

Acknowledgment

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UREAFORMS

Soluble Fraction of Ureaforms—Nitrification, Leaching, and Burning Properties

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The large water-insoluble portion of ureaforms is responsible for their slow nitrogen release properties. However, the lower methyleneureas present are somewhat soluble in water. In the activity index procedure, 25 to 35% of the ureaform nitrogen dissolves. Such solubility, under the conditions of this procedure, does not justify attributing properties of quick availability, rapid leaching, and burning to the water-soluble fraction of ureaforms. Over 90% of the nitrogen in ureaform is combined urea nitrogen. The chemical combination of urea, even in the lowest condensates with formaldehyde, results in decreased rates of nitrification and of leaching, as well as in greatly reduced burning properties.

THE large water-insoluble portion of ureaforms is responsible for their useful slow release properties in comparison with the rapid release from soluble fertilizer materials. In the continuous series of methyleneurea polymers which make up a ureaform, the lowest polymers are the more soluble in water (6). The lowest member of this series, methylenediurea ($\text{NH}_2\text{CONHCH}_2\text{NHCONH}_2$), is 2.5% soluble in water at 25° C.; dimethylenetriurea, the next member, is only 0.1% soluble in water at 25° C.

The activity index procedure, which offers the simplest direct characterization of ureaforms, involves treatment of a finely ground 1-gram sample with 250 ml. of water at room temperature. Under these conditions, 25 to 35% of the ureaform nitrogen dissolves; the widespread use of the activity index has led to characterization of ureaforms as about "one-third water-soluble." Solubilities under less drastic conditions are of a lower order, as indicated by the values stated in the first paragraph. This limited solubility has led to association of the agronomic properties of the low molecular weight portion of ureaforms

with the almost immediate availability, leaching tendencies, and burning properties characteristic of soluble nitrogen sources such as urea and ammonium nitrate (7). Such properties would not be expected, since over 90% of the nitrogen in ureaforms is combined urea nitrogen (commercial ureaforms may contain 6 to 8% free urea) (6). It was of interest, therefore, to determine rates of nitrification and of leaching as well as to consider the burning properties of the soluble fraction of ureaforms and of the lowest condensates of urea with formaldehyde.

Materials

Methylenediurea. This compound was prepared by a modification of the method of Kadowaki (8). Urea (12 moles) and formaldehyde (1.77 moles) yielded 133 grams of crude product, m.p. 185° to 250° C. This product was slurred with 3 liters of hot methanol, cooled to 40° C., and filtered warm. The filtrate was held at 0° C. for 16 hours and the crystalline product filtered off, m.p. 213° C. (Because of the heat sensitivity of methylenediurea and dimethylenetriurea, the sample had to be dropped onto a melting point block

heated to within about 5° C. of the final melting point observed to get complete melting. The melting points quoted were taken in this manner.) The extraction procedure was repeated using fresh methanol and re-using the filtrates until the melting point of the product began to increase. In this way, 70% of the crude product was isolated as sharp melting crystals (m.p. 212–214° C.). The material insoluble in methanol melted at about 265° C.

A composite sample of the recrystallized product was analyzed.

ANALYSIS. Calcd. for $\text{C}_3\text{H}_5\text{N}_4\text{O}_2$: N, 42.4%; CH_2O , 22.7%. Found: N, 41.6%; CH_2O , 22.2%.

SOLUBILITY IN WATER. 2.5 grams per 100 ml. at 25° C.; 7.0 grams per 100 ml. at 50° C.

SOLUBILITY IN METHANOL. 0.03 gram per 100 ml. at 25° C.; 0.35 gram per 100 ml. at 60° C.

Dimethylenetriurea. This compound was prepared by the method of Winsor and Long (14). Dimethylolurea (1.0 mole) and urea (4.0 moles) yielded 62 grams of product, m.p. 275–280° C. (with decomposition). The crude material (50 grams) was recrystallized by slurring in 2 liters of water at 70° C., filtering hot, and storing the filtrate for 16 hours at 0° C. The crystalline

product was separated, washed with ice water, and dried at 30° to 40° C. Yield: 26 grams, m.p. 270° C. (with decomposition).

