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Preliminary Study of Certain Cation-Exchange Properties of Clinoptilolite-Bearing Rockyford Ash Member of the Miocene Sharps Formation at Craven Creek Near Wanblee, South Dakota

By

George A. Desborough[1]

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[1] Denver, Colorado

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ABSTRACT

Preliminary study of the clinoptilolite-bearing Rockyford Ash Member of the Sharps Formation (Miocene) from Craven Creek, near Wanblee, South Dakota, shows that about 40 percent of the potassium and 70 percent of the calcium are cation exchangeable. Nitrogen analysis of ammonium-exchanged material shows that between 1.62 and 1.78 weight percent of ammonium is present even though this material contains only 50-60 percent of clinoptilolite. Using the ammonia selective electrode method indicated a CEC (cation exchange capacity) value of 1.29 meq/g (milliequivalents/gram) which is 0.129 weight percent of ammonium. The potassium content of the rock can be doubled by potassium exchange in KOH solution.

X-ray diffraction of untreated, heated, acidulated and K-, Na-, and NH_4^+-exchanged material shows that the 020 reflection is enhanced substantially for ammonium-exchanged material, compared to untreated, heated, acidulated and K- and Na-exchanged material.

INTRODUCTION

This investigation of cation-exchange capacity of clinoptilolite-bearing Rockyford Ash Member of the Sharps Formation was done chiefly to determine the ammonium-holding capacity for the exchange-fertilizer application of Lai and Eberl (1986). In this exchange-fertilizer application, ammonium-exchanged clinoptilolite is mixed with phosphate rock to induce a slow release of both ammonium and phosphorous from each of these materials, respectively (Lai and Eberl, 1986). Greenhouse tests (potted plants) with this exchange-fertilizer have shown enhanced yields for certain crops (Barbarick and others, 1988). In addition, it appears that use of the exchange fertilizer in certain soils may reduce the nitrogen pollution of groundwater that is caused by highly soluble nitrogen fertilizers that are currently used.

In addition, this study examines the effect of certain exchanged cations on the relative intensities of the X-ray diffraction maxima of clinoptilolite in the Rockyford Ash Member.

Material used was from a single 45 kg sample of clinoptilolite-bearing rock from the basal 1 m of the Rockyford Ash Member (Miocene Sharps Formation) north of Wanblee (Craven Creek) on the Pine Ridge Indian Reservation, South Dakota.

MATERIALS AND LABORATORY METHODS

Previous studies of clinoptilolite-bearing Rockyford Ash Member from the sample locality showed that the rock consists of 50-60 percent of clinoptilolite (Raymond, 1986, fig. 4). X-ray diffraction studies show that in addition to clinoptilolite, quartz and opal are the major diluents; minor amounts of mixed-layer clay, albite and orthoclase are also present. The content of certain cations present in the bulk rock from the interval sampled are given in table 1. The range given for the sample used in the present study represents the variation among several aliquots from a blended 45 kg sample.

Because of the presence of Na- and K-feldspar (albite and orthoclase) and mixed-layer illite-smectite, the amounts of the cations listed in table 1 do not necessarily represent those contained in clinoptilolite.

The 45 kg sample was crushed, blended, screened, and allowed to dry in the laboratory environment (17-20 °C and relative humidity of 15-25%). Cation-exchange experiments were done on several different size fractions to determine the influence of particle size on reaction rates (without agitation). After exchange experiments, samples were rinsed with deionized water several times to remove soluble salts prior to drying.

X-ray diffraction analysis was done with Ni-filtered CuKα-radiation with a diffractometer scan rate of 2° 2θ/min. The same operating conditions and X-ray tube were used for all analyses. Powdered samples were back-packed into 2-mm-thick mounts. X-ray intensities for clinoptilolite were corrected for spectral background. All cation-exchanged samples were dried at 100 °C prior to X-ray diffraction study (except exp. M and N that were dried at 40 °C). This was done to eliminate the influence of adsorbed or interstitial water on X-ray peak intensities. The hkl indices for a clinoptilolite with $\beta = 116^{\circ}20'$, space group = CM(8) as illustrated by Bowles (1972, fig. 4) have been used here (fig. 1).

