THE AMMONIA-FIXING CAPACITY OF CALCIUM SULFATE

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INTRODUCTION

That much nitrogen is lost from manure by the volatilization of ammonium compounds is generally conceded. The extent to which this loss can be prevented by the use of chemicals as preservatives is not well established. The use of calcium sulfate for this purpose is a very old practice. Concerning its efficiency as an ammonia fixer there is little agreement among investigators. There is also a difference of opinion among those who believe it will conserve ammonia as to the manner in which it does it.

Some agriculturists have entertained the view that calcium sulfate has the ability to hold ammonia gas by physical adsorption. Some have contended that the retention of the ammonia may be due to a process of chemical absorption, resulting in the formation of a double sulfate. Far the greater number have considered that the benefit from using calcium sulfate as a preserver depends upon its ability to transform volatile ammonium carbonate into the more stable ammonium sulfate by the process of double decomposition.

According to the results of Haskins (8) physical adsorption plays a very small part, if any, in the fixation of ammonia.

The work of Bell and Taber (3) makes the second of these suppositions appear untenable, since all the conditions necessary to the formation of $\text{CaSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot x(\text{H}_2\text{O})$ would not obtain in a manure heap.

The third assumption, that of double decomposition, is based on rather reasonable grounds both theoretical and experimental. However, the degree to which the reaction takes place in decomposing organic matter is questionable. Since the reaction is a reversible one, and since calcium sulfate is comparatively insoluble, it would appear doubtful whether under the normal moisture conditions in manure, very much ammonium sulfate is formed before a state of equilibrium is reached. Even after being formed, if some of the moisture is lost in any way, the reverse reaction very probably predominates and produces again some of the unstable ammonium carbonate. It is well known that when $(\text{NH}_4)_2\text{SO}_4$ and CaCO_3 are mixed together intimately in the dry state, or at least with only hygroscopic moisture present, a distinct odor of ammonia is noticeable. Obviously this is due to the formation of volatile $(\text{NH}_4)_2\text{CO}_3$. It is also easy to believe that changes of temperature and other physical conditions may have a great influence on the direction in which

the reaction proceeds. Reactions with gypsum in a pile of fermenting material are no doubt somewhat complicated. Sulfates, being oxidizing substances, are likely to be reduced to sulfides by the action of the carbonaceous matter present. The sulfides formed may interact with H_2CO_3 to form carbonates.

HISTORY OF INVESTIGATIONS

Considerable investigational work has been carried on to determine the power of calcium sulfate to fix ammonia. In most cases gypsum in variable quantities has been mixed with manure, allowed to stand for a time, and by analysis of the manure for nitrogen before and after the investigation a conclusion has been reached as to the value of the gypsum as a preservative. The fact that much of the nitrogen is given off in a free state, as shown by Russell and Richards (17) as well as by other investigators (6) has been little considered. A few experiments of a modified type have been carried on.

Although many of these investigations have only a general bearing on the problem under consideration, it seems desirable to review briefly some of the results that have been obtained and some opinions and conclusions that have been reached.

The earlier writers on agriculture have said much regarding the ability of calcium sulfate to fix ammonia. Boussingault (4) states that M. Shattermann, who was a large horse keeper of Alsace during the first half of the nineteenth century, managed large heaps of manure very well and used either sulfate of iron or gypsum as preservatives.

Liebig (9) believed that the beneficial effects which were observed where calcium sulfate had been strewn on a meadow were due to the ability of the salt to fix the ammonia of the atmosphere by the formation of ammonium sulfate. He describes an experiment which was made with growing beans and peas on a garden plot, which had been well manured and strewed with gypsum. Before beginning the experiment it was found by analysis that both soil and gypsum were quite free from carbonates; but on examination of some of the salt taken from the surface of the ground after several weeks, it was discovered that the greater part of the gypsum had been converted into the carbonate of lime and that the soil to a depth of six inches effervesced strongly on the addition of acid. This corresponds to the results obtained by Spatzier and reported by Storer (18). Lemmerman and Fresenius (11) record similar results.

From an extended investigation covering 6 years of time, on how to reduce the loss of nitrogen from manure, Müntz and Girard (13) concluded that the use of chemical agents is unsatisfactory and that, in the case of calcium sulfate, so much must be used to attain the desired result as to make the practice uneconomical.

Burri, Herfeldt and Stutzer (5) inoculated nutrient solutions with manure bacteria, some with bacteria from old decomposing liquid manure and some with bacteria from fresh liquid. Various manure preservatives were added to

the cultures and results noted. One of their conclusions was that "gypsum has no value as a preservative. It does not combine with the carbonate of ammonia already present and does not prevent the further formation of this substance even when used in large quantities."

Aeby, Dorsch, Matz and Wagner (1) found that in case of complete humification and long storage the denitrifying action in manure is lessened by being reinforced with gypsum, but concluded that as a fixer of ammonia it is of little use.