ANALYSIS. Calcd. for $C_5H_{12}N_6O_3$: N, 41.2%; CH_2O , 29.4%. Found: N, 40.0%; CH_2O , 29.5%.

SOLUBILITY IN WATER. ca. 0.1 gram per 100 ml. at 25° C.; 0.6 gram per 100 ml. at 50° C.; 4.4 grams per 100 ml. at 100° C.

Cold Water-Soluble Fraction of Ureaform. This fraction was recovered from the filtrate after extraction of the ureaform in the manner prescribed by the A.O.A.C. activity index method (7). The procedure described previously (6) was adapted to a much larger scale preparation. Five pounds of Hercules Nitroform, ground to pass a 35-mesh screen, was slurried with 110 gallons of water at 25° C. for 5 hours and filtered; the filtration required about 6 hours. The filtrate was evaporated in a stream of air at 30° C., which required 110 hours. The solid product weighed 669.5 grams, which amounted to 29.5% of the original ureaform.

ANALYSIS. Nitrogen, 39.3%; total CH_2O , 18.2%; free urea (urease), 23.8%; moisture, 4.2%; sulfate ash, 3.1%.

Commercial Ureaform	Nitroform, ^a %
Total nitrogen	38.7
Water-insoluble nitrogen (WIN)	25.8
Water-soluble nitrogen (WSN)	12.9
Hot water-insoluble nitrogen (HWIN)	12.5
Activity index (AI)	52
Free urea (by urease)	8.6

^a Hercules Powder Co.

AMMONIUM SULFATE. (Mallinckrodt, A. R.), 21.20% nitrogen.

UREA. (Mallinckrodt, U.S.P.), 46.65% nitrogen.

SOIL. The soil used for both nitrification and leaching was a silt loam taken from pasture land near Elkton, Md. The pH was adjusted to 6.9 to 7.1 with calcium oxide before use and buffered with calcium carbonate (3). (The pH of the soil before adjustment was 5.5.)

Methods

Nitrification Rates. The procedure of Clark and coworkers (3) was used as described previously (6).

Activity Index. The official A.O.A.C. Activity Index procedure (7) was used. Samples for both cold and hot water-solubility tests were crushed to pass a U.S. No. 40 sieve (35-mesh).

Leaching Experiments. PROCEDURE 1. Standard soil, 75 grams, was placed in an 8-inch column (3.35-mm. diameter, 8.81 cm.² or 0.01-sq. ft. area) fitted with a glass filter paper. The soil was tapped to settle it, and 25 ml. of distilled water was added and allowed to stand for 30 minutes for complete penetration and wetting. A fertilizer sample containing 25 mg. of total nitrogen was mixed with an additional 25 grams of soil which was then added to the column. The soil was covered with a 1/4-inch layer of glass wool,

and 40 ml. of distilled water was added. Gentle suction from a water aspirator was applied to draw 35 ml. of filtrate through the column in 15 minutes (35 ml. corresponds to 1.6 inches of water). Total nitrogen in the filtrate was determined by the Kjeldahl method. (When nitrate was present, the chromous chloride reduction modification of the Kjeldahl method was used.) The per cent nitrogen left in the soil after leaching (shown as the ordinate on Figure 3) was determined by subtraction of the total nitrogen in the filtrate (corrected for a small amount leached from the soil) from the nitrogen added in the fertilizer materials. Data by Procedure 1 for Nitroform, cold water-soluble fraction of Nitroform, ammonium sulfate, urea, and potassium nitrate are shown in Figure 3.

PROCEDURE 2. As in Procedure 1, 75 grams of soil was placed in the column, but 25 grams of soil with a fertilizer sample containing 50 mg. of water soluble nitrogen was added before wetting. The column was tapped, 35 ml. of distilled water was added and allowed to stand for 30 minutes. Fifty milliliters of distilled water was added, and 50 ml. of filtrate was drawn through the soil in 20 minutes (50 ml. corresponds to 2.3 inches of water). Total nitrogen was determined on the filtrate by the Kjeldahl method. Data for Nitroform and ammonium sulfate with the use of Procedure 2 are shown in Figure 3.

