IFA Technical Conference

Johannesburg, South Africa

30 September-4 October 1996

International Fertilizer Industry Association - Secretariat: 28 rue Marbeuf - 75008 Paris - France
Tel. +33 1 53 93 05 00 - Fax +33 1 53 93 05 45/47 - ifa@fertilizer.org - www.fertilizer.org

Date of Receipt: 9 May 1996

TOWARDS MORE UNIFORM METHYLENE UREA SLOW RELEASE FERTILIZERS

J. Luhtala and T. Koivumäki
Kemira Agro Oy, Finland

RESUME

La communication présentera un bref historique de la méthylène-urée, sa production et son marché en général ainsi que les progrès de sa fabrication. La chimie du produit sera décrite. Les propriétés varient suivant le procédé de production et les conditions du procédé et l'assimilabilité de l'azote des différents composants seront examinées.

La méthylène-urée est produite soit par le procédé dit en solution diluée, soit par le procédé dit en solution concentrée qui seront décrits en même temps que nos développements du procédé. De même, les possibilités de production d'engrais NPK à base de MU seront abordées. La méthylène-urée et les engrais NPK à base de MU sont utilisés surtout sur les terrains de golf, les jardins et les parcs publics mais des emplois nouveaux intéresseront par exemple les forêts et les cultures spéciales.

◆ ◆ ◆

1. BACKGROUND

1.1 Short history

The reaction products of urea and formaldehyde are the most widely used slow-release fertilizers. Ureaform was launched onto the market in the USA in 1955 and in Europe in 1964. While the production methods have developed, it has been easier to control the reactions connected with the manufacture and a product, called methylene urea, has been developed besides the traditional ureaform. Kemira Agro Oy has started the manufacture of methylene urea, because it was realized that the product can be developed further and on the market there was no product having a suitable release profile for all of Kemira's purposes. The new manufacturing method seems to have benefits compared to the present methods. The factory started production in summer 1996.

1.2 Chemistry

Methylene urea (MU) is a reaction product of urea and formaldehyde and it is a mixture of methylene urea oligomers (Figure 1). It contains also unreacted urea. Traditionally methylene urea which contains longer oligomer chains has been called ureaform or ureaformaldehyde. We prefer to call also ureaform type reaction products as « methylene urea » and use the adjectives short, medium and long to describe the average chainlength of the product.

Figure 1 - The composition of methylene urea. MDU = methylene diurea, DMTU = dimethylene triurea and TMTU = trimethylene tetraurea.

$H_2NCONHCH_2NHCONH_2$ (MDU) + $H_2NCONHCH_2NHCONHCH_2NHCONH_2$ (DMTU) + $H_2NCONHCH_2NHCONHCH_2NHCONHCH_2NHCONH_2$ (TMTU) + LONGER OLIGOMERS+ UREA

The chain-length distribution of oligomers determines the dissolving and agronomic properties of MU. The water solubility of the shortest molecule, methylene diurea is 2.5% at 25°C while the same of dimethylene triurea is only 0.1% at 25°C. The nitrogen of MU is released by the microbes of the soil.

1.3 Fractions

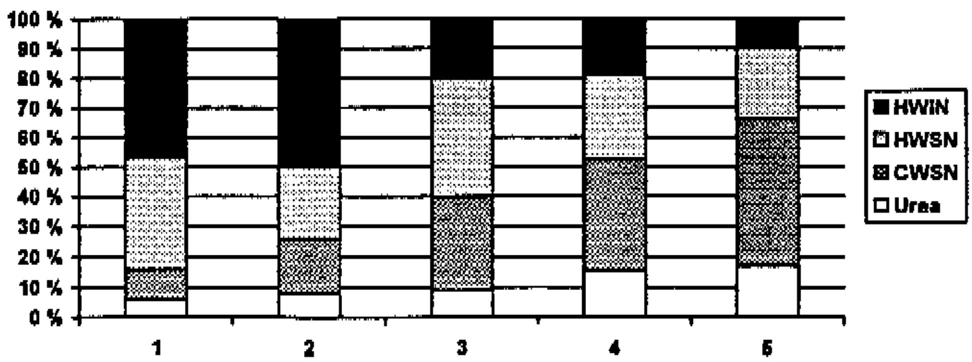
The properties of methylene urea have traditionally been characterized by activity index analysis, an AOAC-method. Because the result of the method (AI) is relative, it does not necessary describe the product unambiguously but based on dissolution trials of that method and on analysis of urea, the determination according EC directive 93/69/EEC can be done:

