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**NITROGEN-LOADING CAPACITIES OF SOME CLINOPTILOLITE-RICH ROCKS**

by

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## ABSTRACT

Clinoptilolite-rich rocks (CRRs) from eight deposits in the western U.S. and one deposit in British Columbia were tested for their nitrogen-holding capacity using two commercial fertilizers. One fertilizer was a mixture of ammonium nitrate plus 10-34-0 (N-P-K) with a total of 18.5 weight percent N and 3.4 weight percent  $P_2O_5$ ; the other solution was 57.1 weight percent ammonium nitrate. For the ammonium nitrate plus 10-34-0 treated CRRs, N capacities ranged from 1.8-3.9 weight percent nitrogen. For the CRRs exposed to the 57.1 weight percent ammonium nitrate solutions with 20 weight percent N, the CRRs held 4.7-8.4 weight percent nitrogen. Some of the N in these CRRs is held as ion-exchanged  $NH_4^+$ ; the remainder is held as water-soluble N salts in the CRR pore space. The CRRs tested were high Ca + K ranging from 3.7 to 5.7 weight percent and with less than 2.5 weight percent Na. Sized 2.0-4.7 mm granules of CRRs were used.

This study demonstrated CRR's N capacity for their potential uses in many agricultural applications. When used as a slow N-release fertilizer, non-point source surface and groundwater N pollution resulting from highly soluble synthetic fertilizers now used can be avoided. In present practices, the use of highly soluble synthetic N-fertilizers in sandy soils results in N losses as high as 35 to 50 percent; this results in serious nitrate groundwater pollution in many parts of the U. S. The use of an N-amended CRR for fertilizer would reduce the N pollution significantly and would also enhance the cation exchange capacity of the soil.

## INTRODUCTION

The objective of this study was to examine the properties of nitrogen-and phosphorous-amended clinoptilolite-rich rocks (CRRs) for agricultural (fertilizer) applications. This was done to develop a slow N-release fertilizer to mitigate non-point source N pollution of ground and surface water caused by widely-used, highly-soluble, synthetic fertilizer (Puckett, 1994). The use of CRRs as an  $NH_4^+$ -exchanged medium to slowly release N for plant availability in the soil was first suggested almost two decades ago by Mumpton and Fishman (1977). The initial concept was that  $NH_4^+$  exchanged into clinoptilolite would be protected from bacterial nitrification, but would be available for plants when exchanged out of clinoptilolite. In these earlier studies an emphasis was placed on the  $NH_4^+$ -ion exchange capacities of both synthetic and natural clinoptilolites. For later studies by Loizidou and Townsend (1987), a maximum of about 2.7 weight percent of N (as  $NH_4^+$ ) was exchanged into a clinoptilolite of a CRR.

Recent studies using granular (2.0-4.7 mm) CRRs exposed to diluted ammonium polyphosphate solutions have 37-88 weight percent N as exchanged  $NH_4^+$ ; the remainder of the N is in pore space of CRRs as soluble N salts. Exposure of CRRs to 57 weight percent ammonium nitrate solutions made N-amended CRRs with as much as 8 weight percent total N, but only 25 percent of the total N was exchanged as  $NH_4^+$  (Desborough, 1996). While the non-exchanged N in CRRs is water soluble, it is temporarily sequestered (in pore space of CRRs) and slowly released because of diffusion-rate limitations that are largely controlled by the CRR particle size. Presumably, the exchanged  $NH_4^+$  in CRRs would dissolve more slowly than the water-soluble, or non-exchanged N salts which are precipitated in the pore space. However, this may only be true in the absence of diffusion-rate considerations, i.e., in very small CRR particles. It is assumed that larger N-amended CRR granules will release soluble, or non-exchanged N, more slowly than smaller particles. Because of the diffusion-rate aspect related to CRR particle size, a range of N-amended CRR granule size (2-4.7 mm) was used for the

laboratory studies done here.

The CRRs used for this study have relatively high concentrations of K plus Ca (e.g., 3.7-5.7 weight percent). CRRs with more than 2.5 weight percent Na were not used because high concentrations of exchangeable Na are deleterious to plants of agronomic interest for human and animal nutrition (Nishita and others, 1968; Nishita and Haug, 1972).

CRRs from deposits in eight western U.S. states and one deposit in British Columbia were chemically analyzed to assure that they could be used without adverse effects in the soil. One CRR from Oregon was determined to have potentially adverse acid-generating reactions in a prior laboratory study (Desborough, 1996) and was not used in the present study.

#### **LABORATORY METHODS**

All CRR samples were crushed and sized. The 10-4 mesh (2.0-4.7 mm) fraction was used for the nitrogen-capacity studies; a 20-50 g sample of this sized material was pulverized to powder (95 % < 0.1 mm) for X-ray diffraction and non-destructive chemical analysis.

Mineralogy of the CRRs was determined by X-ray diffraction (table 1). Chemical composition of the CRRs given in Table 2 were obtained by X-ray fluorescence analysis using radioisotope excitation sources ( $^{55}\text{Fe}$ ,  $^{109}\text{Cd}$ , and  $^{243}\text{Am}$ ) with a Li-drifted silicon detector and the computer program of Yager and Quick (1992). Because clinoptilolite weight varies with relative humidity, all CRR samples were dried at 60°C before weighing. Each group of experiments was done side-by-side, or simultaneously--except for chemical analysis and pH measurements which were done serially. The pH measurements were done with a digital temperature-corrected meter.

