of a weakly acidic product, NH<sub>4</sub>Cl or AN. In calcareous Harkey sicl, Ca reduced the soil pH to as low as 6.5. The reaction of Ca with AC reduced the soil pH values to as low as 5.3. Obviously, the Ca suppression of Ca(OH)<sub>2</sub>-CaCO<sub>3</sub> solubility has resulted in much lower pH than could be produced by adding small amounts of acid to calcare-

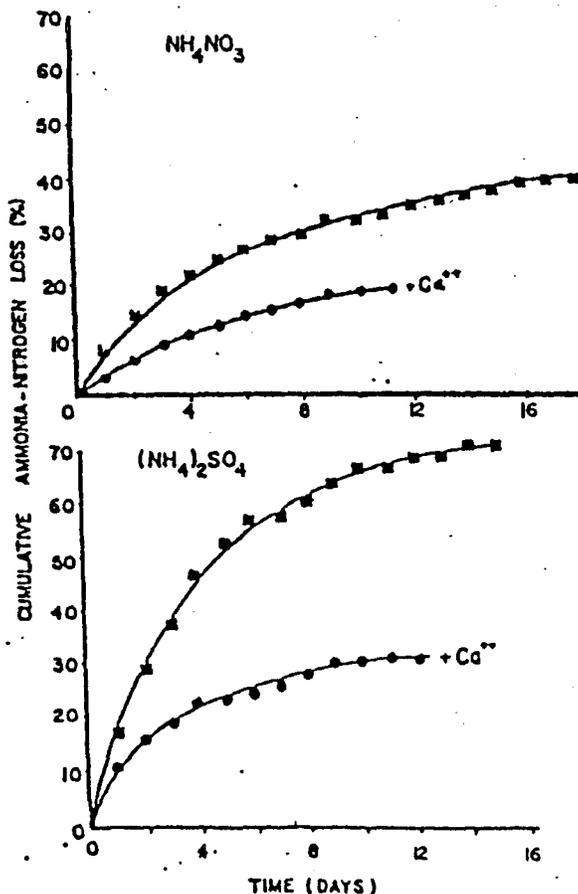


Fig. 4—Ammonia loss from surface applied (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>NO<sub>3</sub> to calcareous Harkey sicl as affected by a Ca salt.

ous soil. Ammonia volatilization at these soil pH values should be minimized.

Expression of this pH effect with urea would be different than with AC. Urea hydrolysis would proceed at a rate determined by urease activity. The initial soil pH would be determined by concentration of Ca salts. Each succeeding amount of AC produced may further reduce pH by  $\text{NH}_4\text{Cl}$  or AN formation. Consumption of the added soluble Ca in  $\text{CaCO}_3$  precipitation, however, lessens Ca-induced pH reduction. Ammonium nitrate without added Ca reduced soil pH of Harkey sicl to 6.7 (Table 1). The additional pH change to 5.3 resulted from the repressive effect of Ca on the  $\text{Ca}(\text{OH})_2\text{-CaCO}_3$  buffer system.

Calcium nitrate and  $\text{CaCl}_2$  with urea on Harkey sicl behaved similarly in depressing  $\text{NH}_3$  losses. The presence of  $\text{CaSO}_4$  with urea reduced  $\text{NH}_3$  losses very little compared to  $\text{CaCl}_2$  and  $\text{Ca}(\text{NO}_3)_2$ . This indicates that the equilibrium of the chemical reaction between Ca and AC is strongly towards AC and  $\text{CaSO}_4$  and not AS and  $\text{CaCO}_3$ . The degree of  $\text{CaCO}_3$  precipitation from an AC solution in the laboratory study (Table 2) indicated less precipitation with  $\text{CaSO}_4$  than found with  $\text{CaCl}_2$  and  $\text{Ca}(\text{NO}_3)_2$ . Even though a considerable tendency exists for  $\text{CaCO}_3$  precipitation from a solution of AC and  $\text{CaSO}_4$ , it is not sufficient to suppress  $\text{NH}_3$  loss in soils. The initial pH of the  $\text{CaSO}_4\text{-AC}$  solutions was similar to AC. However, agitation of the mixture reduced pH to that of  $\text{CaSO}_4$ . A successful reaction of this type requires a cation highly soluble in the reactant form but insoluble in the  $\text{CO}_3$  form. Cations of this type are many, but Ca and Mg behave identically, are readily available, and have no toxic effects.

