Improving Fertilizer Use Efficiency

# Controlled-Release and Stabilized Fertilizers in Agriculture

Dr. Martin E. Trenkel



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### Summary

This publication presents agronomic reasons which have led to the development of controlled-release and stabilized fertilizers. The characteristics, the advantages and the possible disadvantages of controlled-release and nitrification/urease inhibitors are discussed. Particular attention is given to problems of legislation, registration, methodology and standardization.

Leading manufacturers and their product ranges are listed.

Universities and institutes engaged in research on controlled-release fertilizers and nitrification/urease inhibitors and the fields of their main research activities, are indicated. A comprehensive bibliography is added.

As regards controlled-release fertilizers, the publication presents the reason why their production and their distribution costs are significantly higher than those of conventional fertilizers. The difference in cost is identified as the main reason restricting their use to high value crops, specific cultivation systems and non-agricultural sectors (professional horticulture, nurseries, greenhouses, golf courses, household consumers, turf, landscape gardeners and public parks). Only very limited quantities are used on agricultural crops such as fruit trees and high cash-value vegetables.

The total amount of 562 000 t of synthetic controlled-release fertilizers which are applied represents only 0.15% of the world's total mineral fertilizer consumption (approximately 380 mio t of fertilizer material).

Even though in Japan 70% of polymer coated controlled-release fertilizers are used on rice, it is doubtful whether this innovative cultivation system can be transferred to other rice growing countries and to other agricultural crops. Unless the cost of controlled-release fertilizers can be significantly lowered, it is unlikely that these speciality fertilizers will gain widespread use on low value agricultural crops.

With no technical breakthrough in sight, it seems that controlledrelease fertilizers will have no impact on world food production in the foreseeable future.

In contrast to controlled-release fertilizers, nitrification and urease inhibitors are used almost exclusively on agricultural crops. By improving the efficiency of nitrogen use, their application results either in higher and more consistent yields of agricultural crops, or in unchanged yields with reduced nitrogen application rates. The amount of nitrogen applied can be reduced by 15 to 20 % without reducing the yield level. However, even though the economics of their use are much more favourable to farmers compared to controlled-release fertilizers, to date their application has been restricted to very few agricultural crops (mainly corn and root crops), and special climatic conditions.

Apart from the agronomic aspects of controlled-release and nitrification/urease inhibitors, the environmental aspects of their use deserve close attention. Controlled-release fertilizers and nitrification and urease inhibitors, can contribute significantly to environmental protection either by reducing the leaching of nitrate or by reducing the emissions of nitrous oxide and the volatilization losses of ammonia.

Hence, in future the impact of controlled-release fertilizers and nitrification/urease inhibitors may become increasingly important because of the environmental aspects. If environmental legislation should place restrictions on the application of nitrogen on farmland where there is a possibility of polluting groundwater, streams and lakes, farmers may be forced to give preference to these types of nitrogen fertilizers and products.

As regards the volatilization losses of ammonia from amide-N containing fertilizers which are surface applied or applied under flooded conditions, the introduction onto the United States agricultural market in 1996 of the first urease inhibitor, will be observed with great interest.

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### Chapter 1. Introduction

The fertilizer industry faces a permanent challenge to improve the efficiency of its products. This is done either through improvement of fertilizers already in use or through development of new specific fertilizer types (MAENE, 1995; TRENKEL et al., 1988).

Apart from possible technical problems, this is not an easy task due to the mechanisms of plant nutrition. Normally, plants take up nutrients through their roots from the soil and/or the soil solution. However, soil and plants are two antagonistic systems competing for the nutrients available in the soil or applied (AMBERGER, 1996).

This competition is the main problem whenever nutrients in the form of mineral fertilizers are applied to the soil to feed the plants. This is also the main reason why only a proportion of nutrients is taken up and used by the plants and crops grown. There is, however, no universally accepted scientific definition of nutrient efficiency or nutrient use efficiency (NUE). Under practical conditions nutrient efficiency concerns the amount of nutrients taken up from the soil by plants and crops within a certain period of time<sup>1</sup> compared with the amount of nutrients available from the soil or applied during that same period of time.

FINCK (1992) gives the following indications of nutrient uptake. This relates to efficiency of only the nutrients applied in form of mineral fertilizers

- The utilization rate of N in mineral fertilizers is about 50-70% during the first year.
- The utilization rate of P in mineral fertilizers is 10-25% (average 15%) during the first year. However, a further 1-2% per year will be taken up during the following decades.
- The utilization rate of K in mineral fertilizers is about 50-60% during the first year.

The field activities of farmers, particularly all fertilizer application methods - due to the above mentioned competition between soil and plants - must aim to support the plants in this competing system, thereby achieving the greatest possible uptake/efficiency of nutrients.

This support includes:

- all farmers' activities to promote root growth by improving the soil structure (good soil aeration, storage and supply of water), soil reaction (liming), humus content, storage capacity for soluble nutrients and mobility of nutrients (FINCK, 1992; AMBERGER, 1996).
- It includes the use of soil and plant testing methods (soil analyses, N<sub>-min</sub>-analyses, leaf analyses) and a constant crop monitoring (yield expectation and crop development) (STURM et al., 1994).

<sup>1</sup> For special fertilizers the AAPFCO (Association of American Plant Food Control Officials) has introduced the term "Efficiency Design" (see section 7.1. Registration of slow and controlledrelease fertilizers).

- It also includes the application of nutrients corresponding to the plants' need and growth conditions as precisely as possible by choosing the most suitable type and rate of plant nutrient/mineral fertilizer and the most appropriate application technique (for example fertilizer placement or band application, split application, up to socalled 'spoon-feeding').
- It also includes all measures for reducing possible losses of nutrients to the environment (SHAVIV, 1993).

Losses through immobilization, denitrification/volatilization and leaching may occur especially with nitrogen. Consequently, it has been the challenge of the fertilizer industry to develop special types of fertilizers avoiding or at least reducing such losses, in addition to the production of conventional nitrogen-containing fertilizer types (ammonium sulphate, ammonium nitrate, calcium ammonium nitrate, ammonium sulphate nitrate, urea, DAP, and NP and NPK fertilizers) (JOLY, 1993).

These special types can be listed as:

- Foliar fertilizers.
- Slow-release and controlled-release coated/encapsulated fertilizers.
- Nitrification and urease inhibitors/stabilized fertilizers (fertilizers associated with nitrification or urease inhibitors).

In fact, the utilization rate of nutrients could be improved considerably through leaf application, because any immobilization or leaching such as occurs in the soil is avoided. However, the disadvantage of foliar sprays is that in all cases only rather limited amounts of nutrients can be applied. In practice this makes it impossible to economically apply all the necessary nutrients via plant leaves (AMBERGER, 1996).

Another possible route of improving nutrient use efficiency is the use of mineral fertilizers, particularly nitrogen fertilizers, which release the nutrients contained according to the plants' requirements, so-called 'intelligent fertilizers', i.e. by application of slow and controlled-release, or by 'stabilized' nitrogen fertilizers, which preserve the nutrients until plants really require them.

SHOJI and GANDEZA (1992) consider that an ideal fertilizer should have at least the following three characteristics:

- it only needs one single application throughout the entire growing season to supply the necessary amount of nutrients for optimum plant growth,
- it has a high maximum percentage recovery in order to achieve a higher return to the production input, and
- it has minimum detrimental effects on soil, water and atmospheric environments.

Slow, and particularly controlled-release as well as 'stabilized' fertilizers meet these requirements for an ideal fertilizer to a considerable extent.

Though slow and controlled-release and stabilized fertilizers can contribute to improved nutrient efficiency, minimizing negative environmental effects, it has to be kept in mind that errors in field and crop management cannot be compensated for by the use of these special fertilizer types.

### Chapter 2.

# Definitions of Slow and Controlled-Release and Stabilized Fertilizers

### 2.1. Slow and controlled-release fertilizers

Slow and controlled-release fertilizers are fertilizers containing a plant nutrient in a form which either a) delays its availability for plant uptake and use after application, or b) which is available to the plant significantly longer than a reference 'rapidly available nutrient fertilizer' such as ammonium nitrate or urea, ammonium phosphate or potassium chloride (AAPFCO, 1995).

There is no official differentiation between slow-release and controlled-release fertilizers. Also the AAPFCO, the Association of American Plant Food Control Officials, uses both in its Official Terms and Definitions (AAPFCO, 1997). However, the microbially decomposed N products, such as UFs (Urea-Formaldehydes), are commonly referred to in the trade as slow-release fertilizers and coated or encapsulated products as controlled-release fertilizers. The author follows this practice.

The CEN<sup>1</sup> TC260/WG4/Task Force slow-release fertilizers (TFsrf) has made the following proposals (KLOTH, 1996):

	e transformation of a chemical substance into a plant vailable nutrient form (e.g. dissolution, hydrolysis,
	egradation, etc.);
av in pl th	release rate of a chemical substance into a plant vailable nutrient form, which is definitely lower than, a general, the release rate from the application of a lant available nutrient (for slow-release nitrogen e.g. he release rate/plant response to an application of rea, ammonium or nitrate solution);
ni un te cr - i - i - i	fertilizer may be described as slow-release if the utrient or nutrients declared as slow-release meet, nder defined conditions including that of a emperature of 25°C, each of the following three riteria: no more than 15% released in 24 hours, no more than 75% released in 28 days, at least about 75% released at the stated release time.

<sup>1</sup>Comité Européen de Normalisation.

### 2.2. Nitrification inhibitors

Nitrification inhibitors are compounds that delay bacterial oxydation of the ammonium-ion  $(NH_4^+)$  by depressing over a certain period of time the activities of *Nitrosomonas* bacteria in the soil. They are responsible for the transformation of ammonium into nitrite  $(NO_2^-)$ which is further changed into nitrate  $(NO_3^-)$  by *Nitrobacter* and *Nitrosolobus* bacteria. The objective of using nitrification inhibitors is, therefore, to control leaching of nitrate by keeping nitrogen in the ammonia form longer, to prevent denitrification of nitrate-N and to increase the efficiency of nitrogen applied-<sup>2</sup>.

There is considerable confusion concerning the terms **nitrogen stabilizers**, **nitrification inhibitors**, **urease inhibitors** and **stabilized fertilizers**. Nitrogen stabilizers and nitrification inhibitors have been used interchangeably. Strictly speaking stabilized fertilizers are only those which are amended with a nitrification inhibitor during production, such as ALZON<sup>®</sup> and BASAMMON<sup>®</sup>. In all other cases farmers add nitrification or urease inhibitors to their fertilizers only when applying them; they buy nitrification and urease inhibitors and not stabilized fertilizers. This is also the case when the dealer mixes the nitrification or the urease inhibitor into the fertilizer as a service to the farmer. Consequently, the author primarily uses the expressions nitrification and urease inhibitor.

### 2.3. Urease inhibitors

Urease inhibitors prevent or depress over a certain period of time the transformation of amide-N in urea to ammonium hydroxide and ammonium<sup>2</sup>. They do so by slowing down the rate at which urea hydrolyzes in the soil, thus avoiding or reducing volatilization losses of ammonia to the air (as well as further leaching losses of nitrate). They increase the efficiency of urea and nitrogen fertilizers containing urea (e.g. Urea ammonium nitrate solution UAN). Urease inhibitors thus inhibit for a certain period of time the enzymatic hydrolysis of urea, which depends on the enzyme urease (FARM CHEMICALS HANDBOOK '95, 1995).

Though nitrification and urease inhibitors are recognized as nitrogen stabilizers (AAPFCO), nitrification inhibitors in some publications are designated as slow or controlled-release fertilizers. The author is of the opinion that this designation is not correct (see also section 5.2), because all plants are able to take up nitrogen also in form of ammonia.

### Chapter 3.

### Manufacturing Routes for Slow and Controlled-Release and Stabilized Fertilizers

In the production of slow-release or controlled-release fertilizers the slow-release effect may be obtained by various production processes, for example through modification of conventional fertilizers (FUJITA, 1996a, 1996b and 1993; GOERTZ, 1993a and 1993b; HÄHNDEL, 1986).

Their solubility, i.e. the release of plant available nutrients

- is reduced chemically or physically (slow or controlled-release), or
- the transformation of less available or less mobile (in the soil) nutrient forms into plant available or mobile forms is delayed by association with nitrification or urease inhibitors (see Chapter 2 Definitions).

#### Definition for slow and controlled-release fertilizers

Delay of initial availability or extended time of continued availability may occur by a variety of mechanisms. These include controlled water solubility of the material (by semipermeable coatings, occlusion, or by inherent water insolubility of polymers, natural nitrogenous organics, protein materials, or other chemical forms), by slow hydrolysis of water-soluble low molecular weight compounds, or by other unknown means.

(Source: AAPFCO, 1995)

Controlled or slow nutrient release can be achieved through special chemical and physical characteristics. With controlled-release fertilizers the principal procedure is one whereby conventional soluble fertilizer materials are given a protective coating or encapsulation (waterinsoluble, semipermeable or impermeable with pores), controlling water penetration and thus the rate of dissolution, and nutrient release synchronized to the plants' needs.

The most important manufacturing routes are described below.

### 3.1. Slow and controlled-release fertilizers

- 3.1.1. Materials releasing nutrients through low solubility due to a complex/high molecular weight chemical structure following microbial decomposition.
- **3.1.2.** Materials releasing nutrients through a coated surface (coated fertilizers).
- 3.1.3. Materials releasing nutrients through a membrane which may or may not itself be soluble (encapsulation).
- 3.1.4. Nutrient-releasing materials incorporated into a matrix which itself may be coated.
- 3.1.5. Materials releasing nutrients in delayed form due to a small surface-to-volume ratio (super-granules, briquettes, tablets, spikes, plant food sticks etc.).

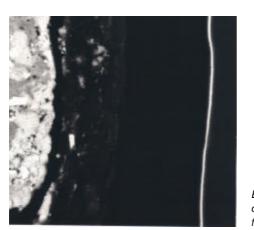
Other materials classified in a broader sense as slow-release fertilizers are not covered in this documentation:

- organic substances, e.g. crop residues, manure, slurry, composts, heat-dried or sun-dried sewage sludge etc.,
- organic or organic-mineral fertilizers, e.g. meat and bone meal, hoof and horn meal, rape meal, treated leather meal etc.
- metal-ammonium phosphates, e.g. magnesium ammonium phosphates (however, generally covered by 3.1.1.).

Electron micrograph of cross-section of polymer-coated controlled-release fertilizer granule (10μm) (BASF AG).

### 3.2. Nitrification and urease inhibitors

3.2.1. Materials/chemical compounds reducing plant availability of nutrients by inhibition of natural soil processes (nitrification inhibitors or urease inhibitors/stabilized fertilizers).



### Chapter 4.

### Advantages/Disadvantages of Slow and Controlled-Release and Stabilized Fertilizers

### 4.1. Their advantages

Slow and controlled-release or stabilized nitrogen fertilizers offer a number of important advantages:

### 4.1.1. Slow and controlled-release fertilizers

- 4.1.1.1. They reduce toxicity (particularly to seedlings), which is caused through high ionic concentrations resulting from the quick dissolution of conventional soluble fertilizers (in some cases also from ammonia, for instance after application of urea) and thus contribute to improved agronomic safety (AGLUKON, 1993 and 1992; GRACE SIERRA, 1994 and 1993; SIERRA, 1991a and 1991b).
- 4.1.1.2. Due to the reduction of toxicity and the salt content of substrates (4.1.1.) they permit the application of substantially larger fertilizer dressings (depot fertilization reducing the application frequency) as compared to conventional soluble fertilizers. This results in significant savings in labour, time and energy, as well as in making the use of the fertilizer more convenient. This latter factor constitutes the greatest advantage for the majority of present consumers of slow- and controlled-release fertilizers.
- 4.1.1.3. They contribute to advanced fertilizer management programmes and to innovative farming systems such as notillage farming with single *co-situs* fertilizer application (FUJITA, 1996a).



Growth of corn plants fertilized • left : with polyolefine-coated controlledrelease N fertilizer (Meister®) and

 right : with a conventional N fertilizer.
 The corn plant fertilized with the conventional N fertilizer shows serious salt injury.
 (KONNO, C).

- 4.1.1.4. They permit the meeting of the full nutrient requirements of crops grown under plastic cover (protected crop cultivation), and multicropping by a single fertilizer application.
- 4.1.1.5. They significantly reduce possible losses of nutrients, particularly losses of nitrate nitrogen, between applications and uptake by the plants through gradual nutrient release. They also reduce evaporation losses of ammonia. This substantially decreases the risk of environmental pollution (KOSHINO, 1993; MIKKELSEN et al., 1994; RIETZE and SEIDEL, 1994; WANG, 1996).
- 4.1.1.6. They also contribute to a reduction in relevant gas emissions  $(N_2O)$  (SHAVIV and MIKKELSEN, 1993; SHOJI and KANNO, 1993 and 1994).

### 4.1.2. Nitrification and urease inhibitors

- 4.1.2.1. Nitrification inhibitors through inhibition of nitrification of ammonia significantly reduce leaching losses of nitrogen and movement of  $NO_3^-$  into water supplies, while maintaining N availability to crops (GRANT et al., 1996b; WATSON et al., 1994).
- 4.1.2.2. They also reduce emissions of N<sub>2</sub>O and NO<sub>x</sub> (BRONSON and MOSIER, 1993 and 1994; BRONSON et al., 1992; BUNDESRAT, 1996; DELGADO and MOSIER, 1996).
- 4.1.2.3. As regards urease inhibitors, they reduce ammonia volatilization losses particularly from top-dressed agricultural fields as well as under reduced tillage when urea is used as a source of nitrogen (BAYRAKLI and GEZGIN, 1996; WANG et al., 1994, 1991a and 1991c).
- 4.1.2.4 Nitrification inhibitors indirectly improve the mobilization and the uptake of phosphate in the rizosphere; see section 5.2 (AMBERGER, 1991b).
- 4.1.2.5. Urease inhibitors furthermore reduce seedling damage when seed-placed levels of urea/urea containing fertilizers are too high (GRANT et al., 1996a; GRANT et al., 1994; XIAOBIN et al., 1994).

Slow and controlled-release fertilizers as well as nitrification and urease inhibitors increase the efficiency of nutrients applied, generally resulting in higher yields of horticultural and agricultural crops.

### 4.2. The possible disadvantages of slow and controlledrelease and stabilized fertilizers

Slow and controlled-release or stabilized fertilizers also have possible disadvantages.

### 4.2.1. Slow and controlled-release fertilizers

- 4.2.1.1. There are no standardized methods for reliable determination of the nutrient release pattern available as yet. Broadly speaking there appears to be a lack of correlation between the data resulting from laboratory testing - which are made available to the consumer - and the actual functioning of the nutrient release pattern in field conditions. Furthermore, when reporting the advantages of slow and controlled release fertilizers in comparison to conventional mineral fertilizers, controlled-release fertilizers have not always been compared to the best existing fertilizer management practices (HALL, 1996; KLOTH, 1996; RABAN, 1995).
- 4.2.1.2. With regard to chemical reaction products, such as ureaformaldehyde fertilizers, it appears that a proportion of the nitrogen contained may be released to the soil solution extremely slowly (or not at all).
- 4.2.1.3. With regards to sulphur coated controlled-release fertilizers the initial nutrient release may be too rapid, causing damage to turf or to the crop. Further, this rapid initial release, even if it does not cause damage, is at a higher cost than that of the equivalent amount of conventional (non slow or controlledrelease) soluble fertilizer nutrient. Also, some of the sulphurcoated granules are usually so thickly coated that the nutrient contained in these granules may not be released during the crop demand period.
- 4.2.1.4. Application of coated controlled-release fertilizers may increase the acidity of the soil. This might be the case if large amounts of sulphur coated urea are applied, since both sulphur and urea contribute to increased acidity.
- 4.2.1.5. Polymer coated or encapsulated controlled-release fertilizers may leave undesired residues of synthetic material on the fields. Some types of polymers used in the coating of conventional fertilizers currently in use decompose extremely slowly or not at all in the soil. Their use may thus lead to an undesirable accumulation of plastic residues (up to 50 kg per ha and year) (HÄHNDEL, 1997). However, even if decomposition takes 10 years, the 500 kg/ha maximum accumulation would

be only 200 ppm of dry soil. Further, if the polymer 'shell' fragments do not compose, the *fragments*, which are smaller than sand size particles, become part of the soil.

- 4.2.1.6. In modern intensive agriculture, where application of optimum rates of mineral nitrogen follows a constant monitoring of growth conditions, farmers prefer to adapt the nitrogen dressings to crop development and yield expectation. This is incompatible with the practice of early depot fertilization with coated or encapsulated nitrogen fertilizers in one single dressing, which cannot be corrected later.
- 4.2.1.7. The cost of manufacturing coated or encapsulated controlledrelease fertilizers is still considerably higher as compared to the production of conventional mineral fertilizers. Thus their cost benefit ratio at present prevents their wide use in general agriculture (DETRICK, 1995; FUJITA, 1996a; GOERTZ, 1993a and 1993b; GORDONOV, 1995; HÄHNDEL, 1997; HALL, 1996; KLOTH, 1996; VAN PEER, 1996).

The higher production costs are due to:

- The more complicated production processes (ready-for-use nitrogen or NP, NK, NPK fertilizers) have to go through a complicated technical process.
- In trying to achieve a perfect coating, the producers usually employ size separation of raw granular materials; this also makes the product more expensive.
- The coating material being several times higher in price than the fertilizer material, and
- The relatively small capacities.
- 4.2.1.8. Coated/encapsulated controlled-release fertilizers call for higher marketing (specialized advisory service) and sales expenses than conventional fertilizers.

### 4.2.2. Nitrification and urease inhibitors

- 4.2.2.1. Stabilized fertilizers i.e. ammonia-containing fertilizers amended with a nitrification inhibitor may favor an increase in ammonia volatilization, if they are not incorporated into the soil immediately after application<sup>1</sup>.
- 4.2.2.2. Depending on the type of nitrification inhibitor the activity of soil bacteria may not only be interrupted for a certain time period, but the soil bacteria may actually be killed. This could be considered an undesirable interference in a natural soil process (STURM et al., 1994; ZACHERL and AMBERGER, 1990).

<sup>1</sup> For ammonia volatilization and denitrification under flooded rice conditions see section 11.2.5. Nitrification and urease inhibitors in tropical crops.

### Chapter 5.

### Types of Slow and Controlled-Release and Stabilized Fertilizers

### 5.1. Slow and controlled-release fertilizers

The two most important groups of slow and controlled-release fertilizers, according to their production process are:

- Condensation products of urea and urea-aldehydes (slow-release fertilizers).
- Coated or encapsulated fertilizers (controlled-release fertilizers).

Of lesser or only regional importance are:

• Supergranules and others.

### 5.1.1. Condensation products of urea and aldehydes (methylene ureas)/ nitrogen reaction products

Among the nitrogen reaction products designed mainly for use on professional turf, in nurseries, greenhouses, on lawn, and for garden and landscaping, three types have gained practical importance (GOERTZ, 1993a; HÄHNDEL, 1986):

- urea-formaldehyde (UF),
- urea-isobutyraldehyde (IBDU<sup>®1</sup>), and
- urea-crotonaldehyde (CDU<sup>®2</sup>).

Whereas the urea-formaldehyde reaction products have the largest share of the slow-release fertilizer market, IBDU<sup>®</sup>- and CDU<sup>®</sup>-based products are less widely used, due to even greater cost constraints in their production.

#### Urea-Formaldehyde (UF) - 38% N

Among the manufactured slow and controlled-release fertilizers, ureaformaldehyde based products still have the largest share worldwide. This is also the first group on which research concerning slow release of nitrogen was carried out. As early as 1924, Badische Anilin- & Soda-Fabrik AG (nowadays BASF Aktiengesellschaft) in Germany received the first patent (DRP 431 585) on urea-formaldehydecondensation fertilizers (BASF, 1965). In the United States they were patented for use as fertilizers in 1947. Commercial production began in 1955 and at present five types of urea-formaldehyde fertilizer products are manufactured as solids and liquids (water solutions and water suspensions) in the United States (GOERTZ, 1993a).

<sup>1</sup> In the United States and North America, Vigoro Industries, Inc. holds the trademark for IBDU slow-release nitrogen.

