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CONTROLLED-RELEASE FERTILISERS

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Abstract

Control of the rate of nutrient release from fertilisers has been cited as a potential means for improving the efficiency of nutrient uptake for minimising losses of nutrient through various mechanisms, for cutting the number of fertiliser applications, and for avoiding contact damage to vegetation. These potential advantages are realisable in various degrees through nitrogen fertilisers of two general types-those inherently slow in dissolving and those coated with a barrier film that slows their dissolution. The first type is illustrated by ureaform, isobutylidene diurea (IBDU), and crotonylidene diurea (CDU)--the second by sulphur-coated urea (an experimental product at TVA) and commercial products in which the coating is a copolymer of dicyclopentadiene with a glycerol ester (trade name, Osmocote). Aside from their specialty uses on lawns, golf courses, and the like, controlled-release nitrogen fertilisers are likely to prove practical for some field crops in some situations, particularly for high-value crops in areas where labour is costly. Prospects are remote for improving phosphate and potassium fertilisers through controlled-release.

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CONTROLLED-RELEASE FERTILISERS

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Fertilisers that release plant nutrients slowly throughout the growing season or even several growing seasons continue to attract the attention of technologists and agronomists. Potential advantages claimed for controlled-release fertilisers are increased efficiency of uptake by plants; minimization of losses by leaching, fixation, or decomposition; reduction in application costs through reduction in number of applications; elimination of luxury consumption; and avoidance of burning of vegetation or damage to seedlings. This is an impressive list of potential advantages.

A substantial amount of research and development has been done on controlled-release fertilisers in recent years. A book (1) on controlled-release fertilisers lists 95 U. S. patents in the period 1952 to 1968. One of these patents described a quick-release fertiliser that could be applied to lawns in large quantities without injury to grass. The other 94 pertained to slow-release fertilisers, mainly nitrogenous.

The term "controlled-release fertilisers," as used in the following discussion, refers to fertilisers that for any reason release their nutrient content over an extended period. Even a simple choice among materials inherently slow to dissolve is viewed as a measure of control.

Controlled-Release Phosphate Fertilisers

Numerous controlled-release phosphorus compounds have been tested, and some are in use. Prominent among them are ground phosphate rock, calcined aluminum phosphate ore, basic slag, defluorinated phosphate rock (tricalcium phosphate), fused calcium magnesium phosphate, Rhenania phosphate, bone meal, dicalcium phosphate, magnesium ammonium phosphate, calcium metaphosphate, and potassium metaphosphate. (The so-called metaphosphates are more properly designated as polyphosphates.)

Ground phosphate rock containing about 1.8 million metric tons of P_2O_5 was applied to the soil in 1969/70 (2). This probably represented some 6 million tons of rock. About half was used in the U.S.S.R., and the remainder was widely distributed among many countries.

The effectiveness of ground phosphate rock varies widely with variation in its reactivity. A good indication of reactivity is solubility in neutral ammonium citrate. The effectiveness of the most reactive rocks, such as those from Gafsa and North Carolina, may approach the effectiveness of water-soluble phosphates on some soils and with certain crops. The least reactive rocks, such as igneous apatite and Udaipur (India) rock, are quite ineffective on all soils. Effectiveness depends on soil pH and is greatest on acid soils; on high-pH soils, even highly reactive rocks are quite ineffective.

Basic slag containing about 1.3 million metric tons of P_2O_5 was applied in 1969/70 (2). Gross weight of the slag probably was about 8 million tons. Basic slag is generally regarded as quite effective except

on calcareous soils. It is also valued for its content of the secondary nutrients calcium and magnesium and for its micronutrient content.

Calcined aluminum phosphate ore is used mainly in France. It tends to be more effective on high-pH than acid soils. The main source of aluminum phosphate ore is Senegal. However, several other occurrences are known, and some is now being mined on Christmas Island. Its effectiveness depends on the calcination temperature and on fine grinding, and may be indicated by solubility in neutral or alkaline ammonium citrate. It is more soluble in the alkaline reagent.