- Ureic nitrogen
- Cold water soluble controlled release nitrogen (CWSN)
- Controlled release nitrogen that is only soluble in hot water (HWSN).

In addition of fractions mentioned above methylene urea contains hot water insoluble nitrogen (HWIN).

The compositions in accordance with EC directive of different kind of methylene urea products can be seen in Figure 2. Bar 1 represent MU that mineralizes slowly and corresponds to the original ureaform. Bar 3 represent MU that is common in Europe and bar 5 newer type of MU that mineralizes fast. Bars 2 and 4 represent other existing commercial MU products.

Figure 2 - Different types of methylene urea products (composition in % of total nitrogen)



The trend is these days towards faster types of MU and the properties of the product can be adjusted more precisely to different use.

1.4 Regulations and practices

In the following, the regulations and practices in the main markets, Europe, USA and Japan will be discussed. Outside these areas there may be own regulations, but generally they follow the outlines defined in these three areas.

1.4.1 Europe

In Europe the requirements for Methylene Urea and for the products containing Methylene Urea have been defined in the directive 93/69/EEC (EEC fertilizer requirements).

The requirements for the straight methylene urea have been given in its Annex 1, number 12: Total nitrogen content shall be minimum 36%. At least 3/5 of the declared total nitrogen content must be soluble in hot water. At least 31% nitrogen shall come from (polymeric) methylene urea and maximum ureic nitrogen content is 5%.

The requirements for nitrogenous fertilizer containing methylene urea are: Product obtained chemically containing methylene urea and straight nitrogenous fertilizer shall have minimum 18% total nitrogen content, and at least 3% of nitrogen in ammoniacal and/or nitric and/or ureic form. At least 1/3 of the declared total nitrogen must be derived from methylene urea. The nitrogen from the methylene urea must contain at least 3/5 nitrogen that is soluble in hot water. The maximum biuret content is (ureic N + methylene urea-N)* 0,026.

For NPK or NP fertilizers there are separate requirements for each nutrients, but the part dealing with methylene urea includes following requirements:

The nitrogen content shall be at least 5%. At least ¼ of the declared content of total nitrogen must derive from methylene urea and at least 3/5 of the declared nitrogen content from methylene urea must be soluble in hot water.

If the fertilizer does not fulfill the above requirements it is not « EEC fertilizer » and must fulfill the local requirements in the country sold.

1.4.2 USA

In USA products containing slow release methylene urea are generally divided into three different classes:

1. Ureaforms, which AAFCO is defined to a product which contains minimum 60% of its total nitrogen as cold water insoluble nitrogen and the Activity Index is minimum 40%.
2. Methylene ureas, where 25-60% of the total nitrogen content is in cold water insoluble nitrogen.
3. MDU/DMTU compositions, where minimum 60% of the polymeric nitrogen is in the form of cold water soluble methylene diurea or dimethylene triurea. Generally in these products cold water insoluble nitrogen is less than 25% of the total nitrogen.

1.5.3 Japan

The requirements of the fertilizer law of Japan for methylene urea fertilizers are:

Minimum amount of nitrogen required is 35%. Maximum amount of biuret is N_{TOT}* 0.02 (%). If (cold) water soluble nitrogen percentage is at least 50%, the ureic nitrogen must not be over 20%. If water soluble nitrogen percentage is less than 50% the Activity Index shall be minimum 40%.

