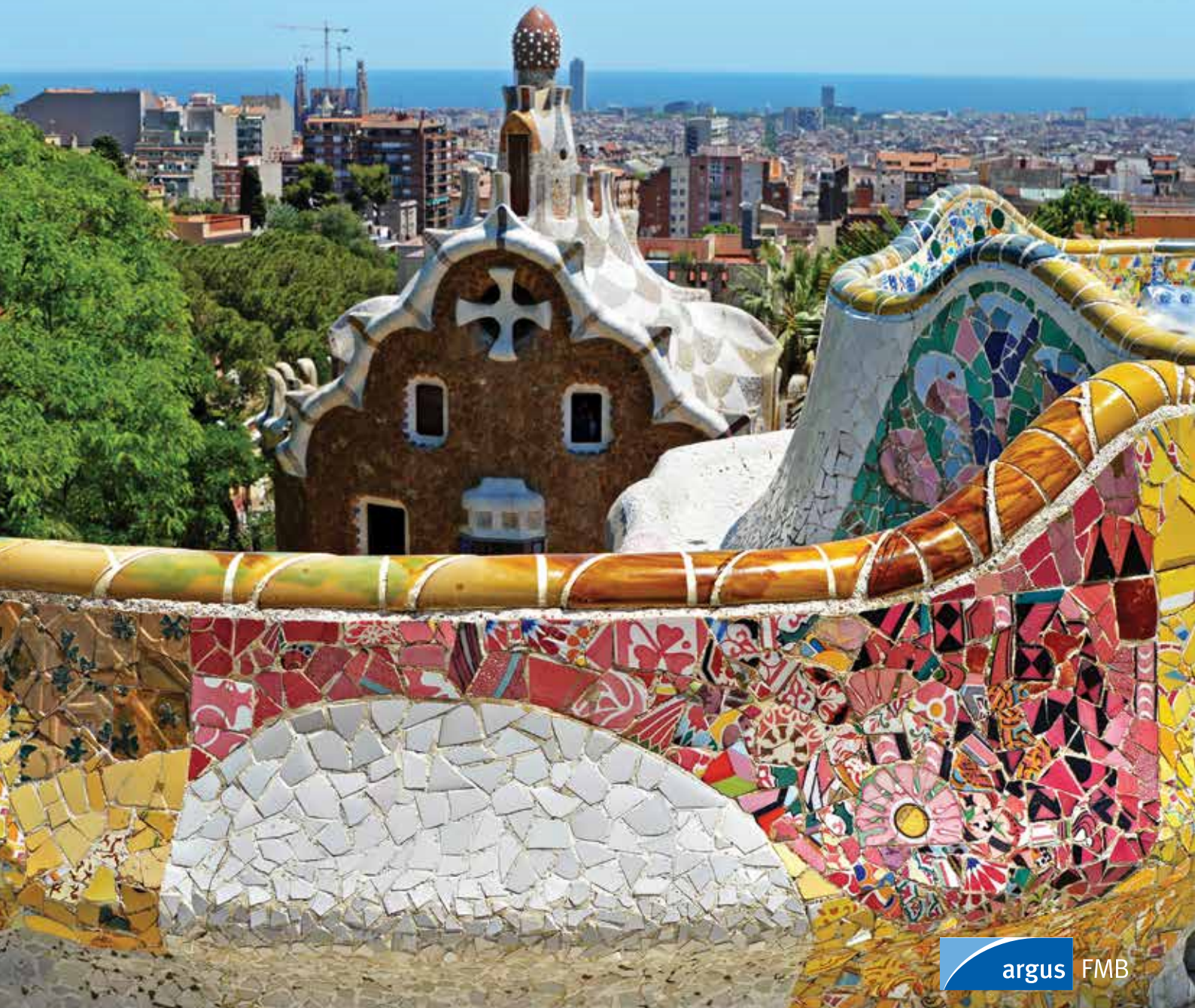


# Fertilizer

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# Clay minerals in the tropics

## Improving nitrogen fertilizer efficiency

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**Tropical soils require liming and a balanced nutrient supply to ensure high crop yield and quality. An adequate agronomic nutrient management involves balanced nutrition and fertilizers are the key factor.**

Different strategies can be employed to increase the efficient use of nutrients in order to maximize the benefits to the plant-soil-atmosphere system.