After numerous thermal and cation-exchange treatments of clinoptilolite-bearing ash, it was noted that the most significant changes in the X-ray pattern involved the intensity of the 020 reflection, and to a lesser extent in the 400, 330 reflection(s) (fig. 1). In order to quantify these differences, the intensities of the 200, 201 and 111 peaks, collectively, were used for reference. One parameter used was 020/NX, where NX = (Sum 200 + 201 + 111)/3, in intensity units; the other parameter was 400/NX. The 330 reflection is included with the 400 because the two cannot be separately resolved. Thus any effects of preferred orientation or variations in clinoptilolite concentrations are reduced, or normalized.

INFLUENCE OF THERMAL TREATMENT ON INTENSITIES OF CLINOPTILOLITE X-RAY DIFFRACTION PEAKS

Because Boles (1972) demonstrated that heulandite group zeolites are highly unpredictable, in terms of their structural or crystallographic response to heating at temperatures above 200 °C, it was necessary to monitor the low and high temperature effects of heating by X-ray diffraction methods.

Heating at temperatures on the order of about 800-900 °C for an hour or more causes significant destruction of clinoptilolite in the Rockyford Ash Member. Heating at temperatures of 500-600 °C for one hour has no major effect on the positions of the reflections, but it has some effect on their relative intensities. Thermal treatment at 500 °C results in a water loss (weight loss) of about 5-6 weight percent, compared with 100 °C dried material. The effect of heating on the intensities of the major clinoptilolite peaks (fig. 2) is shown in table 2, where a single sample was studied after each thermal treatment. Figure 2 shows that the relative intensity of the 020 peak is significantly decreased for material heated at 400 °C.

CATION EXCHANGE AND ACIDULATION EFFECTS

Table 3 gives the X-ray diffraction intensity data for untreated, heated and ammonium-exchanged coarse material (10 g in 5 g of ammonium sulfate and 15 ml of water). The intensities of the 020 and 400 peaks are considerably greater for ammonium-exchanged material than that of untreated or heated material. It is noteworthy that gypsum is present in the ammonium-exchanged material due to calcium made available from the exchange reaction. Quantitative analysis of the exchanged material indicates 22% of the potassium and some calcium was lost (table 4), as compared to untreated material.

Table 1.--Contents of major cations in the basal 1 m of clinoptilolite-bearing Rockyford Ash Member near Wanblee, South Dakota

[n.d. - not determined]

Element	Raymond, 1980 (unpublished) wt. %	Desborough, 1983 (unpublished) wt. %	Sample used for present study wt. %
Ca	1.50	1.98	1.64-1.72
Na	2.00	n.d	n.d.
K	3.00	2.53	2.43-2.72
Mg	0.48	n.d.	n.d.

