

Controlled and renewable release of phosphorous in soils from mixtures of phosphate rock and NH₄-exchanged clinoptilolite

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A controlled and renewable release fertilization system is proposed that employs NH₄ saturated clinoptilolite to aid in the dissolution of phosphate rock (apatite), and thereby to release soluble N, P, and exchangeable Ca for uptake by plants. The system is based on the principle that exchangers can sequester Ca ions released by the dissolution of apatite, thereby leading to further dissolution of the apatite. Experiments show that the quantity of P released by this method is an order of magnitude more than that released by apatite alone. This system offers an alternative technology to the acidulation of phosphate rock, and may circumvent problems associated with highly soluble fertilizers.

Keywords: Phosphorous; phosphate rock; clinoptilolite, NH₄-exchanged; soluble fertilizers

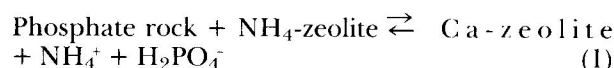
INTRODUCTION

Modern intensive agriculture uses chemical fertilizers that contain highly soluble and concentrated plant nutrients. There is concern that repeated applications of such fertilizers may have long-term, adverse impacts on soils and on environmental quality¹⁻³, and that they may induce imbalances in nutrients supplied to plants, thereby affecting the health of animals and humans^{4,5}. Increasing costs for non-renewable energy also have led to concern about the rising cost of fertilizer in modern food production⁶⁻⁸. These concerns have prompted a reevaluation of our current agricultural practices^{9,10}. Organic farming, which uses less or no chemical fertilizers, has been offered as an alternative¹¹⁻¹⁵. Recently, Frey, Keim, and Nelson, Presidents of the American Society of Agronomy, the Crop Science Society of America, and the Soil Science Society of America, respectively, have stated the problem as follows: 'Whether agricultural production will continue to employ the present intensive system, move to organic farming, or use a mix of the two, will have important overtones on the billions who will occupy the Earth in the next century and beyond'¹⁶.

It is widely held that a period of 3 to 5 years is required during the conversion process to obtain yields from organic agriculture that are commensurate with those obtained by conventional practice¹⁷. Thus, should the conversion from chemical to organic agriculture prove to be necessary or desirable, it would be valuable to have a controlled-release fertilizer that would keep yields large while soil fertility is reestablished. This paper presents the results of experiments that investigated the chemical properties of a potential fertilization system in which nutrient

release can be controlled and renewed, and in which some of the adverse effects associated with highly soluble and concentrated fertilizers are avoided. This system consists of a mixture of phosphate rock and NH₄-zeolite. Nutrient release in this system occurs mainly by ion exchange, thereby mimicking nutrient-release processes that occur naturally in soils. The zeolite in this system, in addition to freeing P, N, and Ca, also serves as a soil conditioner^{18,19}.

Phosphate rock (chiefly apatite) can be applied directly to soil, but its effectiveness as a fertilizer in many soils is limited by its very low solubility²⁰. Its solubility is increased in commercial fertilizers by acidulation²¹. The proposed alternative system is based on the principle that exchangers can sequester ions released by the dissolution of a mineral, thereby leading to further dissolution of the mineral²². A simplified reaction for our system is:



NH₄-zeolite acts as a sink for Ca²⁺ during exchange, thereby releasing NH₄⁺ and lowering the activity of Ca²⁺ in solution. With a lower Ca²⁺ activity in solution, more apatite will dissolve. Phosphate rock can be dissolved completely by this method provided that the system contains sufficient exchanger. In previous studies, Mattson *et al.*²³ used a Na-saturated cation exchanger (Wofatite) to release P from tricalcium phosphate; Møller and Mogenson²⁴ extracted P from calcium phosphate in soil using a Na-zeolite; and Chien and Hammond²⁵ used an H-saturated resin to extract P from phosphate rock. Recently, Wilson and Ellis²⁶ found a linear relationship between P solubility from phosphate rock and Ca²⁺ activity. Pot experiments have shown that the availa-

bility of P for plant growth can be increased greatly by the addition of H-bentonite and other H-exchangers to phosphate rock²⁷⁻²⁹.