Straight decalcium phosphate is manufactured for fertiliser use in relatively small quantities in France and Belgium. However, substantial amounts are present in nitrophosphates and ammoniated superphosphates. It is fully soluble in neutral ammonium citrate and is generally considered to be an effective fertiliser, particularly on acid soils when broadcast in fine particle size and incorporated with the soil.

Fused calcium magnesium phosphate is manufactured mainly in Japan. It is effective on acid soils when finely ground. It supplies magnesium and silica, which may be quite helpful in some soil-crop combinations.

Most of the insoluble or slightly soluble phosphate materials are used either because they are less expensive than soluble phosphates or because they supply other elements. Very seldom if ever can any agronomic superiority be attributed to their slow release of nutrient in the soil. In fact, the slightly soluble materials often give inferior results,

particularly in the first year of application. However, some of them are valued for specialty uses because they may be safely placed in contact with seeds or roots, whereas soluble phosphates might damage seedlings or roots in some situations.

Soluble phosphates react rapidly with the soil to form relatively insoluble products (3). So even fully soluble phosphates become slow-release fertilisers in the soil. The main effort has been to find ways to increase the release rate. When soluble phosphates are applied in granular form, the reaction with the soil is delayed, and pockets of relatively soluble phosphate may persist at the granule sites for several weeks. Thus, good results usually are obtained by placement of soluble granular phosphate fertilisers near the seed.

Even with the best conditions, plants seldom take up more than 10 to 20% of the fertiliser phosphorus in the year of application. The remainder is converted to slightly soluble soil reaction products. Raw phosphate rock may remain largely in its original form. The residual phosphate gradually becomes available, and over a period of many years of continued fertiliser use, crops may take up as much as 75% of the applied phosphorus. This situation is satisfactory on farms with a long history of fertiliser use where the phosphorus content has been built up to the point that annual applications merely maintain the fertility of the soil.

In developing countries where soils are often poor in phosphorus, there is a need for a phosphorus fertiliser that is highly effective in the year of application. The available information indicates that this need

will not be met by slow- or controlled-release materials. On the contrary, the best results on poor soils have been obtained with the most soluble phosphates and with proper placement.

Controlled-Release Nitrogen Fertilisers

Slightly Soluble Materials

One group of controlled-release nitrogen fertilisers comprises chemical compounds that are only slightly soluble. It may be noted that the rate of release of nutrient from most of these slightly soluble compounds is not directly related to water solubility. Instead, the release rate is related to microbiological attack which converts the nitrogen to forms that can be utilized by plants. However, the rate of attack is related to the rate of solution, which depends, in turn, on solubility, particle size, and other factors.

Urea-aldehyde compounds are the principal representatives of this group that are produced commercially. Isobutylidene diurea (IBDU) is produced in Japan through the reaction of urea with isobutyraldehyde in 2:1 mole ratio. When pure, it contains 32.18% N. Hamamoto (4) reported methods for its preparation and discussed its usefulness as a fertiliser. Crotonylidene diurea (CDU) is produced in Japan and Germany through the reaction of urea with crotonaldehyde. It can also be produced from acetaldehyde and urea. The pure compound contains about 32% N.

Ando (5) reported a Japanese consumption of 1800 tons of N as IBDU and 1400 tons as CDU in 1968--a total of 3200 tons of N or 10,000 tons of the two slow-release materials. This was more than twice the 1966 use. The materials were used to prepare compound fertilisers in which about half of the nitrogen was in slow-release form.

Hamamoto (4) discussed agronomic studies made in Japan with IBDU and other slow-acting nitrogen materials. The release rate from these slightly soluble materials is a function of the particle size. Under Japanese conditions, use of these materials was often advantageous in improving yields and in saving labor by decreasing the number of applications. Hamamoto stated that the cost of IBDU to farmers was over twice that of conventional nitrogen fertilisers per unit of nitrogen. Compound fertilisers of 1:1:1 ratio with half of the nitrogen supplied as IBDU cost about 20% more than conventional fertilisers. For this reason they were used mainly on vegetables and cash crops and not so much on grains.

Perhaps the cost could be lowered by manufacture on a larger scale. On the other hand, the aldehydes used in making IBDU and CDU are byproducts from the manufacture of other chemicals; the aldehydes might cost more if they were manufactured specifically for fertiliser materials.