**Table 1.** Locality data, abbreviations, and diluent minerals in clinoptilolite-rich rocks used in the present study. Minerals determined by X-ray diffraction by G.A. Desborough and Richard Sheppard (U.S. Geological Survey). [Minerals listed in decreasing order of abundance; "clay" refers to layer silicates with a 10-angstrom spacing; tr. = trace]

Locality and abbreviation	Diluent minerals
<u>British Columbia</u>	
Princeton-PBC	Opal, feldspar, mordenite, quartz (tr.)
<u>Colorado</u>	
Creede-CCO	Opal, K-feldspar, plagioclase, quartz, clay
<u>Idaho</u>	
Crisman Hill-CHI	Opal, K-feldspar
Preston-PMLI	Opal, plagioclase
PMUI	Opal
POLI	Opal (tr.)
POMI	Opal
PW1I	Opal
PW2LI	Opal, clay
PW2UI	Opal
PW3I	Opal
<u>Montana</u>	
Grasshopper Creek-GCM	Opal, K-feldspar, plagioclase
<u>Nevada</u>	
Fish Creek-FCWN	K-feldspar, quartz, plagioclase
<u>New Mexico</u>	
Winston-SNM	Opal, clay (tr.)
<u>South Dakota</u>	
Rocky Ford-SDH	plagioclase, calcite, quartz, opal, K-feldspar, clay (tr.)
<u>Texas</u>	
Tilden-ZBT	Opal, clay, calcite

**Table 2.** Chemical composition of selected elements in clinoptilolite-rich rocks (CRRs) determined by X-ray fluorescence analysis. (Analyst: G.A. Desborough)

CRR	K	Ca	Fe	Cu	Zn	Rb	Sr	Zr	Y	Nb	Ce	Nd	La	Ba	Pb
	Weight percent			-----Parts per million-----											
CCO	3.6	1.8	0.9	<20	50	200	580	140	15	10	55	20	35	650	50
CHI	4.2	0.9	1.5	30	120	200	150	540	75	40	140	55	90	1600	<30
FCWN	3.4	1.6	0.6	<20	60	190	300	180	30	15	75	25	45	670	35
GCM	2.8	1.9	0.5	20	55	95	530	55	15	15	30	10	30	1480	<30
PBC	2.1	1.6	1.8	25	125	50	490	320	45	5	75	30	30	2000	<30
PMLI	3.2	1.9	1.0	<20	40	130	160	430	60	40	130	45	85	1000	<30
PMUI	3.0	2.0	1.2	20	40	120	270	435	50	40	120	35	70	1000	<30
POLI	3.4	1.9	1.1	<20	60	140	200	400	55	35	120	75	90	950	<30
POMI	2.9	2.4	1.2	<20	50	100	260	420	50	30	120	60	75	1000	<30
PW1I	2.3	2.2	1.3	25	35	120	560	480	55	40	130	45	55	1200	<30
PW2LI	2.5	1.9	1.4	30	<30	120	210	380	65	40	140	60	85	1000	<30
PW2UI	2.4	1.7	1.4	<20	60	120	400	410	60	40	140	40	70	1100	<30
PW3I	3.6	1.7	1.1	<20	55	160	120	350	45	40	120	70	55	1100	<30
SDH	4.0	1.7	1.4	20	60	90	460	170	20	10	65	25	30	700	35
SNM	2.0	2.7	0.9	30	70	70	1700	190	30	20	90	15	40	1000	40
ZBT	1.2	3.1	0.8	<20	45	50	500	160	30	5	60	20	40	800	<30

## REACTIONS OF CLINOPTILOLITE-RICH ROCKS WITH COMMERCIAL AMMONIUM FERTILIZER SOLUTIONS

Commercial liquid fertilizer composed of ammonium polyphosphate (10-34-0), approximately  $(\text{NH}_4)_2\text{H}_3\text{P}_3\text{O}_{10}$ , and ammonium nitrate were used to study N-loading of the CRRs. The ammonium polyphosphate liquid was purchased from a fertilizer dealer. The ammonium nitrate solution was prepared by mixing 57.1 weight percent of  $\text{NH}_4\text{NO}_3$  granules with 42.9 weight percent of water; the fertilizer industry refers to this liquid as AN 20.

### Mixture of Ammonium Polyphosphate and Ammonium Nitrate

For the first experiment, a solution consisting of 1,142 g  $\text{NH}_4\text{NO}_3$ , 222 g ammonium polyphosphate, and 858 g water was prepared; the specific gravity was 1.26 and the pH was 5.6. These proportions make a solution with 18.5 weight percent of N, and 3.4 weight percent of  $\text{P}_2\text{O}_5$ . Twenty four grams of each sized (2.0-4.7mm) CRR was placed in 72 ml (90.7 g) of solution for 48 h at rest; each was stirred for 5 sec. at 18 and 40 hours, respectively, after immersion. After 18 h, a white precipitate was conspicuous in many of the solutions. After 48 h the pH of each solution ranged from 4.8 to 5.8; the solution pH was reduced from 5.6 by all of the CRRs except SDH. CRRs were removed from the solution by filtration after 48 h, and each solution was again filtered with a 0.45 micron filter attached to a syringe. The CRRs were dried (without rinsing) at 60°C and weighed. Because much of the white precipitate was attached to, and could not be removed from the CRR fragments, it is thought that their weight gain might reflect the amount of white precipitate. Samples of the white precipitate were obtained for X-ray diffraction and were shown to be amorphous. Chemical analysis showed the precipitate is an ammonium calcium phosphate, with Ca ranging from about 8 to 13 weight

percent. Similar materials have long been known to form in soils as reaction products from phosphate fertilizers (Lindsay et al., 1962). The precipitate observed in the present study results when  $\text{NH}_4^+$  displaces Ca from the clinoptilolites by cation exchange, and then reacts with the dissolved phosphate to form a similar amorphous precipitate.