Aso and Nishimuro (2), in studies on the comparative value of superphosphate of calcium, gypsum and kainit as manure preservatives found that gypsum and kainit are much inferior to superphosphate as fixers of ammonia.

Lindsey (10) reviewed the results of German investigators and found the consensus of opinion to be against the use of chemical preservatives such as gypsum, on the ground that the nitrogen saved is quite out of proportion to the expense involved.

Pichard (15) compared the action of calcium sulfate and ferrous sulfate in conserving soil nitrogen. The substances were mixed with artificial soils of known composition and placed in enameled earthenware pots. The gypsum, which was added at the rate of 5 gm. per kgm., was found to be more favorable to nitrification and a more effective conserver of nitrogen than ferrous sulfate.

At the Ohio Agricultural Experiment Station (21) work has been carried out to determine the effect on crops of the use of reinforced manure. The manure was applied at the rate of 8 tons per acre, in a 3-year rotation of corn, wheat and clover, and the reinforcing materials were used at the rate of 40 pounds to the ton of manure. In the trial with gypsum-treated yard manure the increase over untreated manure was 7.37 bushels of corn and 473 pounds of stover, 4.07 bushels of wheat and 452 pounds of straw and 581 pounds of hay. In the trial with stall manure the increase was 3.18 bushels of corn and 211 pounds of stover, 2.35 bushels of wheat and 201 pounds of straw, but with a loss of 134 pounds of hay. These are the averages for 16 crops of corn, 16 of wheat and 13 of hay. The results of 5 years' analyses of treated and untreated manure used in these tests, before and after 3 months' exposure to winter weather, showed a nitrogen loss of 29.6 per cent when reinforced with gypsum and 35.5 per cent when no preservative was used (20).

Dietzell (7) placed samples of manure in 12-liter flasks carrying tubes through which a current of air could be drawn. Gypsum and other preservatives were mixed with different samples. The temperature at which the flasks were kept ranged from 10.5° to 25°C. Analysis was made of the manure at the beginning and at the end of the experiment to determine the nitrogen content. The ammonia which passed out through outlet tubes was collected by means of standardized sulfuric acid. Gypsum and kainit proved to be the most efficient preservatives tried in preventing the loss of nitrogen. It was also found that, if the air is excluded from manure, no preservative is needed to

conserve the nitrogen. This corresponds with the recent conclusion of Russell and Richards (17) that the nitrogen loss from manure is least when stored under anaerobic conditions.

Meyer (14) investigated the effect of various preservatives on 100-cc. portions of liquid manure. He found that from 92.8 to 95.9 per cent of the nitrogen of the liquid was in the form of ammonium carbonate, and that it was practically all lost when allowed to stand for some time exposed to the air. Approximately 50 per cent of the nitrogen was saved when gypsum was used as a preservative.

Severin (19) sterilized manure and inoculated it with cultures of manure bacteria. By using 4 per cent of gypsum as a preserver he succeeded in reducing the loss of ammonia by approximately one-half. He also noted a faster decomposition of the manure treated with gypsum than of that not so treated. The greatest loss observed, however, when no CaSO_4 was used was only 0.0739 gm. from 265 gm. of manure in 90 days. Not only was it concluded that gypsum is an efficient preserver of ammonia but also that the value of acid phosphate for this purpose is due to the calcium sulfate it contains.

Palmer (16) carried out an investigation similar in many respects to that of Severin but the quantities of manure were greater and his purpose was only to determine the efficiency of various chemicals as preservatives of ammonia in manure. Fifty-four pounds of horse manure or 150 pounds of cow manure were placed in galvanized iron cans. The chemical preservatives were added at the rate of 80 pounds to the ton of manure. In the case where CaSO_4 was used 32.53 mgm. of nitrogen was lost from 100 pounds of cow manure in 62 days as compared to 52.47 mgm. when no preservative was added. In the trial with horse manure 32.08 mgm. was lost in 44 days compared to 73.18 mgm. when no CaSO_4 was used.

The majority of investigators seem inclined to the view that gypsum possesses some virtue as a nitrogen conserver. The way in which this is done and the quantitative effect are still unsettled problems.

NATURE AND PURPOSE OF THIS EXPERIMENT

Most, if not all, of the attempts to determine the capacity of CaSO_4 to fix ammonia in manure have involved the use of decomposing organic matter and urine as the source of the ammonia. Since many and complicated biochemical reactions take place in a mass of fermenting manure, and since the quantity of ammonia and ammonium carbonate actually formed is not known, it seems desirable to investigate the ammonia-fixing ability of CaSO_4 independent of decomposing organic matter, using as the source of the ammonia a definite quantity of pure ammonium carbonate. In this way many troublesome factors are eliminated. The number of possible reactions also is limited and the actual capacity of CaSO_4 to hold the ammonia of ammonium carbonate by the process of double decomposition of these salts can, it would seem, be more definitely estimated.

EXPERIMENTAL PROCEDURE

Four trains of bottles were arranged as shown in figure 1. The size of the bottles marked A was 2.5 liters. In each of these was placed 250 gm. of filter paper, which had been previously pulped fine and dried, as a substitute for the organic matter of the manure. With the filter paper added to each of two of these bottles, 150 gm. of pure CaSO_4 was intimately mixed. The material in the bottles was compacted and 750 cc. of a solution containing 39.30 gm. of $(\text{NH}_4)_2\text{CO}_3$ was added to each. This amount of $(\text{NH}_4)_2\text{CO}_3$ would be equivalent to 9.645 gm. of nitrogen or 19.29 pounds to the ton of material. The water content was made approximately 75 per cent. The CaSO_4 was added at the rate of 300 pounds to the ton of material. The temperature was varied

FIG. 1. DIAGRAM SHOWING ARRANGEMENT OF APPARATUS USED IN EXPERIMENT

from time to time, as will be seen by reference to tables 1 and 2. Temperatures higher than room temperature were obtained by placing the bottles marked A inside a box lined with asbestos and heated with an electric lamp. Lamps of different candle power were used to obtain the different degrees of heat. By this arrangement it was possible to control the temperature to within a comparatively narrow range. The ammonia which escaped was collected in standard acid solutions in bottles F and G.

The bottles marked C and H contained concentrated H_2SO_4 to absorb the ammonia of the air. Bottle B was partly filled with a 40 per cent solution of KOH to remove the CO_2 from the incoming air and bottle D contained distilled water to insure the entrance of sufficiently moist air to maintain the water content of A. Air was aspirated through the apparatus from time to time for 10-minute periods, the actual number of aspirations being shown in table 1.

DISCUSSION OF RESULTS

It will be noted by an examination of the results of the experiment as summarized in tables 1, 2, and 3 that quite a large amount of nitrogen was given off during the period of the test by bottles containing no CaSO_4 . In those treated with CaSO_4 the quantity given off was 79.7 per cent less. This was a much larger saving of nitrogen than was found by either Severin (19) or

TABLE 1
The effect of CaSO₄ in preventing nitrogen loss

NUMBER OF DAYS	NUMBER OF ASPIRATIONS	RANGE OF TEMPERATURE °C.	NITROGEN LOSS	
			Without CaSO ₄	With CaSO ₄
			gm.	gm.
9	4	20°-25°	A. 0.0240 B. 0.0180	A. 0.0055 B. 0.0030
15	8	20°-25°	A. 0.0460 B. 0.0410	A. 0.0005 B. 0.0015
11	6	20°-30°	A. 0.0754 B. 0.0764	A. 0.0074 B. 0.0079
20	19	20°-30°*	A. 0.2510 B. 0.2560	A. 0.0240 B. 0.0200
12	12	45°-55°	A. 0.1870 B. 0.2620	A. 0.0250 B. 0.0270
10	10	50°-59°	A. 0.3940 B. 0.3090	A. 0.0310 B. 0.0270
9	15	65°-70°	A. 0.7420 B. 0.6260	A. 0.1150 B. 0.1420
5	10	65°-90°§	A. 0.7520 B. 0.7045	A. 0.1120 B. 0.1050
4	7	80°-85°	A. 0.8467 B. 0.8485 A. 0.0105† B. 0.0100† A. 2.6150‡ B. 2.1500‡	A. 0.2565 B. 0.2510 A. 0.0090† B. 0.0095† A. 0.4900‡ B. 0.6200‡
95	91		A. 5.9436 B. 5.3014 Average, 5.6225	A. 1.0749 B. 1.2139 Average, 1.1419

* Temperature for one day of period was over 30°C.

† Ammonia collected in bottles marked G during period of test.

‡ Ammonia absorbed by water condensed in trap bottles.

§ Temperature was 65°-70° during 4 days of period and raised to 90° one day.

Palmer (16), the former having found that CaSO₄ reduced the loss approximately 50 per cent and the latter 38 per cent in the case of cow manure and 56.2 per cent in the case of horse manure. It will be recalled, however, that the quantity of NH₃ given off in their experiments was quite small, due partly to the fact that they depended on the decomposition of manure for the ammonia supply and partly, no doubt, to a lower temperature.

It may be thought that the temperature to which the mixture of filter paper, (NH₄)₂CO₃, etc., was raised in the latter part of this investigation was too high to be analogous to the conditions in a manure heap. While it is true that ordinarily the temperature of manure is not so high, it was found by Russell and Richards (17) that the temperature of fermenting horse manure under cover may rise to 70-80°C. It seemed desirable, therefore, to note the results

at high temperature in order to determine the efficiency of CaSO_4 as a preservative under such conditions.

The quantity of nitrogen given off by the two bottles of a pair is quite different in some cases, especially at the higher temperatures. This can be largely accounted for by the difficulty experienced in keeping the source of heat at the same distance from the bottles of the mixture.

A comparatively large quantity of the nitrogen evolved was absorbed as ammonia by water condensed in the trap bottles. No condensation of mois-

TABLE 2
Daily nitrogen loss with and without CaSO_4

PERIOD	TEMPERATURE	WITHOUT CaSO_4	WITH CaSO_4
	°C.	per cent	per cent
First.....	20°-25°	0.024	0.006
Second.....	20°-25°	0.030	0.001
Third.....	20°-30°	0.072	0.007
Fourth.....	20°-30°	0.132	0.011
Fifth.....	45°-55°	0.197	0.023
Sixth.....	50°-59°	0.365	0.030
Seventh.....	65°-70°	0.854	0.148
Eighth.....	65°-90°	1.511	0.225
Ninth.....	80°-85°	2.197	0.659

Note: The ammonia absorbed in trap bottles and that neutralized in bottles marked G is not included in these calculations.

TABLE 3
Total nitrogen loss with and without CaSO_4

PERIOD	TEMPERATURE	WITHOUT CaSO_4	WITH CaSO_4
		per cent	per cent
During first 55 days.....	Room temperature	4.08	0.33
During last 40 days.....	45°C. and above	54.21	11.50
Total loss 95 days.....		58.29	11.84

ture was noticeable in these bottles until the beginning of the fifth period, when the temperature of the mixture was raised above room temperature. In compiling table 3, therefore, it was thought well to consider that all ammonia collected in the trap bottles was given off during the last forty days.

A consideration of the results as shown by the tables would seem to leave little doubt that CaSO_4 will hold some ammonia and that it does it by interacting with $(\text{NH}_4)_2\text{CO}_3$ to form the non-volatile compound $(\text{NH}_4)_2\text{SO}_4$. This last assumption is based on the probability of other reactions being prevented by the conditions under which the experiment was performed. It is very probable that many reactions take place in a manure heap, subsequent to the formation of $(\text{NH}_4)_2\text{SO}_4$ that would result in an ammonia loss. One of these is the possi-

ble reduction of sulfates to sulfides by the carbonaceous matter present. We know, too, that the reaction $(\text{NH}_4)_2\text{CO}_3 + \text{CaSO}_4 = (\text{NH}_4)_2\text{SO}_4 + \text{CaCO}_3$ is reversible and that it is largely a question of mass action as to which direction the reaction will go.

When a large amount of water is present the formation of $(\text{NH}_4)_2\text{SO}_4$ takes place until equilibrium is reached. When the percentage of water is lowered the reverse reaction no doubt predominates. When the state known as "fire-fanged" is reached in a manure-heap, under which condition a comparatively small percentage of water is present, it would seem reasonable to believe that most of the ammonia of the $(\text{NH}_4)_2\text{SO}_4$, that had been formed, would be changed to the carbonate and be lost. A plentiful supply of moisture, therefore, seems necessary, if CaSO_4 is to be of real service as a manure preservative. Such a condition obtained in this experiment and also in those of Severin and Palmer. It is perhaps the reason also that Meyer (20) found gypsum able to hold practically half the ammonia of liquid manure. It would seem desirable to investigate the amount of ammonia given off during a few weeks of time from a mixture of filter paper, $(\text{NH}_4)_2\text{SO}_4$ and CaCO_3 at comparatively high heat and low moisture content.

An examination of the table will show that CaSO_4 apparently loses some of its ability to hold ammonia as the temperature is raised. The relative amount held at high temperature is not as great as at low.

SUMMARY AND CONCLUSIONS

It appears to be unquestionable that CaSO_4 will prevent to a certain degree the loss of ammonia from a mixture containing volatile $(\text{NH}_4)_2\text{CO}_3$ and it is quite probable that the loss prevention is due to the formation of non-volatile $(\text{NH}_4)_2\text{SO}_4$ by the double decomposition of $(\text{NH}_4)_2\text{CO}_3$ and CaSO_4 , for no other means is thought to be possible under the conditions of this experiment.

The ammonia-fixing capacity of CaSO_4 is apparently dependent on the temperature. The quantity of ammonia given off by the $(\text{NH}_4)_2\text{CO}_3$ increases as the temperature rises and the percentage of it held by the CaSO_4 decreases.

A treatment of 300 pounds of CaSO_4 to the ton of manure would, no doubt, effect a pronounced ammonia fixation, if the water content were comparatively high. Whether subsequent reactions that probably take place in a manure heap would prevent its remaining fixed and whether the practice of reinforcing manure with gypsum is economical are questions beyond the scope of this investigation.

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