<sup>2</sup> Chisso Corporation holds the trademark for 'CDU' urea-crotonaldehyde slowrelease nitrogen. Urea-formaldehyde is formed by the reaction of formaldehyde with excess urea under controlled conditions (pH-value, temperature, molproportion, reaction time etc.) resulting in a mixture of methylene ureas with different long-chain polymers.

Table 1. Urea-formaldehyde (UF solubility)

Fractions	UF Polymers-mixture					
	Cold water soluble (CWS)	Cold water insoluble (CWI*)				
		Hot water soluble (HWS)	Hot water insoluble (HWI)			
	(I)	(11)	(111)			
		The Activity Index (AI) is only concerned with cold water insolubility				
* appears as "W.I.N." on United States Labels. Source: DETRICK (1995).						

The main problem in the manufacture of urea-formaldehyde as a slow-release fertilizer type is to produce condensation-oligomers in a desired proportion. The influence of the proportion of the different methylene ureas on the release of nitrogen and the nitrogen efficiency can be determined by the Activity Index (AI).

- Fraction I: cold water soluble CWS (25°C) containing residual urea, methylene diurea (MDU), dimethylene triurea (DMTU) and other soluble reaction products. The nitrogen of Fraction I is, depending on soil temperature, available slowly (AAPFCO 73, N-29 and N-30).
- Fraction II: hot water soluble HWS (100°C) containing methylene ureas of intermediate chain lengths: slow-acting nitrogen.
- Fraction III: hot water insoluble HWI containing methylene ureas of longer chain lengths insoluble in both cold and hot water; extremely slow-acting or non-available nitrogen.

The AI is calculated on the solubility fractions of the fertilizer under different conditions (DETRICK, 1996):

1. 
$$AI = \frac{II}{II + III} \times 100$$
, or

2. 
$$AI = \frac{The HWS part of the CWI}{CWI}$$
, or

3. 
$$AI = \frac{CWI - HWI}{CWI} = \frac{(\% \text{ N CWI} - \% \text{ N HWI})}{\% \text{ N CWI}} \times 100$$

Whereas in the past urea-formaldehydes had an AI of about 40 to 50, more recent urea-formaldehyde formulations are reaching AI-values of 55 to 65.

The Association of American Plant Food and Control Officials (AAPFCO) are setting an AI of 40 as a minimum with at least 60% of its nitrogen as cold water insoluble nitrogen (CWI N) and a total content of nitrogen of at least 35%. Unreacted urea nitrogen content is usually less than 15% of total nitrogen.

The release pattern of nitrogen from UF fertilizers is a multi-step process (dissolution and decomposition). In general there is some proportion of N slowly released (Fraction I); this is followed by a more gradual release over a period of several (3-4) months (Fraction II), depending on the type of product. However, the release pattern is also influenced by the temperature and moisture as well as by soil organisms and their activity.

In general urea-formaldehyde fertilizers show a significant slow release of nitrogen combined with a good compatibility with most crops. Because of their low solubility they will not burn vegetation or interfere with germination. Since they are more effective at higher temperatures, they are widely used in warmer climates (in the Mediterranean region in Europe and in the southern and southwestern regions of the United States).

#### Isobutylidene diurea (IBDU®) - 32% N

Isobutylidene diurea is formed as a condensation product by a reaction of isobutyraldehyde (a liquid) with urea. In contrast to the condensation of urea with formaldehyde resulting in a number of different polymer chain lengths, the reaction of urea with isobutyraldehyde results in a single oligomer. However, in order to obtain an optimal proportion of IBDU, it is important that the reaction is stopped by neutralization at the point at which it is yielding most IBDU.

The theoretical nitrogen content is 32.18%. The AAPFCO (AAPFCO, 1995) definition requires a minimum of 30%, of which 90% is cold water insoluble (prior to grinding). The release mechanism functions by gradual hydrolysis of the sparingly water insoluble IBDU to urea which is transformed to ammonium ions and further to nitrate (by soil bacteria).

The rate of nitrogen release is a function of particle size (the major influence: the finer the particle size, the more rapid the rate of nitrogen release) and of moisture, temperature and pH.

Agronomic response and safety margin is good with turf, while with greenhouse crops phytotoxicity has sometimes been observed.

#### Crotonylidene diurea (CDU®) - 32.5% N

Crotonylidene diurea is formed by the acid-catalyzed reaction of urea and acetic aldehyde. When dissolved in water it gradually decomposes to urea and crotonaldehyde. As with IBDU, with CDU also particle size greatly influences the rate of nitrogen release (very delayed release with larger particle size).

CDU is decomposed by both hydrolysis and microbial processes in the soil; temperature, soil moisture and biological activity affect the release rate, though even in acid soils the degradation is slower as that of IBDU. The agronomic performance is similar to IBDU.

CDU is produced in Japan (Chisso Corp.) according to a production process developed by Chisso (modified BASF production process; BASF: Crotonaldehyde + Urea, Chisso: Acetaldehyde + Urea). In Japan and Europe, its main use is on turf and in speciality agriculture, typically formulated into granulated NPK fertilizers.

### 5.1.2. Coated/encapsulated controlled-release fertilizers

These are conventional soluble fertilizer materials with rapidly available nutrients which after granulation, prilling or crystallization are given a protective (water-insoluble) coating to control the water penetration and thus the rate of dissolution and the nutrient release. 'A product containing sources of water soluble nutrients, release of which in the soil is controlled by a coating applied to the fertilizer' (AAPFCO, 1995).

There are three different groups of coated/encapsulated controlledrelease fertilizers, using as coating material:

- sulphur<sup>3</sup>
- polymeric / polyolefin materials, and
- sulphur plus polymeric, including wax polymeric materials<sup>4</sup>.

Agents currently used for coating/materials used in manufacturing fertilizers with controlled release of nutrients are:

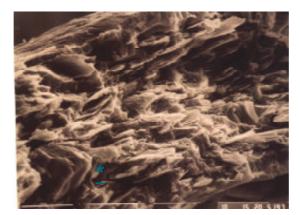
- sulphur,
- polymers<sup>5</sup> (e.g. PVDC-based copolymeres, polyolefine, polyurethane, urea-formaldehyde resin, polyethylene, polyesters, alkyd resins etc.)
- fatty acid salts (e.g. Ca-stereate),
- latex<sup>6</sup>, rubber, guar gum, petroleum derived anti-caking agents, wax,
- Ca+Mg-phosphates, Mg-oxide, Mg-ammonium phosphate + Mgpotassium phosphate,
- phosphogypsum, rock phosphate, attapulgite clay,
- peat (encapsulating within peat pellets: organo-mineral fertilizers, OMF),
- neemcake/'nimin'-extract (extract from neemcake).

<sup>3</sup> O. M. Scott used to produce a sulphur only coated urea with about 19% S.

<sup>4</sup> As for example according to United States Patent Number 5,599,374, Feb. 4, 1997, John H. Detrick "Process for producing improved sulfur-coated urea slow release fertilizers" (DETRICK, 1997).

<sup>5</sup> The kind of polymeric material finally used by the individual manufacturer mainly depends on the chemical and physical properties, the cost, the availability and the patent situation.

6 The word 'latex' originally meant an emulsion of natural rubber, such as is obtained by cutting the bark of rubber trees. However, in chemistry all colloidal dispersions of polymers in an aqueous media are called latex.



Electron micrograph of crosssection of the polyolefine coating of a controlled-release fertilizer granule (Meister®).

• Diameter of granule approximately 2-3 mm

• Thickness of the polyolefine-film 50-60 µm. (CHISSO-ASAHI FERTILIZER CO.)

In comparison to urea reaction products, coated fertilizers, particularly those coated with a multi-layer coating of sulphur and a polymeric material, may present more favourable economics. To obtain a further reduction of total fertilizer costs, coated/encapsulated fertilizers are increasingly used in blends with conventional fertilizers in different ratios (mixtures of encapsulated and non-encapsulated N, NP or NPK fertilizers).

Furthermore, coated/encapsulated controlled-release fertilizers offer greater flexibility in determining the nutrient release pattern. They also permit the controlled release of nutrients other than nitrogen<sup>7</sup>. NYBORG et al. (1995) have found in greenhouse and field tests that slowing the release of fertilizer P into the soil by coating fertilizer granules (polymer coating) can markedly increase P recovery by the crop and the yield.

#### Sulphur coated urea (SCU)

Within the group of coated fertilizers sulphur coated urea has gained the greatest importance to date. The sulphur coating may be considered to be an impermeable membrane which slowly degrades through microbial, chemical and physical processes. The concentration of nitrogen (and other nutrients) and its release varies with the thickness of the coating in relation to the granule or prill size; it is also influenced by the purity of the urea used (EL SHELTAWI, 1982).

The basic production process was developed in laboratory and pilotscale tests in 1961 by TVA (Tennessee Valley Authority, Alabama).

There are four reasons favouring the combination of urea and sulphur:

- Urea with 46% N is highly concentrated, thus coating with sulphur still results in a product with 30-40% N.
- Urea is rather liable to leaching and/or to ammonia losses by volatilization; consequently covering urea granules with an impermeable sulphur membrane significantly reduces such losses.
- Sulphur is a low cost product.
- Sulphur is a valuable secondary plant nutrient.

<sup>7</sup> The sulphur process is not used for producing KNO<sub>3</sub> because of explosive hazard. However, encapsulation according to the Reactive Layers Coating (RLC) polymer process is possible without risk. Preheated urea granules were sprayed with molten sulphur in a rotating coating drum. Then any pores and cracks were closed by adding a wax-like polymeric sealant (2% to 3% of total weight). Finally, a conditioner (2% to 3% of total weight) was applied to obtain a free-flowing and dust free product with good handling and storage characteristics. The final product contained between 31 to 42% N, 10 to 27% S and about 5% of sealant agent and conditioner. Currently manufactured products contain up to 42% N (30% to 42% N) and 6% to 30% S plus various sealants and conditioners.

The nutrient release pattern of SCU particles is directly affected by coating thickness and coating quality. This is because the dissolution of urea from SCU into the soil solution follows the microbial and hydrolytic degradation of the protecting sulphur coating, its micropores and imperfections, i.e. cracks and incomplete sulphur coverage. When wax sealants are used - which is the case with the great majority of sulphur coated fertilizers - microbes first have to attack the sealant to reveal the imperfections in the sulphur coating. Since microbial activities are temperature dependent, the nutrient release pattern of wax-sealed SCUs is also temperature dependent.

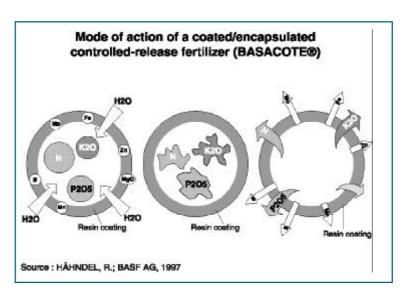
The quality of SCU is characterized by the rate of N released into the soil solution within seven days. This seven-day dissolution rate method (developed by TVA) permits the generating of a leach profile of the tested SCU. Unfortunately, the results obtained cannot be correlated reliably to the release pattern under practical field conditions (GOERTZ, 1993b; HALL, 1996). Currently marketed SCU fertilizers have dissolution values of about 40% to 60%.

'SCU-30' designates a product with a nitrogen release of 30% within seven days, under prescribed conditions. With such a high dissolution rate a rather rapid initial effect is to be expected. In fact, there have repeatedly been claims of a too-rapid release of nitrogen (WILSON, 1988).

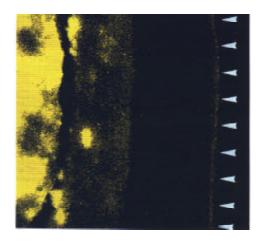
#### Polymer-coated/encapsulated controlled-release fertilizers

Standard SCU has dominated the market for several years. However, horticultural and lawn-garden markets in particular require a more sophisticated control of nutrient release. Thus a whole series of controlled-release fertilizers has emerged. New and modified coating methods have been developed (DETRICK, 1997; FUJITA et al., 1992; FUJITA 1990a, 1990b and 1989; JEFFREYS, 1995; KLOTH, 1989; THOMPSON and KELCH, 1992).

Polymer coatings may be either semipermeable membranes or impermeable membranes with tiny pores. The main problems in the production of polymer-coated fertilizers are the choice of the coating material and the technical coating process applied (GOERTZ, 1993a; HÄHNDEL, 1986; MOORE, 1993; PURSELL, 1995, 1994 and 1992).



Since nutrient release through the polymer membrane/capsule of controlled-release fertilizers is not significantly affected by soil properties, such as pH-value, soil salinity, texture, microbial activity, Redox-potential, ionic strength of the soil solution, but rather depends on temperature and the moisture permeability of the polymer coating, it is possible to predict precisely the nutrient release for a given time (SHOJI and GANDEZA, 1992; FUJITA et al.).



Electron micrograph of cross-section of a controlled-release fertilizer granule showing the distribution of the secondary nutrient sulphur (10 µm). (BASF AG)

The moisture permeability of the capsule can be controlled by changing the composition of the polymeric coating material used; with the technology applied for instance by Chisso Corp. the ratio of ethylene vinyl acetate (high moisture permeability) to polyethylene (low moisture permeability) is changed.

Polymer-coated fertilizer technologies vary greatly between producers, depending on the choice of the coating material and the technical coating process applied: the Pursell RLC<sup>TM</sup> (Reactive Layers Coating) polymer technology (POLYON<sup>®</sup>) is a polyurethane; this is also the case with Haifa (MULTICOTE<sup>®</sup>) and Aglukon (PLANTACOTE<sup>®</sup>); Chisso polymer technology (MEISTER<sup>®</sup>, NUTRICOTE<sup>®</sup>) is a polyolefin; Scotts polymer technology (OSMOCOTE<sup>®</sup>) is an alkyd resin. Thus, the longevity of the polymer coated product, i.e. the rate of nutrient release can - to a certain extent - be controlled by varying the type and the thickness of the synthetic material used in coating (FUJITA, 1993b; FUJITA et al., 1990 and 1989; FUJITA et al., without year; GOERTZ, 1993a and 1993b; DETRICK, 1992; PURSELL, 1994 and 1992).

The quantity of coating material used for polymer coatings of conventional soluble fertilizers depends on the geometric parameters of the basic core material (granules to surface area, roundness, etc.) and the target of longevity. In general the coating material represents 3-4 (RLC<sup>TM</sup>) to 15% (conventional coating with polymers) of the total weight of finished product.

The longer the supply of nutrients needs to last, the smaller has to be the amount of nutrients released per time unit. The producers indicate the period of release, e.g. 70 days release (at constant 25°C), or 140 days release, up to 400 days release.

However, if the polymer coated fertilizers are not straight nitrogen types but NPK fertilizers, particularly when containing secondary and micronutrients, it is generally not stated at what rates the different nutrients N,  $P_2O_5$ ,  $K_2O$ , S, Ca, Mg and micronutrients are released. It is, apparently, very difficult to determine exactly the release mechanism, particularly for secondary and micronutrients.

The problem is that, in order to guarantee the longevity of the polymer coated product, no bio-degradation, chemical-degradation or mechanical destruction of the coating should occur during the active time of the applied fertilizer. Consequently, it is only after the fertilization function of the product, that microbial attack and mechanical destruction of the empty shell should occur to decompose the coating over time (KLOTH, 1996).

Polymer coated urea (PCU) consists of urea granules coated with a polymeric resin; it typically contains about forty percent (40-44%) nitrogen.

Coating material made of photo degradative polymer is easily decomposed by photochemical process in the soil (FUJITA, 1996a). However, some polymer coated fertilizers present an as yet unsolved problem of persistence in the soil of the synthetic material used for encapsulation (but see also 4.21.5.).

A comprehensive compilation of the various complicated technical coating processes (patents) is given by Goertz in 'The O.M. Scott and Sons Company' (GOERTZ, 1993a). Further details on manufacturing processes mainly used in Japan are given by Gandeza and Shoji (SHOJI and GANDEZA, 1992), and particularly on the Pursell RLC<sup>™</sup> (Reactive Layers Coating) Process<sup>8</sup> by Pursell Technologies Inc. (PURSELL, 1995). Models of controlled-release fertilizers developed in Israel are described by SHAVIT et al. (1994) and LUPU (1996) and REISS (1996).

<sup>8</sup>Process developed by Pursell Technologies Inc. United States Patent Nos. 4,711,659 - 4,804,403 -4,969,947 - 5,374,292 and 5,547,486. The much more complex manufacturing processes and high-cost coating materials for polymer coated fertilizers as compared to conventional fertilizers are reflected in significantly higher product costs (also as compared to SCU). Nevertheless, the consumption of polymeric coated fertilizers has increased more than that of any other type during the last 15 years in the United States (about 10% per year, as compared to 2% for UFs) (LANDELS, 1994). In Japan consumption increased by 470% during the period 1985 to 1994 (FUJITA, 1996a). Europe is lagging behind, with an annual growth rate of only 6.5%.

## Sulphur coated/polymer-encapsulated controlled-release fertilizers.

Polymer/sulphur coated fertilizer products (PSCU or PSCFs) have been introduced into the market recently in the United States, with 38.5 - 42% N, 11 - 15% S and less than 2% polymer sealant (LESCO Inc. POLY PLUS® PCSCU 39N, PURSELL TriKote® 9 PCSCU 39-42N and Scott POLY-S® PCSCU 38.5-40N; regular size of all products 1.8 mm to 2.9 mm, nominal 2.4 mm). These products have a primary coating of sulphur and a secondary coating of a polymeric material. The reason for this hybrid coating is to combine the control release performance of polymer-coated fertilizers with the lower cost of sulphur-coated fertilizers (DETRICK, 1997, 1995 and 1992; VAN PEER, 1996; ZHANG et al., 1994).

### Partly polymer-encapsulated controlled-release fertilizers/ Mixtures of encapsulated and non-encapsulated N, NP or NPK fertilizers.

Another possibility in order to combine the advantage of controlled release nutrient supply with the lower cost of conventional fertilizers, is to mix polymer-coated granules for instance in a ratio of 1 : 1 with non-encapsulated granules of the same fertilizer type (HÄHNDEL, 1997). In Germany, an NPK fertilizer (with a minimum content of 3% N, 5%  $P_2O_5$ , 5%  $K_2O$ ), of which only 50% of the granules are polymer-coated, is registered under the German fertilizer law (KLUGE and EMBERT, 1996). In 1997 a similar NPK fertilizer type has acquired registration<sup>10</sup> with only 25% polymer-coated granules, offering a greater flexibility in use and further improved economy. Such partly polymer-encapsulated controlled-release fertilizers, i.e. mixtures of encapsulated and non-encapsulated granules or prills, are also in use in Japan.

#### Neem- or 'Nimin'-coated urea

The Indian neem tree, *Azadirachta indica*, has a number of traditional uses, based on the insect repellent and bacteriostatic properties which are contained in its various parts. The oil obtained from its fruits is a valuable raw material for the production of pharmaceuticals and bodycare products.

9Pursell Trikote<sup>®</sup> PSCU process under United States Patent No. 5,599,374 of Feb. 4, 1997 (see also section 5.1.2. Polymer-coated controlled-release fertilizers). 10Registration issued spring 1997.

The press cake from the production of neem oil has a controlledrelease and nitrification inhibiting effect, besides other possible uses. It is therefore frequently recommended to add neem cake to the N fertilizer (i.e. urea) to form NCU (neem coated urea) or NICU (*nimin = extract from neem cake*) coated urea to improve the nitrogen use efficiency and to reduce losses (WICHMANN, 1997).

However, the use of NCU or NICU is apparently not practiced to any extent by farmers, neither in India where the tree originates, nor in other tropical countries to which it has been brought in the past. The main reason for this might be the difficulty to obtain sufficient quantities of neem cake at village level, the additional labour for blending or the lack of a corresponding technical process.

Since the benefits of the practice of using NCU are not always reliable, this might also be an obstacle to the use of neem as controlledrelease agent or nitrification inhibitor (see Chapter 11 Fields of application).

SURI (1995) regrets that no serious attempt has been made to develop technology to coat urea with neem on a commercial scale.

#### 5.1.3. Supergranules and others

This group of special fertilizer products has been given special attention, particularly in tropical and subtropical regions. Conventional soluble fertilizers are formulated in compacted form, with a relatively small surface-to-volume ratio. This results in a slow release of nutrients, or relatively slower release, into the soil solution. Some of these special formulations also contain urea-formaldehyde (UF) or IBDU<sup>®</sup>.

Whereas in Western Europe such supergranules, briquettes, tablets or sticks are preferably used for fertilizing trees and shrubs, as well as some vegetables, such as tomatoes, pot plants etc., in tropical regions the preferred use is in irrigated rice (GEETHADEVI et al., 1991; GOUR et al., 1990; RAJU et al., 1989).

### 5.1.4. Controlled-release fertilizers in a matrix

The fertilizer particles are incorporated throughout carrier matrices. However, to achieve the desired slow release effect, a large quantity of carrier material is necessary (up to 40%). Therefore only low-grade fertilizer formulations are possible (e.g. NPK 10-10-10 or NPK 5-15-10). In general the carrier material is a mix of molten waxes and of surfactants and polyethylene glycols (polymeric matrices; styrenebutadiene rubber formulations and others).

### 5.2. Nitrification and urease inhibitors - stabilized fertilizers

In the soil ammonia  $(NH_4^+)$  is oxidized to nitrite  $(NO_2^-)$  and nitrate  $(NO_3^-)$  respectively, according to the diagrammatic reaction process:

$$2 \text{ NH}_4^+ \rightarrow 2 \text{ NH}_2\text{OH} \rightarrow 2 \text{ (NOH)} \rightarrow 2 \text{ NO} \rightarrow 2 \text{ NO}_2^- \rightarrow 2 \text{ NO}_3^-$$

Bacteria of the *Nitrosomonas spp* are responsible for the transformation to nitrite. The thus formed nitrite is relatively rapidly further oxidized to nitrate by *Nitrobacter and Nitrosolobus spp*. (AMBERGER, 1996). The process is known as nitrification.

$$2 \operatorname{NO}_{2}^{-} + \operatorname{O}_{2} \xrightarrow{} Nitrobacter \\ 2 \operatorname{NO}_{2}^{-} + \operatorname{O}_{2} \xrightarrow{} Nitrosolobus \\ Nitrosolobus$$

The formation of the environmentally important gases  $N_2O$  and NO may be considered to be a side-reaction of the nitrification process (BUNDESRAT, 1996).

Nitrification inhibitors, when added to nitrogen fertilizers and applied to the soil, delay the transformation of ammonium-ions to nitrite (and further to nitrate) by preventing or at least by slowing down the activities of the soil bacteria *Nitrosomonas spp.* (ZACHERL and AMBERGER, 1990; FARM CHEMICALS HANDBOOK, 1995; STURM et al., 1994).

$$NH_{4}^{+} \longrightarrow NO_{2}^{-}$$

$$NH_{4}^{+} \longrightarrow NO_{2}^{-}$$
*Nitrosomonas spp.*

However, plants are also capable of taking up nitrogen in form of ammonium-ions<sup>11</sup>. By doing so, an additional advantage is given in the form of an improved uptake of phosphorus (P). When plant roots are forced to take up  $\rm NH_4^+$  this results in a strong excretion of protons for charge equilibration in the roots decreasing the pH of the rizosphere (up to two pH units), and resulting in phosphate mobilization (CURL and TRUELOVE, 1986). The effect of phosphate mobilization is intensified by the addition of a nitrification inhibitor which prolongs the  $\rm NH_4^+$  phase in the soil, resulting in a much higher P uptake (AMBERGER, 1992; AMBERGER, 1991b). However phosphate uptake will only be improved if the phosphate fertilizer has been incorporated directly into the rhizosphere (band application).

<sup>11</sup>Consequently, it is not correct to classify fertilizers containing nitrification inhibitors as slow or controlled-release fertilizers. Because ammonium is retained on clay minerals by ion exchange, it is sparingly mobile; nitrate being totally mobile is very much more readily leached from the soil (AMBERGER, 1993b; SCHEFFER, 1994 and 1991; SCHWEIGER, 1991; ZERULLA; 1991). Therefore, addition of a nitrification inhibitor to nitrogen fertilizers will minimize leaching of nitrogen in the form of nitrate as well as denitrification losses of N, by far the greatest source of N loss in the US and in Europe.