Statistics are not readily available on the production of CDU or other slow-release nitrogen materials in Germany. A product called Floranid receives 90% of its nitrogen from CDU and 10% from calcium nitrate.

Urea-formaldehyde reaction products, usually called "ureaform," are produced by about six manufacturers in the United States. Unlike IBDU and CDU, ureaform is not a definite chemical compound. It contains

methylene ureas of different chain lengths; the solubility increases with decrease in chain length. It usually contains about 38% N.

Perhaps the most useful component of ureaform as a slow-release nitrogen material is trimethylene tetraurea; shorter chain lengths are too rapidly decomposed, and longer chains are highly resistant to decomposition. Unfortunately it is very difficult to produce commercially a pure trimethylene tetraurea; ureaform contains both shorter and longer chains.

A typical ureaform may contain 50% of its nitrogen in forms that are soluble in cold water (25°C). The quality of the remaining 70% is judged by the percentage that is soluble in hot (boiling) water as determined by prescribed analytical procedures. At least 40% of the nitrogen insoluble in cold water should be soluble in hot water for acceptable agronomic response; typical values are 50 to 55%.

The consumption of ureaform in the United States is approximately 50,000 tons per year. Most of the production goes into mixed fertiliser for specialty uses, such as for lawns, flower gardens, and golf courses. The wholesale price of ureaform per unit of nitrogen is about three times that of urea, ammonium nitrate, or ammonium sulfate. Solutions containing urea and formaldehyde are marketed for use in compound fertiliser formulations. Formation of ureaform occurs during mixing, granulation, and drying.

In TVA's tests of many other organic nitrogen-containing compounds as fertilisers, some proved readily available, some slowly available, some inert, and some toxic. Among those that showed promise as slow-release

fertilisers were oxamide, glycouril, cyanuric acid, ammeline, and ammelide. For lack of a practical process, none of these materials has been manufactured commercially for fertiliser use.

It was recently reported that guanylurea phosphate (GUP) will be manufactured as a fertiliser material in Japan. The compound when pure contains about 28% N and 35% P_2O_5. Under some circumstances the compound is toxic; under others, including application to paddy rice, it is said to be an effective slow-release fertiliser which minimizes losses by leaching and decomposition. GUP is quite soluble in water, but it is adsorbed or fixed by the soil. Its nitrogen content becomes available as the compound is decomposed by microbiological attack.

Coated Soluble Materials

A wide range of materials and techniques have been explored with the object of making controlled-release fertilisers by coating soluble fertiliser materials with plastic films, resins, waxes, asphaltic materials, or other barriers. The only known commercial production of coated controlled-release fertiliser utilizes a process developed by Archer Daniels Midland Company (ADM). The main component of the coating is a coplymer of dicyclopentadiene with a glycerol ester (1). Applied in several layers that vary in composition, the coating releases fertiliser solution by osmotic exchange with moisture from the soil. The coated granular fertiliser was manufactured by ADM under the trade name Osmocote starting in 1964. It now is produced and marketed by Sierra Chemical Company under exclusive license from ADM. Three grades of Osmocote are available: 14-14-14, 18-9-9, and

36-0-0. The nitrogen in the first two grades is supplied by ammonium nitrate and ammonium phosphate; the third grade is coated urea. The weight of the coating ranges from 10 to 15% of the gross weight.

Osmocote products are recommended for turf, floriculture, nursery stock, and high-value row crops. The retail price was reported to be about $0.55 per kilogram in 1965.

Sulfur-coated urea (SCU) is a controlled-release material that has been under development by TVA for 10 years. Sulfur was selected as the coating material on the basis of economy and efficiency after several coating materials were tried. Urea was selected as the material to be coated because of its high nitrogen content, low cost, and commercial availability.

Initial studies indicated that sulfur alone was not adequately resistant to moisture penetration. The discovery that an oily wax sealant was required with the sulfur provided the breakthrough to a successful coating. The wax was subject to microbial attack in the soil, however, with deterioration of its sealing properties. Need for addition of a microbicide was evident. Coal tar, in the proportion of 0.2%, proved effective and economical.

In early laboratory work, 2- to 15-pound batches of urea were coated in small drums. The development then was shifted to a small continuous pilot plant with a production rate of about 300 pounds per hour. The process is now being developed further in a large pilot plant with a capacity of about 1 ton per hour.

A schematic flow diagram of the pilot plant is shown in Figure 1. Granular urea is preheated in the first rotating drum to 80°C with electric radiant heaters to prevent the sulfur from freezing too rapidly on the granules. The molten sulfur is air-atomized and sprayed onto the rolling bed of granules in the second drum. Wax and coal tar are applied in the third drum. The coated granules are then cooled in a fluidized bed cooler, and a powdery conditioner is applied in a fourth drum to eliminate the tacky condition of the wax.

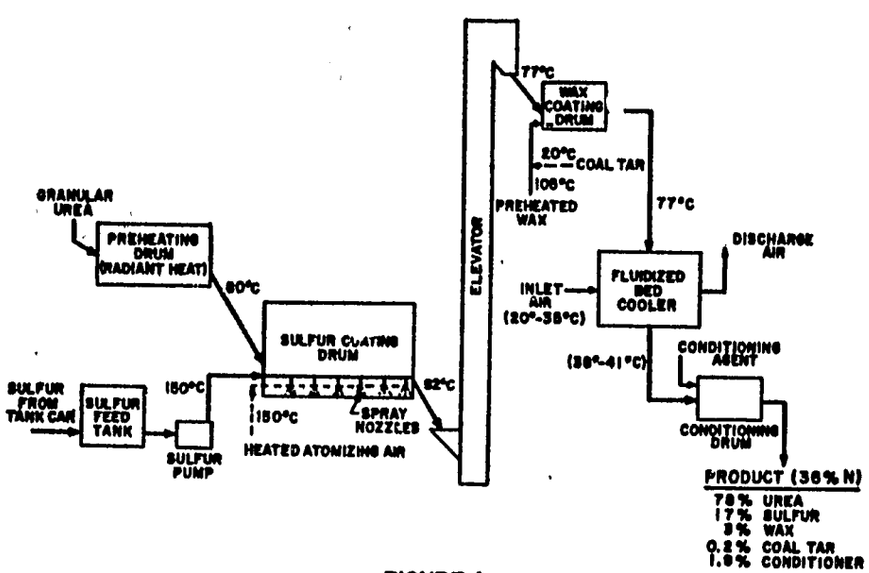

FIGURE I
FLOW DIAGRAM FOR SULFUR-COATED UREA PILOT PLANT

Most of the work was done with commercial granular urea (1.7 to 3.3 mm) produced by the spray-drum granulation process. Some tests were made with prilled urea, but its smaller particle size results in greater surface area per unit weight of urea; this greater surface requires a coating that is higher in percentage by weight of the product for a given coating thickness. For this reason, large, well-rounded granules are preferred for coating.

One cause of the long period required for development of the coating is the time required inherently for agronomic testing of the experimental products. Another cause is the large number of operating variables that affect the quality of the coating. Fourteen variables, some interacting, that affect coating quality have been identified. However, in spite of the large number of variables, they all can be controlled fairly easily to give a consistently uniform product. The difficulty is in finding the optimum combination of variables.

A typical pilot-plant product with a coating weight of about 17% had a dissolution rate of 12 to 18% in the first 7 days and 0.4 to 0.6% per day for the next 7 days. These dissolution rates were determined in the laboratory by immersion in water at 38°C. The higher initial rate of dissolution results from the presence of some granules that are coated imperfectly when they pass under the spray nozzles in the drum. These granules dissolve in a short time when a sample is placed in water. The remaining granules that are well coated have an average daily dissolution rate that is relatively constant. For most purposes it is desirable to have a portion

of the nitrogen available immediately after application of the fertiliser. By varying the coating thickness (or weight), both the initial rate and daily rate of release can be controlled. The desired rate for a given crop and climate has to be determined by field testing.

The dissolution rate in water decreases as the temperature is decreased. The mechanism of dissolution is diffusion of water through the coating into the granule and diffusion of solution outward. Dissolution rates in the soil are not necessarily the same as in water, as they are affected by many other variables.

Estimates indicate that the cost of coating granular urea in a plant of 450 metric tons per day capacity would be about $16 per ton, including a 15% return on investment. If the price of straight urea (46% N) is $77 per ton, the estimated price of coated urea (36% N) would be $76 per ton or about 26% more per unit of nitrogen. Transportation costs per unit of nitrogen would be greater for the coated material because of its lower nitrogen content. However, the results of agronomic tests indicate that the value of increased yield often would more than offset the higher cost. A major advantage of coated urea is the potential saving resulting from a single application of nitrogen at planting time instead of split applications over the growing season.

In addition to the controlled-release characteristics, coated urea has excellent storage and handling characteristics and might even be handled in bulk in humid climates. Also, it may be blended with triple or single superphosphates, which are incompatible with uncoated urea.

The agronomic response of various crops to SCU has been reported by TVA agronomists in several publications (6, 7, 8). Results are summarized below.

- A single application of SCU on Coastal bermuda grass in the spring gave as good or better results than four (split) applications of ammonium nitrate.
- Excessive (luxury) consumption and excessive growth of grass forage shortly after a single application were avoided with SCU.
- SCU produced better distribution of protein throughout the forage growth period.
- The sulfur residues oxidized slowly to plant-available sulfate.
- Heavy surface application of SCU to grasses did not result in burning or in nitrogen losses through decomposition as with uncoated urea.
- SCU resisted leaching and denitrification under conditions of heavy rainfall and resulted in higher yields under these conditions.

Results of the agronomic tests indicated that coated urea was advantageous for use on sugarcane, pineapple, rice grown with delayed or intermittent flooding, and in general for long-season crops and for conditions conducive to heavy leaching or to decomposition losses.

The sulfur-coating technique may be applied to fertilisers other than urea. Experimental work has included coating of diammonium phosphate, potassium chloride, potassium sulfate, and various compound fertilisers.

Nitrification Inhibitors

Nitrogen fertilisers in the ammonium form are immobilized in the soil by sorption on clay particles and hence are resistant to leaching. However, the ammonium form is rapidly converted to the nitrate form in most soils by microbiological processes called nitrification. The nitrate form is more readily available to most plants, although some plants (e.g., rice) can readily use the ammonium form. Thus, some of the purposes of controlled release (resistance to leaching and delayed availability) may be attained by delaying nitrification of ammonium nitrogen.

Numerous organic chemicals have been identified as nitrification inhibitors. The inhibition is due to the toxicity of these chemicals to organisms that convert ammonium nitrogen to nitrite, which is the first step of the nitrification process.

One of the nitrification inhibitors that has received attention in the United States is 2-chloro-6-(trichoromethyl) pyridine. The Dow Chemical Company is promoting it under the trade name N-Serve. A spokesman for Dow says they hope to have a manufacturing unit in operation within a year and that they are aiming for a price level that will permit the grower to use N-Serve at a cost of $6.20 to $7.40 per hectare. The minimum concentration of N-Serve in the soil for delaying nitrification at least 6 weeks is said to range from 0.5 to 10 parts per million.

Dow points out that a nitrification inhibitor is helpful only when conditions favor high nitrogen loss from the soil. Such conditions are heavy rainfall or heavy irrigation, coarse textured soil, soil in the pH range where nitrification readily occurs, and anaerobic soil conditions.

Potassium azide in anhydrous ammonia solutions was effective in lowering the rate of nitrification in tests conducted by the U. S. Department of Agriculture in cooperation with agricultural experiment stations in the states of Louisiana (9) and Washington (10). Formulations containing 0, 2, and 6% KN_3 in liquid ammonia, for example, were applied to fallow soil in eastern Washington in August at a rate of 112 kilograms of N per hectare. The 2% formulation was applied also at a rate of 224 kilograms of N per hectare. Two months later the amounts of nitrate nitrogen recovered from the retention zone--expressed as percent of total extractable nitrogen--were 67 for ammonia alone, 48 for the 2% formulation, and 36 for the 6% formulation. Nitrification inhibition was still evident 6 months after application, particularly at the 224-kilogram rate of application. PPG Industries, Inc., is exploring this and other agricultural uses (e.g., as a herbicide in rice culture) for the azide. They think they may have a commercial production unit in about 3 years.

Another nitrification inhibitor that has received much attention in Japan is 2-amino-4-chloro-6-methyl pyrimidine. It is manufactured by Mitsui Toatsu Chemicals, Inc. (formerly Toyo Koatsu Industries, Inc.) under the trade name AM. Japanese companies produced 15,400 metric tons of NPK fertilisers containing AM in 1968.

Only partial success has been achieved with nitrification inhibitors. Excellent results have been reported in some tests. However, one difficulty is maintaining the desired concentration of inhibitor in the soil for the desired time. Heavy rains may wash it out too soon; too little rain

may result in delaying nitrification too long. Also, there is some concern about the possibility of objectionable residues appearing in ground water.

Possibly there are conditions in which nitrification inhibitors will prove useful; whether these conditions are sufficiently extensive and predictable to warrant commercial use remains to be seen.

Controlled-Release Potash Fertilisers

Little interest has been shown in controlled-release potassium fertilisers. TVA conducted tests with potassium polyphosphates and potassium calcium pyrophosphates. Some of the materials were only slightly soluble in water by the AOAC procedure. Agronomic evaluation of the materials was reported by Engelstad (11). Their only advantage was reduced injury to germinating seeds. Most of the materials were as readily available as soluble potash salts. Some of the least soluble materials showed slow-release characteristics when applied as large particles (about 7 mm), but there was no conclusive evidence of increased efficiency.

More recently, sulfur-coated potassium chloride has been prepared by TVA for agronomic tests. Some of these tests were promising in that yields were increased in comparison with uncoated potassium chloride (12). More information is needed for agronomic and economic evaluation. The low cost of soluble potassium fertilisers tends to discourage efforts to increase their efficiency.

Conclusions

Controlled-release nitrogen fertilisers very probably will prove useful for some field crops in some situations. Much more study will be required, however, to determine the place of controlled-release nitrogen fertilisers in the farm economy.

Controlled-release fertilisers are most likely to prove advantageous where labor is scarce and expensive. In developing countries where labor is plentiful and inexpensive, multiple applications of nitrogen fertiliser can be used to attain improved yields and higher efficiency of utilization with less cost.

Prospects for improvement of phosphate and potassium fertilisers through controlled release seem remote.

References

1. Powell, Robert. "Controlled Release Fertilizers." Noyes Development Corporation, Park Ridge, New Jersey. 1968.
2. World Fertilizer Review, No. 1, 47 (May 1971).
3. Huffman, E. O. Fertiliser Soc. (England), Proc. No. 71 (1962).
4. Hamamoto, Masao. Fertiliser Soc. (England), Proc. No. 90 (1966).
5. Ando, Jumpei. Proc. 20th Annual Meeting Fertilizer Industry Round Table 1970 (Memphis, Tenn.), 85-92. Office of Secretary-Treasurer, Baltimore, Maryland 21212. 1971.
6. Allen, S. E., Mays, D. A., Terman, G. L. Crops Soils 21, 13 (December 1968).

7. Mays, D. A., Terman, G. L. Sulphur Inst. J. 5, No. 3, 7 (1969).

8. Mays, D. A., Terman, G. L. Agron. J. 61, 489 (1969).

9. Parr, J. F., Carroll, B. R., Smith, S. Soil Sci. Soc. Amer. Proc. 35, No. 3, 469-73 (1971).

10. Papendick, R. I., Parr, J. F., Smith, S., Smiley, R. W. Soil Sci. Soc. Amer. Proc. 35, No. 4, 579-83 (1971).

11. Engelstad, O. P. "The Role of Potassium in Agriculture," 63-77, ed. V. J. Kilmer, S. E. Younts, N. C. Brady. American Society of Agronomy, Madison, Wisconsin. 1968.

12. Allen, S. E., Mays, D. A. J. Agr. Food Chem., in press.