2. PRODUCTION OF METHYLENE UREA

Over 50 manufacturing methods for urea and formaldehyde reaction products for fertilizer use have been patented. Though manufacturing methods taking place e.g. in melt urea or organic solvent have been invented, the most remarkable methods can be divided into three groups:

2.1 Concentrated solution process

Urea is dissolved in concentrated water solution of formaldehyde in slightly alkaline conditions, when formaldehyde reacts with urea forming methylol ureas. When acid is added to this solution, methylol ureas are condensed to methylene urea. The reaction is exothermic and the mixture warms up and becomes firm. The acidulated solution is conveyed e.g. on a heated belt where it is also dried.

This concentrated solution method is simple, fast and economical due to low evaporation costs. But the control of the reaction is difficult, which makes it difficult to influence the agronomic properties of the product.

2.2 Dilute solution process

Formaline or urea-formaldehyde concentrate is added to dilute urea solution and the mixture is made acidic. The product is precipitated and the mixture is neutralized. The product is filtered and dried. The mother liquor is recycled. The dilute solution process is carried out in mild conditions and the reaction is easier to control than in the concentrated solution process, thus it is easier to adjust the properties of the product. A disadvantage is more complicated process.

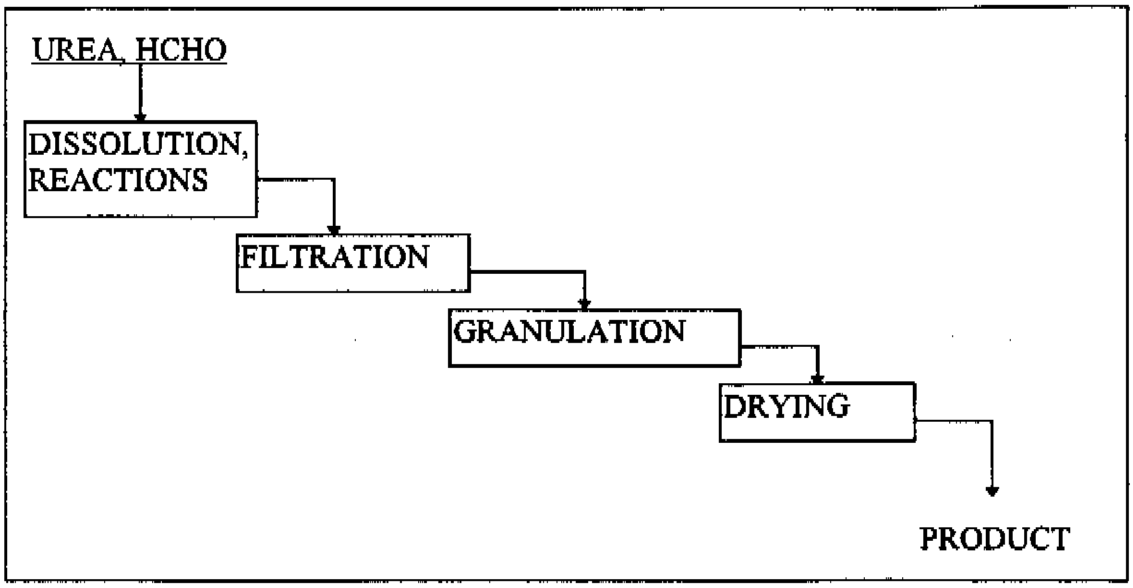
2.3 In situ process

It is possible to manufacture methylene urea simultaneously with compound fertilizer granulation. This method is described more carefully in the chapter 3.1.1.

2.4 Method of Kemira Agro

Kemira thoroughly researched the manufacturing methods of methylene urea for several years. The first process was developed for the equipment of the fertilizer factory in 1991. It was based on the concentrated solution process, where the drying of the product was carried out in the drying drum. The production capacity was about 5 t/h with the plant which was normally able to produce about 30 t/h compound fertilizers. On the basis of tests we found out that the share of HWIN in the product was significant and the best target of the product was forest fertilizers. With further development the share of HWIN could be decreased, but the proportion of other components remained unsatisfactory. The interest in methylene urea remained and after testing various process alternatives a method was developed, in which certain benefits of concentrated and dilute solution processes were combined (Figure 3).