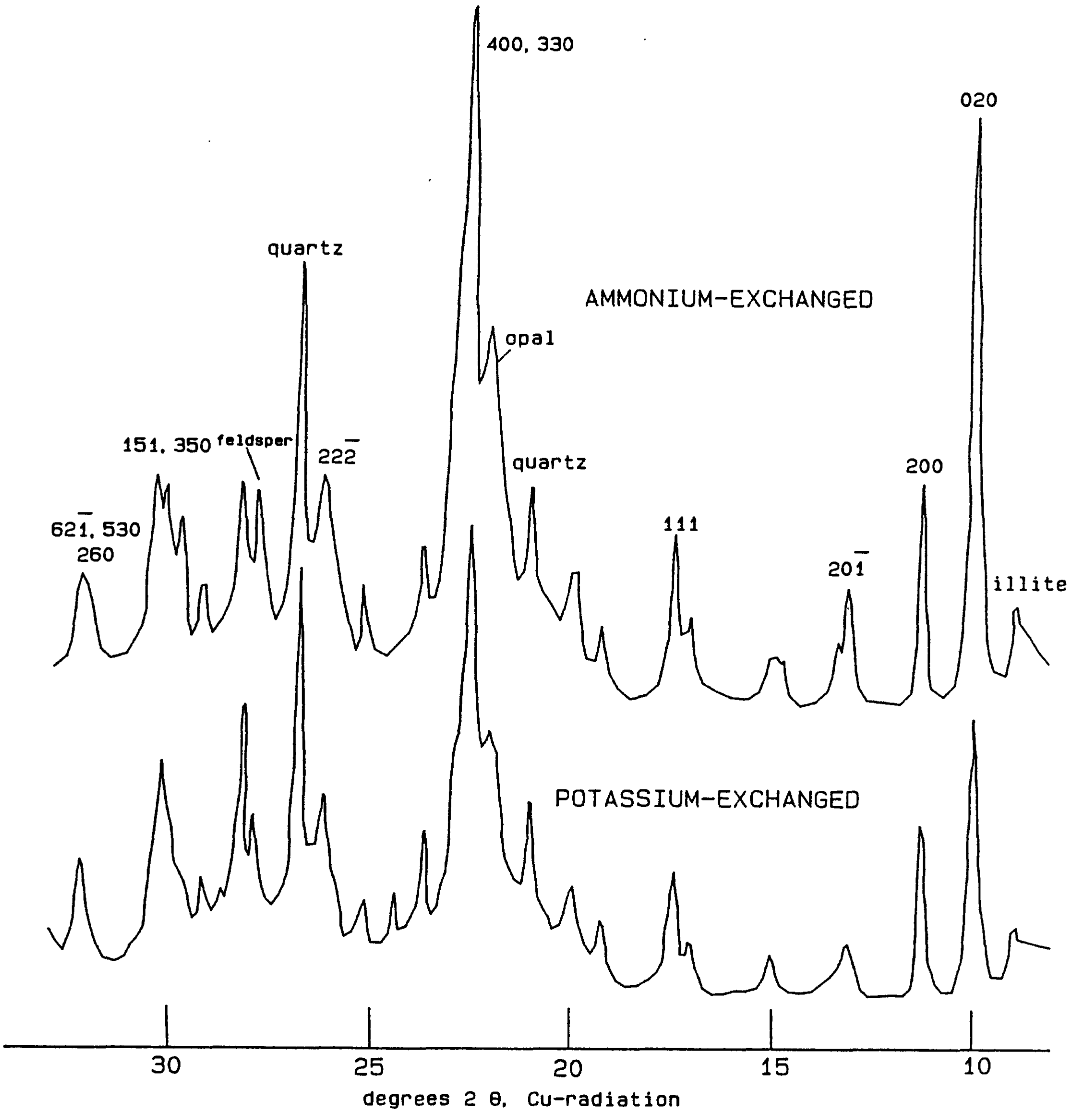

Figure 1.--X-ray diffraction patterns of ammonium- and potassium-exchanged clinoptilolite-bearing Rockyford Ash Member from Craven Creek near Wanblee, South Dakota. Only the strongest clinoptilolite peaks are indexed.