MATERIALS AND METHODS

The phosphate rock (mainly carbonate apatite) used in these experiments is from Florida, and was purchased from Ward's Natural Science Establishment, Inc.* Zeolitic tuff containing >90% clinoptilolite and having a cation-exchange capacity (CEC) of 180 meq/100 g was collected from deposits at Barstow, California. Its properties were described by Sheppard and Gude³⁰. Both phosphate rock and zeolite were ground to <60 mesh. The zeolites were used either in their natural state or were saturated with NH_4^+ , H^+ , or Na^+ by treating them three times with 1 M chloride solutions; the third treatment was by shaking overnight. They then were washed free of chloride and dried.

Three sets of experiments tested the effect of zeolite on phosphate rock dissolution. The first set studied the effect of cation saturation on dissolution by shaking 1 g of zeolite with 200 mg of phosphate rock in 50 ml of distilled water at 25°C for 48 h. The amount of phosphate rock dissolved was measured after centrifugation by analysis of the supernatant for P by colorimetry³¹. A second set of experiments tested the system's capacity to release P in the presence of soil in extraction experiments, and compared this capacity with that of systems containing the same amount of total P in which monocalcium phosphate had been added to the soil. Various proportions of NH_4 -Barstow clinoptilolite and phosphate rock were shaken with 1 g of soil (N-1 from Indonesia, a Typic Paleudults, pH = 4.8, CEC = 18.5 meq/100g). This soil and three other soils used in the next set of experiments (C-19 from New Mexico, a Cumulic Haplustoll, pH = 7.2, CEC = 9.5 meq/100 g; W-1 from Hawaii, a Tropeptic Eustrtox, pH = 5.4, CEC = 22.9 meq/100 g; and NI from Hawaii, a Hydric Dystrandeps, pH = 6.0, CEC = 36.3 meq/100g) are described elsewhere^{32,33}. These systems were allowed to react at 25°C by shaking with 25 ml of distilled water. The supernatant solutions were removed from the solids by centrifugation after every 24 h, and fresh distilled water was added to make up 25 ml (by weighing). The supernatant was analysed for P. Finally, a third set of experiments tested whether or not the system's ability to release P could be renewed by adding 200 mg of additional zeolite to the soil-zeolite-phosphate rock mixtures described above, or by treatment with 25 ml of 0.1 M NH_4Cl solution.

EXPERIMENTAL RESULTS

The first set of experimental results are given in *Table 1*. Dissolution of phosphate rock is favoured by saturation of the zeolite with monovalent exchange

*Use of the firm name is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey

Table 1 Effect of clinoptilolite-rich tuff on the dissolution of phosphate rock

Form of the zeolitic tuff	P released (mg l ⁻¹)	Final pH
Natural	2.84	7.35
NH_4 -saturated	8.28	8.07
Na-saturated	10.38	7.63
H-saturated	67.6	3.75
Phosphate rock only	0.55	7.20

ions (NH_4^+ , Na^+ , and H^+) as compared with the untreated natural zeolite which initially contains some exchangeable calcium³⁰. With Ca^{2+} as the exchange cation, there is no tendency for the zeolite to aid in phosphate-rock dissolution. The large effect found for H-zeolite is related to a lowering of solution pH caused by an exchange of Ca^{2+} for two H^+ by a reaction analogous to Equation 1. More apatite dissolves as the pH decreases, thereby leading to further exchange and further dissolution.

A second set of experiments tested the system's capacity to release P in soil, and compared this capacity to that of a monocalcium phosphate-soil system having the same amount of total P. The curves in *Figure 1* demonstrate that both the rate and the total amount of P released in the zeolite systems are a function of the zeolite/phosphate rock ratio. The curves also show that whereas most of the P in the monocalcium phosphate-soil system is released in the first few extractions, the zeolite systems have a more gradual release. Eventually, zeolite-rock systems surpass the monocalcium phosphate system in total P released, thereby suggesting that, under the proper