Turf Experiments. In the experiments carried out at the University of Rhode Island in 1956 by Mruk (under the direction of DeFrance) (77), Nitroform, Uramite, and Borden's 38 were applied at rates of 4, 8, 12, 16, and 20 pounds of nitrogen per 1000 sq. ft. to establish turf. Each concentration was applied in duplicate for each material on plots 10 feet square. The grass used was Kingston Mixture, containing 35% Kentucky Blue Grass, 15% Astoria Colonial Bent, and 50% Chewing Red Fescue. Application was made on July 3 at a temperature of 88° F. under fair, dry conditions. Observations were made during the first week and at intervals thereafter.

Results and Discussion

Nitrification Rates. Earlier workers (7, 10, 13) have found methylenediurea and dimethylenetriurea to show nitrification rates scarcely distinguishable from that of urea. Similarly, it was reported earlier (6) that the cold water-soluble fraction of a commercial ureaform nitrified to the extent of about 80% in three weeks.

In an attempt to determine whether the lower methyleneureas can be distinguished from urea in nitrification, conversions to nitrate were determined at shorter intervals during the first 3 weeks of incubation. In one series, shown on Figure 1, the reference soil was taken from dry storage, water and the nitrogen fertilizer were added, and the usual incubation was begun. Negligible conversions to nitrate oc-

curred during the first 8 days. Then rapid nitrification began. Urea reached an 80% conversion in 3 days. The rate for methylenediurea was clearly slower, while that for dimethylenetriurea was slower still. A ureaform cold water-soluble fraction (which contained 24% free urea) was intermediate between the latter two.

Since an induction period was observed for ammonium sulfate and urea as well as for the methyleneureas, it was attributed to lag in buildup of the population of nitrifying bacteria. To eliminate this factor, water was added to the standard soil and incubated at 30° C. for 10 days, and then the nitrogen fertilizers were added. As shown on Figure 2, the induction period was almost eliminated for urea and ammonium sulfate, while methylenediurea and dimethylenetriurea still required 8 to 9 days to begin production of significant amounts of nitrate. The ureaform cold water-soluble fraction, with its 24% free urea, began to nitrify immediately but reached its intermediate position between the two methyleneureas in 2 to 3 weeks. The decrease in nitrate values so often seen in studies of this type was rather pronounced in the third week of this experiment and illustrates the variations which may be encountered.

During the induction period shown on Figure 1, while nitrifying bacteria were building up, other soil organisms were

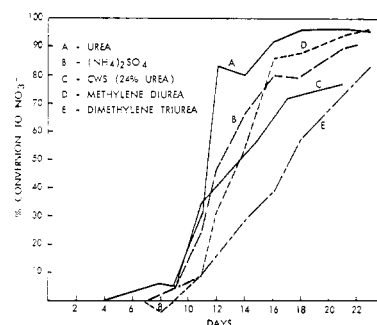


Figure 1. Nitrification of soluble components of ureaform

Without pre-incubation of soil

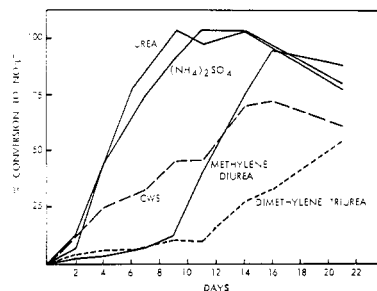


Figure 2. Nitrification of soluble components of ureaform

After pre-incubation of soil

evidently attacking the methyleneureas to produce ammonia, so that production of nitrate began at about the same time from the methyleneureas and from urea and ammonium sulfate. When the nitrogen materials were added to the incubated soil (conditions corresponding more closely to fertilization of turf grass), the onset of nitrification was delayed by the slow rate of the ammonification reaction. The rate of nitrification of methyleneureas under active growing conditions thus appears to be determined by the rate of ammonification, with the rate of this reaction decreasing with increasing molecular weight and decreasing solubility. (In this paper, the term nitrification has been used to cover the combined processes of ammonification and oxidation to nitrate; strictly speaking, it applies only to the latter reaction.)