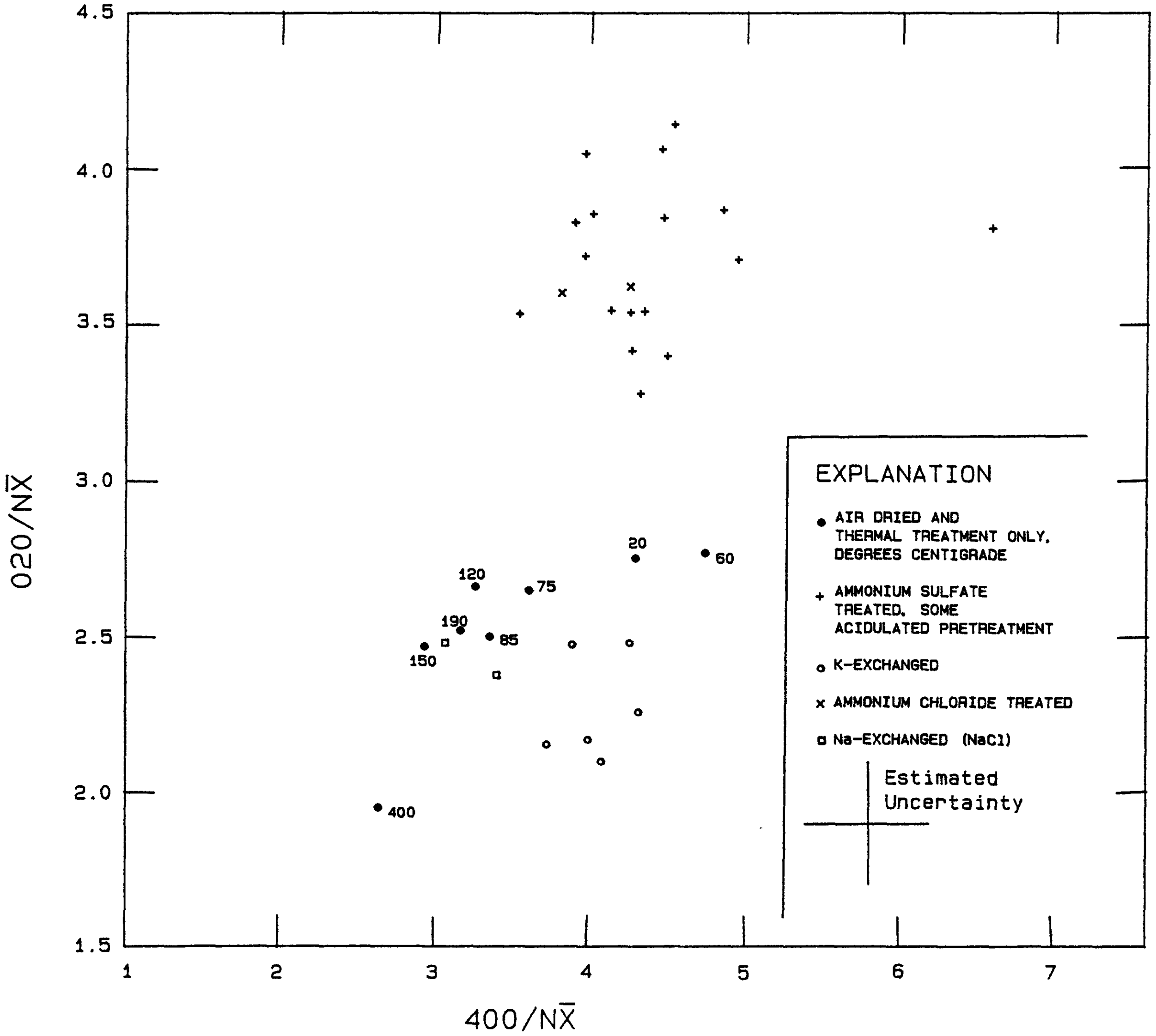

Figure 2.--X-ray diffraction intensity ratios for $020/\bar{NX}$ and $400/\bar{NX}$ [$\bar{NX}$ = Sum (200 + 201 + 111)/3] for air dried, heated, ammonium-, sodium-, and potassium-exchanged clinoptilolite-bearing Rockyford Ash Member from near Wanblee, South Dakota.

Table 2.--X-ray diffraction data for air dried and thermally treated minus 60 mesh clinoptilolite-bearing Rockyford Ash Member
[The same sample was used for all data reported in this table; it was heated incrementally]

Condition:	20°	60 °C	75 °C	85 °C	120 °C	150 °C	190 °C	400 °C
dwell time: (minutes)		60	60	60	60	1,020	30	120
hkl				Relative intensities, in percent (units)				
020	64(44)	58(39)	74(53)	74(55)	82(56)	84(62)	79(61)	73(43)
200	26(18)	28(19)	40(29)	38(28)	40(27)	44(33)	45(35)	52(30)
$20\bar{1}$	13(9)	12(8)	13(9)	15(11)	13(11)	16(12)	14(11)	17(10)
111	30(21)	22(15)	30(22)	36(27)	37(25)	40(30)	35(27)	45(26)
400, 330	100(69)	100(67)	100(72)	100(74)	100(68)	100(74)	100(77)	100(58)
$22\bar{2}$	30(21)	34(23)	35(25)	31(23)	31(21)	27(20)	29(22)	24(14)
151, 350	39(27)	46(31)	40(29)	43(32)	50(34)	40(30)	38(29)	33(19)
$62\bar{1}$,530 260	22(15)	22(15)	24(17)	26(19)	24(16)	24(18)	21(16)	19(11)
				Intensity ratios (units)				
020/$\overline{NX}^{\#}$ =	2.75	2.78	2.65	2.50	2.67	2.48	2.51	1.95
400/$\overline{NX}$ =	4.31	4.78	3.60	3.36	3.24	2.96	3.17	2.63

#, $\overline{NX}$ = Sum (200 + $20\bar{1}$ + 111)/3, intensity units

Table 3.--X-ray diffractometer data for untreated and treated clinoptilolite-bearing Rockyford Ash Member