The filtered spent liquids were analyzed for Na, Mg, K, and Ca and these results are given in Table 3. The amounts of both Mg and Ca given for the spent liquids are about 10-fold less than the results obtained by prior studies using only ammonium polyphosphate as the exchange liquid for CRRs (Desborough, 1996, Table 14).

**Table 3.** Concentrations of Na, Mg, K, and Ca in spent liquids after exchange of clinoptilolite-rich rocks in the mixture of AN20 and ammonium polyphosphate liquid for 48 hours. Initial concentrations of each element were less than 10 % of the concentrations reported.  
[Analysis by ACTLABS, Inc., Wheat Ridge, CO]

CRR	Na	Mg	K	Ca
	-----milligrams per liter-----			
CCO	1,500	11	3,600	290
CHI	1,900	14	11,000	270
FCWN	2,600	26	4,200	320
GCM	2,700	22	2,800	270
PBC	3,900	16	2,700	260
PMLI	600	17	7,300	250
PMUI	680	18	6,500	260
POLI	510	12	7,500	270
POMI	470	10	6,300	260
PW1I	440	16	3,900	260
PW2LI	500	25	2,900	290
PW2UI	520	22	3,600	270
PW3I	1,220	10	8,900	280
SDH	6,400	11	6,600	280
SNM	690	36	1,700	270
ZBT	2,600	22	2,600	280

Table 4 gives the total amounts of nitrogen in the CRRs determined by the Dumont method, and the minimum amounts of exchanged nitrogen in the CRRs, calculated from the amounts of Na and K in the spent liquids (Table 3). It is noteworthy that the amounts of total N in the various CRRs differs by more than a factor of two (table 4 and figure 1).

**Table 4.** Total nitrogen in clinoptilolite-rich rocks after exchange in the mixture of AN20 and ammonium polyphosphate liquid for 48 hours. Minimum amounts of exchanged nitrogen were calculated from the amounts of Na and K in the spent liquids (Table 3).  
 [Total N analysis by Huffman Laboratories, Inc., Golden, CO]

CRR	Total N -----weight percent-----	Minimum exchanged N
CCO	3.39	0.72
CHI	3.06	1.58
FCWN	1.78	0.98
GCM	2.64	0.82
PBC	2.93	1.12
PMLI	3.57	0.92
PMUI	3.88	0.88
POLI	3.59	0.93
POMI	3.36	0.82
PW1I	3.17	0.52
PW2LI	2.57	0.43
PW2UI	2.71	0.49
PW3I	3.48	1.17
SDH	3.45	1.90
SNM	2.75	0.34
ZBT	2.36	0.80

### Ammonium Nitrate

For the second experiment, a solution of 57.1 weight percent  $\text{NH}_4\text{NO}_3$  (AN 20) was prepared having a specific gravity of 1.267 and a pH of 4.75. Forty grams of each sized (2.0-4.7 mm) CRR was placed in 120 ml (152 grams) of solution at rest for 48 h; after immersion, each was stirred for 5 sec at 18 and 40 hours, respectively. The CRR samples were removed by filtration from the spent solution and dried (without rinsing) at 60°C for 48 h and weighed. Each spent solution was then filtered with a 0.45 micron filter for Na analysis (table 5). Five grams of each dried CRR was pulverized and quantitatively analyzed for K and Ca. The concentrations of K, Ca, and N and the percent of weight gain are given in Table 6. Figure 2 shows the amounts of total N in the CRRs.

**Table 5.** Concentration of Na in spent liquids after exposure of clinoptilolite-rich rocks to 57.1 weight percent of ammonium nitrate solutions for 48 hours.  
 [Na analysis by ACTLABS, Inc., Wheat Ridge, CO]

CRR	Na milligrams per liter
CCO	2,200
CHI	2,900
FCWN	3,700
GCM	3,900
PBC	5,600
PMLI	720
PMUI	750
POLI	580
POMI	520
PW1I	430
PW2LI	560
PW2UI	570
PW3I	1,900
SDH	8,600
SNM	720
ZBT	3,800

**Table 6.** Concentrations of K, Ca, and N in clinoptilolite-rich rocks exposed to 57.1 weight percent of ammonium nitrate solutions for 48 hours. Weight gains are also given. [K and Ca analyses by G. A. Desborough; N analysis by Huffman Laboratories, Inc., Golden, CO]

