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CONTROLLED-RELEASE FERTILIZERS USING ZEOLITES

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Introduction

The use of soluble fertilizers can lead to water pollution and to wasted nutrients. For example, nitrogen can leach into ground and surface waters, especially in sandy soils, and phosphate may become fixed and unavailable to plants, especially in tropical soils. Zeolites, a class of minerals that have large cation-exchange capacities and high porosities (both molecular and rock), may be useful in controlling the release of these and other plant nutrients in agricultural systems (Pond and Mumpton, 1984). Zeolites also can free sparingly soluble nutrients already in a soil for uptake by plants, and may improve soil fertility and water-retention. Because zeolites occur in enormous, near-surface deposits, they could be employed on a large scale in agriculture should their use prove to be environmentally beneficial and economically justifiable. The present paper describes several techniques that use zeolites to control nutrient release to laboratory solutions and to plants.

Slow-Release Nitrogen Fertilizer

Urea is one of the most commonly used nitrogen fertilizers. It is very soluble in water, and can be lost from the root zone of plants by leaching. In addition, urea is converted into ammonium ions by urease, an enzyme that is found in most soils. Ammonium ions then are converted into readily leachable nitrate ions by soil bacteria. Zeolitic rocks help prevent these nutrient losses.

A slow-release nitrogen fertilizer can be produced by heating zeolite rock chips to about 400°C to drive out all zeolitic and pore water, and by replacing this water with molten urea, which solidifies at about 132°C (Eberl and Lai, 1992). The rate of nitrogen release from the zeolitic rock is slowed in three ways: (l) by sequestering crystallized urea in the rock and zeolite pores to prevent it from being leached from the root zone; (2) by slowing the release of urea to urease enzyme in soil thereby delaying the formation of ammonium ions; and (3) by taking up ammonium ions onto exchange sites in the zeolite to "protect" them from nitrifying bacteria. Potassium-saturated chabazite from Bowie, Arizona, prepared by the above method was found to hold about 17 wt. % elemental N. The rate of N release, which was controlled by changing the particle size of the rock chips, followed the equation:

$$\text{wt. \% slow-release N} = 20 + 40(\text{log of mean particle size in mm})$$

Controlled-Release Phosphorous Fertilizer

Phosphate for uptake by plants can be released from phosphate rock (mostly composed of the calcium phosphate mineral apatite) by mixing the rock with zeolite containing a monovalent exchange ion, such as ammonium (Lai and Eberl, 1986). The approximate reaction in soil solution is:

$$\text{P-rock} + \text{NH}_4\text{-zeolite} = \text{Ca-zeolite} + \text{NH}_4^+ + \text{H}_2\text{PO}_4^-.$$

The zeolite takes up Ca^{2+} released to the solution from the phosphate rock, thereby releasing both phosphate and ammonium ion. Unlike soluble P fertilizers (e.g., superphosphate), phosphate is released in the above system by a chemical reaction that occurs in the soil. As phosphate is removed from the soil solution by plants or by soil fixation, more is released as the above reaction is driven to the right to reestablish equilibrium. Therefore P concentration in the system is buffered. The rate of P release is controlled by varying the P-rock/zeolite ratio. Phosphorous also is released from the rock by a lowering of soil pH related to the nitrification of ammonium ions.

This system was tested in greenhouse pot experiments with sorghum-sudangrass using NH_4-saturated clinoptilolite from the Fort Leclede deposit, Washakie Basin, Wyoming, and P-rock from North Carolina, with a P-rate of 340 mg P/kg soil, and zeolite/P-rock ratios ranging from 0 to 6 (Barbarick *et al.*, 1990). Total P-uptake and P-concentration measured for the grass were related linearly to the zeolite/P-rock ratio, and yields summed over four cuttings were as much as four times larger than companion experiments performed using a soluble P source (monocalcium phosphate).

Release of Trace Nutrients

Greenhouse experiments similar to those described above indicate that zeolite in soil can aid in the uptake of some trace nutrients by sorghum-sudangrass. The concentrations of Cu and Mn in the grass (in mg/kg) were found to be significantly related to the zeolite/P-rock ratio (x) in experimental systems that used two different NH_4-saturated clinoptilolites (Washakie Basin, Wyoming, and Craven Creek, South Dakota), two different soils (Weld from Colorado and Keith from South Dakota), and P-rock from North Carolina and Idaho. For example, the relation for systems using the Washakie Basin zeolite, the Weld soil, and P-rock from North Carolina was:

$$Cu = 2.78 + 0.83x - 0.06x^2 \ (R^2 = 0.94); \text{ and } Mn = 40.03 + 18.49x + 0.76x^2 \ (R^2 = 0.99).$$

The mechanism for this effect may be similar to the reaction shown above: sparingly soluble minerals are dissolved by the sequestering effect of the exchanger, thereby releasing trace nutrients to zeolite exchange sites where they are more readily available for uptake by plants. A lowering of soil pH by nitrification of ammonium ions also aided trace element uptake in some experiments.

Harmful Effects

Zeolites can be harmful as well as helpful to plant growth. For example, zeolites containing sodium as the chief exchange ion can be toxic to plants (Pirela *et al.*, 1984), and K-, Ca-, and NH_4-poor zeolites can scavenge these ions from soil solutions and thereby limit plant growth if they are used in soils that are deficient in these nutrients (Barbarick *et al.*, 1990; Marcille-Kerslake, 1991). These negative results emphasize the need to use well-characterized zeolites during agricultural experimentation (see Sheppard, 1984).

Conclusions

The ultimate fertilizer should be inexpensive and long lasting; it should tend to increase soil fertility through repeated use, and it should release nutrients as they are needed by plants (buffered systems), thereby eliminating fertilizer inefficiencies. Whether or not such systems will be realized will depend on a movement in agricultural research towards technologies that are advanced and fine-tuned to ecologically friendly and sustainable methods. The preliminary experiments reported here indicate that zeoagriculture is a promising avenue for such research.

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