[Material used was plus 10 mesh-minus 6 mm. 1B and 2B were heated to 450 °C for 45 minutes and cooled to room temperature before immersion in $(NH_4)_2SO_4$ saturated water for 160 minutes at 20 °C. 6B was heated at 100 °C prior to ammonium exchange in $(NH_4)_2SO_4$ saturated water]

hkl	20 °C	100 °C	450 °C, 45m rehydrated in air for 275 min	Ammonium-exchanged 160 min, 20 °C		
				450 °C, 30 min		100 °C
	1AB	1BB	3BB	1 B	2 B	6 B
	Relative intensities, in percent (units measured)					
020	75(48)	73(45)	57(36)	78(64)	71(59)	92(80)
200	31(20)	42(26)	37(23)	33(27)	33(27)	31(27)
$20\bar{1}$	19(12)	16(10)	14(17)	21(17)	16(13)	16(14)
111	33(21)	32(20)	37(23)	28(23)	25(21)	21(18)
400, 330	100(64)	100(62)	100(63)	100(82)	100(83)	100(87)
$22\bar{2}$	38(24)	32(20)	37(23)	35(29)	27(22)	30(26)
151, 350	39(25)	39(24)	40(25)	29(24)	28(23)	27(24)
$62\bar{1}$, 530 260	22(14)	21(13)	19(12)	17(14) gypsum	18(15) gypsum	14(12) gypsum
	Intensity ratios (units)					
$020/\overline{NX}^{\#}$ =	2.72	2.42	1.71	2.87	2.91	4.06
$400/\overline{NX}$ =	3.64	3.33	3.00	3.68	4.09	4.42

($^{\#}\overline{NX}$ = Sum (200 + $20\bar{1}$ + 111)/3), intensity units

Table 4.--Contents of potassium and calcium in exchanged clinoptilolite-bearing Rockyford Ash Member

[Quantitative analysis for K and Ca was done using non-destructive energy dispersive analysis with standards. Air dried -60 mesh Wanblee standard material contains 1.64-1.72 wt. % Ca and 2.43-2.72 wt. %. All samples were allowed to equilibrate to a relative humidity of about 15-20% prior to quantitative analysis]

Sample No.	Exchange treatment	Dwell time, min	wt.% K (% loss or gain)	wt.% Ca (% loss)
6B	Ammonium sulfate, 20 °C	160	1.96(-22)	1.62(6) g
C1	-do-	60	1.80(-28)	1.52(12)
C2	-do-	120	1.78(-29)	1.32(23)
C3	-do-	180	1.49(-40)	1.52(12) g
C4	-do-	13,260	2.05(-18)	1.49(13) g
D1	-do-	4,080	1.76(-30)	1.34(38) g
D2B	Acid then ammonium	60	1.70(-32)	1.46(15) g
D3A	Sulfuric acid	20	1.68(-33)	1.52(12) g
D3B	Acid then ammonium	30	1.64(-34)	1.36(21) g
E1	Ammonium sulfate, 60 °C	20	2.03(-19)	1.28(26) g
E2	-do-	30	2.06(-18)	1.34(22) g
E3	-do-	40	1.88(-25)	1.38(20) g
E4	-do-	60	2.22(-11)	1.51(12) g
E5	Acid then ammonium	25	1.56(-38)	0.70(59) g
G1	Sodium hydroxide	80	2.51 (0)	1.52(12)
G5A	Sodium, potassium	40	5.40(+116)	1.52(12)
G5B	-do-	80	5.63(+125)	1.46(15)
G2	Potassium hydroxide	60	4.68(+87)	1.60(7)
G3	-do-	3,960	5.12(+105)	1.49(13)
G4	-do-	120	4.85(+94)	1.59(7)
G6	-do-	120	4.30(+72)	1.42(30)
3H	Ammonium hydroxide	960	2.48(-1)	1.39(33)
5H	-do-	1,170	2.35(-6)	1.67(3)
6H	-do-	1,080	2.45(-2)	1.50(13)
2K	-do-	25	2.46(-2)	1.72(0)
1kk	Ammonium, potassium	60	4.75(+90)	1.47(14)
1HCl	Hydrochloric acid	30	2.33(-7)	0.92(44)
3HCl	-do-	90	2.15(-14)	0.82(50)
4HCl	-do-	4,165	1.76(-30)	0.66(60)
	Acid then ammonium	3,990	1.55(-38)	0.41(75)
	Acid then NaOH	5,340	2.10(-16)	1.00(39)