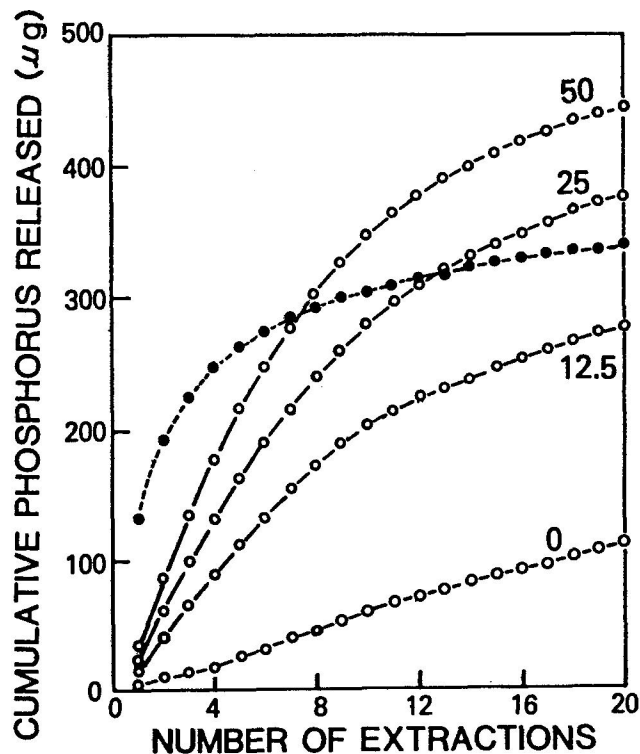


Figure 1 Capacity of the zeolite systems (open circles) to release P as compared to a monocalcium phosphate system (solid circles) having an equivalent amount of P. Both types of systems contained 1 g of soil N-1. Numbers next to the curves refer to the NH_4 -zeolite/phosphate rock ratio, with each zeolite system initially containing 4.0 mg of phosphate rock

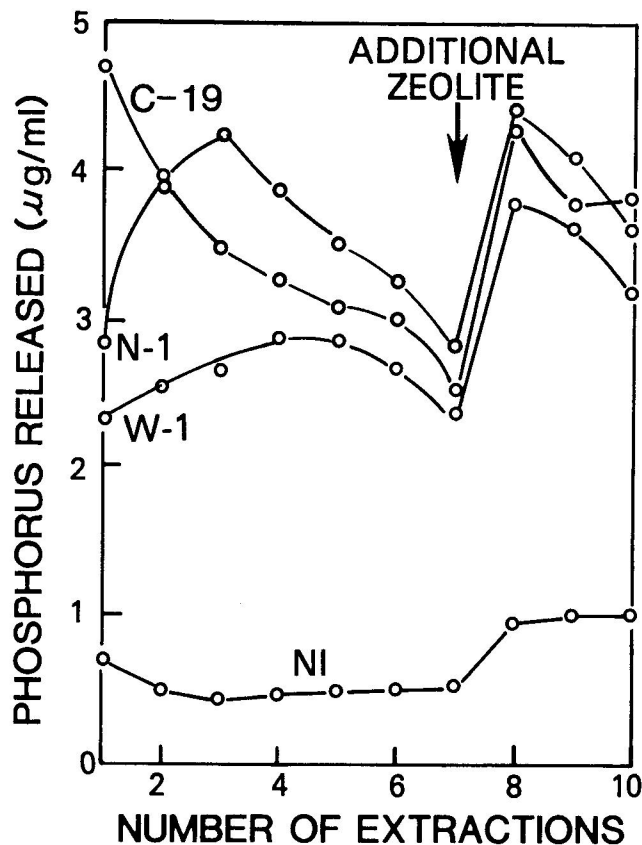


Figure 2 Renewal of P-release from zeolite-phosphate rock-soil systems by adding 200 mg additional NH_4 -exchanged clinoptilolite after seven extractions. Four different soils are represented. See text for a description of soils

soil conditions, zeolite systems could surpass commercial superphosphate and triple superphosphate, which are composed chiefly of monocalcium phosphate.

The gradual decrease in slope of the zeolite-system curves in *Figure 1* shows that the zeolite-system's ability to release P decreases as the number of extractions increases. The likely cause is a filling of exchange sites by Ca^{2+} . Thus, it should be possible to renew the system's ability to release P from phosphate rock still present in the soil either by adding more NH_4 -zeolite, or by resaturating zeolite already present in the soil with NH_4^+ . The third set of experiments was conducted to test these proposals by adding additional NH_4 -zeolite to soil-zeolite-phosphate rock mixtures. *Figure 2* shows that renewal is evident for all four soils. *Figure 3* shows the effect of adding NH_4Cl to systems undergoing extraction. At first, P release is inhibited because excess NH_4^+ competes with Ca^{2+} for exchange sites according to Equation 1. As this NH_4^+ (and Ca^{2+} released to solution from the zeolite) is washed from the system with each additional extraction, however, the ability of the system to release P increases and finally surpasses that of the initial system. Evidently, cation-exchange sites in the soil also have been converted into the NH_4 -form, thereby aiding dissolution.