Nitrogen (N) is part of all living cells and is an essential constituent of amino acids. Fertilizers are the most important source of nitrogen used in large-scale cultivation of various non-legumes crops.

About 40–70 pc of N-fertilizers are lost, because nutrient application is often not synchronized with the needs of the specific crop. The low nitrogen use efficiency (NUE) of N-fertilizers occurs as a result of leaching, mineralization, erosion and de-nitrification processes.

In general, some changes in agricultural management can increase the efficiency in the use of N fertilizers such as: removing physical,

**“ Fertilizers are the most important source of nitrogen used in large-scale cultivation**

chemical and biological limiting factors to plant growth, balanced fertilization, adequate water supply, adjusting fertilizer supply to plant demand, optimization of rate and timing of fertilizer supply, split fertilization, fertilizer soil-incorporated, use of crop rotation and green manure, and finally, using slow or controlled release fertilizers and nitrification inhibitors with N-fertilizers.

### Slow release

The controlled and slow release fertilizers are designed to release their nutrient content gradually, and if possible, match the release with the crops' nutritional requirements. The advantages of these nutrient sources are that they; eliminate the use of top-dressing fertilization, save labour and fuel, minimize soil compaction

and root damage, as well as reduce environmental contamination.

Due to lower cost per unit of N, N-urea has been the one of the most used N-source. But N use efficiency of urea may be reduced due to losses from the agricultural system via volatilization of ammonia to the atmosphere. This is one of the main factors responsible for the low efficiency of urea.

Mulch form no-tillage or pasture systems may also increase the amount of N lost by volatilization, especially when urea is applied on soil surface. One method to enhance the efficiency of N fertilizer is the use of modified sources with lower or controlled release of nutrients. Fertilizers with agronomic, economic or environmental benefits over the conventional forms are called 'enhanced efficiency fertilizers' (EEF).

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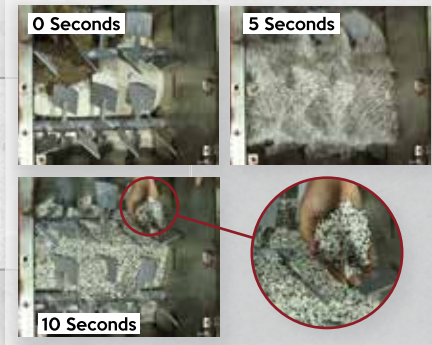
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The N-urea losses can be minimized using zeolites as additives in the fertilizers to control the retention and release of  $\text{NH}_4^+$  and convert it as an EEF. Two processes are cited as the kinetics of ion-exchange process in zeolites: the process starts with diffusion within the zeolite in the former and diffusion transport through the liquid film surrounding the particle in the latter have been assumed. However, the preference of a zeolite for a particular cation in a multicomponent system depends on various factors, viz. Si/Al ratio, the exchangeable cation in the zeolite which should be analyzed for a better understanding of the ion-exchange mechanism.

The use of minerals for agricultural purposes is becoming widespread and zeolites concentrates have a special niche in this category. Zeolite minerals are crystalline hydrated aluminosilicates of alkali or alkaline-earth metals, structured in three-dimensional rigid crystalline network, formed by the tetrahedral  $\text{AlO}_4$  and  $\text{SiO}_4$ , which come together to compose a system of canals, cavities and pores at nanoscale. These minerals are characterized by the retaining and releasing water and exchange cations without changes in structure. Other hydrated layered silicates clay minerals, like bentonite, are able to exchange cations, and intercalate neutral molecular species between the interlayer regions by interaction with structural water.

### Greenhouse gas

The worldwide number of identified natural zeolitic concentrates demonstrates both their great variety and the present-day interest on their potential applications in the industry and the agriculture.

The use of natural aluminosilicates together with fertilizers is considered to be of strategic importance, contributing to an N-loss reduction, increase of NUE, and also a reduction of negative impacts of fertilizers on soil resources. Among the natural zeolites, clinoptilolite is most commonly used in agriculture. Zeolites containing micropores of

## *The use of natural aluminosilicates with fertilizers is considered to be of strategic importance*

molecular dimensions of  $<1$  nm, play an important role in modifying the physics, chemistry and biology of soils.