M1	Ammonium sulfate, 40 °C	60	1.98(-27)	1.31(23)	g
M2	-do-	120	1.80(-34)	1.36(20)	g
M3	-do-	1,080	1.70(-37)	1.07(37)	g
N1	Ammonium chloride, 40 °C	90	1.08(-40)	0.80(51)	
N2	-do-	180	1.72(-37)	0.72(56)	
N3	Sodium chloride, 40 °C	90	2.11(-22)	1.04(36)	
N4	-do-	180	2.20(-19)	1.03(37)	

g, gypsum is present, all exchanged calcium was not removed

Table 5 gives the X-ray intensity data for heated and unheated material exposed to ammonium sulfate solution for different periods of time using 10 grams of coarse material. Quantitative analysis of exchanged material (table 4) shows that 18-40 percent of the potassium was exchanged and at least 12-23 percent of the calcium was exchanged. For the two samples which did not contain gypsum, more potassium was exchanged than calcium.

Table 6 contains the X-ray diffraction data for unheated, acidulated and heated plus acidulated and ammonium-exchanged coarse material (10 g in 5 g ammonium sulfate and 15 ml water). The ammonium-exchanged acidulated material has enchanced 020 and 400 intensities, as compared to material that was only acidulated. Between 30-35 percent of the potassium was exchanged by either acidulation or ammonium-exchange, whereas more than 15-38 percent of the calcium was exchanged (table 4).

Table 7 gives X-ray diffraction intensity data for unheated, acidulated and 100 °C treated material that was ammonium exchanged (5 g in 2.5 g ammonium sulfate and 15 ml water) at 60 °C for periods of time from 20 to 60 minutes. Gypsum was present in all samples except for the one pretreated at 100 °C. The intensity ratios 020/NX and 400/NX for these ammonium-exchanged samples are plotted on figure 2, and it is clear that the intensity of the 020 peak is enchanced, compared to samples that have not been ammonium exchanged. Quantitative analysis of potassium and calcium (table 4) shows that between 11 and 38 percent of the potassium was displaced and more than 12 to 59 percent of the calcium was displaced. Quantitative analysis of nitrogen for E5 (table 7), using two different methods gave 1.37 weight percent (Dumont method) and 1.39 weight percent (Kjeldahl method). This is equivalent to 1.76 and 1.79 weight percent ammonium in the ammonium-exchanged sample. Measurement of the ammonium-exchange capacity of the same sample using an ammonia selective electrode gave an ammonium CEC (cation exchange capacity) value of 129 milliequivalents per 100 grams, equivalent to 0.129 weight percent of ammonium.

Table 8 shows the X-ray diffraction intensity data for coarse material that was sodium- or potassium-exchanged at 20 °C using 0.1 molar sodium hydroxide and 0.5 molar potassium hydroxide solutions (5 g of sample in 17 ml of solution). The sample that was only sodium-exchanged, lost no potassium and only lost 12 percent of calcium (G1, table 4). The two samples that were sodium-exchanged prior to potassium exchange gained more than 100 percent of potassium, but lost only 12-15 percent of calcium. For the four samples treated only with potassium hydroxide, the gain in potassium ranged from 87-105 percent, and the loss in calcium was 7-30 percent. It is noteworthy that sample G6, heated to 100 °C prior to potassium hydroxide treatment, lost more calcium, but gained less potassium than the unheated materials.

Table 9 shows the X-ray diffraction intensity data for coarse material treated with ammonium hydroxide. Samples 1H-4H had 2 g of material in 7 ml of solution; 5H and 6H had 5 g of material in 15 ml of solution. Maximum potassium exchanged was 6 percent; calcium exchange ranged from 3-33 percent. This indicates that ammonium hydroxide solutions cause very minimal ammonium-exchange for this clinoptilolite.

Table 10 gives the X-ray diffraction intensity data for material treated with a 4 molar solution of ammonium hydroxide; one of these was then potassium exchanged in 0.5 molar potassium hydroxide. The contents of potassium and calcium were essentially unchanged by the ammonium hydroxide treatment (2K, table 4). The potassium-exchanged sample gained 92 percent of potassium, and 14 percent of the calcium was lost.