The rates of nitrification of the lower methyleneureas are, thus, clearly slower than that of urea; there appears to be a delay of about a week before nitrification of the nonurea, soluble ureaform components begins, and the subsequent rate is a function of molecular weight. While the soluble portion of a ureaform is converted largely to nitrate in 3 or 4 weeks, the observed rates would make this fraction less likely to cause an undesirable flush of growth (12) than a similar amount of urea or other soluble fertilizer.

Leaching Properties. The insolubility of the major portion of ureaform in water makes it resistant to leaching. Since the water-soluble portion dissolves in a large excess of water, the resistance of this fraction to leaching and its effect on the leachability of commercial ureaforms under use conditions is of interest.

Figure 3 shows the results of leaching experiments on a commercial ureaform, its cold water-soluble fraction, ammonium sulfate, urea, and potassium nitrate in columns with a standard soil. Under arbitrarily selected conditions which gave 90% leaching of the nitrogen of urea and 100% leaching of the nitrogen of potassium nitrate, the commercial granular ureaform still retained about 90% of its nitrogen. The granular form was somewhat more resistant to leaching than the finely ground (35-mesh) material, as would be expected (6). The cold water-soluble fraction was much more readily leached than the total ureaform, but still not so readily leached as urea, which in turn moved out of the soil at a detectably slower rate than the nitrate, in agreement with more comprehensive studies (2).

The results with ammonium sulfate are interesting in that they show the well-

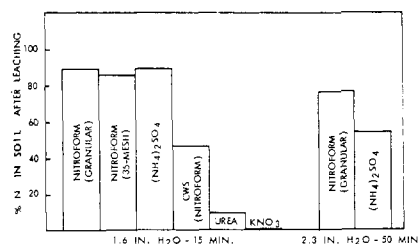


Figure 3. Comparison of ureaform leaching with that of soluble nitrogen fertilizers

recognized binding of the ammonium ion by soil components. As shown by the nitrification experiments in this same soil, the ammonium ion, although resistant to leaching, was still readily available for oxidation to nitrate by soil bacteria. With a somewhat more drastic leaching method (Procedure 2), the retention of ureaform nitrogen was reduced to 76%, but retention of ammonium sulfate was reduced to a greater extent, dropping to a value of 54%. Retention of the nitrogen of ureaform is due to low solubility; the observed retention of ammonium nitrogen appears to depend on the cation exchange capacity of the soil.

Analogous to the slower rate of nitrification, the leaching tendencies of the cold water-soluble fraction, as well, of course, as those of the total ureaform, are markedly decreased by the chemical combination of the urea in the methyleneureas.

Burning Properties. Relatively large amounts of ureaform fertilizers can be applied to grass without the danger of burning which may occur if soluble nitrogen fertilizers are not applied carefully under ideal conditions. Thus, DeFrance found that highest quality turf could be obtained from a single application of 8 pounds of ureaform nitrogen per 1000 sq. ft. (5). This rate was safe even when applied in the seedbed at the time of seeding (12). A direct comparison has also shown that methylenediurea does not burn at concentrations at which urea does damage (9).

An impressive demonstration of the lack of burning with ureaforms was also obtained by Mruk (17) who applied 4, 8, 12, 16, and 20 pounds of ureaform nitrogen to well established turf in July and found no evidence of burning over the first week. However, very lush growth was obtained at the high rates, and the bent grass component of the mixture used developed brown patch after one month. Thus, much higher ureaform nitrogen rates can be applied without burning than are warranted in sound turf management.

Effect on Turf Management. As shown in the information presented, the soluble fraction does not lead to serious problems in leaching or burning when ureaforms are used on turfgrass in reasonable amounts. Its relatively rapid rate of release, although slower than for materials such as urea or ammonium nitrate, still leads to a desirably quick response. However, the rate of release of the soluble fraction is a major factor in leading to the limiting of recommendations for single applications of ureaforms (e.g., Nitroform) to 4 to 6 pounds of nitrogen per thousand square feet. This means that a commercial ureaform is best applied two or more times per year, depending on the type of grass and climatic conditions. Soluble fertilizers must be applied much more frequently to get the same results and to avoid damage to turf.

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