In addition, there are several investigations through which it has been proven that nitrification inhibitors not only reduce leaching of nitrate nitrogen, but also show a suppression of methane ( $CH_4$ ) emissions and a reduction of nitrous oxide ( $N_2O$ ) emissions (BRONSON and MOSIER, 1994 and 1993; BRONSON et al., 1992; BUNDESRAT, 1996; KLASSE, 1991; KOSHINO, 1993; SCHWEIGER, 1991).

These are highly important positive environmental aspects of nitrification inhibitors' use. Reduced losses of N not only protect the environment, but are also increasing nitrogen use efficiency, resulting in higher yields on a more consistent basis.

It should be part of Best Agricultural Practices that farmers should fine-tune nitrogen application particularly in environmentally sensitive areas, by using nitrogen fertilizers amended with a nitrification inhibitor (MINISTÈRE, 1994).

This also applies to urease inhibitors. In world agriculture, urea has become the most widely used nitrogen fertilizer, particularly in the tropics (out of world total of 77.3 million tons of N in 1995/96, approximately 37.9 million tons were in the form of amide-N in form of urea, UAN and others, corresponding to approximately 49%) (IFA, 1996). However, urea has its leading position in the world fertilizer market not due to particular advantages for agriculture, but to its advantageous production process making use of the  $CO_2$  by-product from the manufacture of ammonia, resulting in a highly competitive product.

When amide-N, as in urea, UAN or in some NPK fertilizers, is applied to the soil, it is transformed relatively rapidly through the activity of the enzyme urease to ammonia, CO, and H<sub>2</sub>O (AMBERGER, 1996):

 $\label{eq:constraint} \begin{array}{c} \text{Urease} \\ \text{CO(NH}_2)_2 + \text{H}_2 \text{O} & \longrightarrow 2 \ \text{NH}_3 + \text{CO}_2 \end{array}$ 

The full equation is:

 $CO(NH_2)_2 + H_2O \longrightarrow H_2NCOONH_4 \longrightarrow 2NH_3 + CO_2$ 

i.e. in a first step urea is transformed into the - unstable - ammonium carbamate:



This transformation has two major drawbacks:

• it is subject to - sometimes very high - volatilization losses of ammonia if urea is surface-applied, (GRANT et al., 1996b; WATSON et al.; 1994) or under flooded conditions (FILLERY and VLEK; 1986), and

it can produce severe seedling damage (by ammonia NH<sub>3</sub> and nitrite NO<sub>2</sub>) if seed-placed levels are too high (GRANT et al., 1996a).

Depending on the conditions of its use, for a certain period of time, urease inhibitors inhibit or reduce the formation of the enzyme urease, which is ubiquitous in surface soils and necessary for the transformation of urea to ammonia,  $CO_2$  and  $H_2O$ , thus slowing down the rate at which urea hydrolyses in the soil, and preventing or at least depressing the transformation of the amide-N to ammonium hydroxide and ammonium (NH<sub>4</sub><sup>+</sup>).

Therefore, the use of urease inhibitors added to urea or to UAN solutions may be able to increase the efficiency of surface applications or applications to flooded rice (BYRNES et al., 1995) and to reduce the toxicity of seed-placed urea (KINCHELOE and SUTTON, 1996).

### 5.2.1. Types of nitrification and urease inhibitors

Note: The abbreviations of the names of the chemical compounds are those commonly used and are not in all cases corresponding the IUPAC-Regulation (International Union of Pure and Applied Chemistry).

12 Soil fumigants also show nitrification inhibiting properties.

13 Nitrification as well as urease inhibitor. In the United States, ATS is also used as a source of sulphur in liquid fertilizers or as stand alone N-S liquid fertilizer.

14 Nitrification as well as urease inhibitor.

There are several types of nitrification and urease inhibitors known in Europe, India, Russia and the United States. Compounds and materials investigated in scientific research, laboratory, pot and field experiments concerning their *nitrification inhibiting* properties are (DRESSEL, 1995):

Nitrapyrin: 2-chloro-6-(trichloromethyl)-pyridine,

DCD: dicyandiamide,

CMP: 1-carbamoyle-3-methylpyrazole, and its main metabolite MP: 3-methylpyrazole, (MPC: 3-methylpyrazole-1-carboxamide),

Terrazole: etridiazole<sup>12</sup>,

5-ethoxy-3-trichloromethyl-1,2,4-thiadiazole,

AM/AT/ATC: 4-aminotriazole,

CP: 2-cyanimino-4-hydroxy-6-methylpyrimidine,

2-ethylpyridine,

ATS<sup>13</sup>: ammonium thiosulphate,

ST: sodium thiosulphate,

ZPTA: thiophosphoryl triamide,

Thiourea<sup>14</sup>,

Guanylthiourea (GTU)

AMP: ammonium polycarboxilate,

Ethylene urea,

Hydroquinone,

Phenylacetylene,

Phenylphosphoro diamidate

NCU: neemcake coated urea,

NICU: 'nimin' (neemcake extract) coated urea,

CCC / ECC: wax coated/encapsulated calcium carbide.

Of these, the following nitrification inhibitors have sometimes been used in agriculture:

AM (which had some importance in Japan),

Terrazole (5-ethoxy-3-trichloromethyl-1,2,4-thiadiazole),

Ethylene urea,

Thiourea<sup>15</sup> (TU), and others,

Up to now only two nitrification inhibitors have gained practical or commercial importance in agricultural and other crops:

Nitrapyrin: 2-chloro-6-(trichloromethyl)-pyridene,

DCD: dicyandiamide, (CMP has been used only in combination with DCD).

*Urease inhibitors* are a more recent development. Compounds which have been investigated in scientific research, laboratory, pot and field experiments during the last five years include:

Thiophosphoro triamides:

NBTPT (or NBPT): N-(n-butyl)thiophosphoric triamide,

and the main metabolite BNPO (or NBPTO): N-(n-butyl) phosphoric triamide,

TPT: thiophosphoryl triamide,

PPD/PPDA: phenyl phosphorodiamidate,

CHTPT: cyclohexyl thiophosphoric triamide,

CNPT: cyclohexyl phosphoric triamide,

PT: phosphoric triamide,

HQ: hydroquinone,

p-benzoquinone,

ATS<sup>16</sup>: ammoniumthiosulphate,

HACTP: hexaamidocyclotriphosphazene,

Thiopyridines, thiopyrimidines, thiopyridine-N-oxides,

NN-dihalo-2-imidazolidinone,

N-halo-2-oxazolidinone,

NCU: neemcake coated urea / NICU: neem cake extract coated urea

However, only one urease inhibitor has gained practical and commercial importance:

NBTPT (or NBPT): N-(n-butyl)thiophosphoric triamide.

### Nitrapyrin

2-chloro-6-(trichloromethyl) pyridine (and related chloronated pyridines, such as: 4,6-dichloro-2-trichloromethylpyridine).

Nitrapyrin is exclusively produced by DowElanco in the United States and distributed under the trade name 'N-Serve'<sup>®</sup> (NS), (DOWELANCO, W.Y.; DOWELANCO, 1989; HUFFMAN, 1996).

15See footnote 14. 16 See also footnote 13. The product has a very selective effect on *Nitrosomonas* bacteria; however, in contrast to DCD and CMP, it has some bactericidal effect, i.e. the *Nitrosomonas* bacteria are not only depressed or inhibited in their activity for a certain period, but part of the population in treated soil is killed (HUFFMAN, 1996; STURM et al., 1994; ZERULLA, 1996).

In the United States nitrapyrin is registered by EPA (United States Environmental Protection Agency) as a pesticide. From 1997 onwards all nitrification inhibitors will have to be registered as pesticides (excluding DCD-containing fertilizers).

The toxicity,  $LD_{50}$ , is 2140 mg/kg oral, female rat (N-Serve24<sup>®</sup>) and 3616 mg/kg oral, female rate (N-Serve24E<sup>®</sup>).

In the soil (and the plants) nitrapyrin rapidly degrades by both chemical and biological processes into 6-chloropicolinic acid, the only significant chemical residue from its use, and further to N, Cl,  $CO_2$  and  $H_2O$ . Decomposition is normally complete in 30 days or less in warm soils that are conducive to crop growth. However, nitrapyrin is very persistent in cool soils, thus providing excellent activity from fall or winter applications. For product applied in warm soils, measurable activity against *Nitrosomonas* is normally 6 to 8 weeks, but activity can be 30 weeks or longer when applied to cool soils in the late fall or winter.



#### N fertilization of corn.

• Corn on the left received a commercial rate of anhydrous ammonia applied in spring prior to planting.

• Corn on the right received the same N rate plus Nitrapyrin (N-Serve®).

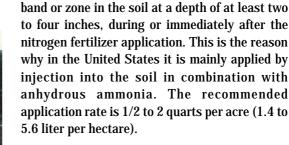
Note the difference in firing (caused by nitrogen deficiency) where the nitrification inhibitor was not used. (HUFFMAN, J. - DowElanco)

The technical incorporation of nitrapyrin into conventional fertilizer material is difficult due to its vapor pressure. Decreasing the vapor pressure equally reduces nitrification inhibiting efficiency. The active ingredient is, therefore, formulated as liquid product:

- N-Serve 24<sup>®</sup> Nitrogen Stabilizer with 2 pounds active ingredients per gallon (240 g /l); for use with anhydrous ammonia and impregnation onto urea.
- N-Serve 24E<sup>®</sup> Nitrogen Stabilizer with 2 pounds active ingredients per gallon (240 g / l); for use with liquid fertilizers and animal manure (slurry).

There are three crops to which N-Serve<sup>®</sup> is labelled for use: corn, sorghum and wheat. However, the present (1995) usage of nitrapyrin in the US is 90% on corn, 9% on wheat and about 1% on grain sorghum.

Whatever type of ammonium-N containing fertilizer is applied in combination with N-Serve<sup>®</sup>, the material has to be incorporated into a



The main reason for use of nitrification inhibitors by American farmers is the time management, i.e. preferring fall-N plus nitrification inhibitor instead of spring N, and spring N plus nitrification inhibitor instead of side-dress N.



Incorporation of the N fertilizer and the nitrification inhibitor into the soil. (HUFFMAN, J., DowElanco)

#### DCD - dicyandiamide (about 67% N)

DCD as a technical product is produced by one producer each in Germany, Japan and Norway, whereas nitrapyrin is exclusively produced by only one manufacturer in the United States. Some lower quality material is produced in the PR China. It is produced in the form of white or colorless crystals from calcium cyanamide, water and carbon dioxide (CO<sub>2</sub>), which have wide industrial use (ODDA, 1995). It has low water solubility and contains at least sixty-five percent (65%) nitrogen (AAPFCO). In the soil it is decomposed (partly abiotically and partly biotically by specific enzymes) and converted via guanyle urea and guanidine to urea, a conventional fertilizer (AMBERGER, 1991 and 1989; HALLINGER, 1992; HAUSER and HASELWANDTER, 1990; VILSMEIER, 1991a and 1991b)<sup>17</sup>.

In Western Europe, there is no uniform legislation on DCD. In individual Member countries of the EU it is designated in fertilizer legislation as a nitrification inhibitor and classified under several N fertilizer types amended with DCD as a nitrification inhibitor (for instance in Germany 'dicyandiamide-containing ammonium sulphate nitrate') (BUNDESMINISTER, 1995; KLUGE and EMBERT, 1992; ZERULLA; 1996).

17This multi-step degradation might be the reason why DCD as such is recognized as slow release nitrogen (AAPFCO); however, this is not the case when DCD is used in concentrations of a nitrification inhibitor in combination with ammonium nitrogen containing fertilizers.

> 18Bundesgesundheitsamt, Berlin, Germany.

With an  $LD_{50}$  of >10.000 mg/kg oral, female rat, it is practically non-toxic. The Ames Test with dicyandiamide did not reveal any mutagenic activity. Furthermore, long-lasting studies have shown that dicyandiamide has no cancerogenity. The Official Institute for Public Health of the Federal Republic of Germany<sup>18</sup> has therefore confirmed that any risk to the health of humans can be excluded when dicyandiamide is used. This also applies to its residues (ROLL, 1991; ZERULLA, 1996). In the soil DCD has a bacteriostatic effect on the *Nitrosomonas bacteria*, i.e. the bacteria are not killed, but only depressed or inhibited in their activities for a certain period of time. Even several applications have only led to a depressive effect on *Nitrosomonas bacteria* (STURM et al.; 1994).

Depending on the amount of nitrogen applied and the moisture and temperature of the soil, the ammonium-N in nitrogen fertilizers (or in slurry) is stabilized for several weeks (6 to 8), through the nitrification inhibiting effect of DCD.

Compared with the application of conventional nitrogen fertilizers, there are larger amounts of ammonium, and significantly less of nitrate, found in the soil solution when the nitrogen fertilizer used was amended with DCD. This applies particularly to light textured soils and to heavy precipitation within the 6-8 weeks following application (AMBERGER, 1993a and 1993b; KLASSE, 1991; ZERULLA and KNITTEL, 1991a and 1991b).

The use of DCD-stabilized fertilizers is therefore recommended for most of the agricultural crops fertilized with ammonium-N containing mineral fertilizers (or slurry) under these growing conditions. A growing area of application of DCD-containing nitrogen fertilizers is protected in water catchment areas.

Most DCD is technically incorporated into conventional ammonium containing fertilizers (AS, ASN - ammonium sulphate, ammonium sulphate nitrate, urea, UAN) making up about 5 - 10% DCD-N of the total N content. It is thus automatically applied in the correct proportion to the ammonia content (BASF, 1993 and 1991; WOZNIAK, 1997; ZERULLA, 1996).

Types of fertilizers distributed in Western Europe are:

- ALZON<sup>®</sup> 27 with 27% total N of which 1.6% (or 1.6 N- units) is dicyandiamide-N (DIDIN<sup>®</sup>) and 13% S,
- ALZON<sup>®</sup> 47 with 47% total N of which 3% (or 3 N- units) is dicyandiamide-N (DIDIN<sup>®</sup>),
- BASAMMON<sup>®</sup> stabil with 27% total N of which 1.6% (or 1.6 N-units) is dicyandiamide-N (ENSAN<sup>®</sup>) and 13% S, and
- NITROPHOSKA<sup>®</sup> stabil 12-8-17 with 12% total N of which 1.1% (or 1.1 N-unit) is dicyandiamide-N (ENSAN<sup>®</sup>), plus 2% MgO and 7% S.

In 1996 SKW Stickstoffwerke Piesteritz have obtained registration within the German Fertilizer Law (KLUGE and EMBERT, 1996) for the mixture of DCD and 3MP, (3-methylpyrazole, the main metabolite of CMP) in a proportion of 15:1 PIADIN<sup>®</sup> and a mixture of dicyandiamide and ammonium-thiosulphate.

The regulation states: this combination of products may be added as nitrification inhibitors to nitrogen fertilizers containing at least 40% of the total nitrogen content in form of ammonium-N, carbamide-N or cyanamide-N (KLUGE and EMBERT, 1996: WOZNIAK, 1997). The registered combination of DCD and 3MP is contained in ALZON<sup>®</sup>-liquid with 28% total N, a combination of PIASIN 28 (solution of UAN) with PIADIN<sup>®</sup> (mixture of DCD and 3-methylpyrazole in a of ratio 15:1).

#### СМР

1-carbamoyle-3-methylpyrazole

This nitrification inhibitor had been developed by Agrochemie Piesteritz (now SKW Stickstoffwerke Piesteritz GmbH, Wittenberg, Thuringia). There has been substantial laboratory research and rigorous field testing, practically exclusively in the former GDR, in Central Eastern Europe and in the Former Soviet Union (there called KMP).

For this research and field testing it was formulated as a 50% CMP-formulation, to be mixed into solid ammonium-N containing fertilizers or into solutions. However, because CMP is liable to hydrolysis when incorporated into solid or liquid fertilizers, the CMP-formulation had to be added at the time of applying the fertilizer (or the slurry). This was also the reason for the recommendation that CMP could be mixed with water (at a rate of CMP of 1 - 3 kg/ha) and applied with a pesticide sprayer at rates of 200 to 300 l of spray per ha.

As with nitrapyrin, CMP has to be incorporated into the soil during or immediately after application.

CMP has a bacteriostatic effect on *Nitrosomonas* bacteria, i.e. it only reduces their nitrifying activities for a certain period, thus preventing the conversion of ammonia into nitrite (and further to nitrate).

CMP has a  $LD_{50}$  of 1580 mg/kg, oral, rat, the main metabolite 3MP an  $LD_{50}$  of 1312 mg/kg, oral, rat.

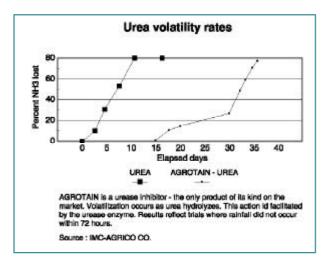
However, apparently this product has never reached the stage of being marketed and used in agricultural practice. One recent exception is its metabolite 3MP, which is used in combination with DCD (PIADIN<sup>®</sup>) added to UAN (urea-ammonium-nitrate-solution) (WOZNIAK, 1997).

#### Neem- or 'Nimin'-coated urea

(see sections 5.1.2. Neem- or Nimin-coated urea, and 11.1).

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18AGROTAIN is a registered trademark

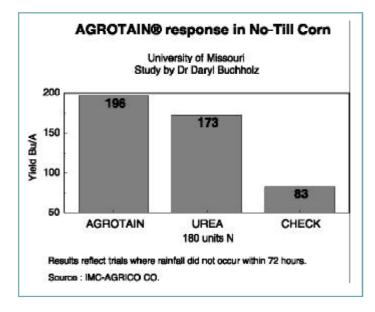


#### **NBTPT** - (or NBPT)

N-(n-butyl) thiophosphoric triamide

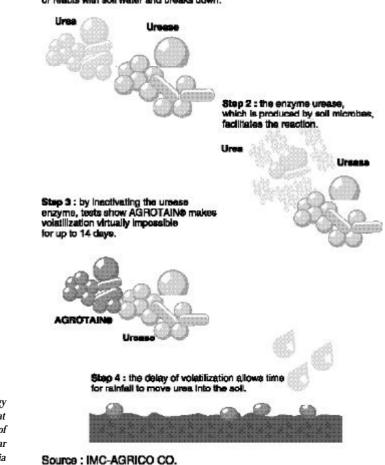
NBPT, and its main metabolite BNPO (or NBPTO): N-(n-butyl) phosphoric triamide, at present the only urease inhibitor of commercial and practical importance for agriculture, has been marketed since spring 1996 by IMC-Agrico Company under the trade name AGROTAIN<sup>®18</sup> in the United States (IMC GLOBAL, 1996).

Surface applied urea or urea containing fertilizers have the potential for significant volatilization losses (KINCHELOE, 1997b; KINCHELOE and SUTTON, 1996).



Such losses will occur particularly if the urea or UAN solution is not incorporated into the soil with the help of rainfall or tillage within 72 hours after application (no-till, high residue conservation tillage and minimum tillage<sup>19</sup>), or when it is applied to flooded rice. Furthermore, seed-placed urea may produce severe seedling damage.

AGROTAIN<sup>®</sup> has consistently demonstrated its ability to inhibit the activity of the enzyme urease (GARDNER, 1995; MARKING, 1995). The effect of preventing the activities will last up to 14 days.



Urea volatilization

Step 1 : volatilization occurs when urea hydrolyzes or reacts with soil water and breaks down.

19The CTIC (Conservation Technology Information Centre) estimates that conservation tillage may reach 27% of the worldwide cropland by the year 2000, including rice in Southeast Asia (KINCHELOE, 1997b). AGROTAIN<sup>®</sup> is formulated (as a green clear liquid) containing (IMC AGRICO, 1995)

- 25% N-(n-butyl) thiophosphoric triamide, as active ingredient,
- 10% N-methyl-pyrrolidone (NMP),
- 60-65% other non-hazardous ingredients.

As regards the toxicology of NBPT, the following data have been determined: acute toxicity oral  $LD_{50} = 1\ 000$  to 4 000 mg/kg. The Ames tests (*in vitro* mammalian cell gene mutation and *in vitro* mammalian chromosome damage) were each negative (WILKINSON, 1996). The product has received EPA approval. It is being registered as a TSCA (Toxic Substances Control Act) substance.

According to IMC-Agrico Company, in the soil the product degrades into fertilizer elements: nitrogen, phosphorus and sulphur. Degradation studies have also been carried out when applied to flooded rice (BYRNES et al., 1989b).

The recommended rate of application depends exclusively on the quantity of amide-N applied as urea, UAN or in form of NPK fertilizers: 0.14% by weight, corresponding to 2.8 lb active ingredient/t (1.4 kg/t) of urea. This will require a concentrate loading of approximately 5 quarts per ton (5.21 l/t) of urea. Urea impregnated (see box below) at this concentration will be effective in inhibiting the activity of the enzyme urease regardless of pounds per acre (kg/ha) of urea applied. In dry bulk blends, the urea should be impregnated prior to the introduction of other fertilizer materials.

The half-life of bulk-stored urea impregnated with the urease inhibitor AGROTAIN<sup>®</sup> at the 5.21 lt concentration is about three months (KINCHELOE, 1997b).

When urea is applied at a rate of 150 lb of N per acre (168 kg/ha N) the amount of AGROTAIN<sup>®</sup> to be added is 1.65 pints per acre (1.93 l/ha). When UAN solution is applied at a rate of 150 lb of N per acre (168 kg/ha N) the necessary amount of the urease inhibitor to be added is 1.3 pints per acre (1.52 l/ha).

AGROTAIN<sup>®</sup> urease inhibitor may be used for a wide variety of crops. It is primarily recommended for pre-plant surface application of urea



Spreading of UAN treated with the urease inhibitor AGROTAIN<sup>®</sup>. (IMC-AGRICO CO.)

and urea-containing fertilizers but may be used as pre-emergence, sidedress, top-dress or other post-planting applications. It is not recommended for use if rain is imminent. If rainfall exceeding 0.75 inches (approximately 2.0 cm) is expected immediately after application, the urea would be carried below the surface and there would be little opportunity for the urease inhibitor to perform.

Some IMC-Agrico Company recommendations for the impregnation procedures

#### **Equipment required**

• An accurate balance or scale to weigh materials.

• Equipment suitable for rolling or blending the urea particles with a spray of AGROTAIN<sup>®</sup> solution. A rotary device that can tumble the urea and allow for uniform contact with the urease inhibitor without spillage is appropriate. Auger and paddle mixers may also be used. Exposed inner surface should be clean, dry and dust-free.

#### Procedure

• Use with adequate ventilation. Respiratory protection not required under normal use.

•Weigh the urea and transfer into the equipment for contact with AGROTAIN® concentrate.

• Measure the desired quantity of AGROTAIN® concentrate.

Transfer the AGROTAIN<sup>®</sup> solution to the spraying equipment and apply to the urea. AGROTAIN<sup>®</sup> urease inhibitor impregnated urea should not be stored for more than two weeks prior to application.
Tumble the urea in the spraying equipment allowing adequate time for uniform coverage. A non-hazardous dark blue/green dye is included in the concentrate to assist in evaluating the uniformity of coverage.

#### For mixing with UAN (Urea-Ammonium-Nitrate) solutions

After donning proper personal protection, ... fill spray tank half full with UAN solution. With agitators on, add the appropriate amount of AGROTAIN<sup>®</sup> concentrate for the desired concentration in the full volume, mix well and then add the remainder of the UAN solution. Use blended UAN solution soon after mixing. There is a gradual decomposition of the urease inhibitor when stored in the presence of water.

### Chapter 6. Research

In Australia, Canada, PR China, Germany, France, India, Israel, Italy, Japan, the Netherlands, Russia, the UK and the United States there are a number of research institutes, universities and industrial companies involved in research on slow and controlled-release and stabilized fertilizers. Some investigations have also been carried out in the Czech Republic, Denmark, Egypt, Ghana, the Republic of Korea, the Philippines, Poland, Malaysia, South Africa, Spain and Thailand.

The main fields of research are described below.

#### 6.1. Controlled-release fertilizers

SHAVIV and MIKKELSEN (1993) list the following issues, regretting that the use of slow and controlled-release fertilizers is still very limited due to their relatively high cost, in spite of the potential benefits.