Fig. 3. MU process description



The process differs from today's patented continuous dilute solution methods as far as the process conditions and dimensions of the reactors and dissolving method of urea are concerned. The patent application for the process has been filed.

Advances of Kemira-MU process:

- *Continuous process*

  Compared to the batch dilute solution process the reactor has all the time constant conditions in regard to the mole ratio of urea and formaldehyde. The operating costs are low in the continuous process.

- *Reactors small in size*

  Concentrated solutions (total reactant concentration 35-65%) and continuous operation make it possible to use small reactors by volume compared to the conventional dilute solution process. When compared to some patented continuous processes this is beneficial especially in interrupted production, when starting and particularly shutting down are faster and easier compared to the use of large reactors.

- *Easy to control*

  In spite of concentrated solutions the temperature of the reaction in the condensation step can be kept low. The water balance can be controlled without using urea-formaldehyde concentrate as raw material.

- *Good opportunities to adjust the properties of the product*

  The mole ratio of urea and formaldehyde has a big influence on the chain length distribution of the product. In this process the mole ratio is easy to be adjusted and it can be kept constant during the process. Changing slightly the mole ratio the properties of the product can be finely adjusted and with big changes it is possible to make products for different purposes. Changes in temperature and in pH of the reaction mixture can also be utilized in making minor chances. Retention time can be also influenced.

Our target is to manufacture originally three different types of MU:

Long; the solubility properties correspond chiefly to the original ureaform product. One difference is the small cold water soluble controlled release and ureic nitrogen. The mineralization speed of this product is slow.

Medium; the properties correspond mainly to the product which is used in Europe at present, but in which the shares of cold and hot water soluble controlled release nitrogen are maximized.

Short; the target is to keep the hot water insoluble nitrogen as low as possible, but the amount of ureic nitrogen below 7%. The mineralization speed is fast.

3. PRODUCTION OF MU CONTAINING COMPOUND FERTILIZERS

3.1 Production methods

Compound fertilizers (NPK-, NP- or NK-fertilizers) containing methylene urea as a raw material can be produced with several methods. Perhaps the most common method after in situ production of these fertilizers is production with compaction granulation. Also conventional granulation methods, drum, blunger or pan granulation are used. Bulk blending is one of the simplest method to produce compound MU-fertilizers.

3.1.1 In situ production

Generally the production is considered to be the in situ method if the production of methylene urea is done simultaneously with compound fertilizer granulation. Methylene urea is generally produced in one or several reactors most often through concentrated solution process. Methylene urea reaction can be stopped either in reactor or immediately after the reactor before the granulation process. There are several ways to feed the MU solution or suspension into the granulation. The separation step is not needed because the evaporation is done in normal drying of the fertilizer. The advantages of this method include simple and inexpensive equipment (in existing fertilizer process), and possibility to utilize reaction heat in the granulation process. The most serious disadvantage is inflexibility, i.e. possibility to change the release characteristics of methylene urea is very limited. With these methods it seems to be fairly easy to produce very slow methylene ureas with high amount of hot water insoluble nitrogen. Production of the product with low free urea content and with low hot water insoluble nitrogen content seems to be very difficult with in situ method although these type products are the most commonly used outside forestry.

3.1.2 Compaction process

Compound fertilizers can be produced from solid raw materials through compaction granulation. The production principle is as follows. Solid raw materials (including methylene urea), which are either in powder form or in small granules, are mixed in the proper ratio. The mixture is compacted between two rollers into a flake, which is subsequently crushed into irregular shaped granules. Proper granule size is separated with screens and the oversize and undersize material is recycled back to the compaction step. Product size granules are normally polished mechanically and coated with anticaking treatment.

The biggest advantage of compaction granulation in the production of methylene urea containing compound fertilizers is the simplicity of the process and also good possibility to vary slow release characteristics of the final product. Wide variety of products can be produced and also the methylene urea content can vary widely. The process does not require drying and so it is not as sensitive as conventional granulation methods. Crushing is the main problem, material becomes easily sticky if free urea content is high or if compaction temperature is high. The granule is fairly soft and thus degrades easily in the soil which normally is a preferred property with these types of fertilizers. Product dustiness may sometimes be considered as disadvantage but this can be fairly well prevented by proper surface treatment of the granules.