CRR	K ----weight	Ca percent----	N	weight gain percent
CCO	2.6	0.5	6.80	13.7
CHI	1.0	0.5	7.01	12.4
FCWN	1.7	0.9	4.69	7.2
GCM	1.9	0.7	5.79	8.4
PBC	1.2	0.7	5.35	9.5
PMLI	1.0	0.4	6.42	9.0
PMUI	1.1	0.5	6.72	13.3
POLI	1.2	0.3	6.61	14.1
POMI	1.0	0.4	6.37	12.9
PW1I	1.3	0.5	6.39	11.9
PW2LI	1.6	0.5	5.87	13.1
PW2UI	1.6	0.6	5.81	12.7
PW3I	1.0	0.4	6.41	11.9
SDH	1.6	1.1	8.40	18.7
SNM	1.3	1.1	6.22	15.8
ZBT	0.3	2.0	6.73	19.0

### Leaching of N-amended Clinoptilolite-rich Rocks

Ten grams of each CRR exposed to the 57.1 weight percent ammonium nitrate solution for 48 hours was placed in 100 ml of near-neutral tap water at rest for 23 hours. After 23 hours each of the CRRs was removed from the leachate by filtration and dried at 60°C and weighed to determine weight loss. After the second leach, each leached CRR was pulverized to 95 percent <0.1 mm, and each sample was then leached a third time for 24 h. The results of these leaching tests are given in Table 7.

For 13 of the 16 CRRs, the first leach of 2.0-4.7 mm granules removed more than 70 percent of the soluble salts removed after the third leach of pulverized CRRs (table 7). The amounts of leachable salts in these N-amended CRRs range from 11.8 to 19.9 weight percent--which is a relative difference of about 41 weight percent. This difference accounts significantly in the differences for total nitrogen capacity of FCWN and SDH, which is a relative difference of 44 weight percent (table 6).

**Table 7.** Cumulative weight loss from leaching clinoptilolite-rich rocks exposed to 57.1 weight percent ammonium nitrate solution for 48 hours. Ten grams of each CRR were placed in 100 ml of tap water at rest.

CRR	First leach, 23 h (2.0-4.7 mm)	Second leach, 26 h (2.0-4.7 mm)	Third leach, 24 h (95 % < 0.1 mm)
-----cumulative weight percent lost-----			
CCO	12.5	12.7	14.9
CHI	11.7	12.7	17.2
FCWN	7.5	7.6	15.6
GCM	9.7	9.7	11.8
PBC	10.8	11.0	15.0
PMLI	10.2	10.5	15.0
PMUI	12.9	13.0	16.7
POLI	13.9	14.2	17.4
POMI	13.6	13.8	16.3
PW1I	12.5	12.5	15.5
PW2LI	12.9	12.9	15.6
PW2UI	12.7	12.9	15.0
PW3I	12.4	12.6	15.8
SDH	17.3	18.9	19.9
SNM	12.4	13.2	16.2
ZBT	16.6	17.3	19.3

The alteration of near-neutral pH tap water leachate by 10 g of each CRR exposed to 57.1 weight percent ammonium nitrate solutions for 48 h are shown for the three successive exposures to 100 ml of leachate in Table 8. The leachate solutions of both the first and second leach had significantly depressed pH due to the soluble salts held in CRR pore space even though the ratio of leachate:CRR was 20:1 after the second leach (two 10:1 leaches). This may be significant in N-amended fertilizer applications because pH depression should solubilize phosphates in the soil to provide essential P in the early plant-growth stages.

It is inferred that soluble  $\text{NH}_4^+$  salts in the CRRs cause the depression of the initially near-neutral leachate pH; the initial pH of the AN 20 solution was 4.75.

**Table 8.** Alteration of tap water leachates by clinoptilolite-rich rocks exposed to 57.1 weight percent ammonium nitrate solution for 48 hours. Ten grams of each sample were placed in 100 ml of each leachate. Initial pH and final pH of each leachate are given for each sample. [- lost liquid]

CRR	First leach, 23 h (2.0-4.7 mm) initial pH = 6.5	Second leach, 26 h (2.0-4.7 mm) initial pH = 6.5	Third leach, 24 h (95 % < 0.1 mm) initial pH = 6.8
CCO	4.6	4.8	6.5
CHI	4.4	4.3	6.5
FCWN	4.9	5.0	7.4
GCM	4.7	4.7	7.1
PBC	5.4	-	7.0
PMLI	4.5	5.0	6.8
PMUI	4.6	4.8	6.4
POLI	4.7	4.5	6.9
POMI	4.6	4.7	6.9
PW1I	4.5	4.7	6.9
PW2LI	4.6	4.8	6.8
PW2UI	4.6	4.7	6.7
PW3I	4.6	4.8	7.0
SDH	5.6	4.6	7.6
SNM	4.5	4.5	6.9
ZBT	5.4	5.1	7.2

Table 9 gives the amounts of soluble K and Ca in the CRRs exposed to 57.1 weight percent ammonium nitrate for 48 hours. Where present, these two elements are readily available plant nutrients as soon as N-amended CRRs are wet. It is uncertain why there is so much variation in the amounts of soluble K and Ca.

