



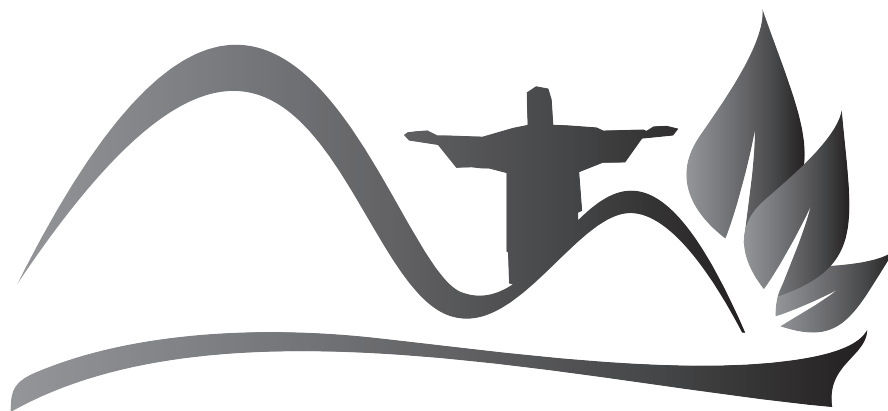
16th WORLD FERTILIZER CONGRESS OF CIEC

TECHNOLOGICAL INNOVATION FOR A
SUSTAINABLE TROPICAL AGRICULTURE

PROCEEDINGS



International Scientific Centre of Fertilizers (CIEC)



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PROCEEDINGS

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THE USE OF CLAY MINERALS TO IMPROVE NITROGEN FERTILIZER EFFICIENCY

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Introduction

Diferent strategies can be taken to increase the efficient use of nutrients from to maximize its benefits to the plant-soil-atmosphere system. Nitrogen is part of all living cells and is an essential constituent of amino acids and hence the proteins, enzymes and metabolic processes involved in the synthesis and transfer of energy, and is part of chlorophyll, the green pigment responsible for photosynthesis. Fertilizers are the most important sources of nitrogen used in large-scale cultivation of various non-legumes crops.

In general, some changes in agricultural management can increase the efficiency in the use of N fertilizers such as: removing physical, chemical and biological limiting factors to plant growth; balanced fertilization; adequate water supplying; adjustment of fertilizer supplying to plant demand; optimization of rate and timing of fertilizer supplying; 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.

The controlled and slow release fertilizers are prepared to release their nutrient content gradually, and if possible, match their release with the crop nutritional requirements, or to extend their availability much more than high solubility fertilizers. The advantages of these nutrient sources are the eliminate the use of topdressing fertilization, labor and fuel saving, soil compaction and root damage minimizing, and preventing crop damage, as well as reducing environmental contamination.

Urea nitrogen has been the most used N-source in Brazil, due to lower cost per unit of N. But N use efficiency of urea may be reduced because of losses from agricultural system by volatilization of ammonia to atmosphere. This is one of the main factors responsible for the low efficiency of urea, and may reach extreme values, close to 80% of N

applied, even so in acid soils, since the liming increases soil pH and favors volatilization. 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.

The N-urea losses can be reduced using zeolites as additives in the fertilizers to control the retention and release of NH_4^+ . 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 AlO_4 and 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. 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. In Brazil there are three regions with sedimentary zeolite which widely varies in the depth of the occurrence and the stilbite concentration. The largest zeolite reservoirs are found in the Parnaíba river valley, where the stilbite form of the heulandite group dominates reaching approximately 50% of sediment (Rezende & Angelica, 1999; Monte et al., 2009; Bernardi et al., 2013b).

The main action of zeolite in partial reduction on 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 NH_4^+ and

NO_3^- soil concentrations and may increase the soil emissions of the greenhouse gas (GHG) as NH_3 and N_2O . 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.

There are many reports in literature demonstrating the increased efficiency of N utilization when urea is used together with aluminosilicates. In a laboratory test, Baptista-Filho et al. (2008) demonstrated the ammonia retention by zeolite using a photoacoustic set-up, which simulated tropical weather temperatures. The positive effect of zeolite was confirmed in a field experiment with rose buds.

In a field experiment Bernardi et al. (2011) evaluated dry matter yield and nutritional levels of nitrogen of silage corn fertilized with urea + zeolite. Treatments comprised two types of stilbite zeolite (natural and concentrated), four levels of nitrogen (0, 50, 100 and 200 kg ha^{-1}) and four ratios of zeolite (25%, 50% and 100% of N level). Treatments were applied 60 days after planting in the topdressing fertilization. The use of concentrated (650 g kg^{-1} of stilbite) or natural (470 g kg^{-1} of stilbite) zeolite with urea increased, respectively 5.5% and 3.6% the silage corn dry matter production and N leaf concentrations.

In a pot experiment with Italian ryegrass Bernardi et al. (2013a) observed differences in the rate of N- NH_3 volatilization with addition of 20% of zeolite to urea with an 8% decreasing of accumulated volatilized N- NH_3 . Results indicated that approximately 21% of applied N was lost as N- NH_3^+ when there was no addition of zeolite to urea. Addition of 20% zeolite reduced losses to 19.6%. As expected based on previous results, the lowest percentage of loss was obtained from ammonium nitrate N-source which was similar to the control (without N).

Clinoptilolite is the most known and used zeolite species for retaining ammonium cation. Werneck et al. (2012) achieved reductions of losses by ammonia volatilization when urea was applied with clinoptilolite. Baptista et al. (2011) showed that the Brazilian zeolite stilbite has the ability to retain half of the quantity of ammonium held by the clinoptilolite type.

Rech (2014) tested urea-based formulations of nitrogen fertilizer with the addition of urease inhibitors (NBPT, Cu, B), elemental sulfur and clay minerals of the zeolite group. The results showed that formulations produced with urease inhibitor alone (NBPT, B, Cu) embedded in beads and those inhibitors combined with the clay mineral showed greater efficiency in reducing losses by volatilization compared to commercial coated fertilizer with the same inhibitors. Ammonium and nitrate leaching and soil accumulation showed no significant differences between produced formulations and commercial fertilizers. The N accumulation in corn plants grown with the new formulations was similar to commercial fertilizer, being higher to commercial urea. However, it is clear that the incorporation of a urease inhibitor in urea fertilizer is more efficient in the reduction of losses by volatilization compared to coated fertilizers produced with the same additives.

However, the property of cation exchange is shown by the aluminosilicate, represented not only by zeolites, but especially by 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 exchangeable ions and structural water. The crystalline structures are classified into 2 types: structures 1:1 (kaolinite, serpentine) and structures 2:1 (talcpyrophyllite, 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} $\text{meq}\cdot\text{g}^{-1}$ (phyllites) to 1 $\text{meq}\cdot\text{g}^{-1}$ (montmorillonites and vermiculite).

Pereira et al. (2012) demonstrated that a nanocomposite formed from a montmorillonite exfoliation in a urea matrix controlled the solubilization process, delaying the N release. The results showed that it was possible to obtain by cold extrusion, a high N content and adequate strength compatible to commercial fertilizer. Microstructural analysis of composites indicated that the extrusion process generated two regions, one comprising the nanocomposite itself (montmorillonite and

urea), and other regions with urea granules. Thus, the authors attributed the release process not only to the clay mineral-urea interaction, but also to the creation of barriers to free urea diffusion out of the granule.

Conclusions

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

Keywords: Zeolite, stilbite, clinoptilolite, slow-release fertilizer, N losses, ammonia volatilization.

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