3.1.3 Conventional compound fertilizer processes

Methylene urea containing compound fertilizers can be produced also with conventional granulation processes, especially if the amount of methylene urea is reasonably small. Large amounts of methylene urea may cause granulation and/or drying difficulties, especially if the amount of nitrates are high. Normally methylene urea powder or small granules are fed either directly into granulator; drum, blunger or pan, or alternatively to recycle belt with or without mixing. Mixing of course makes the feed more uniform and so improves the granulation possibility. Because methylene urea always contains also free urea, it means that the drying must be done carefully avoiding high temperatures so that the fertilizer do not become sticky in the drying drum.

By using solid methylene urea in compound fertilizer process one can formulate best release characteristics for the specific purpose for the final compound fertilizer. The physical properties of these granulated products are usually better than with the compaction process.

3.1.4 Bulk blends

Bulk blended compound fertilizers are very often used especially in USA and in some countries of Europe. The advantage generally considered is the big flexibility to formulate different compositions according to the specific needs of farmers even in fairly small volumes. Methylene urea can be used also in bulk blend fertilizers although there may be some additional risks: The specific gravity of methylene urea granules are lower than that of other raw material granules and thus the risk of segregation is increased.

3.2 Methylene urea content in compound fertilizers

There are not any fixed limits in the amount of methylene urea in compound fertilizers. Most generally the limit, however, comes because of the price. The unit price of methylene urea is several times the price of most often used raw materials and this generally means that from the economical point the limit is between 5 and 10% methylene urea nitrogen in the final product. In some specific cases the product may however be produced almost totally from methylene urea. From agronomic point of view often the best result can be achieved if the product contains all the different forms of nitrogen.

Although it is recommendable to have all nitrogen forms in the same granule, the restriction comes if both nitrate and ureic nitrogen is preferred in the same granule. From production point of view it has been shown that in nitrate containing fertilizers about one percent ureic nitrogen can be included, otherwise the production due to its hygroscopic properties will be impossible. This first becomes evident in wet granulation processes where drying is needed.

4. AGRONOMIC ASPECTS

4.1 Mineralization

The mineralization of methylene urea is a microbiological process. Methylene urea chains are degraded by microorganisms to urea in several stages.

The time needed for the mineralization process is strongly dependent on the length of methylene urea chains. The longest chains, the amount of which is indicated by the amount of HWIN, will decompose within several months - usually more than half year to several years. Methylene urea components with medium length - about three to four urea units - decomposes within few months to about half a year. Shortest compounds - MDU and DMTU will decompose mainly within some weeks.

The above mentioned mineralization scheme gives only an indication of the relative mineralization speed of different compounds. In practice mineralization is affected by several parameters, the most important of which are temperature and soil structure. The better place the soil is to live for bacteria, i.e. fertile soils, the faster will be the mineralization speed. Generally it has been accepted that the microbial activity is doubled if temperature is increased by ten degrees. Microbial activity will cease if the temperature goes down below five degrees centigrade and so will also the mineralization of methylene urea chains. Moisture also has an effect on soil microbial activity so it also indirectly has effect on the mineralization speed. It has been shown that soil pH and particle size have no big effect on mineralization.

4.2 Use in turf, golf courses, sports fields, etc.

Professional turf growers responsible of golf courses were among first ones to recognize the economic value of slow release nitrogen sources. Methylene urea is one of the most widely used nitrogen sources in modern compound fertilizers made for turf.

The number of green keepers using methylene urea containing fertilizers for turf is increasing. The most important benefits recognized are esthetic, economical and environmental. Besides a better color, uniform growth and less scorch other factors like a decrease in the number of applications per season or less leaching of nitrogen have been the motives for switching to a slow-release type of nitrogen. There is also indications that the amount of *Poa annua*, a grass weed, has not been increased on golf courses when compound fertilizers containing methylene urea have been used.