**Table 9.** Concentrations of soluble K and Ca in clinoptilolite-rich rocks exposed to 57.1 weight percent ammonium nitrate for 48 hours. Determined by the difference in K and Ca concentrations of N-amended CRRs before leaching and after the third leach. [Analyses by G. A. Desborough]

CRR	K weight percent	Ca
CCO	0.6	>0.1
CHI	0.3	0.1
FCWN	>0.1	0.1
GCM	>0.1	0.1
PBC	0.3	>0.1
PMLI	0.2	0.2
PMUI	0.4	0.3
POLI	0.2	0.1
POMI	0.3	0.2
PW1I	0.5	0.2
PW2LI	0.4	0.1
PW2UI	0.3	0.1
PW3I	0.2	0.2
SDH	0.5	0.5
SNM	0.4	0.7
ZBT	0.1	0.2

The calculated amounts of exchanged N as  $\text{NH}_4^+$  are given in Table 10, and shown graphically on Figure 3. These values were calculated from the concentrations of Na in the spent ammonium nitrate solution, and the amounts of K and Ca remaining in the CRRs after the third leach (table 7) of the CRRs exposed to the ammonium nitrate solution. The calculated amounts of  $\text{NH}_4^+$ -exchanged N, based on analysis of the major exchangeable cations in the CRRs (Na, K, and Ca) varies by more than a factor of two (table 10). Figure 4 shows the amounts of total N, as both  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , held in pore space of the CRRs.

**Table 10.** Calculated amounts of N exchanged into clinoptilolite-rich rocks as  $\text{NH}_4^+$  based on the amounts of Na in the spent ammonium nitrate solution (table 5) and the amounts of K and Ca lost from the CRRs after the third leach (tables 7 and 8).

CRR	weight percent N exchanged as $\text{NH}_4^+$
CCO	1.43
CHI	2.02
FCWN	1.57
GCM	1.52
PBC	1.80
PMLI	1.63
PMUI	1.64
POLI	1.60
POMI	1.70
PW1I	1.28
PW2LI	1.10
PW2UI	1.30
PW3I	1.85
SDH	2.95
SNM	1.33
ZBT	1.48

## SUMMARY AND INFERENCES

Experiments with exposure of CRRs to a solution of ammonium polyphosphate plus ammonium nitrate resulted in total N-loading capacities ranging from 1.8 to 3.9 weight percent. Precipitation of amorphous Ca-phosphate occurred due to the displacement of Ca from the clinoptilolites by  $\text{NH}_4^+$ . This dissolved Ca combined with the phosphate in solution and caused precipitation of the Ca-phosphate in the pore space of, and upon the surface of CRR granules. This precipitation of Ca-phosphate in and on the CRR granules caused a liquid permeability barrier that impeded or arrested further interaction between the CRRs and the N-rich solution. This resulted in relatively small amounts of nitrogen in all of the CRRs.

It is well known that when Ca-rich soils of near-neutral pH that are fertilized with ammonium polyphosphate, an amorphous Ca-phosphate is precipitated rather rapidly (Lindsay and others, 1962). The solubility of these amorphous Ca-phosphates in soils is not well understood. It is suspected that there is probably an abundance of these amorphous Ca-phosphates in the near-neutral pH and alkaline soils to which synthetic phosphate fertilizers have been added during the last 20-30 years.

Rothbaum and others (1979) have shown that the application of superphosphate to neutral or slightly calcareous soils that "contains 20-30 percent clay in arable soils, little P has been leached below plow depth (about 23 cm), except where farmyard manure ( $35 \text{ t ha}^{-1} \text{ year}^{-1}$ ) has been applied." Their study clearly demonstrated that the use of superphosphate fertilizer applied at rates of  $68\text{-}76 \text{ lbs P}_2\text{O}_5 \text{ acre}^{-1} \text{ annum}^{-1}$  increase the amounts of total phosphorous in

fertilized soils, as compared to adjacent soils where no P fertilizer was applied.

For the CRRs exposed only to the 57.1 weight percent ammonium nitrate, the amounts of total N, as both exchanged  $\text{NH}_4^+$ , and water-soluble N in CRR pore space, ranged from 4.7 to 8.4 weight percent (94-168 lbs N t<sup>-1</sup>). Due to the pH (4.75) of the ammonium nitrate solution, the CRRs exposed to it contain salts that depress the pH of near-neutral water when they become wet. This property of the N-amended CRRs should induce some phosphate dissolution in the soil. In addition, phosphate solubility should be promoted by the acid generated during bacterial nitrification of ammonium released from the pore space of N-amended CRRs.

If high N capacity (e.g., 6-8 weight percent) CRR could be applied at planting for row crops by banding, and could eliminate further crop N-fertilizer applications during the growing season, there could be two immediate economic benefits. One benefit would be the reduction in application costs, the second being reduced cost of N use.