The main action of zeolite in partial reduction on  $\text{NH}_3$  loss by volatilization occurs by the control of retention of ammonium ion, formed by urea hydrolysis in the soil, due to zeolite high cation exchange capacity and ammonium retention from soil solution. N inputs from fertilizers increase  $\text{NH}_4^+$  and  $\text{NO}_3^-$  soil concentrations and may increase the soil emissions of the greenhouse gas (GHG) as  $\text{NH}_3$  and  $\text{N}_2\text{O}$ . However, information on how urea–aluminosilicate slow-release nanocomposites might affect volatilization, nitrification and denitrification processes in the soil still need more studies. Besides retaining large quantities of ammonium ion, these minerals also interfere in the process of nitrification. Zeolites also can decrease nitrogen loss due to leaching, since the cation is bind by negative charges and leads to the reduction of nitrogen leaching.

Zeolites also improve the efficiency of nutrient use by increasing the availability of P from phosphate rock, the utilization of N- $\text{NH}_4^+$  and N- $\text{NO}_3^-$  and reduced losses by leaching of exchangeable cations.

There are many reports in literature demonstrating the increased efficiency of N utilization when urea is used together with aluminosilicates. Clinoptilolite is the most known and used zeolite specie for retaining ammonium cation, and reductions of losses by ammonia volatilization when urea was applied with this mineral. However, the property of cation exchange is shown by the aluminosilicate, represented not only by zeolites, but by clay minerals.

### Clay minerals

Clay minerals are crystalline hydrated aluminum silicates, structurally oriented as silicate lamellae bonded to aluminate lamellae. These lamellae are spatially arranged by stacks separated by exchange able ions and structural water. The crystalline structures are classified into 2 types: structures 1:1 (kaolinite, serpentine) and structures 2:1 (talc-pyrophyllite, mica, smectite, vermiculite, chlorite, attapulgite, sepiolite).

Only a small number of clay minerals are components of industrial clays: kaolinite (kaolin); montmorillonite (bentonite); talc (talc); vermiculite (vermiculite) and chrysotile (asbestos). Just as zeolites, the cation exchange capacity in clay minerals is quite pronounced, however, values may range from  $10^{-3}$  meq·g<sup>-1</sup> (phyllites) to 1 meq·g<sup>-1</sup> (montmorillonites and vermiculite).

Zeolites are characterized due to the retention and release of water and exchange cations without any change in the crystal structure. The worldwide number of identified natural zeolites minerals demonstrates both their great variety and the present-day interest on their potential applications in the industry and the agriculture. Zeolite structure allows the formation of channels (mesopores) of around 78 to 115Å for clinoptilolite zeolite. This mesoporous structure provides high surface area (8 to 72 m<sup>2</sup>·g<sup>-1</sup> for clinoptilolite zeolite). However, the ionic charge of the aluminosilicates are not neutral, it requires cations to stabilize it, and the most common ions are Na<sup>+</sup> and K<sup>+</sup>. These cations, associated with high surface area, provides one of the

most important properties of these minerals: the high cation exchange capacity as 2.6 meq·g<sup>-1</sup> (stilbite) and 3.0 meq·g<sup>-1</sup> (clinoptilolite) Zeolite stilbite has the ability to retain half of the quantity of ammonium held by the clinoptilolite type.

Bentonite, a hydrated layered silicates clay mineral, is also able to exchange cations, and intercalate neutral molecular species between the interlayer regions by interaction with structural water. Nanocomposites formed from a bentonite exfoliation in a urea matrix obtain by cold extrusion, a high N content and adequate strength compatible to commercial fertilizer can control the urea solubilization process, delaying the N release.

The lower release process was not


**“ The results indicate that aluminosilicates minerals are able to improve the efficiency of nitrogen use**

only due to the clay mineral-urea interaction, but also to the creation of barriers to free urea diffusion out of the granule.

Although the results have showed that the aluminosilicate and urea mixture can reduce ammonia volatilization, the utilization of these minerals by farmers will depend on their cost. Zeolite natural reserves are present in many countries, and the cost of this mineral may vary due their availability and effectiveness.

### Nitrogen efficiency

The reduction in ammonia losses by volatilization and the increased efficiency of N utilization when urea is used together with aluminosilicates was demonstrated in laboratory, greenhouse and field experiments. These results indicate that aluminosilicates minerals are able to improve the efficiency of N use, contribute to increasing N uptake through the control of retention of ammonium ion. ■





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