4.3 Use in forestry

The use of methylene urea in forests has been studied already since 1970's. Good growth of trees fertilized with methylene urea nitrogen was demonstrated 10 years after fertilization. Soil microbial studies[1,2] revealed that slow-release methylene urea had not increased nitrification activity in the soil. It had a positive effect on microbial activity even with high doses, and hence proved to be good alternative for forest fertilization. In the studies of Vasander and Lindholm[3] slowly soluble methylene urea applied together with slowly soluble apatite and biotite seemed to have longer effect on basal area growth than readily soluble urea, superphosphate and potassium salts. The growth results of an unpublished Kestilä trial has been presented in Figures 4 and 5.

Figure 4 - The growth of pine in Kestilä trial (m^3/ha)

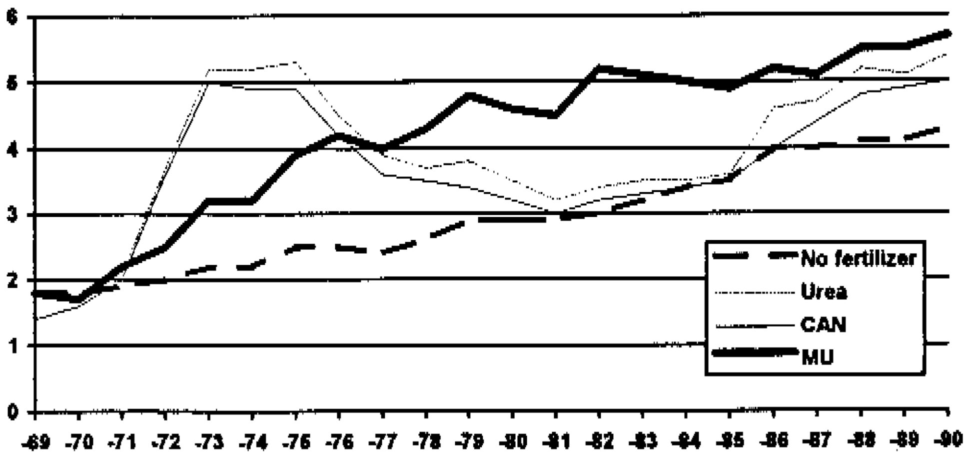
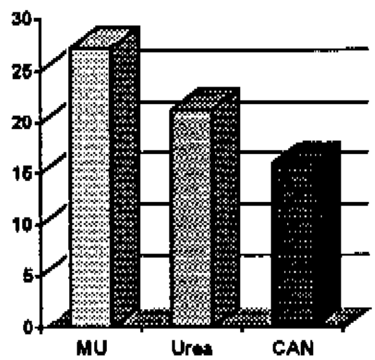


Figure 5 - Growth increase of pine (m^3/ha/20a) compared to the nonfertilized in Kestilätrial. The growth increase with MU is still 1,5 m^3/ha/a, which means that the difference will still increase.



Based on the positive results in forestry Kemira has developed the Vitality Fertilizers range for forestry use.

4.4 Other potential uses

A lot of trials with several different plants has been done during the years. The benefits received from the trials include: reduced number of applications, increased yields and decreased levels of nitrates and nitritesin vegetables, lower nitrogen leaching and greater germination and higher nitrogen efficiency. With

---

1 P.J. Martikainen, T. Aarnio, V-M. Taavitsainen, L. Päivinen and K. Salonen, Mineralization of carbon and nitrogen in soil samples taken from three fertilized pine stands: Long term effects; Plant and Soil 114: 99-106 (1989).

2 T. Aarnio, P.J. Martikainen, Mineralization of C and N and nitrification in Scots pine forests soil treated with nitrogen fertilizers containing different proportions of urea and its slow-releasing derivative, ureaformaldehyde; Soil Biol. Biochem. Vol. 27, N° 10, 1325-1331 (1995).

3 H. Vasander, T. Lindholm, Effect of readily and slowly soluble fertilizers on the growth and needle nutrient contents of Scots pine in Southern Finland, proceedings of International Peat Congress 1992.

speciality crops there seems to be good possibilities for economical use of compound fertilizers based on methylene urea, the chain length of which generally is fairly short. However, this is still an area which needs additional, long term trials to evaluate all the benefits.

5. SHORT MARKET OVERVIEW

5.1 USA

USA is the largest market of methylene urea and MU based products. The total market size is about 200 kt/a. Mainly two types of products exists: ureaform type products with fairly low Activity Index and product with relatively high amount of cold water soluble nitrogen (methylene urea - type products). This is the newer product type and has gained market share from ureaform - type products. Product type with relatively large only hot water soluble controlled release nitrogen fraction is not common in the USA. There has been fairly big changes in the producer side during the last year and now it can be said that the market is mainly dominated by three separate producers. The wholesale price level due to big volumes and high competition has dropped down to level USD 750.-/mt and even below.

5.2 Europe

In Europe the market volume of fertilizers containing methylene urea has been fairly evenly about 30 kt/a, which means about 10 kt/a calculated as methylene urea. There has been two producers as well as some material has been imported from the USA. In summer 1996, however, Kemira Agro Oy has started its new methylene urea plant. In Europe three different types of product are available: same two as in the USA but in addition to that also a product where the amount of cold water insoluble but hot water soluble nitrogen is fairly high. This is the most common product type in Europe and it is used in many applications where only a few applications per season are wanted. The price level of straight methylene urea has remained fairly high, most probably due to small production, at the level of USD 1000.- / mt.

5.3 Japan

Japan is the smallest of the three main markets of methylene urea. The compound fertilizers containing methylene urea sold amount to about 5 kt/a. Two producers use methylene urea in their compound fertilizers

5.4 Other areas

Outside the three main market areas fairly small amounts of methylene urea are sold e.g. in Far East countries, Australia and New Zealand. Although the market size in these countries is growing it is still small.

6. FUTURE TRENDS

6.1 Environmental questions

More and more emphasis has been and will be paid on environmental aspects of fertilization. This trend clearly has impact also for the consumption of slow and controlled release fertilizers. Slow release fertilizers can reduce nitrogen losses through two ways. Compared to free urea, nitrogen losses through ammonia emissions, which normally are between 10-25% but depending on soil alkalinity may be even 40%[4], can be reduced significantly by using methylene urea (7,7%) instead of urea (20,4%)[5]. The nitrate leaching in ground waters can also be reduced by using properly slow release methylene urea fertilization, e.g. Owens et al[6] has found that within a long term study, during 9th and 10th year of high application , the seasonal nitrate levels in the ground water were 10-16 mg/l for watersheds receiving ammonium nitrate whereas 7-14 mg/l for methylene urea.

Methylene urea is mineralized through the soil microbial activity, which is greater when the temperature is higher. The growth of plants and hence the nitrogen need of the plant is also higher when the temperature is

---

4 G. Kongshaug, Fertilizers for the future, The Fertilizer Society Proceedings No. 374.

5 Chakraborty, A., Bhattacharya, B., Volatilization losses from slow-release nitrogenous fertilizers compared to urea applied to alluvial soil, Indian Agriculturist (19929 vol. 36, No. 2, pp. 83-87.

6 Owens, L.B.; Edwards, W.M.; Van Keuren, R.W., Nitrate levels in shallow groundwater under pastures receiving ammonium nitrate or slow-release nitrogen fertilizer, J. Environ. Qual. (1992), 21(4), 607-613.

high. These two things together means that the nitrogen release from methylene urea fertilizer and uptake from the plant can have good correlations. By using properly chosen methylene urea type, the nitrogen efficiency of fertilizer can be improved compared to conventional fertilizers.

6.2 Methylene Urea composition

If we look back to the history of methylene urea, there has been clearly a change towards methylene urea which mineralizes faster. Generally this trend can and probably also will continue in the future, but it is also clear, that for certain applications slower products will be needed. This means that for a certain application there will be a need for more and more uniform methylene urea, with a release characteristic corresponding as closely the need of the plant as possible. The target of Kemira by starting the production of three types of methylene urea products is to fulfill these needs.