#### REFERENCES CITED

- Desborough, G.A., 1996, Clinoptilolite-rich rocks in agricultural use for soil amendment and potential nitrogen-pollution mitigation: U.S. Geological Survey Open-File Report 96-065, 32 p.
- Lindsay, W.L., Frazier, A.W., and Stephenson, H.F., 1962, Identification of reaction products from phosphate fertilizers in soils: Soil Science of America Proceedings, v. 26, p. 446-452.
- Loizidou, M., and Townsend, R.P., 1987, Ion-exchange properties of natural clinoptilolite, ferrierite and mordenite: Part 2. lead-sodium and lead-ammonium equilibria: Zeolites, v. 7, p. 153-159.
- Mumpton, F.A., and Fishman, P.H., 1977, The application of natural zeolites in animal science and aquaculture: Journal of Animal Science, v. 45, p. 1188-1203.
- Nishita, H., and Haug, R.M., 1972, Influence of clinoptilolite on Sr<sup>90</sup> and Cs<sup>137</sup> uptake by plants: Soil Science, v. 114, p. 149-157.
- Nishita, H., Haug, R.M., and Hamilton, M., 1968, Influence of minerals on Sr<sup>90</sup> and Cs<sup>137</sup> uptake by bean plants: Soil Science, v. 105, p. 237-243.
- Puckett, L. J., 1994, Nonpoint and point sources of nitrogen in major watersheds of the United States: U.S. Geological Survey Water-Resources Investigations Report 94-4001, 9 p.
- Rothbaum, H.P., McGaveston, D.A., Wall, T., Johnston, A.E., and Mattingly, G.E.G., 1979, Uranium accumulation in soils from long-continued applications of superphosphate: Journal of Soil Science, v. 30, p. 147-153.
- Yager, D.B., and Quick, J.E., 1992, SuperXap Manual: U.S. Geological Survey Open-File Report 92-13, 45 p.

CRR wt. % N after AN20 plus  
10-34-0 for 16 CRRs

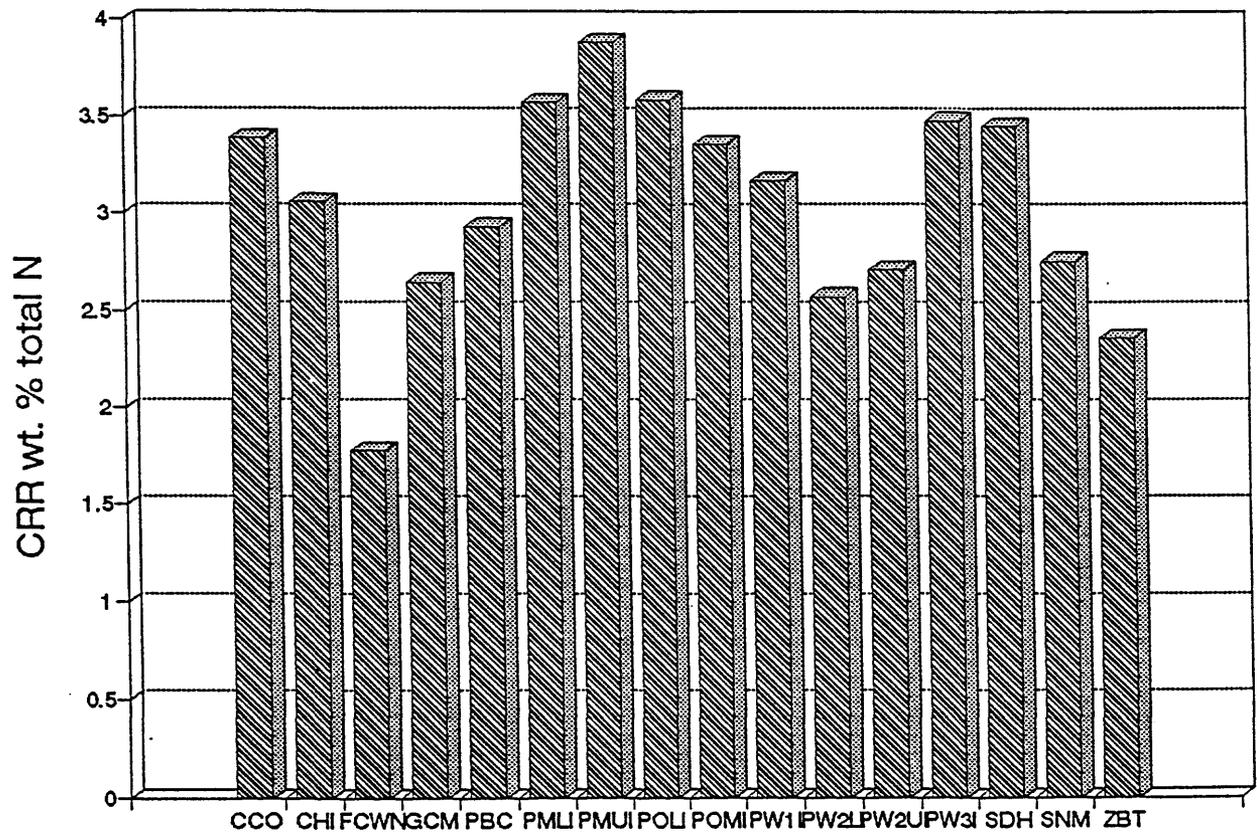


Figure 1. Graph showing total nitrogen in 16 clinoptilolite-rich rocks exposed to a mixture of AN20 plus 10-34-0 liquid for 48 hours. (abbreviations in table 1)