Table 5.--X-ray diffractometer data for heated and unheated ammoniated clinoptilolite-bearing Rockyford Ash Member

[Material used was plus 10 mesh minus 6 mm. For samples C1, C2 and C3, the material was heated about 30 minutes at 450 °C prior to hot immersion into a solution containing 5 g of ammonium sulfate in 15 ml of water. Sample C4 was unheated material immersed into a solution of the same ammonium concentration. All exchange at 20 °C]

	C1	C2	C3	C4
	Heated at 450° for 30 min.			Unheated
Ammonium solution: dwell time	60 min.	120 min.	180 min.	13,260 min.
hkl	Relative intensities, in percent (units)			
020	65(47)	73(58)	62(47)	84(69)
200	32(23)	33(26)	22(17)	35(29)
$20\bar{1}$	15(11)	15(12)	13(10)	15(12)
111	21(15)	24(19)	20(15)	21(17)
400, 330	100(72)	100(79)	100(76)	100(82)
$22\bar{2}$	28(20)	28(22)	30(23)	28(23)
151, 350	32(23)	34(27)	39(30)	32(26)
$62\bar{1}$, 530 260	19(14)	18(14)	21(16) Gypsum	16(13) Gypsum
	Intensity ratios (units)			
$020/N\bar{X}^{\#}$ =	2.88	2.82	2.57	3.56
$400/N\bar{X}$ =	4.41	3.83	4.15	4.24

#, $N\bar{X}$ = Sum (200 + $20\bar{1}$ + 111)/3, intensity units

Table 6.--X-ray diffractometer data for unheated, acidulated and heated plus acidulated ammonium-exchanged clinoptilolite-bearing Rockyford Ash Member

[D1 was air dried and ammonium-exchanged only. D2A was acidulated for 20 minutes and ammonium-exchanged for 60 minutes. D3A was heated at 400 °C for 30 minutes and ammonium-exchanged for 20 minutes. D3B was heated at 400 °C for 30 minutes and acidulated for 20 minutes, then ammonium-exchanged for 30 minutes. Ammonium solution was saturated with ammonium sulfate. Material used was plus 10 mesh and minus 6 mm. Acid solution ratio: 4:1 vol., $H_2O:H_2SO_4$]

	D1	D2A	D2B	D3A	D3B
		dried @ 100 °C			
	unheated NH_4-exchanged 4,080 min.	acidulated 20 min. NH_4-exchanged 60 min.		heated @ 400 °C 30 min. acidulated 20 min. NH_4-exchanged 30 min.	
hkl	Relative intensities, in percent (units)				
020	58(33)	70(38)	75(53)	66(39)	65(47)
200	16(9)	33(18)	28(20)	22(13)	26(19)
$20\bar{1}$	12(7)	19(10)	13(9)	12(7)	15(11)
111	10(18)	28(15)	20(14)	25(15)	24(17)
400, 330	100(57)	100(54)	100(71)	100(59)	100(72)
$22\bar{2}$	19(11)	26(14)	30(21)	27(16)	29(21)
151, 350	44(25)	26(14)	37(26)	34(20)	30(22)
$62\bar{1}$, 530 260	18(10) Gyspum	22(12)	18(13) Gypsum	17(10) Gypsum	18(13) Gypsum
	Intensity ratios (units)				
$020/N\bar{X}$[#] =	3.80	2.65	3.70	3.30	3.00
$400/N\bar{X}$ =	6.58	3.77	4.96	5.00	4.60

[#], $N\bar{X}$ = Sum (200 + $20\bar{1}$ + 111)/3, intensity units

Table 7.--X-ray diffractometer data for unheated, acidulated and 100 °C dried clinoptilolite-bearing Rockyford Ash Member ammonium-exchanged at 60 °C in 3.895 wt. % of NH_4^+ in sulfate solution for periods of 20 to 60 min.

[E5 was -60 mesh material that was acidulated for 20 minutes in a solution of water: sulfuric acid of 4:1, the other samples were plus 10 mesh-minus 6 mm material. The ammonium sulfate solution was preheated to 60 °C for all samples; for E1 the rock was preheated to 60 °C also. