

the water-insoluble residue is extracted with neutral ammonium citrate. The phosphorus dissolved in this step is assumed to be the sum of that present as dicalcium phosphate and basic calcium phosphate. The percentage of basic calcium phosphate is obtained by subtraction. While this relationship seems to be valid on most fertilizers, it may not be applicable to those containing unusual proportions of hydroxyapatite or compounds other than those discussed herein.

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## FERTILIZER COATINGS

# The Effect of Coatings on the Dissolution of Fertilizers and the Uptake of Fertilizer Potassium by Plants

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Several fertilizers containing potassium were coated with vinyl acetate, acrylic resin spray, paraffin, and polyethylene emulsion to alter their dissolution properties. Leaching losses of potassium were significantly reduced by several coating materials. Germination of wheat seed in contact with uncoated fertilizer and emergence of seedlings were lower than with similar placement of coated fertilizer in greenhouse trials. In addition, in a field study of alfalfa top-dressed with a large application of mixed fertilizer, coatings reduced luxury consumption of potassium by this legume. Thus, coatings on granular fertilizer can reduce loss of soluble nutrients by leaching in coarse textured soils, minimize salt injury due to seed-fertilizer contact, and level out excess absorption of fertilizer nutrients such as potassium.

NITROGEN and potash salts such as ammonium nitrate or sulfate, urea, and potassium chloride or sulfate dissolve very rapidly in moist soils. Even the more soluble, well granulated phosphorus carriers such as concentrated superphosphate and ammonium phosphates lose a large part of their phosphorus after 12 to 24 hours of exposure to moist soil (5, 6).

Most of the fertilizer used in American agriculture is applied before or at the time a crop is planted. Since the nutrient requirements of seedlings or transplants are small, the components of soluble fertilizers are largely free to react with soil minerals or may be subject to considerable movement within the soil profile as a result of leaching. The concept of a slow release of plant nutrients from fertilizers to be used by crops as they require them has been proposed for slightly soluble materials. Urea-formaldehyde as a nitrogen source (7)

and the meta- and pyrophosphates of potassium (8, 9) have been developed with this idea in mind. It is possible that coatings on soluble or partially soluble fertilizers may accomplish the same objectives.

The benefits that agronomists have speculated might be attributed to such coatings include reduction of leaching and volatilization losses of nitrogen, reduction of leaching losses of potassium applied to sandy soils, and minimization of plant absorption of excessive amounts of mineral elements, such as potassium, beyond normal crop requirements (3). In addition, fixation of soluble phosphate moving out of fertilizer granules or bands might be lessened and salt injury resulting from seed-fertilizer contact might be greatly reduced.

This study examines several materials which could serve as coatings for fertilizers and determines their performance

under laboratory, greenhouse, and field conditions.

### Materials and Methods

The following materials were employed as coatings for fertilizers.

**Acrylic Resin.** Made up of 5% resin in aromatic hydrocarbons and chlorinated solvents with fluorinated hydrocarbons as the spray propellant. This material was sprayed on fertilizer particles as they were rotated on a flat paper surface. These particles were then air-dried, and the spray was repeated. By this procedure, a glassy-like, water-resistant coating was prepared which filled or covered most of the pores and crevices of the particle surface.

**Vinyl Acetate.** Contained 10 grams of vinylite dissolved in 100 ml. of acetone. This viscous liquid was poured over fertilizer granules in a funnel, and the excess allowed to drain off. Between

successive treatments the fertilizer was placed on a paper surface to dry at room temperature; otherwise the vinyl acetate films tended to fuse at their points of contact. A water-resistant film equivalent to 1 to 2% of the particle weight was formed by this method.

**Polyacrylic Acid.** Acrysol A-3 (Rohm and Haas Co.) diluted 1 to 3 with 95% ethyl alcohol. This clear, viscous liquid was poured over fertilizer granules in a funnel, and the excess was allowed to drain off. After the fertilizer particles were dried on a flat surface at room temperature, they were coated a second time. This procedure produced a film which approximated 1 to 2% of the weight of granules within the size range found in commercial fertilizers.

**Paraffin.** A near-saturated solution of Parawax in *n*-hexane. This solution was poured over fertilizer particles in a Büchner funnel and excess solution was removed under suction. The particles did not stick together, and evaporation of the solvent was facilitated by drying at 70° C. on a flat surface. Two or three successive coatings produced a waxy, dull-appearing film which approximated 1 to 2% of the weight of the fertilizer particles.

**Emulsifiable Polyethylene.** Epolene E Type I (Eastman Chemical Products, Inc.) diluted 1 to 3 with distilled water. This emulsion was poured over fertilizer granules in a funnel, producing a soft, waxy-like coating as excess emulsion was drained away. A kind of curd formed as a result of soluble salts dissolving out of the fertilizers, causing an apparent flocculation of the emulsion. To avoid this problem, the fertilizer particles were coated with acrylic resin or vinyl acetate before an additional film of polyethylene emulsion was developed.

Dissolution characteristics of some coated and uncoated fertilizers were evaluated in the laboratory using distilled water as the leaching agent. Fertilizers included in this study were -4+6-mesh potassium-calcium pyrophosphate, 0-35-25, potassium metaphosphate, 0-55-35 (TVA materials), and a -6+10-mesh commercial granulated 5-20-20 fertilizer. Weighed fertilizer samples (approximately 1 gram) were leached in funnels with successive portions of water at the rate of 1 liter per hour. Potassium in these leachates was determined using a Coleman flame photometer.

A greenhouse experiment was conducted using flats 4 inches deep to determine the effect of fertilizer coatings on the germination and emergence of winter wheat seedling. Granular 5-20-20 fertilizer was applied at the rate of 300 and 600 pounds per acre in furrows 1½ inches deep in a Coloma sandy soil. Fifteen wheat seeds were placed directly on the fertilizer band and the soil was firmed over the row. The soil moisture content at time of seeding was 6.5% or

approximately field capacity, and this moisture level was essentially maintained until seedling emergence by loosely covering the flats with a polyethylene film. At 1-day intervals the cumulative number of seedlings that had emerged were counted until no further emergence was noted. During the 8-day emergence period, water was added four times to the flat by spraying the soil surface.

A similar experiment with oats was conducted in the field using coated and uncoated 5-20-20 fertilizer applied at the rate of 600 pounds per acre. Weighed quantities of oat seeds (variety Gary) were placed by hand in furrows 1 inch deep and 7 inches apart and the fertilizer was dribbled uniformly on top of the seed. The moist field soil was then firmed over the seed and the planting was completed on April 29th. Each plot consisted of three rows 24 feet long with two replicates per fertilizer treatment. The following day the area received 0.4 inch of precipitation and during the first 4 weeks in May, the rainfall amounted to 0.6, 0.5, 0.9, and 1.5 inches, respectively. No attempt was made to evaluate emergence, but height measurements were taken at three dates during the 67-day growth period, and evaluation of stand and dry weight of oat plants was made at full heading stage on July 6.

To study the influence of fertilizer coatings on plants absorption of nutrients from a large application of fertilizer, an experiment was initiated using a young established alfalfa stand. Granular fertilizers of -6+10 mesh and having an analysis of 5-20-20 were top-dressed on plots 5 × 10 feet at a rate of 1200 pounds per acre. Date of application was April 24 when the alfalfa plants were 2 to 3 inches tall. A simple randomized block involving three replications was employed with one half of the plot used for sampling and the other half used for yield measurement. Representative plant samples were taken at approximately 2-week intervals on May 8, 18, 30, and June 15. Approximately 35 granules were collected from the surface of each treatment plot on May 1, 19, June 2, 19, and July 5. Both plant tissue and recovered granules were analyzed for total potassium and phosphorus. Yield data were calculated from hay cut from a 3 × 4 foot area of each plot.

### Results and Discussion

Leaching studies in the laboratory indicated that fertilizer coatings markedly reduced the rate at which potassium was dissolved from granular or coarse sized fertilizers. According to data presented in Figure 1, a paraffin coating reduced dissolution from 81.3% loss for an uncoated sample of 5-20-20 fertilizer to a 5.4% loss of potassium for a

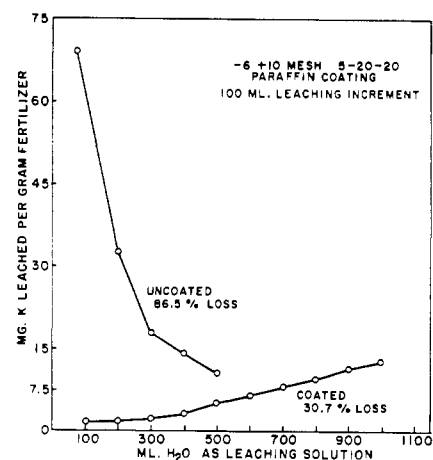


Figure 1. Dissolution of potassium from a granular mixed fertilizer with and without a coating of paraffin

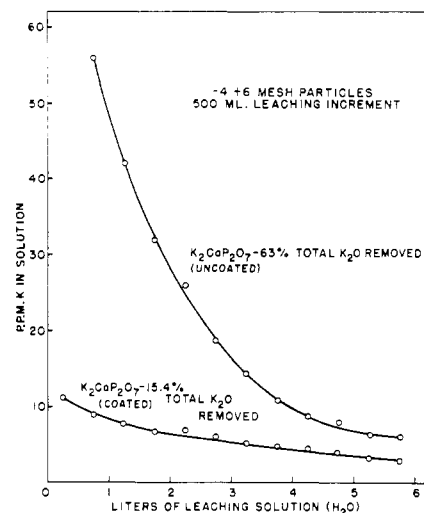


Figure 2. Dissolution of potassium from potassium-calcium pyrophosphate particles with and without a coating of vinyl acetate

coated sample after 24 minutes of leaching (400 ml. of water). After 1 hour of leaching the paraffin-coated fertilizer had lost only 30.7% of its total potassium content. While the rate of dissolution rapidly decreased with successive increments of leachate for the uncoated fertilizer, the rate of loss from the coated granules increased with time. This trend suggests that over the leaching period, the paraffin coating was slowly disintegrating, thus allowing more pores or exposed surface for dissolution.

The effect of coating particles of potassium-calcium pyrophosphate, a slightly soluble fused potassium phosphate, on its dissolution properties is given in Figure 2. With this fertilizer, a coating substantially minimized the dissolution of potassium over a 6-hour leaching period. In this case, particles coated with vinyl acetate lost only 15.4% of their total K content, while the

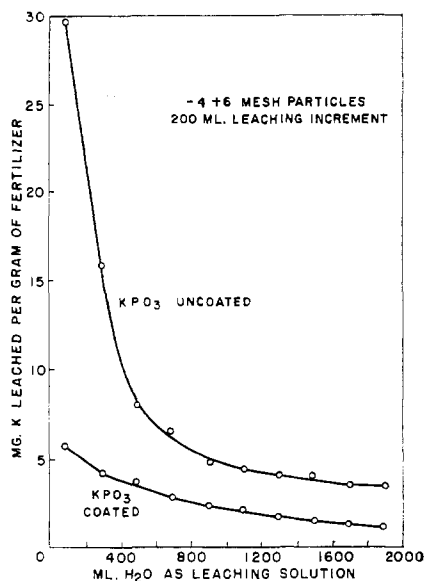


Figure 3. Dissolution of potassium from potassium metaphosphate particles with and without a coating of acrylic resin

uncoated fertilizer lost 63% of its potassium under the same conditions. Solubility curves for both uncoated 5-20-20 and 0-35-25 were very steep, indicating potassium moved out of these fertilizers quite rapidly at first, followed by a slower diffusion from the interior of the particles. The vinyl acetate coating on the pyrophosphate particles probably remained intact during the leaching period since the slightly downward sloping dissolution curve describes the loss of potassium from rather small pores or surface imperfections as it slowly diffuses from the inner matrix. If it is assumed that continued release from the uncoated and coated pyrophosphate would be 4.0 and 8.0 mg. of K per liter of leachate, then it would require about 55 more liters of water to remove all the potassium from the coated particles and 10.6 liters for the uncoated particles.

The solubility curves of coated and uncoated  $KPO_3$  particles closely resemble those of potassium-calcium pyrophosphate. Data presented in Figure 3 show that acrylic resin applied as a spray coating distinctly reduced the solubility of potassium in the early part of the leaching period. However, after four or five 200-ml. portions of water at a leaching rate of 1 liter per hour, the rate of dissolution for the uncoated material paralleled that for the coated particles. The shape of the dissolution curves after the first liter of leachate suggests that diffusion of potassium through the pores or crevices or from the edges of the fertilizer matrix is the rate limiting factor. Apparently the coating of the metaphosphate particles was not complete, since the rather slow and uniform release of potassium is

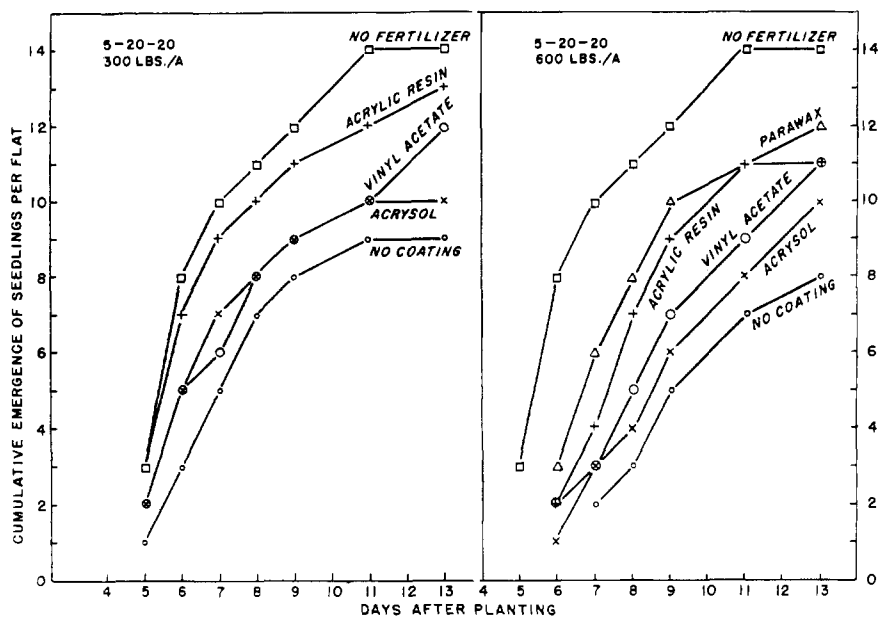


Figure 4. Emergence of wheat seedlings from a sandy soil as influenced by various coatings on fertilizer placed in contact with seed in greenhouse

indicative of an imperfect film coverage. During the leaching of 2 liters of water, the uncoated and coated particles lost 28.9 and 9.1%, respectively, of their original potassium contents. Since this fused potassium phosphate has about 60% of its potassium in a water-soluble form, an amount equivalent to about one half of this fraction was removed from the uncoated -4+6-mesh fertilizer. The coated particles, on the other hand, retained the bulk of the water-soluble potassium under similar conditions.

Detrimental effects resulting from close contact of soluble fertilizer with field crop seeds have been noted many times, particularly with large amounts of fertilizer on coarse textured soils and in periods of moisture stress (2, 4, 7). The results of a greenhouse study of the effects of contact of wheat seed and coated fertilizers on emergence are presented in Figure 4. Extremes in rate of emergence were obtained for the uncoated granular fertilizer at both rates of application and the no fertilizer treatment. For example, 7 days after planting, twice as many seedlings had emerged where no fertilizer was applied, while after 13 days, there were 56% more plants in the nonfertilized soils as compared with the treatment involving 300 pounds per acre of commercial fertilizer. A similar, but more pronounced trend was evident when the quantity of uncoated fertilizer was doubled.

Coating the 5-20-20 fertilizer significantly improved both rate of emergence and production of viable seedling in the sandy soil. However, not all the coatings studied were of equal benefit. Although there was some variation in behavior of

the individual coatings during the emergence period, they could be ranked in preventing salt injury as follows for the 300 pound per acre application: paraffin = acrylic resin > vinyl acetate > polyacrylic acid > vinyl acetate + emulsifiable polyethylene. When the fertilizer rate was doubled, the paraffin coating was again one of the most effective, while polyacrylic acid was of least benefit. However, more extensive studies are needed to study the behavior of these coatings under a variety of conditions with respect to soil moisture and texture before one coating can be recommended in preference to others.

The benefits ascribed to fertilizer coatings in the greenhouse were not evident in a subsequent field trial. Data in Table I show that oat plants grew as well when the seed was in contact with uncoated fertilizer as when coated material was used. Only in the very early stage of growth was there a visible reduction in growth with uncoated 5-20-20 fertilizer. At harvest time the number of stalks and total dry weight of plants per plot for each fertilizer treatment were rather similar. It is believed that contrasting results for the various fertilizers might have been obtained if soil moisture levels had been substantially lower, particularly at the time of germination. For example, on the day following seeding, there was 0.45 inch of precipitation, followed by 0.55 and 0.46 inch on May 7 and 10, respectively.

The effect of various coatings on the absorption of potassium by alfalfa from a granulated 5-20-20 fertilizer applied as a top-dressing is given in Table II. As early as 2 weeks after application, there was a distinct dif-

ference in the potassium content of alfalfa plants from the check area and between plots receiving coated and uncoated fertilizer. Luxury consumption was quite evident in alfalfa treated with uncoated fertilizer, while alfalfa plants receiving coated materials contained significantly less potassium. This trend continued up to first harvest on June 15 when the per cent K in alfalfa top-dressed with uncoated fertilizer was 2.89, or approximately 0.67% greater than the average composition of alfalfa treated with coated fertilizers. Accordingly these data indicate a reduction in the rate of dissolution of potassium where coatings were used.

At this same sampling date, the alfalfa which received no fertilizer was very close to the critical level of plant K for deficiency conditions. The benefit from top-dressed fertilizer, which was largely the result of added potash, was about 0.65 ton per acre of air-dry hay greater than the yield from the check plots. However, all fertilizer treatments, regardless of the presence of or kind of coating, resulted in hay yields of approximately the same value, 2.30 tons per acre.

Approximately 1 month after the first harvest, there was still a marked difference in the potassium content of alfalfa from the coated and uncoated fertilizer treatments. In contrast to the absorption trend for the initial growth period, a greater amount of potassium was taken up by plants where the coated materials had been applied. A logical explanation for this reversal is that most of the potassium from the uncoated granules had dissolved out into the soil by the middle of May. The coated fertilizers, on the other hand, as late as the first part of July were still releasing potassium as shown in Table III. Apparently potassium dissolving slowly out of fertilizer granules was more readily absorbed by alfalfa feeder roots near the soil surface than were potassium ions which had been in contact with soil minerals for over a 2-month period.

Some measure of the loss of potassium from the top-dressed fertilizer granules during alfalfa growth can be noted from data in Table III. However, since the original weight of the recovered granules was not known, and an indeterminate amount of nitrogen and phosphorus was also probably leached from the fertilizer particles, the values for per cent K will be necessarily high when compared with the original composition. Dissolution of potassium from the uncoated granules proceeded very rapidly. Within a week after application, during which time precipitation amounted to 1.35 inches, these fertilizer residues contained very little potassium. During the same period, losses from the coated particles were minor, and even by May 19,

**Table I. Effect of Coated Fertilizer on Growth, Stand, and Dry Matter Production of Oats Seeded in Contact with Fertilizer**

Coating on Granular 5-20-20 Fertilizer	Height of Plants, Inches <sup>a</sup>			Stand and Dry Wt. <sup>b</sup> per 24 Feet of Row	
	May 31	June 15	July 6	No. of stalks	Grams
No fertilizer	5.0	17.0	28.0	107	445
No coating	6.0	21.0	34.5	125	565
Paraffin	7.0	23.5	35.0	137	555
Acrylic resin	7.0	23.5	36.5	127	575
Vinyl acetate	7.0	21.5	36.0	133	615
Acrylic resin + paraffin	7.5	21.5	34.5	123	560
Vinyl acetate + paraffin	7.5	22.0	35.0	129	575
Vinyl acetate + Epolene	7.0	22.0	36.0	120	580

<sup>a</sup> Average of 6 measurements taken in two replications.

<sup>b</sup> Values for stand and dry weight taken on July 6 and represent an average for 6 rows.

**Table II. Effect of Various Coatings on Absorption of Potassium by Alfalfa from a Granulated 5-20-20 Fertilizer**

Fertilizer Treatment <sup>a</sup>	Per Cent Potassium in Alfalfa Tissue				
	May 8	May 18	May 30	June 15 <sup>b</sup>	July 15
No fertilizer	2.15	1.98	1.64	1.30	1.65
No coating	3.30	3.14	3.07	2.89	2.05
Paraffin	2.75	2.50	2.62	2.24	2.45
Acrylic resin	2.55	2.56	2.56	2.30	2.28
Vinyl acetate	2.50	2.55	2.60	2.15	2.40
Acrylic resin + paraffin	2.45	2.62	2.59	2.07	2.36
Vinyl acetate + paraffin	2.48	2.62	2.46	2.20	2.45
Vinyl acetate + Epolene	2.75	2.60	2.80	2.14	2.30
L.S.D. 5% level	0.31	0.37	0.28	0.24	0.25

<sup>a</sup> 1200 pounds of 5-20-20 fertilizer per acre top-dressed on April 24.

<sup>b</sup> First cutting taken on June 15.

**Table III. Potassium Content of Fertilizer Residues Recovered from Soil Surface of an Established Stand of Alfalfa Top-Dressed with Coated and Uncoated Fertilizers**

Fertilizer Treatment	Per Cent Potassium in Recovered Fertilizer Granules <sup>a</sup>			
	May 1	May 19	June 2	July 5
No coating	2.48	0.45	0.22	...
Paraffin	13.64	10.80	7.65	4.04
Acrylic resin	13.50	9.65	6.14	4.60
Vinyl acetate	14.15	11.10	8.30	4.55
Acrylic resin + paraffin	14.70	10.80	7.78	5.22
Vinyl acetate + paraffin	13.96	11.45	7.52	4.16
Vinyl acetate + Epolene	14.42	11.00	8.15	4.28

<sup>a</sup> Original fertilizer contained 16.67% K; approximately 35 granules recovered at each date except for noncoated fertilizer on July 5 when granules had disintegrated.

when a total of 2.75 inches of rain had fallen on 7 out of 26 days, the residues contained appreciable potassium. By July 5, precipitation from the date of top-dressing amounted to 7.15 inches and there was still a distinct difference between the potassium content of the coated and uncoated fertilizer residues.

Many problems are involved in the development of suitable coatings for fertilizers. Materials used to encase granules may either be slightly permeable to water and dissolved salts, allowing slow dissolution in the surrounding soil, or the coating may be essentially water impermeable. In the latter case, a breakdown of the coating must occur as a result of chemical or biological reactions

or there must be weak or thin spots in the covering of some or all of the fertilizer particles.

Well developed granules of spherical form are rather easy to cover with a relatively thin coating, which may not amount to more than 1 to 5% of the original granule weight. Angular or irregular-shaped particles are much more difficult to coat uniformly since the rough surfaces and corners or edges result in weak surface films or coverings. In such instances, the development of a more spherical pellet by tumbling the fertilizer particles with an inert substance and binder may be more satisfactory. This technique has been used in developing pelleted vegetable

seed (1, 77). However, the inert coating will necessarily make up a greater proportion of the pellet weight and thereby will lower the analysis of the original fertilizer.

Optical examinations of fertilizer particles often show extremely irregular surfaces with evidence of pores, crevices, and many small, exposed crystal forms. The nature of this surface including the aggregation of crystals in mixed fertilizers and its polarity must be studied before adequate coatings can be developed. It is more difficult to prepare coatings for granular, single salt fertilizers such as potassium chloride, ammonium nitrate, or urea than for granules involving mixed salt systems. For instance, a very small imperfection in the coating on a granule of KCl allows the potassium to diffuse away rapidly in water or moist soil. With an

aggregation of small crystals in a matrix which contains partially soluble salts such as calcium phosphates, the dissolution properties are quite different.

Experimental work indicates that fertilizers can be coated satisfactorily to change the rate at which they dissolve in moist soils. When large quantities of fertilizer are used under farming conditions, this reduction will help to alleviate seed-fertilizer contact injury, reduce leaching losses of fertilizer nutrients in sandy soils, and minimize luxury absorption of potassium by crops.

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## AMMONIA LOSSES FROM SOILS

# Gaseous Loss of Ammonia from Surface-Applied Nitrogenous Fertilizers

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This work was done to determine if ammonia was lost from urea that was surface-applied to turf or bare soil even in the acid range, or from urea or ammoniates applied to turf which had been surface limed. Volatile loss of ammonia was measured by direct absorption and by crop response. Losses following application of 100 pounds of urea nitrogen averaged 29% for unlimed turf and 39% for limed turf. Respective losses from  $(\text{NH}_4)_2\text{SO}_4$  were 0.4 and 19.7%; and from  $\text{NH}_4\text{NO}_3$ , 0.3 and 3.4%. Losses from urea surface-applied to bare sandy soil averaged 25% in 7 days, while loss from  $\text{NH}_4\text{NO}_3$  was negligible. Greenhouse cropping of field-treated soil supported the general trend in data obtained by direct measurement. Losses were greater from large pellets than from fine. Dusting with  $\text{CuSO}_4$  or gypsum did not retard volatile loss. For maximum efficiency under certain conditions, urea, ammoniates, and lime should be incorporated if practical.

**G**ASEOUS LOSS of nitrogen from the soil following application of nitrogenous materials is not a new concept; but only within the last few years has it been recognized to be sufficiently large to justify intensive study. Tests of efficiency of applied nitrogen generally show maximum plant recoveries of between 50 and 75%. Even when leaching losses and residual nitrogen in the soil are considered, there still is a significant amount of nitrogen which cannot be accounted for and must be assumed lost from the soil in gaseous form.

The work of Loewenstein *et al.* (5) and Hiltbold and Adams (4) shows very definitely that nitrogen, if not kept in the plant utilization cycle, rapidly disappears in gaseous form, except for a fraction held in the soil at equilibrium with the

particular type of soil and environment. That major losses as  $\text{N}_2$  and  $\text{N}_2\text{O}$  gases occur was shown by the work of Hauck and Melsted using nitrogen-15 (3). Thus, to conserve nitrogen, it must be kept in the plant uptake cycle as far as practicable.

The volatile loss of ammonia following surface or shallow application of ammoniacal materials or urea to slightly acid or calcareous soils has been demonstrated by Martin and Chapman (6) and Earnst and Massey (2). The latter workers also showed the effect of soil moisture in increasing ammonia loss. The factors which have been largely overlooked are the limitations of ammonia-absorbing mechanisms in well developed sods and in light sandy soils in the moderate to strong acid range.

A second major factor which apparently has been ignored is the massive effect of surface liming of grass pastures or other turfs on the pH of the top fraction of an inch of soil, although the soil immediately below may still be acid. The potential loss of ammonia under such conditions may approach that from a naturally calcareous soil.

The primary purpose of this report is to present the latest results of continuing studies on volatile loss of ammonia from turf or bare soils. The approach to the problem of evaluation of volatile loss of nitrogen as ammonia is along two lines: the direct measurement of ammonia as it volatilizes from the soil, and the indirect estimate of this loss by differential crop response to the nitrogen remaining in the soil. The first method became