CRR wt. % N after AN20  
for 16 CRRs

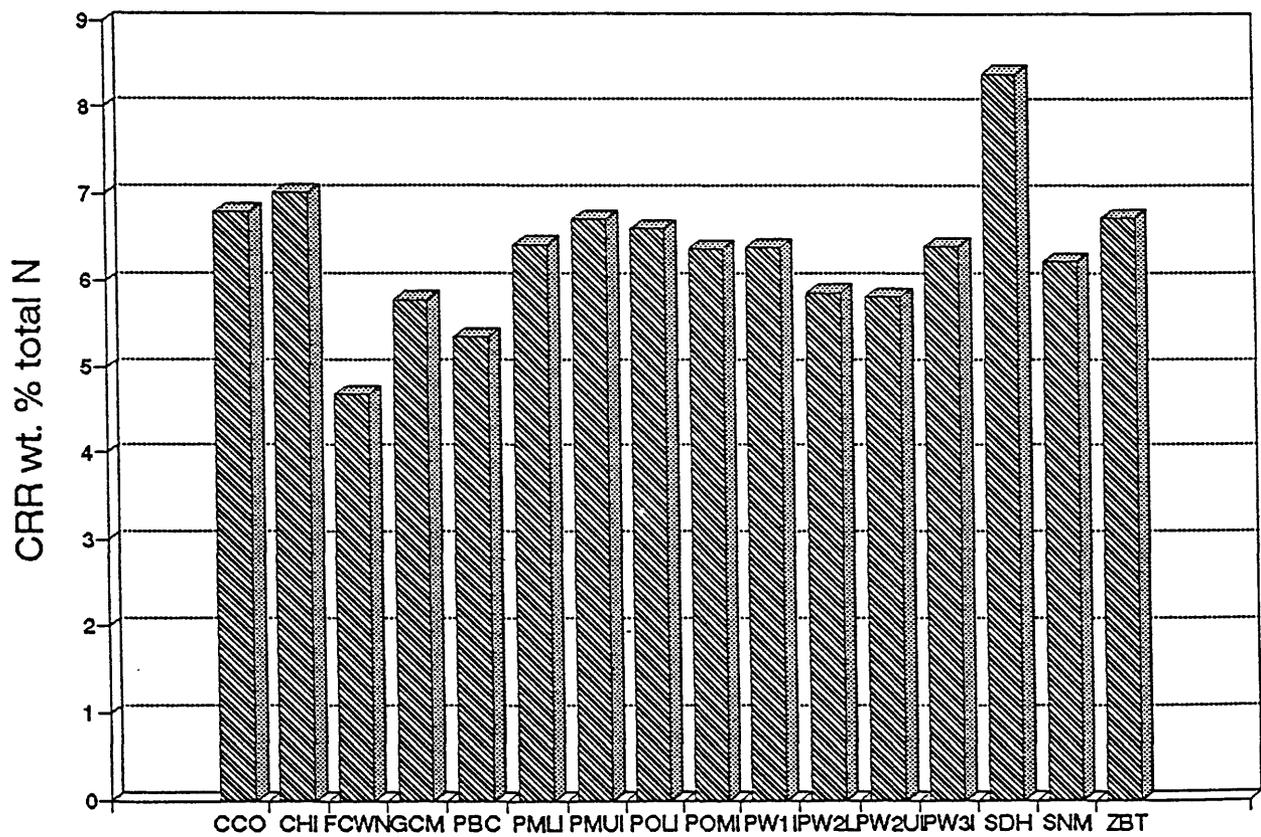


Figure 2. Graph showing total nitrogen in 16 clinoptilolite-rich rocks exposed to 57.1 weight percent ammonium nitrate liquid for 48 hours. (abbreviations in table 1)