"Yet there exist several other issues related to the efficient use of SRF/CRF that deserve much more attention and deeper insight. If properly treated, these issues should lead to a more significant contribution of SRF/CRF to agriculture and the environment. Among these are:

- utilization of advanced technologies and development of new concepts for preparing more cost effective SRFs.
- better assessment of expected benefits to the environment from using SRF/ CRF. This should include estimates of the economic significance of reducing pollution of ecosystems (air, water, etc.) and sustaining soil productivity.
- quantification of the economic advantages resulting from reduced losses of nutrients and from labour saving.
- improved assessment of economic benefits expected from reduced osmotic stress and specific toxicity as a result of synchronizing nutrient supply (release) with plant demand.
- induction of synergistic effects between chemical forms of nutrients by controlling the exposure of plants to desired compositions.
- better understanding of the mechanisms controlling release rate and pattern and the major environmental factors (e.g. temperature, moisture, microorganisms, acidity, soil type, etc.) which affect them.
- development of tests for characterizing the release performance of SRF/CRF in order to improve industrial quality control and farmers decision making process.
- construction of mechanistic-mechanical models for predicting release of nutrients under laboratory and field conditions and as design tool for the technologist.

Achievements in the above-mentioned directions will greatly depend on the possibility of organizing multi-disciplinary R&D work for dealing with such complex problems, and probably even more on the priority and support given to such work by our society."

- 6.1.1. Nitrogen efficiency of conventional mineral fertilizers as compared to controlled-release (sulphur coated urea and encapsulated) fertilizers. Correlating data from laboratory testing to the efficiency under field conditions. Assessment of the economic benefits resulting from the use of controlledrelease fertilizers (value/cost-ratio - VCR).
- 6.1.2. Factors influencing nutrient release from sulphur coated urea and encapsulated mineral fertilizers, such as type of coating, coating agents/coating process (polymerization coating processes), coating thickness, solvent agents etc. Another very important factor is the physical characteristic of the substrate onto which the coating is applied: particle size, shape and surface profile (irregularity), prills which often have holes in their surface or granules (whether granulation e.g. of urea is smooth, or whether it is rough and irregular when using agglomeration granulation and compaction granulation).
- 6.1.3. Factors and mechanisms influencing nutrient release from sulphur coated urea and encapsulated mineral fertilizers, such as soil type, humus content, acidity, temperature, moisture (irrigation), microbial activity.
- 6.1.4. Decomposition/degradation (biological, physical, chemical) of coating agents, particularly polymeric coating materials, under specific soil and climatological conditions.
- 6.1.5. Effect of controlled-release fertilizers on nitrate leaching and emissions of N<sub>2</sub>O and NO<sub>2</sub>.
- 6.1.6. Development of (standard) methods for the evaluation of nutrient release rates from controlled-release fertilizers.
- 6.1.7. Development of new coating and encapsulating materials, specifically of more rapidly degradable synthetic materials/ polymers.
- 6.1.8. Development of new, improved, lower-cost and environmental friendly technologies in coating/encapsulating processes.

Producers in Japan and in Israel, as well as the leading manufacturers in the United States, are working intensively on the development of new lower-cost controlled-release fertilizer products. In Japan, another particular field of research is the degradation of the polymeric material used in coating.

Though there are no fundamental changes to be expected, improved and more economic products may enter the market within the next few years (particularly in Japan and in the United States).

In the United States, in addition to the research departments of the leading manufacturers, among the many research institutes and/ or universities working on agronomic and ecological applications and considerations of slow and controlled-release fertilizers, the following may be named (DETRICK, 1997 and 1995): University of California, Riverside **Cornell University** University of Florida University of Georgia **University of Illinois Iowa State University** Louisiana State University **Michigan State University Mississippi State University** North Carolina State University **Ohio State University Oregon State University Pennsylvania State University Purdue University Rutgers University** Texas A+M University V.P.I and Southern University University of Wisconsin

In Western Europe all research work in practice is done in horticulture. Technical research (particularly on the degradation of the polymeric material used in coating) is only undertaken by manufacturers (HÄHNDEL, 1997).

In Japan, in addition to the research department of the leading producers, the following research institutes and universities are working on polyolefin-coated fertilizers (FUJITA, 1996a):

Paddy rice:

- 1. Ohgata Branch, Akita Prefectural Agr. Exp. Sta.
- 2. Aichi Sogo Agr. Exp. Sta.
- 3. Okayama Agr. Exp. Sta.
- 4. Kawatabi Farm, Faculty of Agr., Tohoku University
- 5. Faculty of Agr., Yamagata University

**Upland field crops:** 

- 1. Kawatabi Farm, Faculty of Agr., Tohoku University
- 2. Faculty of Agr., Tohoku University

3. Iwate Agr. Exp. Sta.

Vegetables and horticultural crops:

1. Fertilizer Institute, Chisso Corp.

2. Kumamoto Agr. Exp. Sta.

3. Aichi Sogo Agr. Exp. Sta.

#### **Environmental problems:**

- 1. National Institute of Agro-Environmental Sciences
- 2. Fukushima Agr. Exp. Sta.
- 3. Gifu Agr. Exp. Sta.
- 4. Akita Prefectural Agr. College.

In Israel, in addition to the intensive research and development programme carried out by Haifa Chemicals Ltd., the Faculty of Agricultural Engineering, Technion - Israel Institute of Technology, Haifa is working on controlled-release fertilizers (GORDONOV, 1995).

#### 6.2. Nitrification and urease inhibitors - stabilized fertilizers

#### Main research topics

- Nitrogen efficiency of mineral fertilizers used with and without nitrification/urease inhibitors. Assessment of the economic benefits to the farmer resulting from the use of nitrification/urease inhibitors (value/cost-ratio - VCR). Assessment of the expected benefits to the environment from using nitrification/urease inhibitors.
- Effect of nitrification and urease inhibitors on soil (soil-life), water and atmosphere.
- Effect of nitrification inhibitors (nitrapyrin/DCD/CMP and other compounds) on *Nitrosomonas* bacteria under varying soil (particularly high temperature soils), climate and use (flooded) conditions.
- Effect (including the long-lasting effect on the nitrogen cycle in soils) of nitrification inhibitors on reducing losses/leaching and volatilization of nitrous oxide and methane.
- Effect of urease inhibitors on the hydrolysis of urea and volatilization losses of ammonia.
- Factors influencing the degradation of nitrification and urease inhibitors in the soil, such as soil type, pH, humus content, temperature, moisture (irrigation), microbial activity.

Significantly more difficult than the development of new coating technologies and coated/encapsulated fertilizers is that of new nitrification and urease inhibitors. In addition to the development cost the requirement for registration as a pesticide or a fertilizer/fertilizer or soil amendment, the development of nitrification and urease inhibitors is subject to such costly and time-consuming testing (for instance toxicity on rats, mice etc., decomposition of the active ingredient, decomposition and toxicity of metabolites, crop residue studies), that the majority of fertilizer manufacturers have neither the preconditions for research nor the capital needed.

The problem is that the cost (and time) of developing new acceptable nitrification and urease inhibitors is equal to the development of a new plant protection product. The margin, however, which may be expected from their marketing, is more or less in the range of that of conventional fertilizers. The profitability of nitrification (and urease) inhibitors to producers is too small to justify the effort. There are more opportunities for acceptable levels of economic returns from investing in herbicides, insecticides, fungicides and (conventional fertilizers) than in nitrification or urease inhibitors. Consequently, there are only three or four companies in the world which at present are directing their costly and time-consuming research to the development of new nitrification and urease inhibitors.

In addition to these industrial companies the following research institutes/universities are working on nitrification and/or urease inhibitors:

In the United States<sup>1</sup> (HUFFMAN, 1996):

University of Illinois Ohio State University Clemson University University of Nebraska University of Minnesota Pennsylvania State University Purdue University University of Kentucky Kansas State University Iowa State University Southern Illinois University

In Western Europe (DRESSEL, 1995):

Lehrstuhl für Pflanzenernährung der TU München, Freising, Germany.

Bayerische Landesanstalt für Bodenkultur und Pflanzenbau, Freising, Germany.

Niedersächsisches Landesamt für Geowissenschaft, Bodentechnisches Institut Bremen, Bremen, Germany.

Institut für Angewandte Mikrobiologie der Justus-Liebig-Universität, Gießen, Germany.

Instituto sperimentale per la cerealicoltura, Sezione specializata per la risicoltura, Vercelli, Italy.

IVIA - Instituto Valenciano por Investigacion Agraria, Valencia, Spain.

Department of Plant Ecology and Evolutionary Biology, University of Utrecht, Utrecht, The Netherlands.

Station d'Agronomie de Quimper, Quimper, France.

Centre d'Etudes Nucléaires de Cadarache, Département de Biologie, Saint-Paul-lez-Durance, France

University of Edinburgh School of Agriculture, Edinburgh, Scotland, UK.

In Israel (GORDONOV, 1995) - The Faculty of Agricultural Engineering, Technion, Isreal Institute of Technology, Haifa.

In Malaysia - Department of Soil Science, University Pertanian Malaysia Serdang, Selangor.

In The Philippines - IRRI, Division of Soil and Water Science, Manila.

Further information on research is given in the chapters References and References for Further Reading.

<sup>1</sup> For clarification: These universities have field programmes verifying the activity of nitrification and/or urease inhibitors, but are not developing new products.

### Chapter 7. Legislation and Methodology

#### 7.1. Registration of slow and controlled-release fertilizers

In Israel, Japan, the United States and in Europe a wide range of slow and controlled-release fertilizers is produced and distributed. The products are for specific applications, fertilizing purposes and strategies.

According to the producers, slow and controlled-release fertilizers are classified into (SH0JI and GANDEZA, 1992)

- an ordinary release group, and
- a delayed release group.

Fertilizers of the ordinary release group release their nutrient contents at a specific rate starting at the time of application. Nutrient dissolution of fertilizers of the delayed release group starts nutrient release only 30 or 40 days after application (in water at a constant temperature of 25°C).

Slow and controlled-release fertilizers may contain only nitrogen or potassium, NP or NK (with different forms of K), NPK or NPK plus secondary nutrients and/or whole series of micro-elements. All the products are given with different longevities ranging for instance from one month to 18 months.

In spite of this highly specialized and diversified market no universally accepted legislation exists as yet to protect the consumer, neither in the United States, nor in Western Europe nor in Israel. Only Japan has introduced obligatory test methods. However, it is obvious that legislation and regulations are becoming more urgent as more slow and controlled-release fertilizers may be used in agriculture in the future (AAPFCO, 1995; BUNDESMINISTER, 1995; KLUGE and EMBERT, 1992).

In April 1988, at the conference of The Fertiliser Society in London, WILSON (1988) read a paper with the title: 'Slow-release - true or false? A case for control.' Wilson has seen a strong emphasis on protection for agriculture rather than for the home gardener, grower or amenity manager. He asked: "How does an individual come to an informed opinion when examining pack copy or associated literature? Does he know which materials have been included in a compound or NPK fertilizer? If some slow release ingredient is named as present, how does he tell how much has been included? What help does he get from our fertilizer regulations?" He suggested potentially suitable test methods and the additional information which should be necessary to be shown on labels in order to regulate claims of slow-release. In the United States, 50 states regulate their own agricultural policies, including fertilizers (CRAWFORD, 1995; CRAWFORD and DUBBERLY, 1995; HALL, 1996; PIGG, 1995; YELVERTON, 1995). There are some guidelines and Federal EPA regulations which can be imposed on the individual States if their policies and laws do not meet or exceed the Federal regulations. This is predominantly the case concerning registration of pesticides under 'RECRA' (Resource Conservation and Recovery Act) in the EPA.

However, fertilizers are excluded. Therefore, the AAPFCO (1995) has formulated definitions for controlled-release fertilizers (Official Publication No. 48).

#### Definitions for controlled-release fertilizers

- 3. Slowly Released or Controlled Plant Nutrients.
- a) No fertilizer label shall bear a statement that connotes or implies that certain plant nutrients contained in a fertilizer are released slowly over a period of time, unless the slow-release components are identified and guaranteed at a level of at least 15% of the total guarantee for that nutrient(s) (Official 1991).
- b) (Under b) the different types of fertilizers with slow nutrient release characteristics are listed)
- c) Until more appropriate methods are developed AOAC International method 970.04 (15th Edition) is to be used to confirm the coated slow-release and occluded slow-release nutrients and others whose slow-release characteristics depend on particle size. AOAC International method 945.01 (15th Edition) shall be used to determine the water insoluble nitrogen of organic materials (Official 1994).

(Source: AAPFCO, 1995)

### Example of AAPFCO label statements which imply slow-release properties

17. Coated Slow-Release or Occluded Slow-Release Nutrients When nutrients in a fertilizer are coated or occluded to obtain slowrelease properties, then the guarantees for those components may be shown as footnotes rather than as a component following each nutrient. For example, a fertilizer with one coated material:

#### Fertkote 10-15-20

Guaranteed Analysis	
Total Nitrogen (N)	10%
2.5% Ammoniacal nitrogen	
2.5% Nitrate nitrogen	
5.0% Urea nitrogen*	
Available Phosphate $(P_2O_5)$	15%
Soluble potash (K <sub>2</sub> O)	20%
Sulfur (S)	14%
*% Slowly available Urea nitro	gen from

Regulatory models for slow-release fertilizers were also given by TERRY (1990).

In its latest (Tentative 1995) Policy Statement on Slow Release and Stabilized Fertilizers (AAPFCO, 1997): "AAPFCO affirms that one of the goals of its model legislation is to provide for consumer protection while encouraging free commerce. Pursuent to this goal, AAPFCO endorses and recommends that: The term 'Efficiency Design (ED)' be adopted to describe fertilizer products with characteristics that minimize the potential of nutrient losses to the environment, as compared to a 'reference soluble' product."

AAPFCO further declares: The AAPFCO, through its body of model legislation, develop and promote simple and effective regulatory procedures for ED products. These include:

- identification of methodology for determining 'release rate' or 'longevity of response' that is straight-forward and universally accepted;
- development of definitions and labeling requirements that confirm with this policy statement, and that are readily understood and supported by industry;
- development of guidelines for consistent and effective enforcement of regulations for ED products; and
- flexibility to include future product concepts and technology that may be developed and brought to market.

Table 2 gives examples of procedures for extraction and acceleration of controlled nutrient release in use with manufacturers, as presented by HALL (1995), Vigoro Industries/IMC Global, at the 45th The Fertilizer Industry Round Table, Raleigh/United States, October 1995.

To meet present and future needs for regulation and methodology a Task Force was formed jointly by AAPFCO and TFI in the United States. Members of the Controlled Release Task Force come from Departments of Agriculture, Manufacturers, AAPFCO and TFI. It has the following five subcommittees:

- Methodology,
- Labeling,
- Enforcement,
- New Products/Concepts,
- Policy.

The new method for extraction and analysis of efficiency design (see above) of fertilizers would have to meet the following requirements:

**1.**Must be able to categorize materials tree structure with logic for computer base.

2. Status of current materials will not change significantly.

3. Can be run in an analytical laboratory.

- 4. Can be run in seven days, preferably less.
- 5. Would be able to be performed by technicians using available equipment, thus gaining wide acceptance.

Source/ Company	Scope	Solvent System	Temp.°C	Sample Water Ratio	Total Samp/ Water Ratio Water Change	Samp Freq	Test
Vigoro	N-P-K-Mg PC & LS	Water	20°	5g/500ml	5g/2000ml Complete	1H/1D 3D/7D	N-P-K Minors
Vigoro	N-P-K-Mg PC & LS	Water	40°	5g/500 ml	5g/2000ml Complete	1H/1D 3D/7D	N-P-K Minors
Scotts	SCU/PCU	Water	25°	25g/250ml	25g/1000ml Complete	1H/1D 3D/7D	N
Scotts	SCU/PCU	Water	60°	15g/150ml	15g/600ml Complete	1H/1D 3D/7D	N-P-K
Scotts	N-P-K PC	Water	Room Temp	4g/300ml	4g/600ml Comp. Sand	3D/10D X7D	N-P-K Cond.
Scotts	N-P-K PC	Water	High Temp	20g/170ml	20g/170ml No	15M/1H 2H	N-P-K Cond.
ICI	SCU	Water	Low ?20°	12.5g/2500ml	12.5g/2500ml	1D/?	N
ICI	SCU	Water	High	40g/200ml	40g/200ml	1H/?	Density
Fisons	PC N & N-P-K	Water	25°	10g/500ml	10g/1000ml Refilling	1D/7D	ISE/ICP
Fisons	PC N & N-P-K	Water	High	10g/200ml Complete	10g/2600ml Complete	1D/7D	Ν
Aglukon	PC N-P-K	Water	Low	10g/800ml	10g/800ml No	1D/7D	N-P-K & Cond
Aglukon	PC N-P-K	Water	High	10g/800ml	10g/800ml No	8H/1D 2D/	N-P-K & Cond
Pursell	PC N-P-K & Sizes	Water	22°	20g/100ml	20g/100ml No	2H/3D 7D	Ref. I
Pursell	PC N-P-K & Sizes	Water	30°	10g/100ml	10g/100ml No	2H/6H 12H	Ref. I
Pursell	PC N-P-K & Sizes	Water	50°	10g/100ml	10g/100ml No	2H/6H 12H	Ref. I

 Table 2. Matrix Chart - Controlled Release Procedures for Extraction and Acceleration

6. Would be applicable to a wide variety of blended material.

7.Can be correlated to agronomic data.

8. May be used for extraction of multiple nutrients (N-P-K-Minors).

Here, one of the most important points is point No. 7 'correlation of laboratory to agronomic data', i.e. the development of tests, the application of which matches laboratory findings and practical field data, must be initiated.

In Western Europe there are not, as yet, general regulations of the EU Commission imposed on slow and controlled-release fertilizers; they are non EEC regulated fertilizers. To date, there are no coated controlled-release fertilizers within the EU type list.

As in the United States, a Task Force had been formed; this CEN TC260/WG4/Task Force slow-release fertilizers (TFsrf)<sup>1</sup> has the challenge of presenting proposals to the official authorities/legislator on the classification of these fertilizers.

The aim has been to define the conditions under which a type of fertilizer which is already included in the list of EU fertilizer types, may be newly categorized as a slow or controlled-release fertilizer (for the limits already proposed see section 2.1.). The enforcement of these limits will probably be the decisive point of any new regulation.

The CEN TFsrf started with the development of an adapted analytical method on how to evaluate encapsulated, water soluble fertilizers. In 1995, such an adapted analytical method was tested in parallel by 14 European and one United States laboratories. The results of this test have been analyzed and represent the basis for the formulation of a 'CEN-Norm'.

Furthermore, the CEN TFsrf has proposed manufacturers' responsibility for the biological testing of their products. Also, the manufacturers will be asked to prepare a comparative study between an official CEN-standard - long time cold water leaching (in preparation) - and an accelerated short time control measurement (in preparation), which has to be declared on the label combined with the longevity of the said nutrients.

CEN TC260/WG4/TFsrf has made their proposals for slow and controlled-release fertilizer definitions and has handed them over to the EU-Commission to add as a general note to the official EU-list of fertilizer types. This will avoid the generating of a number of individual new slow and controlled-release fertilizer types.

However, there are regulations concerning definitions and classification in the individual member states. Under some national fertilizer legislations there are types available such as coated NPK, partly coated NPK, coated urea etc., e.g. limited to a minimum amount of coated product of 50% or 70% - the coated part of partly coated fertilizer has to be stated - but without saying anything about the percentage of surface, mass, number of granules, and even without saying anything about the effectiveness.

<sup>1</sup> Information supplied by the chairman of the CEN Task Force, Dr. Bernhard Kloth, AGLUKON Spezialdünger GmbH, Düsseldorf, Germany (KLOTH, 1996).

The coating has to be certified to be harmless.

In Germany, CDU, IBDU and UF are classified as individual fertilizers; in addition fertilizer legislation covers the group of N fertilizers (N, NPK, NP and NK fertilizers) containing CDU, IBDU or UF. Furthermore, the fertilizer legislation covers coated N fertilizers as well as coated and encapsulated NPK fertilizers.

For analyzing for example the slow release nitrogen content in UFbased slow-release fertilizers, in most of the Member States of the EU methods are used which are adapted from corresponding methods of the AOAC. For IBDU- and CDU-based as well as for coated and encapsulated slow and controlled-release fertilizers, national or manufacturers' methods are in use. France and the Netherlands prescribe special procedures.

At present, the following methods are generally used to test the slow release pattern of slow and controlled-release fertilizers:

- plant tests: ornamentals, vegetables, lettuce, grass,
- different leaching procedures: e.g. percolation, substrate storage, cold water, tempered water, cumulative, incremental,
- Chemical analysis: e.g. amount of coating/product.

In Israel the following recommendation for the registration of slow and controlled-release fertilizers were made in 1995:

Recommendation for the registration of slow and controlledrelease fertilizers

Authorities and users should be interested in proper registration of Controlled Release products, because the use of fertilizers that are declared as CRFs but do not have real Controlled Release properties, will not bear any agronomic or environmental benefits.

Compilation of systematic registration instructions regarding SRFs and CRFs is essential for proper introduction of these fertilizers into routine use. Complete formal definition of Controlled Release products has to refer to:

- · identification of the mechanism that controls the release, and
- the expected release curve, and the factors that might affect the release.

In addition, strict instructions have to be given regarding product labeling. Apart from the basic information that describes nutrient content, labels should describe the release characteristics of the product.

(Source: RABAN, 1995; GORDONOV, 1995)

RABAN (1994) prepared a conceptual model describing the nutrient release from coated granules. Further models of controlled release of nutrient from coated fertilizers have been developed and investigated by ZAIDEL (1996). RABAN and SHAVIV (1995) have defined the mechanism controlling the release of nutrients from coated fertilizers as either coating failure or as diffusion. In an investigation they try to give a systematic assessment of the release mechanism of four different types of coated urea. An evaluation of the solute diffusion coefficient of a controlled release fertilizer using wetting and dissolution characteristics in a gel based controlled-release fertilizer has been made by SHAVIT et al. (1995).

In Japan the registration instructions require a dissolution test. A product is defined by the nutrient release rate obtained in water under well defined conditions.

Annex VII gives the three test methods: the laboratory methods (release in water and release in soil) and the field method (FUJITA, 1996a).

In order finally to achieve *international standardization*, the Controlled Release Task Force formed in the United States by AAPFCO and TFI has established relations with members of the corresponding CEN-subcommittee (CEN TC260/WG4/Task Force slow release fertilizers (TFsrf) in Brussels.

#### 7.2. Nitrification and urease inhibitors

In the United States fertilizers, but *not* additives to fertilizers, are excluded from 'RECRA' regulations in the EPA (United States Environmental Protection Agency). Therefore nitrapyrin - the active ingredient in N-Serve<sup>®</sup> -, the leading nitrification inhibitor in the United States, is classified as a pesticide under the EPA registration. In 1996 it was decided that all nitrification inhibitors have to be EPA registered as a pesticide in the United States (HUFFMAN, 1997).

Officials claim that manufacturers or distributors of DCD (DCDcontaining fertilizers) should also have to apply for registration under 'RECRA' in the EPA. Experts disagree, being of the opinion that nitrification inhibitors such as DCD, thiosulphate and others are not pesticides and that the EPA regulations for registration of these types of nitrification inhibitors would therefore have to be changed. In consequence, in spite of the new regulation, DCD will not require registration as a pesticide<sup>2</sup>.

In Western Europe, there is no uniform regulation for DCD, the leading nitrification inhibitor. As in the case of slow and controlledrelease fertilizers individual countries have established national classification and legislation (in Germany: N fertilizers with DCD; for instance dicyandiamide-containing ammonium sulphate nitrate) (BUNDESMINISTER, 1995; KLUGE and EMBERT, 1992; MINISTÈRE, 1994). CMP (in combination with DCD) also comes under fertilizer legislation.

The regulations under which a nitrification or urease inhibitor has to be registered have a significant influence on future research and the development of new nitrification and urease inhibitors, since the costs involved may be a decisive factor.