The pH values of the Darco and Beaumont soils were reduced by the addition of Ca (Table 1). Much of the pH decrease resulted from replacement of hydrogen or aluminum. Soil pH values of the Beaumont and Darco soils were as low as 3.86 and 4.48, respectively, after the addition of Ca; but these values increase with the addition of AC. There can be no  $\text{CO}_3$  precipitation at low pH values. The  $\text{CO}_3$  would be lost through  $\text{H}_2\text{CO}_3$  decomposition until the pH reached neutrality where  $\text{CaCO}_3$  formation might begin. This formation, however, would still serve as a check on  $\text{NH}_3$  volatilization. The addition of AC alone to this acid soil resulted in a very alkaline pH. Obviously, the acidity on the soil surface did not neutralize added alkalinity. With addition of Ca, however, the pH values were maintained below 8.0.

The existence of  $\text{CaCO}_3$  was determined in the Darco fs. Acid soils will have little permanent  $\text{CaCO}_3$  since land preparation and rainfall would result in the loss of  $\text{CaCO}_3$ . Calcium carbonate produced from the application of soluble Ca and AC tends to exist only on the surface of an acid soil. The significant loss of soluble and exchangeable Ca and Mg from Harkey sicl showed that Ca and Mg readily disappear in the presence of urea. The loss of soluble Ca and Mg in the presence of  $\text{CO}_3$  may be the result of  $\text{CaCO}_3$  formation. This study relied strongly on indirect soil evaluations to indicate the probable formation of  $\text{CaCO}_3$ . Labelled C would be necessary to precisely quantify the  $\text{CO}_3$  formed from AC and added Ca and Mg in Darco fs. Carbon-14 would definitely need to be used in a calcareous soil to accurately measure new

$\text{CaCO}_3$  but, considering the evidence,  $\text{CaCO}_3$  is probably formed in all cases.

### Inorganic Nitrogen Fertilizers

Ammonium sulfate is representative of inorganic-N fertilizers that react with  $\text{CaCO}_3$  to form AC. Surface placement of AS on Harkey sicl will produce  $\text{NH}_3\text{-N}$  loss identical to urea. Since the reaction product is AC, soluble Ca should reverse the reaction and reform  $\text{CaCO}_3$  and AS or form  $\text{CaSO}_4$  directly from the added Ca avoiding the AC pathway. An additional explanation should be that soluble Ca depresses the solubility of  $\text{CaCO}_3$ , thus preventing AC formation. Calcium, applied at a ratio of one chemical equivalent of  $\text{CaCl}_2$  with one chemical equivalent of AS, significantly reduced  $\text{NH}_3$  loss. The speed of the initial reaction to AC is more rapid than with urea; consequently, Ca is less effective with AS than with urea. Calcium also cannot be applied in liquid form with AS, so an irregular distribution of AS with Ca is likely. It is therefore possible that some AS reacted with  $\text{CaCO}_3$  without being influenced by Ca. The use of AC on the surface of the Harkey sicl treated with Ca (data not presented) resulted in a similar, smaller reduction in  $\text{NH}_3$  loss.

Ammonium nitrate does not form an insoluble reaction product in calcareous soils. Ammonia loss was reduced by the presence of Ca. Percentage reduction was less than with AS. The likely mechanism of loss reduction is depression of soil pH discussed earlier.

Divalent cations are effective means for depressing  $\text{NH}_3$  losses from surface-applied N fertilizers. The mechanism is especially effective with urea. Ammonia losses from inorganic-N compounds are depressed to a smaller extent by Ca and Mg but the depression is still substantial.

### LITERATURE CITED

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