CRR wt. % exchanged N after  
AN 20 for 16 CRR samples

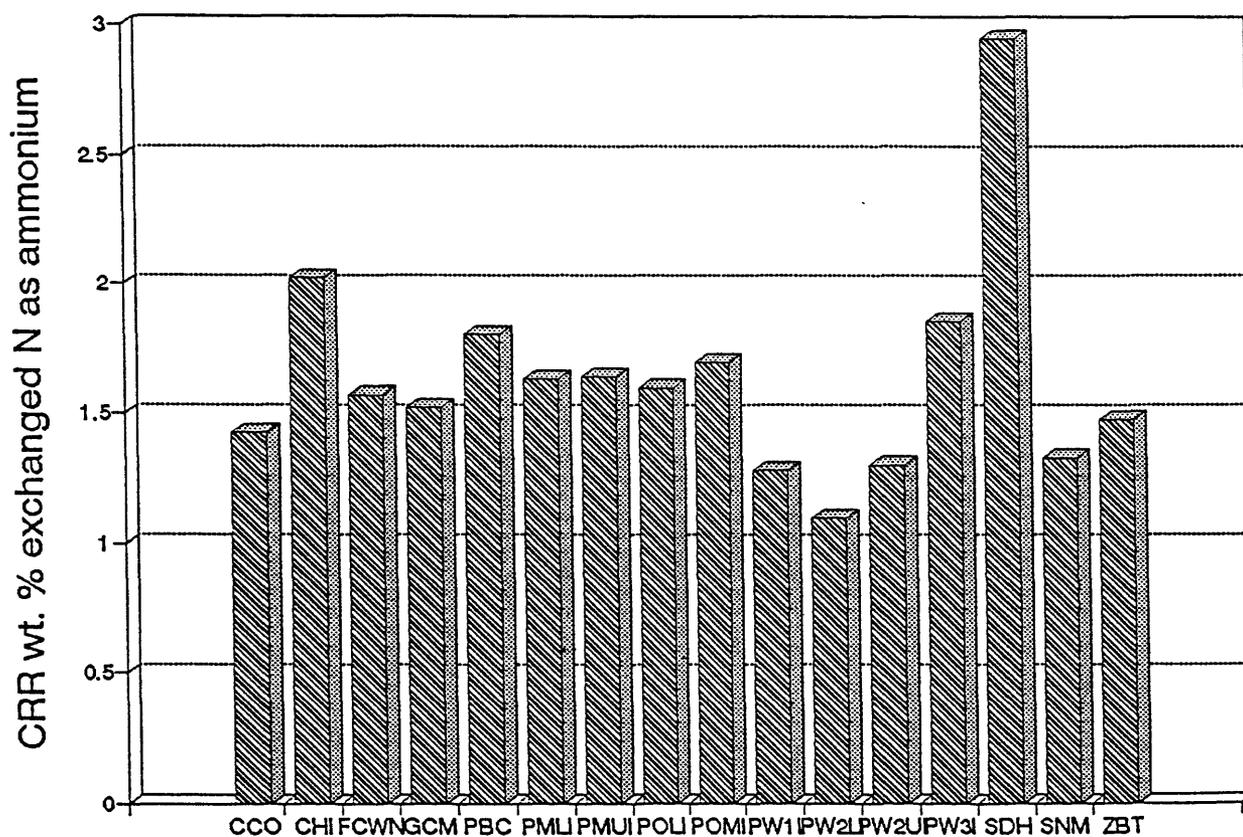


Figure 3. Graph showing nitrogen exchanged as  $\text{NH}_4^+$  in 16 clinoptilolite-rich rocks after exposure to 57.1 weight percent ammonium nitrate for 48 hours. Calculated from Na, K, and Ca concentrations in the exchange solution. (abbreviations in table 1)

CRR wt.% non-exchanged or pore space N  
after AN20 for 16 CRR samples

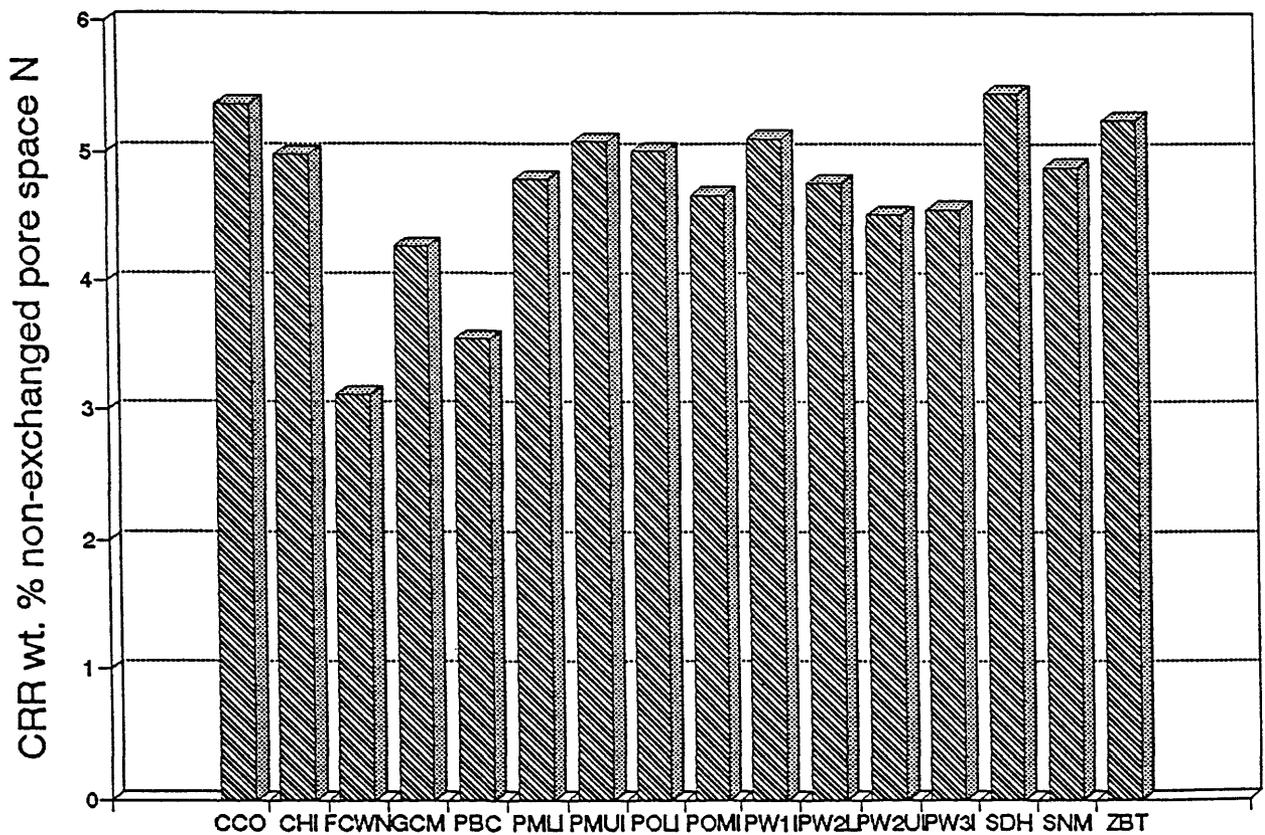


Figure 4. Graph showing non-exchanged nitrogen or pore space nitrogen in 16 clinoptilolite-rich rocks after exposure to 57.1 weight percent ammonium nitrate for 48 hours. Amounts of nitrogen are the difference in total nitrogen (table 6) and nitrogen exchanged as ammonium (table 10). (abbreviations in table 1)