### Chapter 8.

### Manufacturers/Distributors of Slow and Controlled-Release Fertilizers and Nitrification and Urease Inhibitors

#### 8.1. Slow and controlled-release fertilizers: Regions

#### 8.1.1. United States

In the United States/Canada the leading producers and/or suppliers of slow and controlled-release fertilizers are:

- Pursell Technologies Inc.<sup>1</sup> (Annex I)
- The Scotts Company (Annex II)
- Vigoro Industries/IMC Global
- Lebanon Seaboard Corp.<sup>2</sup>
- LESCO, Incorporated
- Nu-Gro Corp. Canada/Omnicology, Inc.<sup>3</sup>

Vigoro Industries, who until now have produced IBDU<sup>®</sup>-based products and who began production of coated fertilizers in 1996, was acquired by IMC Global in the spring of 1996. This merger has created one of the world's largest fertilizer suppliers (HALL, 1996).

According to SRI International (LANDELS, 1994), these companies supplied 92% of the US market. The other 8% consisted of imports of sulphur-coated urea from Canada (Terra International), and polymercoated material from Japan and Israel (CRAWFORD and DUBBERLY, 1995; DETRICK, 1995; VAN PEER, 1996).

#### <sup>2</sup> Formerly Lebanon Chemical Comp., Lebanon, PA, producer of granulated NPKs containing UF and isobutylidenediurea IsoTek<sup>TM</sup> <sup>3</sup> Nu-Gro Corporation, Canada, has

<sup>1</sup> Formerly Pursell Industries, Inc.

acquired Terra's SCU production. Also Nu-Gro is the principal shareholder in Omnicology, Inc. in Gloversville, N.Y., since Nov. 1995. AgrEvo after going out of the lawn-fertilizer business in June 1996 has given the corresponding rights (use of registered trade marks 'Nitroform<sup>®</sup>' and 'Nutralene<sup>®</sup>' as well as distribution rights) to Omnicology, Inc.

#### 8.1.2. Western Europe and Israel

The leading manufacturers and/or suppliers in Western Europe are (GORDONOV, 1995; HÄHNDEL, 1995; KLOTH, 1996; VAN PEER, 1995):

- AGLUKON Spezialdünger GmbH, Germany (Annex III)
- BASF Aktiengesellschaft, Germany (Annex IV)
- Scotts Europe B.V., The Netherlands (see Annex II)
- EniChem SpA, Agricultural Div., Italy

In Israel the leading manufacturer and supplier is:

• Haifa Chemicals Ltd. (Annex V).

#### 8.1.3. Japan

The leading manufacturers and/or suppliers are (FUJITA, 1996a):

- Chisso Corporation (Annex VI)
- Asahi Chemical Industry
- Central Glass
- Mitsubishi Chemical
- Mitsui Toatsu
- Nissan Chemical Industry

Other suppliers are: Coop Chemical, Katakura Chikkarin, Nippon Fertilizer, Sumitomo Chemicals and Ube.

#### 8.2. Slow and controlled-release fertilizers : Products

United States		
Granular products		
Ureaform 38-0-0	The Scotts Company Omnicology, Inc. (AgrEvo) Hydroagri	'Scotts Granuform' 'Nitroform'®; production contract with Hercules, the original UF producer HydroformTM
Methylene ureas	The Scotts Company	'Scotts MU-40'
40-0-0	Omnicology, Inc. (AgrEvo) Hydroagri The Homestead Nitrogen Corp.	'Nutralene' <sup>®</sup> (Scotts has sale rights). 'HydroleneTM' METH-EX 40 methylene urea.Former producer of Nutralene <sup>®</sup> 40N.
NPK grades containing UF and/or isobutylidenediurea	The Scotts Company Lebanon Seaboard Corp.	'ProGrow'®, 'ProTurf'®, 'TurfBuilder''® 'IsoTekTM', 'Country Club''®, 'Greenskeeper''®, 'Greenview''®
Urea-Isobutyl Aldehyde Products		
31-0-0	Vigoro Industries, Inc. IMC Global	'IBDU''®
Liquid products Urea-formaldehyde solutions		
30-0-0	Georgia-Pacific Corp. Hickson Kerley, Inc.	'GP-4340', 'GP-4341'(30-0-2) 'Formolene'®-Plus'
29-0-0	CoRoN Corp.	'Folocron''®
28-0-0	CoRoN Corp.	'CoRoN''®
Urea-formaldehyde suspensions		
18-0-0	Georgia-Pacific Corp.	'Resi-Grow''®
Urea-triazone solutions		
28-0-0	Hickson Kerley, Inc.	'N-Sure''®
NPK grades	Hickson Kerley, Inc.	'Trisert'®

#### 8.2.1. Urea reaction products/slow-release fertilizers

ne'®, 'Nitroform'®, III).
J - 'Crotodur <sup>®</sup>
15-7-7 and 14-16-8

Japan	
Urea reaction products	
Mitsui Toatsu Fertilizers Inc.	Urea-formaldehyde
Mitsubishi Kasei Corp.	IBDU
Chisso Corp.	CDU <sup>®</sup> (see Annex VI)

#### 8.2.2. Coated/encapsulated controlled-release fertilizers

Sulphur coated urea	
Nu-Gro Canada, Inc.	Sulphur coated urea - SCU, sulphur coate potassium
Polymer coated products	
The Scotts Company <sup>₄</sup>	'Osmocote'®, 'Sierra'®, 'Sierrablen'®, 'Agrifor 'High N' 'Prokote'®, 'Scottkote'®, NPK formulations; 'Scottkote'® coated urea and potassium sulphate, (see Annex II).
Pursell Technologies Inc.	'POLYON <sup>®</sup> PCU', polymer coated urea; 'POLYON <sup>®</sup> coated potassium nitrate; 'POLYON <sup>®</sup> coated MAP, POLYON <sup>®</sup> coated NPK fertilizers (see Annex I).
Vigoro Industries, Inc./ IMC Global	'Escote' <sup>®</sup> , imported from Chisso Corp., Jap Used for blends to be applied in nurseries ('Woodace' <sup>®</sup> )
	'V-COTE <sup>(®</sup> , polymer coated (polyvinylidene chloride)
Agrivert Inc. (Nichiman Trad. Co.)	'Nutricote <sup>®</sup> polymer coated NPK fertilizer, imported from Chisso Corp., Japan
Agrium, Canada⁵	<ul> <li>'Duration'<sup>®</sup>, clay coated PCU (marketed in United States by Western Farm Service).</li> <li>'ESN'<sup>®</sup>, clay coated PCU (marketed in the United States by United Horticultural Supp</li> </ul>

<sup>4</sup>Also 'The Sierra Horticultural Products Company, Subsidiary'.

<sup>5</sup> Sherritt, Canada, acquired Esso Canada's Imperial Oil Chemical Division in early 1994 and the PCU developments (before with EXXON United States) some months later. Sherritt Fertilizer became Viridian, Inc. in 1995/96. Viridian Inc. has been acquired by Agrium Inc., Calgary, in 1996, now owning ESN<sup>®</sup> and DURATION<sup>®</sup>, CCPCU. Agrium Inc. has been until early 1996 Cominco, Inc., Calgary, Alberta Canada.

#### Polymer/sulphur coated products

Pursell Technologies Inc.	'TriKote <sup>®</sup> - several polymer-sealed sulphur coated fertilizer types (see Annex I).
The Scotts Company	'Poly-S' <sup>®</sup> - Polymer encapsulated sulphur coated urea (see Annex II)
LESCO Inc.	'Poly Plus' polymer/sulphur coated urea

#### Western Europe and Isael

Polymer coated products	
Sierra Europe B.V., The Netherlands	'Osmocote'®, 'Sierrablen'®, 'Sierraform'® (see Annex II)
Aglukon Spezialdünger GmbH, Germany (Subsidiary of AgrEvo)	'Plantacote <sup>®</sup> , (see Annex III)
BASF Aktiengesellschaft, Ludwigshafen, Rhein, Germany	'Basacote'®, (see Annex IV)
Haifa Chemicals Ltd., Israel	'Multicote <sup>®</sup> , several types of resin-coated compound fertilizers (see Annex V)
Mixtures of polymer coate	d and uncoated fertilizers
BASF Aktiengesellschaft, Ludwigshafen, Rhein, Germany	BASF NPK fertilizers, Nitrophoska <sup>®</sup> TOP, Basatop ™ Sport

#### Japan

Sulphur-coated products	
Mitsui Toatsu Fertilizer	Sulphur coated compound fertilizers
Nissan Chemical Industry	Nissan Mild, sulphur/polyolefin-coated
Polymer coated products	
Chisso Corp.	'Meister'®, Polyolefin coated urea, KCl and $K_2SO_4$ . 'Nutricote'®, (see Annex VI).
Asahi Chemical Industry Co.	'Nutricote <sup>®</sup> , Polyolefin coated compound fertilizers
Mitsubishi Chemical	M cote, polyolefin coated urea
Nissan Chemical Ind.	Polyolefin- /sulphur-coated
Ube Industries	UC cote, polyolefin coated fertilizers; pilot plant
Central Glass	Cera cote, alkyd resin coated
Coop Chemical	Coop Cote, several grades of alkyd-resin- coated potassium chloride and potassium sulphate
Katakura Chikkarin	Alkyd resin coated products

### 8.3. Nitrification and urease inhibitors

#### 8.3.1 United States

The principal manufacturers and distributors in the United States are (HARRELL, 1995; HUFFMAN, 1996; KINCHELOE and SUTTON, 1996):

DowElanco	Producer of nitrapyrin, which is distributed under the trade name 'N-Serve'®
IMC-Agrico Company Vigoro Industries Inc.	'AGROTAIN <sup>®</sup> , first commercial urease inhibitor NBPT, marketed since spring 1996.
Freeport-McMoRan Res. Partners Terra Nitrogen Corp.	They are distributing nitrogen fertilizers amended with DCD, which is all imported into the US from PR China, Norway and Germany.

#### 8.3.2 Western Europe

The principal manufacturers and distributors in Western Europe are (ODDA, 1995; WOZNIAK, 1997; ZERULLA, 1996):

SKW Trostberg, Germany	Manufacturer of DCD ('Didin <sup>®</sup> ) and distributor of DCD liquid ('DIDIN®-liquid'), as well as of DCD-containing nitrogen fertilizers under the trade name 'Alzon <sup>®</sup> , produced by BASF.
SKW Stickstoffwerke Piesteritz, Wittenberg, Germany	Until 1989 producer of DCD, however, exclusively for industrial use.Producing DCD and CMP-/DCD-combination product (PIADIN <sup>®</sup> ).
BASF Aktiengesellschaft, Germany	Manufacturer and distributor of nitrogen and NPK fertilizers containing DCD, which is produced by SKW Trostberg. Nitrophos <sup>®</sup> stabil and Nitrophoska <sup>®</sup> stabil; Basammon <sup>®</sup> stabil (see Annex IV).
ODDA Smelteverk AS, Norway	Manufacturer of DCD for industrial and agricultural use.

Producers of nitrification inhibitors in the PR China (ODDA, 1995): Around 20 different small producers

### Chapter 9.

### Consumption of Slow and Controlled-Release and Stabilized Fertilizers

#### 9.1. Slow and controlled-release fertilizers

The following figures given are based on information from companies marketing the products concerned, on notes in fertilizer magazines, reports and official publications (these are also referred to in chapter 10. Prices of slow and controlled-release and stabilized fertilizers).<sup>1</sup>

World consumption of synthetic slow and controlled-release fertilizers in 1995/1996 is estimated at 562 000 metric tons (table 3):

Table 3.	World consumption of manufactured slow and controlle			
	release fertilizers (in tons of fertilizer material)			

Region	1983	1995/96	% 1995/96	
United States*	202 000	356 000	64	
Western Europe**	76 000	87 000	15	
Japan***	44 000	119 000	21	
Total	322 000	562 000	100	
Plus 1 000 tons for Central and Eastern Europe ****				
<ul> <li>* LANDELS, (1994).</li> <li>** Instead of 1983 = 1980, estimated; including Israel.</li> <li>*** Arbitrated by the Ministry of Agriculture, Forestry and Fisheries (FUJITA, 1996).</li> <li>**** KLOTH, 1996.</li> <li>Source: Information received from producers.</li> </ul>				

In Central/Eastern Europe, the actual consumption of controlledrelease fertilizers is estimated at 1 000 t p.a. (approximately 500 t UFbased and 500 t coated/encapsulated products) (KLOTH, 1996).

According to the IFA's estimates (IFA, 1997), the world consumption of fertilizer nutrients in 1995/96 was:

Ν	77 302 mio. t
$P_{2}O_{5}$	31 047 mio. t
K <sub>2</sub> 0	21 015 mio. t

This total of N +  $P_2O_5$  +  $K_2O$  = 129 364 mio. t., corresponds to approximately 380 000 mio. tons of fertilizer material. Consequently,

 Several editions 1992-1996 of 'IFA Fertilizer Product Consumption/Fertilizer Production Forecasts', IFA, Paris; 'Commercial Fertilizers', Tennessee Valley Authority, Muscle Shoals, AL; 'FERTECON, European Fertilizer Fax', London; 'Fertilizer Week', London; 'Green Markets', Bethesda, MD, United States; 'Eurostat', Luxembourg. the estimated quantity of slow and controlled-release fertilizer consumption in 1995/96 still amounts to no more than 0.15% of total world fertilizer consumption.

This is on the one hand a negligible market but on the other hand it is a market with large growth rates. In the United States the supply of manufactured slow and controlled-release fertilizers (material) increased from 202 000 t in 1983 to approximately 356 000 t in 1995/ 96, i.e. by 76%. In Japan the production of slow and controlled-release fertilizers increased from 44 000 t in 1980 to 119 000 t in 1995/96, that is by 257%. Polymer-coated fertilizers (mainly NPK fertilizers) have become the most important (tables 3 and 4).

Whereas the total slow and controlled-release fertilizer world market is growing at an annual rate of 4.5 to 5.0%, Western Europe is significantly lagging behind the United States and Japan in consumption growth rate. In Western Europe the total consumption (production plus imports) of slow and controlled-release fertilizers only increased from approximately 76 000 t in 1980 to approximately 87 000 t in 1995/96 (an annual increase of less than 1.0%).

The potential for increased use, also in agriculture, is tremendous considering the advantages of:

- labour saving
- increased nutrient recovery, (N use efficiency/efficiency design)
- improved yields, and
- reduced negative environmental effects.

Whereas in the United States urea-formaldehyde condensation products represent more than half (53%) of the total consumption of slow and controlled-release fertilizers (table 4), in Western Europe IBDU-formulations comprise the largest group. The increase (1995/ 1996 as against 1980) in consumption there consists exclusively of IBDU-based slow and polymer-coated controlled-release fertilizers.

In the United States and in Japan polymer-coated controlled-release fertilizers have a 9 or 10% p.a. constant growth rate in consumption, in contrast to the yearly growth rate of 4.5% for all slow and controlledrelease fertilizers.

As regards the fertilizer types the greatest increase in consumption has been with polymer-coated types (PC), with polymer-coated NPK fertilizers accounting for the larger share.

In 1996, Pursell Technologies Inc. launched on the market POLYON<sup>®</sup> PC-NPKs-Homogenous Prills, 3-1-2 and 1-1-1 substrates produced by the RLC<sup>TM</sup> process such as POLYON<sup>®</sup> PC-NPK 18-6-12 and 14-14-14. Norsk Hydro have recently introduced 1-1-1 45% NO<sub>3</sub> prills onto the market. Scotts have introduced various PC-NPK combinations in Western Europe and in the United States. In Germany partly encapsulated NPK fertilizers have obtained registration. Haifa Chemicals has brought to the market PC-NPK granular fertilizers with micronutrients and a release time of 6 and 12 months.

Region Type	Year	United States	Western Europe*	Japan	Total	%
UF	1993/94	180 000	30 000	5 000	215 000	42
	1995/96	190 000	30 000	5 000	225 000	40
SCU/ SCU + P/SCU	1993/94	91 000	neg.	5 000	96 000	19
	1995/96	100 000	2 000	6 000	108 000	19
PC**	1993/94	36 000	15 000	58 000	109 000	21
	1995/96	45 000	20 000	72 000	137 000	24
IBDU/CDU	1993/94	14 000	35 000	31 000	80 000	16
	1995/96	14 000	35 000	33 000	82 000	15
Others	1993/94	7 000	-	3 000	10 000	2
	1995/96	7 000	-	3 000	10 000	2
TOTAL	1993/94	328 000	80 000	102 000	510 000	100
	1995/96	356 000	87 000	119 000	562 000	100

### Table 4. Consumption of Slow and Controlled-Release Fertilizers by Region and Type (in tons of material - 1993/94 and 1995/96)

1 000 tons material for Central / Eastern Europe should be added.

\* including Israel

\*\* PC = Polymer coated: PC urea, PC NPKs and PC others.

Source: 1993/94: Landels, 1994; Japanese Ministry of Agriculture, Forestry and Fisheries 1994/95 1995/96: Estimate based on information received from leading producers. 1993/94 and 1995/96: Several editions 1992-1996 of FERTECON, European Fertilizer Fax, London; 'Fertilizer Week', London; 'Green Markets', Bethesda, MD, United States; 'Eurostat', Luxembourg.

#### 9.2. Stabilized fertilizers - nitrification and urease inhibitors

There are no reliable statistics available publicly on the use of nitrification and urease inhibitors, nor of fertilizers containing these products. Due to the unique production structure - there is only one manufacturer of nitrapyrin in the United States - there are no figures available on the annual production of nitrapyrin.

The same holds true for DCD in Western Europe. Although there are some producers of DCD in the world, and although the total world production is estimated at 38 000 t in 1995/96, there are only two fertilizer manufacturers incorporating DCD (and only one CMP) into nitrogen fertilizers in Western Europe. This is also the reason why there are no statistics publicly available on DCD-containing fertilizer production.

The producers of DCD are (ODDA, 1995):

<ul> <li>SKW Trostberg, Germany</li> </ul>	11 000 t
<ul> <li>Nippon Carbide Industries, Japan</li> </ul>	3 000 t

- Various small producers, China 10 000 t
- Odda Smelteverk AS, Norway
   14 000 t

The Canadian producer Cyanamide of Canada stopped production of DCD in 1992.

However, these figures give no indication of the available capacities, which in some cases might be several times higher than the abovementioned production. It has also to be taken into account that DCD is a widely used industrial intermediate for the manufacture of pharmaceutical products, textile and paper chemicals, fire retardence products, water treatment chemicals, guanidines and guanamines etc. Therefore, these figures are also no indication of the amount of manufactured DCD finally used as a nitrification inhibitor in agriculture, added to ammonium-containing N, NP and NPK fertilizers.

The importance of nitrapyrin and DCD as nitrification inhibitors in agriculture may therefore be demonstrated by an estimate of the cropland acreage on which nitrification inhibitors containing N, NP and NPK fertilizers are applied:

For the United States the total acreage treated is estimated for 1994/1995 at 1.820 million hectares (4.15 million acres). Of the total area, approximately 1.620 million ha were treated with nitrapyrin and 200 000 ha with DCD-containing N fertilizers. Favoured by wet weather and environmental considerations in 1995/96, the treated area increased to approximately 1.860 mio ha. In relation to the total acreage of 160 mio. ha in 1995/96, this amounts to 1.16%.

For Western Europe, a very rough estimate only can be made concerning the agricultural area treated with DCD-containing fertilizers. Approximately 200 000 ha of the arable cropland may have been treated with DCD-containing N, NP and NPK fertilizers. In relation to the total arable acreage of the EU of 68 mio. ha this amounts to 0.29%. An additional marginal quantity of DCD may be used in liquid animal waste/ slurry (SKW TROSTBERG, 1993).

There are no figures available yet on the area which has been treated with the urease inhibitor NBPT (AGROTAIN<sup>®</sup>) during its first year of market introduction 1996 in the United States.

### Chapter 10.

# Prices of Slow and Controlled-Release and Stabilized Fertilizers

#### 10.1. Prices of slow and controlled-release fertilizers

The main obstacle to the wider use of slow and controlled-release fertilizers, particularly in agriculture, is the high cost of these special types of fertilizers as compared to conventional fertilizers.

The price difference is:

- lowest with SCU (generally less than 2 to 1),
- higher with UF products (per unit N, 3-5 times higher than in conventional fertilizers) and
- highest with polymer coated controlled-release fertilizers (ranging between 4 to 8 times that of corresponding conventional fertilizers).

This is a result of several important reasons:

• High prices of the ingredients used for encapsulated/coated products, particularly the price of the coating materials. 'The organic polymer coating materials, which consist primarily of single polymers, polymer mixtures or copolymers, may cost 10 to 30 times that of the fertilizer itself. To put this in perspective, the following example is given of a fertilizer with a cost index of 100 and a coating polymer with a cost index of 3 000. A coated fertilizer, comprised of 12% by weight polymer coating and 88% by weight fertilizer encapsulated by the coating, would have a materials cost as follows (DETRICK, 1996):

### Table 5. Cost Comparison of Urea versus Conventional Polymer-Coated Urea

Component	Cost Index	Weight %	Materials Cost Index	
Urea 46-0-0	100	88	88	
Polymer coating	3000	12	360	
PCU 40-0-0		100	448	
Note that the PCU is only a 40-0-0 grade, since the 12% coating results in only 88% urea in the PCU (88% x 46 N = 40 N) Source: DETRICK, 1996.				

The above calculation demonstrates that the materials cost of the coated fertilizer is four times that of the basic fertilizer and "in addition, the cost of production adds to this cost" (DETRICK, 1995).

- Low production capacities: Some producers manufacture their products in special batches (1 000 to 5 000 kg).
- To achieve perfect coating quality, producers usually employ size separation of raw granular materials. This process further adds to the cost of encapsulated/coated fertilizers.
- There are significantly higher marketing and sales expenses associated with slow and controlled-release fertilizers. The use of the products has to be explained much more carefully than conventional fertilizers to ensure the correct application.

However, the use of partly polymer-coated controlled-release fertilizers (see 5.1.2) or that of 'hybrid-coating' (sulphur plus polymeric material) may become more economic.

The newly developed RLC process of Pursell Technologies (reactive layers coating) also reduces the cost of encapsulation significantly. This may be demonstrated by the following theoretical calculations according to DETRICK (1996):

Table 6.	Cost Comparison of Urea versus (RLC) Ultra-Thin
	Polymer-Coated Urea

Component	Cost Index	Weight %	Materials Cost Index
Urea 46-0-0	100	96	96
RLC polymer	2200	4	88
PCU 44-0-0		100	184
Source: DETRICK,	1996		

As can be seen from tables 5 and 6, the materials cost index of the PCU produced by the RLC-process is significantly less than the materials cost index of the more conventional coated PCU (184 versus 448).

An economic guideline for the farmer to determine the profitability of an investment in fertilizer is the calculation of the value/cost ratio (VCR). Unfortunately, there is practically no data available from reliable field experiments with slow and controlled-release fertilizers permitting the exact calculation of the value/cost-ratio. Such field experiments are urgently needed worldwide. The minimum profitability is fixed normally at a VCR of 2. However, under more risky conditions, i.e. with tropical and subtropical farming conditions, the VCR should at least be 3 (TRENKEL, 1993). DETRICK (1996) gives two calculations (table 7 and table 8) showing the VCR when using controlled-release fertilizers on low cash value (LCV) crops and high cash value (HCV) crops:

## Table 7. Low Cash Value Crop with 50% Controlled-Release Urea-Nitrogen Standard Fertilizer Practice vs. Experimental Fertilizer Practice

Standard Fertilizer Practice	US\$ / acre
150 lb N / acre x US\$ 0.30 / lb N (urea-N)	45
Application costs, basic- & side-dressing	20
Total costs	65
Crop Yield Value	300
Experimental Fertilizer Practice, 50% CR Urea-N	US\$ / acre
75 lb N / acre x US\$ 0.60 / lb N - CR Urea-N	45
75 lb N / acre x US\$ 0.30 / lb N - urea-N	23
150 lb N / acre - total N	68
Application costs, basic-dressing	10
Total costs	78
Crop Yield Value (with 10% yield increase)	330
Value - incremental increase	30
Cost - incremental increase	18
Value / Cost-Ratio (VCR)	1.7
Source: DETRICK, 1996.	

The above calculation clearly shows that the application even of only 50% of total N in the form of controlled-release urea-N would not give a satisfactory value/cost ratio. In addition, it has to be noted that the cost of controlled-release urea-N in this example is only 2 times the cost of urea-N. Such a low level is generally not reached by conventionally encapsulated products.