CONCLUSIONS

Judging from plant growth experiments which used

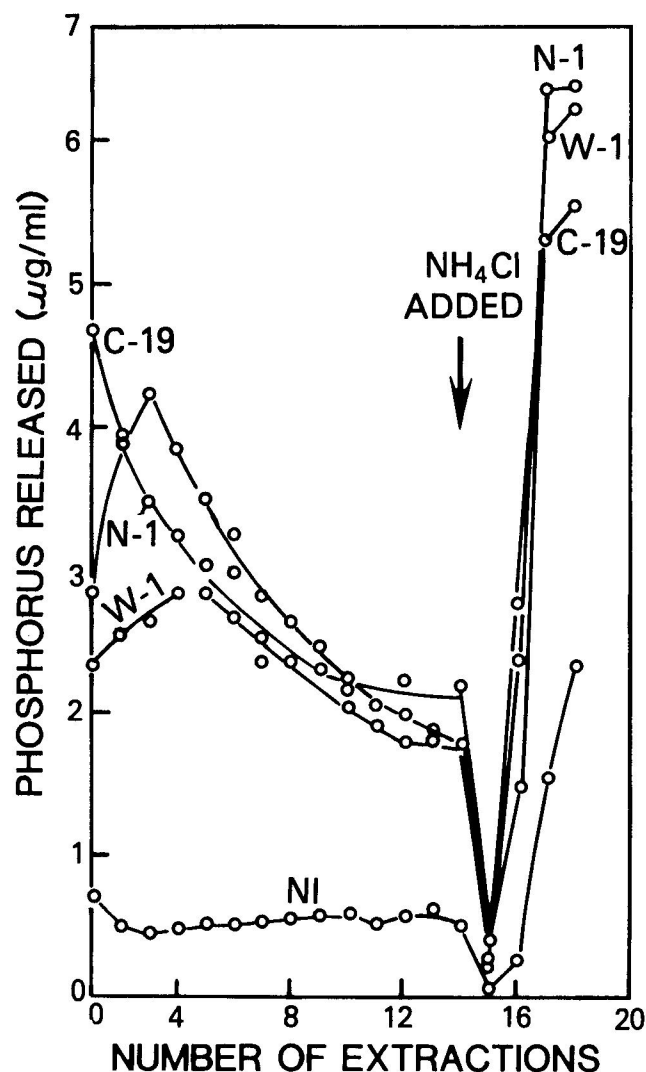


Figure 3 Renewal of P-release from zeolite-phosphate rock-soil systems by adding 25 ml of 0.1 M NH_4Cl after 14 extractions. Other experimental conditions are the same as in *Figure 2*

mixtures of H-exchangers and phosphate rock as sources for P^{27-29} and from experiments which used ammonia-treated exchangers or NH_4 -exchangers as effective sources for $\text{N}^{34,35}$, the proposed system should work for plants. Plant growth experiments that are currently underway in our laboratory demonstrate that 2:1 and 5:1 ratios of zeolite to phosphate rock are effective as fertilizer. The experiments reported above have shown that the system yields a steady release of P. The rate of this release can be varied to meet a variety of growth requirements by varying the zeolite/rock ratio, as has been demonstrated with plants for H-bentonite/phosphate rock systems by Cook²⁷. In addition, exchangeable Ca (in the zeolite) is readily available for plant uptake²⁰ and K can be added to the system by using K-zeolite or by letting NH_4 -zeolite dissolve a sparingly soluble K-mineral such as feldspar or mica³⁶. Thus, the system has the potential to supply all of the major plant nutrients. Trace nutrients could be added in a similar manner. The system's effectiveness, however, probably is limited to noncalcareous soils because NH_4 -zeolite will dissolve the more soluble calcite before it dissolves much apatite.

The economic viability of the system remains to be determined. Phosphate rock is available worldwide.

The exchanger can be substances available locally, such as zeolite, bentonite, and smectite-rich shale or soil. Enormous, near-surface deposits of clinoptilolite are found in North America³⁷. Clinoptilolite can be converted into the NH₄-form by using it to remove ammonia from sewage effluent and industrial wastes³⁸. Another method is to wash zeolite with dilute acid and then to expose it to NH₃ gas. Many questions remain to be answered, however, such as the relative and absolute amounts of zeolite and phosphate rock required for optimum plant growth, the efficiency of nutrient uptake by plants from this system compared with that from standard fertilization systems, the chemical stability of zeolite in soil, and the resistance of NH₄⁺ in zeolite to leaching and microbial attack.

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