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The situation is different with high cash value (HCV) crops:

### Table 8. High Cash Value Crop with 44% Controlled-Release Urea-Nitrogen

Standard Fertilizer Practice vs. Experimental Fertilizer Practice

Standard Fertilizer Practice	US\$ / acre
300 lb N / acre x US\$ 0.30 / lb N (urea-N)	90
Application costs, basic- & 2 side-dressing	30
Total costs	120
Crop Yield Value	3000
Experimental Fertilizer Practice, CR Urea 44% of total N	US\$ / acre
133 lb N / acre x US\$ 0.90 / lb N - CR Urea 44% of total N	120
167 lb N / acre x US\$ 0.30 / lb N - urea-N	50
300 lb N / acre - total N	170
Application costs, basic- & 1 side-dressing	20
Total costs	190
Crop Yield Value (with 10% yield increase)	3300
Value - incremental increase	300
Cost - incremental increase	70
Value / Cost-Ratio (VCR)	4
Source: DETRICK, 1996	

Even though, with high cash value crops, a controlled-release urea fertilizer is used at a cost at 3 times that of urea-N, the value/costratio is 4. In this case it is profitable to use at least part of the urea applied in form of a controlled-release fertilizer. This is even more to be recommended when taking into consideration that high cash value crops are managed with fertility pushed to much higher levels, thus increasing the potential for greater nutrient losses.

However, these comparative calculations clearly demonstrate that the main obstacle to the wider use of slow and controlled-release fertilizers, particularly in low cash value agricultural crops, is the high cost of these fertilizers as compared to conventional fertilizers.

This is also emphasized by comparing present market prices for slow and controlled-release fertilizers with those of conventional fertilizers.

#### 10.1.1. Market prices for slow-release fertilizers

40% of world consumption, and in the United States at present the largest group of slow and controlled-release fertilizers, are ureacondensation products. Therefore, some price relationships between conventional urea and urea-condensation products are given below:

With the price of granulated urea in the United States at about US\$ 300.00 per  $t^1$  in autumn 1996, the prices for slow-release fertilizers were approximately:

- UF-based products 38-0-0, 40-0-0: = US\$ 600.00 per t
- IBDU<sup>®</sup>-based products 30-0-0: = US\$ 900.00 to 1 100,00 per t.

The prices per unit of nitrogen within the different types of fertilizers demonstrate the difference more clearly. For granulated urea with 46% N the price is approximately US\$ 0.66 per kg of N, corresponding to approximately US\$ 300.00 per t (or US\$ 276.00 per short ton). For UF-based products with 38% N, the price is between US\$ 1.50 and 1.58 per kg of N, (corresponding to approximately US\$ 600.00 per t (or US\$ 545.00 per short ton).

For IBDU<sup>®</sup>-based controlled-release fertilizers with 31% N the price is approximately US\$ 2.90 to 3.55 per kg of N, corresponding to approximately US\$ 900.00 to 1 100.00 per t (or US\$ 817.00 to 1 000.00 per short ton).

In Western Europe, in the autumn of 1996 the price for prilled urea was approximately DM 370.00 per t fot<sup>2</sup> - bulk. In comparison, prices for the urea condensation product Ureaform were in the range of DM 1 800.00 to 2 300.00 per t.

These prices correspond to the following prices in DM/kg N:

- 1 t = metric ton.2 Free on truck.
- Urea = DM 0.80 per kg N,

on truck. • Ureaform = DM 5.40 per kg N.

#### **10.1.2.** Market prices for controlled-release fertilizers

In the *United States* encapsulated granular urea (Pursell POLYON® PCurea granular) is sold at a price of US\$ 600.00 to 1 000.00 per t. Encapsulated NPK fertilizers (Pursell POLYON® PC-NPK 3-1-2 and 1-1-1) are sold at prices from US\$ 1 500.00 to 2 500.00 per t.

In *Japan* polyolefine-coated urea (Chisso Asahi 'Meister'<sup>®</sup>) is sold at a price of 150 000 yen (= US\$ 1 500.00 per t).

In *Western Europe*, the average user prices are DM 3 500.00 to 5 000.00 per t.

In comparison the average price in the autumn of 1996 of NPK complex fertilizer 15-15-15 was approximately DM 360.00 per t fot bulk, and Urea 46% N granular, DM 370.00 per t bulk.

The price difference is considerably less between conventional urea and sulphur-coated urea (SCU). With the above mentioned prices in Western Europe of granular urea in the range of US\$ 245.00 per t and sulphur coated urea (SCU) with about US\$ 380.00 per t, the price per kg of N in sulphur-coated urea is approximately US\$ 1.00 per kg of N. This is approximately double the price per kg of N than in conventional granular urea.

This may be considered to be an acceptable difference for use in agriculture. However, it has to be kept in mind that SCU unfortunately has some shortcomings in performance, i.e. high initial release, while another portion of the nutrient is not being released over the necessary time period (lock-off).

As mentioned under 5.1.2 manufacturers are, therefore, trying to combine the controlled release performance of polymer-coated fertilizers with the lower cost of sulphur-coated fertilizers by 'hybrid'-coating (sulphur *plus* polymeric material).

#### 10.2. Economics of nitrification/urease inhibitors

In the United States, at the recommended standard rate of 0.5 lb/acre (560 g/ha), the grower cost for nitrapyrin (N-Serve<sup>®</sup>) is approximately US\$ 8.00 per acre (approximately US\$ 19.80 per ha). Applying 150 to 200 kg/ha N in form of UAN solution (with 32% N) costs (without application cost) approximately US\$ 100.00 to 130.00. Thus, using nitrapyrin increases the material cost by 20 to 15%.

Some companies incorporate imported DCD into solid nitrogen fertilizers, for example Super N<sup>®</sup> (UAN solution of Terra Nitrogen). When applying these DCD-containing nitrogen fertilizers the 'per acre grower cost' may be somewhat higher than that using nitrypyrin, adding approximately US\$ 9.00 to the fertilizer material cost per acre (approximately US\$ 22.20 per ha). With other formulations, depending on the application rates, fertilizer material costs increase by US\$ 7.00 to 12.00 per acre (US\$ 17.30 to 29.65 per ha). However, these fertilizers do not need to be immediately incorporated into the soil.

In Western Europe the most widely used nitrogen fertilizer is calcium ammonium nitrate (CAN) with 27% N (2.6 mio t of N out of a total of 9.5 mio t N consumption in 1994/95) (EFMA, 1994; FAO, 1995).

In Germany the price for CAN in autumn 1996/spring 1997 was DM 300.00 per t fot bulk, corresponding to DM 1.11 per kg of N.

However, the main nitrogen fertilizer actually used as a carrier material for DCD is ammonium sulphate nitrate (ASN) containing 26% N and 16% S. With 19 units of nitrogen in form of ammonium-N, ASN contains more ammonium-N than CAN. The price for ASN without DCD is approximately 10% higher than that of CAN: approximately DM 1.20 to 1.25 per kg of N.

If DCD is incorporated into ASN (the final product containing 27% N, of which 1.6% N is in form of DCD-N) the price increases by about 20%, corresponding to DM 1.45 per kg of N fot bulk.

If the amount of nitrogen applied per ha is, for example reduced by 20 kg/ha of N without affecting the yield level when using ASN amended with DCD, the fertilizer material cost per ha is the same as with the application of ASN without DCD (120 kg/ha N ASN at approximately DM 144.00 versus 100 kg/ha N ASN+DCD at approximately DM 145.00). However, with the application of ASN with DCD generally one extra application round can be saved. This corresponds to a saving of approximately DM 25.00/ha. Consequently, including the cost of application, the result is as follows:

- 120 kg N/ha ASN *without* DCD including application cost (1 basic, 1 side-dressing) = DM 194.00,
- 100 kg N/ha ASN *with* DCD including application cost (1 basic dressing) = DM 170.00.

Thus, the farmer - at lower cost but same yield level - additionally saves labour at a time with high work load.

Even if in agricultural practice (with exception of sulphur deficient soils or crops) the application of ASN with DCD is compared with that of CAN (DM 132.00 plus DM 50.00 = DM 182.00), there remains a difference in favor of ASN with DCD of DM 12.00. However, this is not the case when farmers have to buy ASN with DCD in bags, unfortunately still the majority. In bags the price per kg of N is about DM 1.85 (as against DM 1.45 in bulk). Furthermore, in the case of agricultural crops which do not allow a reduction of the rate of nitrogen applied or the saving of one extra application round, the price difference still constrains the wider use of DCD-containing nitrogen fertilizers. A different situation may arise should special regulations enforce the use of nitrogen fertilizers associated with a nitrification inhibitor in protected water catchment areas.

In the United States the cost of treating urea with the urease inhibitor AGROTAIN<sup>®</sup> would be in the range of US\$ 66.00 to 68.00 per (metric) t of urea. At that price it would cost US\$ 19.70 to impregnate solid urea at an application rate of 120 lb N per acre (135 kg/ha N), and US\$ 9.85 to treat UAN solution 28% N (at the same application rate of N).

Results from rigorous trials demonstrate that AGROTAIN<sup>®</sup> treated urea has increased corn yields by 14.2 bushels per acre in 316 nitrogenresponsive sites (table 9).

N source	No. of sites	Bushels per acre (t per ha)					
		With Agrotain <sup>®</sup>	Without Agrotain <sup>®</sup>	Agrotain <sup>®</sup> response			
Urea	316	127.9 (8.02)	113.7 (7.13)	14.2 (0.89)			
UAN	119	130.9 (8.21)	121.6 (7.62)	9.0 (0.56)			
Source: KINC	CHELOE (1997a),	SUTTON (199	97).				

 Table 9. Corn response to the urease inhibitor AGROTAIN<sup>®</sup>

 United States national average (more-years field-testing)

With a price of US\$ 3.40 per bushel of corn (fall 1995/spring 1996) an increase in production of 14.2 bushels results in an additional gross income of US\$ 48.28 or in a net income of US\$ 28.58.

In situations where an extra 15 to 20 lb of N per acre have been applied on no-till or low-tillage operations to compensate possible ammonia losses, this practice can be discontinued, further improving the economics of the use of AGROTAIN<sup>®</sup>.

# Fields of Application of Slow and Controlled-Release and Stabilized Fertilizers

## 11.1. Application of slow and controlled-release fertilizers in general

The indications given on prices of slow and controlled-release fertilizers as compared to conventional mineral fertilizers clearly explain why there is only very limited use of these highly priced fertilizer specialties on low cash value agricultural crops. However, these premium price products have established niches in highly specialized market sectors (KAFKAFI, 1996).

Where these highly priced fertilizer specialties are considered to be used in agriculture, even this depends on the definition of agriculture. Referring to the situation in the United States, William L. Hall/VIGORO Industries said at the 45th The Fertilizer Industry Round Table (HALL, 1995):

"We could say growing turf on a golf course in Florida is an agricultural crop, but we won't. We could say 100 acres of strawberries in Southern California is an agricultural crop but we won't. We could say 500 hectares of rice paddy in Japan is an agricultural crop, but we won't. Why? Use of controlled release technology is already an accepted practice by most users in these areas."

In the United States the agricultural crops in which controlledrelease fertilizers are mainly used are:

- strawberries,
- · citrus and other fruits, nuts and
- vegetables.

There is no doubt that it is cost-effective to apply encapsulated controlled-release fertilizers in (per area) high value crops. In relation to the high annual investment cost in laying a plastic mulch and in setting 30 000 to 60 000 strawberry plants, the expenditure on fertilizer/ m<sup>2</sup> is relatively low. This applies even when extremely expensive (as compared to conventional fertilizers) polymer-coated controlled-release products are used. Furthermore, with plastic mulch the most practical and responsible way of using fertilizers, is to apply them in form of a polymer-coated fertilizer with a longevity of 8 to 9 months, before laying the plastic mulch and setting the plants.

A California lettuce grower, for example, will have an annual crop investment of US\$ 6 500.00 - 8 500.00/ha and, to minimize risk of losing yield, may choose trickle fertigation over  $CAF^1$  use as a more dependable and controllable way of crop fertilization, in the absence

<sup>1</sup> CAF = Controlled availability fertilizers



Application of a controlled-release N fertilizer (Meister®) to a tomato nursery pot (before mixing). The total amount of N for the whole growing season is applied. (CHISSO-ASAHI FERTILIZER CO.)

of convincing evidence to the contrary (HAUCK, 1993). Approximately 70% of California strawberries are grown using CAFs under mulch.

For a high cash value horticultural crop (strawberry), SCOTTS (SIERRA, 1991a) gives the following example of nutrient saving or improved nutrient efficiency:

Research objective: Decrease fertilizer quantity, specially nitrogen and increase yield. Standard strawberry crop, planted in August, at a density of 30 000 plants/ha. Average nitrogen consumption of strawberries is 80-90 kg N per ha per crop. The mineralization process of the soil provides 30-40 kg N per ha during the growing season. Additional N needed is about 50 kg/ha.

Comparison: Grower practice - Conventional granular fertilizer. 1 200 kg/ha per crop of which 200 kg nitrogen. Nitrogen efficiency is 25%. Controlled-release fertilizer Agroblen<sup>®</sup> 17-9-8-3MgO, at 15 gram per plant = 450 kg/ha fertilizer with 76 kg N/ha. Nitrogen efficiency 66%.

SALMAN et al. (1990) obtained in an experiment with tomatoes the highest yield with a polymer-coated urea (6% coating). The yield was 67% and 45% more than that of uncoated urea and commercial sulphur coated urea.

On permanent crops, particularly when they are grown on more leachable soils which call for up to 15 split applications of N fertilizers per season (for example in Florida), the use of slow-release fertilizer significantly reduces labour costs. Reducing the number of applications as well as the amount of nutrients applied may compensate for part of the much higher cost of polymer-coated fertilizers.

HALL (1995) compares the costs and the amount of nutrients applied in young citrus trees in Florida, comparing six applications per year with a conventional fertilizer to one application of an IBDU + ESCOTE<sup>®</sup> slow-release fertilizer.

1.	8-4-8 all fertilizer material US\$ 193.10 / t 6 applications per year at 1 lb each = US\$ 0.58 / tree / year
2.	8-4-8 1/2 IBDU <sup>®</sup> at US\$ 323.00 / t 3 applications per year at 1 lb each = US\$ 0.48 / tree / year
3.	10-3-7 85% IBDU <sup>®</sup> at US\$ 433.00 per t 2 applications / year at 1 lb each = US\$ 0.44 / tree / year
4.	19-6-12 IBDU <sup>®</sup> + ESCOTE <sup>®</sup> at US\$ 1524.00 / t 1 application at 8 oz. / tree / year = US\$ 0.38 / tree / year.



Growing of tomato seedlings fertilized with a controlled-release fertilizer in the greenhouse. (CHISSO-ASAHI FERTILIZER CO.)

While this comparison appears to be most convincing, it is not clear, and therefore only assumed, that with each fertilizer regime used, the yield and the quality of the harvested fruit is of the same level. Furthermore, to show the true result of this practical field experiment, it would be indispensable also to report the yield and quality of the zero-plot (or that of the trees without any fertilizer application).

Comparing the nutrients applied with the conventional fertilizer (system 1) and that with the  $IBDU^{\otimes} + ESCOTE^{\otimes}$  fertilizer (system 4), the following amount of nutrients is applied:

- system 1: 218 g N 109 g P<sub>2</sub>O<sub>5</sub> 218 g K<sub>2</sub>O per tree,
- system 4: 47 g N 15 g P<sub>2</sub>O<sub>5</sub> 30 g K<sub>2</sub>O per tree.

Even assuming much better nutrient use efficiency (NUE), the question of whether such a difference in the amount of nutrients applied will conserve a sustainable soil fertility, should be monitored carefully over a considerable period of time.

ALVA (1993a and 1993b) concludes from experiments in a citrus orchard in Florida, that the frequency and rate of N application for young citrus trees can be reduced and  $NO_3$ -leaching can be minimized by using polyolefin coated controlled-release fertilizer without adversely affecting tree growth.

ZEKRI (1991a and 1991b) also states from an experiment on young Valencia orange trees that, with the use of controlled-release fertilizers, the application frequency could be reduced from a total of 15 to 6 applications with no adverse effects on tree growth. His conclusion is: combining soluble and controlled-release fertilizers in a plant nutrition programme offers an economical and effective strategy for citrus growers.

The experiments show that by using controlled-release fertilizers the amount of nutrients to be applied can be reduced significantly as compared to common practice. This saves labour and energy costs and the greater nitrogen use efficiency rate from controlled-release fertilizers will minimize possible leaching losses of nitrate to the ground water.

However, in some instances higher amounts of nutrients from controlled-release fertilizers might be applied. This is the case where the extended delivery of nutrients from the controlled-release fertilizer enhances growth, and, therefore higher nutrient demand by the plant over time.

The environmental aspects of controlled-release fertilizers have been investigated by SHAVIV and MIKKELSEN (1993). Comparing several types of polymer-coated urea SHAVIV (1995) found that increasing N use efficiency and lowering environmental damage by using controlledrelease nitrogen fertilizers can be critically affected by the release characteristics of the controlled-release N fertilizer in relation to the pattern of N demand of the crop.

Positive environmental aspects of controlled-release fertilizers in reducing nitrate (NO<sub>3</sub>) leaching and nitrous oxide (N<sub>2</sub>0) emissions are

reported by SHOJI and KANNO (1994), using controlled-release fertilizers in combination with innovative rice farming systems.

In the United States out of the 356 000 t of total slow and controlledrelease fertilizer consumption only about 25 000 t, mainly SCU and polymer coated fertilizers, are used on these agricultural crops, i.e. about 8%. The vast majority, i.e. 92%, is applied in non-agricultural sectors such as:

- nurseries and greenhouses,
- golf courses,
- consumers (home and garden),
- landscape gardeners and other professional lawn care, etc.

In Western Europe, with the exception of some protected vegetables, the whole quantity of the estimated 87 000 t of slow and controlledrelease fertilizers consumed in 1995/96 was used in greenhouses and nurseries (professional horticulture), containerized plants, on turf and public parks, by consumers (home and garden).

Encapsulated controlled-release fertilizers are optimal products designed to solve a number of the specific technical and environmental problems in professional horticulture, in fertilizing lawn and turf, in landscaping and for use by consumers. These sectors can also afford the use of such highly priced specialties.

It is only in Japan (see 11.1.1.), with its unique structure of agriculture and protectionist agricultural policy, that a larger proportion of slow and controlled-release fertilizers (urea-formaldehyde- and CDUbased as well as polymer-coated) is applied on rice (though large amounts are blended with conventional fertilizers), in addition to use on vegetables and in professional horticulture. In Japan professional horticulture is included in agriculture.

## **11.1.1.** Slow and controlled-release fertilizers in tropical crops (rice)

The possibilities of making use of controlled-release fertilizers on agricultural field crops in tropical countries should be much greater than in the agriculture of temperate regions. This applies especially to regions with light-textured soils under heavy rainfall or irrigation. Under these conditions losses of nitrogen from conventional fertilizers are high.

Controlled-release fertilizers are significantly less sensitive to air humidity and temperature fluctuations (better storage caracteristics) and less susceptible to leaching or denitrification. For these reasons, coated and encapsulated controlled-release fertilizers have been tested in rice, rice nurseries, soybeans, sugarcane, pastures and other agricultural crops, as well as on tree crops like oil-palm and rubber.

In rice, the soil-fertilizer regime is completely different from that of other crops, particularly as concerns applied fertilizer nitrogen (ALLEN, 1984; BOULDIN, 1986; GARCIA et al., 1982). Under flooded soil conditions, losses through denitrification may be high. When  $NO_3$ -N containing fertilizers are applied or if  $NH_4^+$ -N nitrifies prior to flooding, losses through denitrification may be large.  $NH_3^-$ N may also be lost to the atmosphere, when floodwater becomes alkaline during daylight hours, as algae consume all available carbonate (IFA, 1992).

For this reason, ammonium-N or amide-N containing fertilizers have been given preference in the fertilization of paddy rice. If these types of fertilizers are applied in floodwater, losses may be reduced. However, losses are significantly higher where flooding and drying (lack of irrigation water, cultivation under natural rainfall conditions) alternate.

Where farmers simply broadcast urea into standing floodwater (DE DATTA, 1986), urease activity at the flooded soil surface leads to rapid urea hydrolysis, high ammoniacal-N concentrations in the floodwater and potentially high volatilization losses when weather conditions facilitate the removal of  $NH_3$  from the water-air interface (BYRNES et al.; 1989a); (see also section 11.2. Nitrification and urease inhibitors). Under such conditions slow and controlled-release fertilizers should be much more effective, in particular polymer-coated fertilizers.

Since the introduction of sulphur coated urea (SCU) in the 1960s a number of rice experiments have been carried out, mostly in Asia. In a field experiment with wetland rice, RAJU et al. (1989) found that among a number of different N fertilizer types, sulphur-coated urea and urea supergranules gave the highest grain yields.

However, despite the facts that:

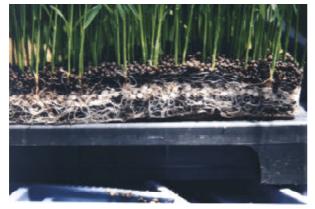
- the price ratio between SCU and conventional urea is generally less than 2 to 1, and
- when applied as a basal treatment, SCU has proved superior to urea in the majority of field experiments,
- sulphur is a necessary, and increasingly deficient plant nutrient,

the wider use of SCU has not become a general fertilization practice in rice cultivation (or for other agricultural field crops).

Most of the experiments carried out in wetland rice with polymercoated urea or NPK fertilizers, are of a more scientific character, i.e. they compare the nitrogen recovery from different N sources. In general, it can be shown that N recovery is greater from controlled-release fertilizers than from conventional fertilizers, such as urea or ammonium sulphate.

In India, in a field trial on rice conducted by SINGH and SINGH (1994), neem cake (as a slow-release agent) coated urea (NCU) produced substantially higher yields than prilled urea. Also BUDHAR et al. (1991) in a trial on rice achieved a significantly higher yield with NCU as compared to conventional urea. DE et al. (1992) came to the conclusion that more than 30 kg/ha N can be saved in rice with neem-extract (nimin) coated urea (NICU) in comparison to prilled urea. Also GEETHADEVI et al. (1991) produced higher yields in field experiments in rice with NCU than with prilled urea. However, in these experiments urea super granules gave the highest yield. Also JENA et al. (1993) and KUMAR et al. (1993) obtained the highest yields in rice with NCU. However, PANDEY and TRIPATHI (1994) did not obtain improved yields with NICU.

Although in the majority of cases neem-coated or nimin-coated urea, NCU or NICU, was equal in yield - or even better - than uncoated or other coated urea fertilizer types, this has apparently not led to commercialization and accordingly, there is no practical use of neemcoated urea in the fertilization of rice in India (see section 5.1.2. Neemor 'Nimin'-coated urea).



Layered application of a controlledrelease fertilizer (Meister®) in a rice nursery box (from bottom to top: soil - controlled-release fertilizer rice-seedlings - soil). (KANETA, Y.) According to FUJITA (1996a) the only country in which substantial quantities of polymer coated urea as well as coated NPK fertilizers are applied in rice is Japan. This is so in spite of the fact that also in other countries special types of polymer-coated urea granules have been developed which do not float, but sink immediately on application (Pursell Technologies POLYON® PCU - AF/Anti-Float, marketed in Japan by Sumitomo; Haifa Chemicals resin-coated anti-floating urea MULTICOTE®).

KANETA (1995) and KANETA et al. (1994) compared coated urea with a conventional compound fertilizer in one single application in a nursery box of non-tillage rice. In his experiment the absorption of N from coated urea was greater than that from the conventional fertilizer (recovery of 79% of N from coated urea at maturity). This also resulted in a greater number of grains and a higher yield.

SHOJI and KANNO (1994) report the comparative recovery of basal N through rice plants as follows.

	ontheastern sapa	••				
Placement	Fertilizer	Recovery, %	Reference			
Broadcast	Ammonium sulphate or urea	22 - 23	SHOJI and MAE, 1984			
Broadcast	POCU-100*	48 - 62	UENO, 1994			
co-situs	POCU-S 100	79	KANETA et al., 1994			
* POCU-100 = polyolefin-coated urea, release type 100 days Source: SHOJI and KANNO (1994)						

### Table 10. Comparative recovery of basal N by rice plants in northeastern Japan

Another example of N recovery comparing top-dressed AS (ammonium sulphate) and POC-Urea 70 (MEISTER®) is given by SHOJI and GANDEZA (1992).

Table 11. Recovery of top-dressed AS and POC-Urea	(40-0-0)-70* by rice in Yamagata, northeastern
Japan (NAKANANISHI et al., 1990)	

Application	Top-dressing date (days before heading)	Amount of N applied (kg/ha)	Recovery %					
			14 July	27 July	11 Aug.	25 Aug.	25 Sept.	
Conventional top- dressing	20 10	20 20		43	40 50	41 60	40 55	
POC-Urea-70 top-dressing	35	60	6 (44)**	17 (55)	3 (72)	53 (74)	(78)	
* Release type 70 da	* Palease type 70 days							

\* Release type 70 days

\*\* Recovery based on the amount of N released at each sampling date.

Source: SHOJI, S.; GANDEZA, A.T. (1992)

Table 12. Recoveries of basal N by rice

	Conventional	fertilizers	POC-Urea			
Farming	Conventional transplanting	Direct sowing	Conventional transplanting	No-till direct sowing		
Fertilization	Broadcast	Broadcast	Broadcast	co-situs		
Recovery	20-30%	10%	60%	70-80%		
Source: Personal communication from Dr. T. FUJITA (1996a), Chisso Corp., Japan						

Results from experiments (FUJITA, 1996a) showing the possible reduction of the amount of nutrients applied by use of controlled-release fertilizers without affecting the grain yield are given below.

### Table 13. No-till transplanting rice (Cultivar: Akitakomachi) using seedlings with single basal fertilization in Akita pref., NE Japan

Plot	Applied N (kg/ha)	Kind of fertilizer	Brown rice yield (ton/ha)
Conventional	100	Compound fertilizer	5.76
New farming	41	LPS-100*	6.04
New farming	62	LPS-100*	6.51
*LPS-100: Delayed days. To release nit water at 25°C. Source: KANETA (*	trogen takes 100	/ / /	

25°C.

Source: KITAMURA H., IMAI, K. (1995)

Site	Plot	Applied N (kg/ha)	Brown rice yield (ton/ha)				
Anjo	Conventional	84	6.04				
	New fertilization*	56	6.17				
Yatomi	Conventional	74	5.51				
	New fertilization*	56	5.52				
* LPSS-100 : LP-70** : conventional fertilizer = 6 : 3 : 1. ** LPSS-100: Delayed release (sigmoid curve) type; the latent period is 45 days. To release nitrogen takes 100 days for 80% (N/total N) release in water at 25°C. LP-70: Ordinary (linear curve) type with no latent period							

 Table 14. Conventional transplant rice (Cultivar: Koshihikari) by

 single basal fertilization in Aichi pref., Central Japan

In Japan, in addition to the possible reduction in the rate of nitrogen applied (or increase in yield), other advantages related to the use of polyolefin-coated fertilizers are:

To release nitrogen takes 70 days for 80% (N/total N) release in water at

- Their use permits innovative fertilizer applications, e.g. *co-situs* placement, one single basal application, simplification of planting.
- They contribute to multicropping by a single fertilizer application and large cultivation saving from no-till culture;
- No or reduced lodging due to the more gradual release of nitrogen from resin-coated fertilizers (TANAKA, 1990).

Though polyolefin coated urea (POCUrea or MEISTER<sup>®</sup>) is also expensive, it can contribute to the innovation of fertilizer applications and farming systems, whereby the total farming costs can be notably reduced (KIMOTO, 1992). For example, new rice farming systems (notill transplanting rice culture using seedlings with single basal fertilization - no extra fertilization in paddy fields and no-till direct seeding of the rice culture with single basal *co-situs* fertilization) can reduce by 30 to 50% the total rice farming cost.

SHOJI and KANNO (1994), referring to experiments carried out by KANETA, even report a decrease in farming cost by 65% with no-till rice cultivation by transplanting of rice seedlings with a single basal fertilization as compared to conventional rice cultivation. This suggests that controlled-release fertilizers such as POCU may widely be used for low cash-value crops if their farming systems can be innovated by including controlled-release fertilizers. In addition, because of serious agro-environmental problems, some Prefectures recommend the use of controlled-release fertilizers in order to control fertilizer pollution. This will also stimulate the introduction of the new innovative farming systems including the use of controlled-release fertilizers.

As a result of this, in Japan a large proportion (approximately 70%) of the total of polyolefin-coated fertilizers produced and used, is applied

on paddy rice (1995); another 20% is used on vegetables such as tomato, carrot, lotus, egg plants etc.

However, it has to be added, that POC-Urea is mostly blended with conventional fertilizers at blending ratios of 10-30 : 90-70, to reduce the increase in total fertilizer costs.

Considering the interest of this practice and the experience gained, it must be regretted that no benefit and value/cost ratio calculations of the different fertilization systems have been made. Such calculations are indispensable for any possible assessment as to the extent to which such innovative fertilizer management systems including controlledrelease fertilizers could be transferred from Japan to countries:

- which practice less intensive rice growing,
- where prices of encapsulated controlled-release fertilizers are significantly higher than in Japan,
- with a completely different structure of marketing, costs and wages.

Also in Japan, new open market laws are making the life of local farmers much harder. As a result, growth in the use of controlledrelease fertilizers in rice is slowing down. For 1996 FUJITA (1997) reports that polymer-coated fertilizers have mainly gained market share in horticultural crops, such as strawberries, tomato, eggplant, spinach, and cyclamen.

There is no doubt that rice is one of the most interesting agricultural crops for the use of encapsulated controlled-release fertilizers. Therefore, any further development in practical application (economic blends), in the characteristics of polymer-coated fertilizers, the granules of which do not float, but sink down immediately on application, and in production processes (mass production) reducing the production costs, will undoubtedly contribute to the use of controlled-release fertilizers in rice also in countries other than Japan.

However, further extensive testing under practical field conditions comparing controlled-release fertilizers with the most advanced conventional fertilizer management systems followed by the calculation of the respective benefits (the different value/cost ratios), is indispensable.

### 11.1.2. Future aspects

The main obstacle to the wider use of controlled-release fertilizers will remain the high cost of these special fertilizer types, as compared to urea, ammonium sulphate and conventional NPK compound fertilizers. Consequently, it is assumed that also in the future controlled-release fertilizers will have no - or only a very limited - impact on world food production in comparison to the amount of conventional fertilizers actually used on food crops, whether in tropical or temperate regions.

In spite of the advantages of slow or controlled-release fertilizers in significantly improving nutrient efficiency (mainly of nitrogen) and minimizing undesirable losses to the environment, unless the cost of slow and controlled-release fertilizers can be significantly lowered, it is unlikely that these types of fertilizers will gain widespread use on low cash value (i.e. in conventional agricultural) crops. To achieve widespread use, the value/cost ratio (VCR) would need to be at least 3 to 1.

If the industry succeeds in the production and distribution of slow and controlled-release fertilizers at costs permitting a value/cost-ratio of at least 3 to 1 in agricultural crops, there is an enormous potential.

Under such circumstances, the conclusions of the AAPFCO and TFI in early 1994 might materialize:

"...slow-release fertilizers achieve improved efficiency of nutrient use and minimize the potential of nutrient losses to the environment through mechanisms that slow release of plant available nutrients in the soil. These products provide important tools in environmentally responsible plant nutrition; therefore, increased use and market share for these products over the next few years is predicted, especially in agricultural crop markets".

Their impact could be particularly great as concerns environmental aspects. If environmental legislation places restrictions on the application of nitrogen on farmland where there is a possibility of pollution of groundwater, streams or lakes (e.g. in the United States in the States of Florida and Nebraska, in Western Europe in Denmark, Germany, Netherlands, Sweden, UK, and in Japan in some Prefectures), farmers may be forced to use these types of nitrogen fertilizers. Under such conditions, the public or social interests may be in conflict with farmers' interests. Farmers are generally well aware of the challenge they face to develop environmental-friendly farming and fertilization systems. However, if due to the application of fertilizer types which are significantly more expensive, new fertilizer management systems lead to a reduction in farm income, than the common agricultural policy (CAP) has to offer particular incentives (or compensation) for their introduction.

This applies equally to the use of nitrification and urease inhibitors.

## 11.2. Nitrification and urease inhibitors

Fertilizers containing nitrification or urease inhibitors (in contrast to slow and controlled-release fertilizers) are exclusively used on agricultural crops, on some longer standing vegetables and in orchards and vineyards.

## 11.2.1. Nitrapyrin (N-Serve<sup>®</sup>)

Because nitrapyrin (N-Serve<sup>®</sup>) requires injection or immediate incorporation into the soil due to volatility, this limits interest and acceptance in regions where N is not commonly injected.

Therefore, N-Serve<sup>®</sup> is commercially available only in the United States, though there are research programmes which have documented benefits in several other areas of the world.

In the United States, N-Serve<sup>®</sup> is labelled for use on corn, sorghum, wheat, cotton and strawberries (restricted). However, the actual use is more than 90% on corn, the rest on wheat and some on grain sorghum (HUFFMAN, 1996; CHRISTENSEN and HUFFMAN, 1992). Of the total sales volume of nitrapyrin in 1995, corn received 90 %, wheat 9 % and grain sorghum 1 %. Out of the total of 28.5 million ha grown with grain corn, approximately 5.6% were treated with nitrogen fertilizers plus the nitrification inhibitor nitrapyrin.

Nitrapyrin is very stable in cool soils, providing excellent activity from fall or winter applications. This meets the interest of American farmers concerning time management: farmers prefer to apply fall-N plus a nitrification inhibitor instead of spring-N, and spring-N plus nitrification inhibitor instead of side-dressed N.

In cooperation with the Iowa State University, Cooperative Extension Service, DowElanco have developed a special computer programme for the estimation of nitrogen loss (Fate of anhydrous ammonia in Iowa soils) (KILLORN and TAYLOR, 1994). The programme relies on state and county soil temperatures, rainfall levels, and established risk of leaching and denitrification. This computer programme can be used as a tool to help make nitrogen management decisions.



N fertilization of corn without and with the addition of a nitrification inhibitor. The light colored strip of corn in the center of the photo received fall-applied nitrogen;

- corn to the left received the same rate of fall-applied N plus N-Serve;
- corn to the right received spring applied nitrogen.
   Yields were:
- 227 bu/ac for fall +N-Serve.
- 194 bu/ac for fall N and
- 217 bu/ac for spring-applied N.

This is the type of pattern expected with similar yields with fall nitrogen plus a nitrification inhibitor and springapplied nitrogen with both being superior to fall-applied nitrogen.

(HUFFMAN, J. - DowElanco)

Field shot of a spring-applied nitrogen rate/nitrification trial, Iowa State University, Ames, IA, 1996. This was a



wet season, and nitrogen deficiencies are obvious in the zero N check and in the low N rate plots. Also corn size varied in response to N rate and to nitrification inhibitor. Vield response to the nitrification inhibitor, N-Serve, averaged 10% (160 vs 145 bu/ac). Typical of what is seen on somewhat poorly drained soils in a wet year. (HUFFMAN, J. - DowElanco)

> In most years the majority of nitrogen losses occur before corn becomes a major user of nitrogen. It is to the advantage of the farmer and to the environment to retain a maximum amount of the available nitrogen in the root zone until the major period of nitrogen loss is past. N-Serve<sup>®</sup> results in delayed nitrification and, accordingly, may reduce the risk of nitrogen loss by leaching and by denitrification (KILLORN and TAYLOR, 1994).

> CHRISTENSEN and HUFFMAN (1992) demonstrated in several years of experiments with corn (*Zea mays* L.) that the nitrogen rate could be reduced without loosing yield when nitrogen fertilizers were applied amended with nitrapyrin.

> The response of corn to preplant applications of nitrogen and to nitrogen plus nitrapyrin is given in table 15.

Treatment		Year						
Nitrogen	Nitrapyrin	1982	1983	1984	1985	1986	1987	1988*
kç	g / ha				t / ha			
0	0	7.44	2.63	4.34	5.42	4.10	4.18	3.94
90	0	8.68	5.03	6.60	7.09	9.10	7.76	5.51
90	0.56	9.44	5.94	7.51	7.61	10.81	8.67	5.88
134/179	0	9.14	5.98	7.19	7.52	11.10	8.70	5.80
134/179	0.56	10.38	6.50	7.59	8.41	12.38	9.18	6.58
CV (%)		3.90	7.10	3.90	2.60	11.9	7.80	5.20

### Table 15. Response of corn to nitrogen rate and to nitrapyrin, 1982 to 1988

\*No treatments applied in 1988. The high rate in 1982, 1983 and 1984 was 120 lb/acre N and was 160 lb/acre N for 1985, 1986 and 1987.

Adapted from: CHRISTENSEN and HUFFMAN (1992)

Emphasis in research is shifting to the precision application of N-Serve<sup>®</sup>, targeting applications to soils where N losses are high, such as poorly and somewhat poorly drained soils and sandy soils. According to HUFFMAN, 1997, this will:

a. lower grower cost of N by allowing growers to use lower N rates without fear of yield loss,

b. lower costs of N-Serve® per field by applying only where it offers good potential return, and

c. help to reduce movement of  $NO_3$ -N into water supplies due to both reduced N rates and reduction of leaching of N.

Further environmental benefits from the use of nitrapyrin are described in section 11.2.4. Environmental aspects of the use of nitrification and urease inhibitors.



Application of dry nitrogen fertilizer in a research trial. (HUFFMAN, J. - DowElanco)



Application of a nitrification inhibitor over the nitrogen band. (HUFFMAN, J. - DowElanco)

## 11.2.2. Dicyandiamide - DCD

For the United States, it is assumed that nitrogen fertilizers amended with DCD are applied more or less to the same crops as those receiving fertilizers with nitrapyrin. However, the importance of DCD-containing fertilizers (UAN solutions) is growing, particularly on "no-till" corn and soybeans in the Midwest.

The economics of the use of nitrification inhibitors for farmers are significantly better as compared to those of slow and controlled-release fertilizers (HALL, 1995).

Corn planted on soybean resid	ue			
N-Tech SR <sup>®</sup> preplant broadcast		UAN preplan	nt injected	
Gross income				
189 bu.	US\$ 396.90	168 bu.	U\$ 352.80	
N fertilization expenses				
N-Tech SR	US\$ 39.25	UAN	U\$ 30.80	
Application with herbicide	US\$ 3.50	Application	US\$ 5.00	
		Herbicide application	US\$ 3.50	
Net income after N fertilization and application	US\$ 354.15		US\$ 313.50	
Corn planted on corn residue				
N-Tech SR <sup>®</sup> preplant broadcast		UAN preplant injected		
Gross income:				
162 bu.	US\$ 340.20	152 bu.	US\$ 319.20	
N fertilization expenses				
		UAN	US\$ 30.80	
N-Tech SR	US\$ 39.25	Application	US\$ 5.00	
Application with herbicide	US\$ 3.50	Herbicide application	US\$ 3.50	
Net income after N fertilization and application	US\$ 297.45		US\$ 279.90	

Table 16. Economics to farmers, Purdue University data

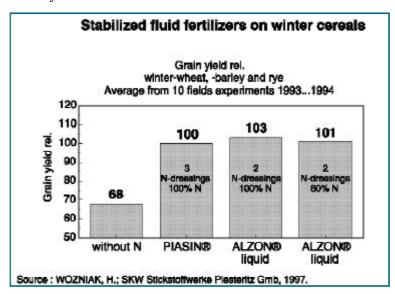
In Western Europe, the use of fertilizers in which ammoniacal-N is stabilized with DCD (as well as with DCD plus 3MP) is recommended for most of the agricultural crops fertilized with ammonium-N containing fertilizers or slurry. This holds true primarily when grown on light textured soils or with heavy rainfall within the 6-8 weeks following the application (AMBERGER, 1995, 1993b and 1989; STURM et al., 1994). Preferably they are used on corn and root crops with a relatively slow growth during the early growing stages, such as potatoes and sugar beet (AMBERGER, 1995; AMBERGER and GUTSER, 1986; ZERULLA and KNITTEL, 1991a and 1991b) as well as on malting barley.

In addition to the saving of one round of fertilizer application (at a cost of approximately DM 25.00/ha), through improved yields these crops have shown the best reaction to nitrification inhibitors (ZERULLA, 1996). It is, however, necessary to define clearly the soil and growing conditions under which such positive results can be expected. This is of particular importance where nitrification inhibitor - containing nitrogen fertilizers are used on cereals such as winter wheat and winter barley (BRENNER and SOLANSKY, 1990; MOKRY and AMBERGER, 1992).

NPK complex fertilizers containing DCD are also used in orchards, vineyards (KANNENBERG, 1993) and longer standing vegetables.

AMBERGER (1991) emphasizes the following advantage of DCDcontaining fertilizers. With only one or two applications of stabilized fertilizers the application costs of fertilization can be reduced significantly as compared to several dressings with calcium ammonium nitrate. SPIELHAUS (1991) also confirms that same yield can be obtained from only one or two applications of stabilized fertilizers, as that from conventional fertilizers which have to be applied in more dressings.

BRENNER (1991) found in extensive field experiments from 1977 to 1990 that the nutrient efficiency from stabilized fertilizers is 20 to 30% greater than that of conventional nitrogen fertilizers. This leads to the conclusion that with stabilized fertilizers the N rate can be reduced by 20 to 30% (as compared to conventional fertilizers) without fear of yield loss.



A higher nitrogen efficiency is also reported by STURM et al. (1994), leading to the conclusion that the rate of nitrogen applied to maize, root crops (potatoes and sugar beets) and rape can be reduced by 20 -30 kg/ha N when using DCD-stabilized fertilizers without reduction in yield.

In field experiments carried out over several years by HEGE and MUNZERT (1991), DCD-stabilized fertilizers gave different degrees of efficiency with different crops. The increase in yield as well as the economic benefit was significant with crops planted at a greater row width (maize, maize for silage - with fertilizer band application), with a longer vegetative period and with a 'preference' for ammonium-N (potatoes). However, with winter cereals, winter rape and sugar beet no increase or only an insufficient increase in yield was obtained.

For promoting the use of DCD-containing fertilizers the leading distributors in Western Europe are following a strategy similar to that of the manufacturer of nitrapyrin / N-Serve<sup>®</sup>, DowElanco in the United States.

In Germany and neighbouring countries, BASF Aktiengesellschaft has over many years carried out a large number of precise field experiments with its own research and advisory staff to clearly define the conditions for an efficient use of nitrogen fertilizers amended with DCD. In these experiments the relation between soil type, rainfall, temperature, level of nitrogen rate applied and the crop grown have been investigated (BASF, 1993; BASF, 1991).

Further comprehensive data have been obtained from research in cooperation with official institutes and universities. Such research work has also been carried out by SKW Trostberg AG, primarily in close cooperation with the Technical University of Munich, Institute of Plant Nutrition, Freising, as well as by SKW Stickstoffwerke Piesteritz, Wittenberg (AMBERGER, 1989 and 1986; AMBERGER and GUTSER, 1986; WOZNIAK, 1997).

These activities will undoubtedly motivate farmers to apply more fertilizers with DCD.

However, no substantial breakthrough is expected, neither in the United States nor in Western Europe, at least for the time being. This is due to the still prevailing disparity in prices with conventional nitrogen fertilizers.

## 11.2.3. NBPT or NBTPT - AGROTAIN®

The principal advantages of urease inhibitors are:

- the significant reduction of ammonia losses to the atmosphere,
- the improvement of nitrogen efficiency from amide-N,
- the reduction of seedling damage, and
- the depressive effect on environmentally relevant gases.

For the urease inhibitor NBPT, GRANT et al. (1996a) listed the circumstances under which it will increase yield through reduced volatilization losses from surface-applied urea / urea-containing fertilizers. This will be the case if:

- a. Nitrogen fertility is limiting to crop yield when the NBPT is not applied and
- b. volatilization losses from the applied fertilizer are sufficient to impact on crop yield.

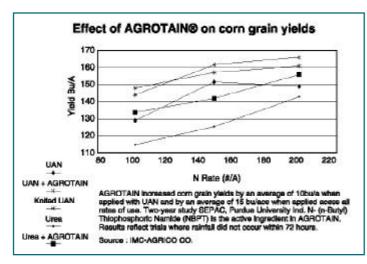
As regards reducing damage from seed-placed fertilizer, NBPT generally appears to be effective where conditions are such that damage will occur (XIAOBIN et al., 1994).

GRANT et al. (1996a) conclude: "Maximum benefits of NBPT use can therefore be expected where crop yield potential is high, soil N levels are low and soil and environmental conditions promote extensive volatilization losses." And: "Since we cannot effectively predict far in advance when environmental conditions will occur that will lead to either volatilization losses or seedling damage, use of NBPT can help

N Rate	Irrig	ated 1993	Osage Co 1993		N. Farm 1994		Sandyland 1994	
	Urea	U.+NBPT	Urea	U.+NBPT	Urea	U.+NBPT	Urea	U.+NBPT
0	5.08	5.08	1. 25	1.25	3.07	3.07	8.97	8.97
67	5.39	6.96	2.76		4.26	4.64	10.91	11.79
135	7.52	8.65	2.76		5.27	6.65	11.91	12.04
202	8.03	8.90	3.89	4.45	6.21		12.29	12.41
Mean	6.96		3.14		5.52		11.66	12.10
LSD (0.05)Means	0.69		0.56		0.75		NS	
Source: GRAN	Source: GRANT et al., 1996a.							

 
 Table 17. Effect of surface-applied urea fertilizer, with and without the addition of NBPT, on corn yield (t/ha) in trials in Kansas (LAMOND et al., 1993, 1994 Unpublished data)

to reduce the risk of damage, if weather conditions become detrimental. This will help to improve the long-term economics of crop production."



Further data on corn response to the use of the urease inhibitor AGROTAIN<sup>®</sup> on an United States national average has been given in table 9 section 10.2.

In Western Europe urease inhibitors are not yet in use. Some first field tests are being carried out.

In Italy, PALAZZO et al. (1995) have studied the effect of NBPT over a 3year period in field experiments on maize. They found that the addition of NBPT resulted in significant decreases in NH volatilization. The

grain yield increased from 11% (normal urea) to 30.6% with the inhibitor.

In Turkey, BAYRAKLI and GEZGIN (1996) have tested NBPT with surface-applied urea in sugar beet. The greatest decrease in  $NH_3$  losses of 44.5% resulted from 0.5% NBPT. The same treatment also produced the highest refined sugar yield.

With a consumption of 1.2 mio t of N in form of urea and 0.9 mio t of UAN solutions, containing about 0.45 mio t of amide-N, there also exists a great potential and need in Western Europe for the application of an urease inhibitor, to the benefit of farmers and of the environment (EFMA, 1994; FAO, 1995; IFA, 1996).

## 11.2.4. Environmental aspects of the use of nitrification and urease inhibitors

In assessing the value of nitrification and of urease inhibitors it is not only the better utilization of the applied nitrogen which has to be taken into account, but also the possibility of maintaining safe and clean ground water and of reducing emissions of ammonia and other environmentally relevant gases/greenhouse gases to the atmosphere.

In the United States a long-term leaching study has been completed at the University of Minnesota and will be published within 12 to 18 months. It shows that the use of nitrapyrin reduced leaching of nitrate-N by about 15% annually (when averaged across 7 years), with fall applied anhydrous ammonia compared to fall application of ammonia without nitrapyrin (HUFFMAN, 1997). Yields were increased by 6% for the fall comparison. Fall applied ammonia plus nitrapyrin produced similar yields and similar levels of nitrate-N leaching as the same rate of N applied in the spring.

In Germany SCHEFFER (1991) found in a field experiment of 7 years' duration that the leaching of nitrate could be reduced substantially with DCD-stabilized fertilizers as compared to calcium ammonium nitrate (27% reduction on a podsol-gley soil and 40% on a loamy soil). AMBERGER (1993a and 1991) and GUTSER (1991) also emphasize that the leaching of nitrate, particularly in humid spring, and under crops like maize or sugar beets, can be prevented (AMBERGER and GERMANN-BAUER, 1990).

As regards the reduced leaching of nitrate-N, a growing sector of application will be in water catchment areas with restrictions on nitrogen fertilizer use. Here the following recommendation is given:

"If in water catchment areas with restrictions or due to other reasons, a reduction in N fertilization is required, the N application can be reduced by approximately 20 kg/ha N without losing yield."

As indicated in sections 4.1.2.2. and 4.1.2.3 nitrification and urease inhibitors contribute significantly to the reduction of emissions of ammonia and nitrous oxide gases. Global budgets for atmospheric  $NH_3$ emissions have been calculated by SCHLESINGER and HARTLEY (1992). With regard to emissions from fertilizer application a compilation of recent studies suggests that at least 20% of urea-N and 10% of  $(NH_4)_2SO_4$ -N are lost in a short period after application to upland soils.

A "Three-Dimensional Model of the Global Ammonia Cycle" has been used by DENTENER and CRUTZEN (1994) to determine the global distribution of ammonia ( $NH_3$ ) and ammonium ( $NH_4^+$ ), calculating a volatilization fraction of the nitrogen applied for urea of 15%, for ammonium nitrate of 2%, for ammonium sulphate of 8% and for other nitrogen fertilizers of 3%. KINCHELOE (1997b) calculates that there are 30% or more losses, if urea is not incorporated, mixed or moved into the soil by rainfall or tillage.

For the developing countries, long-term scenarios with regard to emissions of ammonia (NH<sub>a</sub>), nitrous oxyde (N<sub>a</sub>O) and methane (CH<sub>a</sub>)

into the atmosphere from animal waste products and fertilizer use have been compiled by BOUWMAN (1995).

McTAGGERT et al. (1993) studied  $N_2O$ -emissions following the application of urea and ammonium nitrate on a grassland site over two growing seasons. The nitrification inhibitors DCD and nitrapyrin combined with the nitrogen fertilizers reduced the emissions from ammonium-based fertilizers significantly. They conclude 'The results reported here suggest that there is considerable scope for reducing emissions of  $N_2O$  by the application of nitrification inhibitors, and also by the judicious choice of the form of fertilizer applied depending on the likely environmental conditions'.

BRONSON and MOSIER (1993) studied the emissions of methane (CH<sub>4</sub>) and nitrous oxyde (N<sub>2</sub>O) from application of urea on irrigated corn (*Zea mays* L.). The use of the nitrification inhibitors nitrapyrin and ECC (encapsulated calcium carbide) reduced the greenhouse effect of N<sub>2</sub>O derived from urea by 41% and 71-74%, respectively.

Of particular interest concerning the positive environmental properties of nitrification inhibitors is the report of the German 'Scientific Advisory Committee on Fertilizers' (*Wissenschaftlicher Beirat für Düngungsfragen*)<sup>2</sup> (BUNDESRAT, 1996): "Experience with the use of nitrification inhibitors with reference to their possible influence on the vitality of soil organism and the formation of climatic relevant trace gases like  $N_2O^3$ ", published by the German Federal Government as Drucksache 239/96 (BUNDESRAT, 1996).

Important conclusions of this highly interesting report are:

"Various investigations on the influence of nitrification inhibitors on  $N_2O$ , primarily by using DCD but also acetylene (in pot experiments) and nitrapyrin, clearly demonstrate, that the emissions of climate relevant gases such as  $N_2O$  can be reduced by up to 50%, methane up to 35%, through nitrification inhibitors."

"Primary quantities of nitrate (also originating from fertilizers) and the related  $N_2O$  emissions through denitrification cannot be influenced by nitrification inhibitors. In the case of NO, an emission product which contributes to soil acidification and which can be released through nitrification, the reduction through DCD is as high as 92%."

"Taking into account that nitrification and denitrification occur continuously in nature even without the use of fertilizers, and that soils at least in the highly industrialized countries - are supplied with nitrogen extremely well, then the use of nitrification inhibitors in case of applying ammonium-containing organic or mineral fertilizers offers the chance to limit the emission of undesirable climate-relevant trace gases in addition to thereby improving the utilization rate of nitrogen in agricultural crops and on pastures."

<sup>2</sup> Translations by the author.

<sup>3</sup> Erfahrungen mit dem Einsatz von Nitrifikationsinhibitoren bezüglich ihres möglichen Einflusses auf die Vitalität von Bodenorganismen und auf die Bildung klimawirksamer Spurengase wie N2O. "Vielfältige Untersuchungen zur Beeinflussung der N<sub>2</sub>O-Emissionen durch Nitrifikationsinhibitoren, hauptsächlich unter Einsatz von DCD aber auch von Acetylen (in Gefäßversuchen) und Nitrapyrin durchgeführt, zeigen eindeutig, daß durch Nitrifikationsinhibitoren die Emissionen von klimaverändernden Gasen wie N<sub>2</sub>O um bis zu 50%, bei Methan um bis zu 35% gesenkt werden können."

"Primär vorhandene Nitratmengen (auch Nitrat aus Düngemitteln) und damit verbundene  $N_2O$ -Emissionen durch Denitrifikation sind durch Nitrifikationshemmstoffe nicht beeinflußbar bzw. hinsichtlich ihres "Emissionsanteils" nicht erfaßbar. Für NO, einem zur Bodenversauerung beitragenden Emissionsprodukt, das bei der Nitrifikation freigesetzt werden kann, liegt die Senkung der Emissionsrate für DCD sogar bei 92%."

"Stellt man in Rechnung, daß Nitrifikation und Denitrifikation auch ohne Einsatz von Düngemitteln in der Natur kontinuierlich ablaufen, die Böden zumindest in den hochindustrialisierten Ländern außerordentlich gut mit Stickstoff versorgt sind, so eröffnet der Einsatz von Nitrifikationshemmstoffen im Falle des Einsatzes von ammoniumhaltigen organischen und mineralischen Düngemitteln die Chance, neben der dadurch möglich gewordenen verbesserten Ausnutzung des Stickstoffs in landwirtschaftlichen Kulturen und Weideland auch die Emission unerwünschter klimabeeinflussender Spurengase zu begrenzen."

In a greenhouse experiment with transplanted rice BYRNES et al. (1989a) found that losses from the split application of urea were less than 10% when the urease inhibitor NBPT was added. In two other experiments on flooded and puddled soils, BYRNES and AMBERGER (1989) demonstrated the inhibition of urea hydrolysis through NBPT; essentially no ammoniacal-N concentrations developed in the floodwater, which indicates that ammonia volatilization losses were completely stopped.

### **11.2.5.** Nitrification and urease inhibitors in tropical crops

Though nitrapyrin (N-Serve<sup>®</sup>) is commercially available only in the United States there are research programmes, which have documented benefits also in areas other than the United States, for instance in cotton in the Tashkent area of the FSU.

Based on field trials on the growth and yield of maize conducted in Egypt in 1991-92 to assess the efficiency of different rates of nitrogen (from 15 to 105 kg/feddan N) with and without nitrapyrin, HAMMAM (1995) came to the conclusion that the use of nitrapyrin permits a saving of 40 kg/feddan N (96 kg/ha N).

As regards DCD, SERNA et al. (1994 and 1993) tested ammonium sulphate nitrate (ASN) in several experiments on citrus without and with DCD. The nitrification inhibitor DCD reduced  $NO_2$  losses and improved the N fertilizer efficiency minimizing the economic and environmental risks that are inherent in the irrigated production of citrus.

YADAV et al. (1990) compared urea super granules, neem cake coated urea (NCU) and DCD coated urea in sugar cane. There was, however, no significant difference in yield resulting from the three different treatments. JOSEPH and PRASAD (1993) also compared urea coated with neem cake and with DCD in wheat. Coating urea with DCD was the most efficient treatment. VYAS et al. (1991) obtained similar yields of rice with 70 kg/ha N in form of NCU as with 100 kg/ha N applied as uncoated urea. VIMALA and SUBRAMANIAN (1994) produced higher yields with nimin-coated urea (NICU) than with NCU and prilled urea in field trials on rice. Though GOUR et al. (1990) obtained better yields of rice with NCU than with prilled urea, the highest yields in his trials were given by urea super granules. TOMAR and VERMA (1990) produced nearly equal yields with 80 kg/ha N when urea was applied in combination with nitrification inhibitors (among others NCU) as with 120 kg/ha N in form of prilled urea without nitrification inhibitor. KETKAR (1974), in a rice trial, investigated how far neem cake coated urea (NCU) was able to increase the efficiency of applied N as compared to urea alone. The result was: on acid soils NCU at the rate of 50 kg/ha N significantly increased paddy yield over uncoated urea. With higher N rates, increases in yields were not significant. The opposite was true in case of neutral soils, NCU at the high rate of 100 kg/ha N increased the yield of paddy significantly, whereas the increase in yield was not significant at lower levels of N application.

KHANIF and HUSIN (1992) obtained the highest grain yield, N uptake and fertilizer N recovery in flooded rice from ammonium sulphate nitrate (ASN) plus DCD (2%). However, TRACY (1991) concluded from field trials on cotton that the application of DCD is not cost-effective for use in short season cotton in Missouri since it did not improve cotton yield or N uptake. The influence of temperature on the mineralization kinetics with a nitrification inhibitor (DCD and ATS) has been investigated by GUIRAUD and MAROL (1992). SACHDEV and SACHDEV (1995) concluded from a laboratory experiment with DCD that it is effective only at relatively low temperatures. At higher temperatures (35°C) it has no influence on the nitrifying bacteria in the soil. Hence, in India DCD will be more useful during the winter rabi season than during the monsoon kharif season.

These results indicate further research is needed to investigate the effectiveness of nitrification inhibitors also under high temperature soil conditions.

According to BYRNES et al. (1995) research in tropical rice systems indicates that urease inhibitors such as N-(n-butyl) phosphoric triamide, NBPT, and cyclohexylphosphoric triamide, CNPT, can play an important role in increasing urea efficiency.

As discussed in section 11.1.1 slow and controlled-release fertilizers in tropical crops (rice), in flooded rice the soil-fertilizer regime is completely different from that of upland crops (DE DATTA, 1995). The active biology and warm conditions of tropical rice paddies cause urea hydrolysis to be complete in 2 - 4 days, though in some studies it has taken up to 10 days. When farmers are simply broadcasting urea into standing water (DE DATTA, 1986) high NH<sub>3</sub> volatilization losses have to be expected due to the rapid hydrolysis of urea, causing high aqueous NH<sub>a</sub> concentration in the flooded water (BYRNES and AMBERGER, 1989; BYRNES et al., 1989a and 1989b). The high pH-conditions, due to urea hydrolysis and algae growth, sustain the NH<sub>2</sub> volatilization. Comparing two urease inhibitors, BYRNES et al. (1989a) found that PPDA (phenyl phosphorodiamidate) is a powerful urease inhibitor in flooded rice soils. However, under the high pH conditions of floodwater the urease inhibition effect of PPDA ends abruptly. In contrast to PPDA, with NBPT the inhibition of urea hydrolysis in the flooded soil sustained for a long period of time at a particular level. With a loss of N from urea alone of 49.9%, BYRNES et al. assume that, although this loss is thought to be principally from NH, volatilization, the loss of 7.8% to 9.6% with NBPT is likely through denitrification, since there was essentially no NH<sub>3</sub> in the floodwater to volatilize. This finding does not support the position that N saved from NH<sub>3</sub> volatilization would be largely lost by denitrification when NH<sub>2</sub> loss is eliminated. Most of the N preserved was not denitrified but was maintained in the soil (BYRNES and AMBERGER, 1989).

In experiments in which the urease inhibition was only partially successful the addition of an algicide, to reduce ammonia losses, and that of nitrification inhibitors, to reduce losses by denitrification, improved the efficiency of the urease inhibitor. This is supported by studies made by CHAIWANAKUPT et al. (1996) and by FRENEY et al. (1995) in experiments in flooded rice in Thailand.

However, further research on tropical soils in different environmental conditions with urease inhibitors is required to prove their efficiency in reducing N losses and increasing yields under upland, but particularly under flooded soil conditions (in combinations with nitrification inhibitors and algicides). This research is urgently needed. Taking into account that more than half of all nitrogen actually used in agriculture is in form of urea and that a large proportion is still surface-applied or used on flooded rice, there is an enormous potential for urease inhibitors.

## 11.2.6. Future aspects

Environmental restrictions may force farmers to use nitrogen fertilizers in certain protected zones or regions only in association with nitrification or urease inhibitors. As already mentioned with slow or controlled-release fertilizers, some states of the United States and some countries in Western Europe have already placed such restrictions on nitrogen fertilizer application on farmland. Thus, nitrification and urease inhibitors may, in the future, have a greater impact on environment protection than on world food production.

With urease inhibitors, there is a tremendous potential as well as an urgent need for their use. Approximately 49% of nitrogen (out of 77.3 mio. t of N annually) is manufactured as urea and consumed in agricultural and non-agricultural sectors in this form (as well as in the form of UAN solutions). Urea is a type of fertilizer which - in contrast, for example to NPK complex fertilizers - has not been developed technically to meet a particular agricultural demand. Its leading position is due to the specially advantageous production process, utilizing by-product  $CO_2$  from the manufacture of ammonia, resulting in a highly competitive nitrogen fertilizer.

Following the application of urea in agriculture, there is extensive data demonstrating high losses of ammonia. In the literature concerning ammonia and the atmosphere, calculations of volatilization losses are based on losses of 15%, 20% and more of the amount of nitrogen applied in form of urea (DENTENER and CRUTZEN, 1994; KOSHINO, 1993; SCHLESINGER and HARTLEY, 1992; STURM et al., 1994). This occurs especially when urea is not incorporated into the soil immediately after spreading. Losses are especially high on calcareous soils, and in the tropics on flooded rice and on crops which are not tilled, such as bananas, sugar cane, oil palms, rubber and others.

Out of the 77.3 mio. t of N used in world's agriculture 1995/96, about 38 mio. t N were amide-N in urea. Based on 20% volatilization losses, 7.6 mio. t of N were lost to the atmosphere. At a price of US\$ 0.66 per kg of N in urea, this amounts to US\$ 5.01 billion.

Even assuming that only one third of the urea and N fertilizers containing nitrogen in form of amide-N are used under conditions leading to such losses of ammonia, these losses still surmount to 2.11 mio. t of N, corresponding to a value of approximately US\$ 1.39 billion (wholesalers price).

Taking into account these economic aspects - in addition to the extremely important environmental aspects - everything should be done to drastically reduce these losses.

The application of urea (or UAN solution) amended with an urease inhibitor would permit a substantial reduction in nitrogen losses to the atmosphere, and consequently also in the application rates without affecting growth and yield of fertilized crops. In this respect, the market performance of the urease inhibitor, AGROTAIN<sup>®</sup>, introduced onto the United States market in spring 1996, will be of gratest interest.

The future, and in particular the wider use of nitrification and urease inhibitors primarily depends on the development of new, effective, lowprice and non-toxic products. But no such developments are known, and even if a new promising nitrification or urease inhibitor should be developed, due to lengthy, time-consuming tests and data collection for registration purposes, the introduction to the market would take several years.

Taking into consideration the extremely high costs involved in research and the technical development of nitrification and urease inhibitors in particular, the proposal is made to establish an international fund, which would support future research (screening of chemical compounds, investigation of their characteristics as well as those of their metabolites, development of large scale technical production processes). Such international funding could run in parallel to the funding of the different international agricultural research centers on the world's basic food crops.

The increased use of nitrification and urease inhibitors in world agriculture would benefit farmers, but it is also urgently needed for the protection of the environment.

# Chapter 12. Conclusion

BONTE-FRIEDHEIM (1996), Director of the International Institute for Agricultural Research, at the IFA Annual Conference 1996 at Berlin, proposed the following tasks for industry and agriculture:

- The fertilizer industry is challenged to do more research and more development work.
- The fertilizer industry must assist in providing farmers with the right types of fertilizers.
- The fertilizer industry must help to ensure that farmers neither waste resources nor pollute the environment.

The intention of this document is to demonstrate that the industry is already meeting these requirements to a considerable extent. It has developed a series of specific fertilizer types, i.e. slow and controlledrelease and stabilized fertilizers and has improved the efficiency of nutrients applied, making better use of given resources and in minimizing negative environmental effects.

Unfortunately, there is still a considerable disparity between the price of these products compared to conventional fertilizers, particularly in the case of encapsulated controlled-release and DCD-stabilized fertilizers. This disparity in price still limits the wider use of these more efficient fertilizers in conventional agriculture.

More basic research and more investment in manufacturing facilities is needed. The industry is prepared to meet this challenge. The authorities should ensure that this urgently needed development and further investment in research and production are not paralyzed by an overload of regulations and legislation.

## **Appendix I**

## Pursell Technologies Inc. - Sylacauga, AL, United States

In the manufacture of encapsulated controlled-release fertilizers Pursell Technologies uses the 'Reactive Layer Coating (RLC<sup>TM</sup>) Process'. This technology polymerizes two reactive monomers as they are applied to the fertilizer substrate in a continuous coating drum or in a batch coating drum.

A large number of products are marketed under the trade name 'POLYON'":

- POLYON coated urea PCU
- POLYON coated sulphate of potash
- POLYON coated N-P-K (homogeneous prills)
- POLYON coated MAP
- POLYON coated KNO<sub>3</sub>, potassium nitrate.

- TriKote polymer/sulphur coated urea.
- TriKote polymer/sulphur coated MAP
- TriKote polymer/sulphur coated sulphate of potash

### **Pursell Technologies Inc**

203 w. 4<sup>th</sup> Street P.O. Box 1187 Sylacauga, AL 35150 USA Tel: +1-205 249 6855 Fax: +1-205 249 7491

# **Appendix II**

## **Scotts - United States**

## Scotts use:

- alkyd resin technology for the following product lines:
  - 'Osmocote'®
    - 'Osmocote Plus'™
    - 'High-N'®
    - 'Sierra'®, and
    - 'Sierrablen'®.
- polymer coated technology in the 'ProKote'® and 'Scottkote'® product lines.
- polymer encapsulated sulphur coated technology in the 'ProTurf'®, 'ProGrow'®, and 'Scotts'® consumer product lines.
- methylene urea (MU) technology in the 'ProTurf'<sup>®</sup>, 'ProGrow'<sup>®</sup>, and 'Scotts'<sup>®</sup> consumer product lines.

### **The Scotts Company**

Professional Business Group 14111 Scottslawn Road Marysville, OH 43041 USA Fax: +1-513 644 7308

## **Appendix III**

## Aglukon Spezialdünger GmbH - Düsseldorf, Germany

Aglukon Spezialdünger GmbH coated slow release products are resin coated products with a patented coating process:

- PLANTACOTE<sup>®</sup> DEPOT, PLANTACOTE CONTROL, (NPK), with longevity of 4 to 18 months.
- PLANTACOTE MIX (blends of PLANTACOTE DEPOT and PLANTACOTE START),
- a compacted NPK Mg-TE-fertilizer, with longevity of 4 to 14 months.
- the PLANTACOTE DEPOT 4M, 6M and 8M are labelled 14-9-15,
- the PLANTACOTE DEPOT 12M and 18M are labelled 13-8-15,
- the PLANTACOTE MIX 4M, 6M and 8M are labelled 15-10-15-(2) with TE,
- the PLANTACOTE MIX 12M and 18M are labelled 14-9-15-(2) with TE.

In addition, Aglukon Spezialdünger GmbH manufactures and distributes UF-based and methylene urea fertilizer formulations:

- PLANTOSAN<sup>®</sup> is an UF-based NPK fertilizer with controlled release effect containing magnesium and micronutrients.
- NUTRALENE<sup>®</sup>, AZOLON<sup>®</sup> and NITROFORM<sup>®</sup> are methylene urea N and NPK fertilizer formulations with longevities from 3 to 16 months.

Aglukon Spezialdünger GmbH Postfach 270125 D-40524 Düsseldorf Germany Fax: +49-211 5064 247

# **Appendix IV**

## **BASF Aktiengesellschaft - Limburgerhof, Germany**

BASF produces and distributes controlled-release and stabilized fertilizers:

- Encapsulated NPK compound fertilizers are marketed under the trade name 'Basacote'®.
- Various controlled-release fertilizers based on IBDU ('Isodur')<sup>®</sup> are marketed under the trade name 'Floranid'<sup>®</sup>, and those based on CDU ('Crotodur'<sup>®</sup>) under the trade name 'Triabon'<sup>®</sup>.

The nitrification inhibitor in BASF's nitrogen fertilizers is DCD. The products are marketed under the trade names:

- 'Nitrophoska'<sup>®</sup> and 'Nitrophos'<sup>®</sup> stabil (NPK and NP complex fertilizer associated with DCD), and
- 'Basammon'® stabil (ASN associated with DCD).

### **BASF AG**

P.O. Box 120 D-6114 Limburgerhof Germany Tel: +49 -621 6028122 Fax: + 49-621 6027115

# **Appendix V**

## Haifa Chemicals Ltd. - Haifa, Israel

This company has developed a line of resin-coated products. Fertilizer granules are heated in a rotating pan and treated with a fatty acid and metal hydroxide.

Several coated NPK compound fertilizers, coated urea and coated  $KNO_3$  are marketed under the trade name 'multicote<sup>®</sup> 4'.

#### Haifa Chemicals Ltd

Research & Development P.O. Box 10809 Haifa Bay 26120 Israel Fax: +972-4 846 9825 Email: laborat@actom.co.il

# **Appendix VI**

## Chisso-Asahi Fertilizer Co., Ltd. - Tokyo, Japan

This company uses thermoplastic resins, such as polyolefins and ethylene vinyl acetate as coating materials.

The polyolefin-coated urea, KCl and  $K_2SO_4$  with varying longevities are marketed under the trade name: 'MEISTER'<sup>®</sup>.

A large number of polyolefin-coated NP, NK and NPK compound fertilizers with longevities from 40 to 360 days are marketed under the trade name 'Nutricote'<sup>®</sup>.

## **Chisso Corporation**

Fertilizer Research Center 46-70 Nakabaru Sakinohama Tobata Ku Kitakyushu-City 804 Japan Fax: +81-93 882 4213

## **Appendix VII**

## Japan: Controlled-Release Fertilizers - Test Methods<sup>1</sup>

## 1. Laboratory methods

## 1.1 Release in water

Ten grams each of POCF are put into net bags and the net bags are placed in plastic bottles containing 200 ml of water at different temperatures (15-35°C). After given periods of dissolution, the solution is taken for analysis.

#### 1.2 Release in soil

In order to examine release of POCF in the soil, a variety of soils and soil conditions (moisture, pH, etc.) are selected. 2.5 grams of POCF is put into a plastic bottle of 200 ml containing the soil (100 g dry weight) which is subjected to the different conditions. Then it is maintained at 25°C for given periods. Then POCF particles separated from the soil are used for analysis. Release in the soil is compared with release in water.

## 2. Field method

Two to three grams of POCF mixed with 5 to 10 grams of 2 mm sieved soil are placed in net bags and the net bags are left in the ploughed layer. The net bags are removed after given periods and POCF particles separated from the soil are used for analysis. The observed release of POCF is compared with the calculated release taking account of the soil temperature data for the ploughed layer.

<sup>1</sup> Supplied by Dr. Toshio FUJITA, Director Fertilizer Institute Chisso Corp., Japan. (FUJITA, 1996a).

## **Appendix VIII**

## **Contacts - Nitrification and Urease Inhibitors**

#### **BASF Aktiengesellschaft**

P.O. Box 120 67114 Limburgerhof Germany Tel: +49-621 6028122 Fax: + 49-621 6027115

### DowElanco

9330 Zionsville Road Indianapolis IN 46268-1054 USA Fax: +1-317 337 7374

### IMC Global Inc.

2100 Sanders Road Northbrook, IL 60062 United States Tel: + 1-847 2729200 Fax: + 1-847 2054805

#### **IMC-Agrico Compagny**

2345 Waukegan Road, Suite E-200 Bannockburn, IL 60015 United States Tel: + 1-918 4967711 Fax: + 1-918 4921719

### SKW Stickstoffwerke Piesteritz GmbH

Landwirtschaftliche Anwendungsforschung Cunnersdorf Am Wieseneck 7 D-04451 Cunnerdorf Germany Fax: +49-342 91 80204

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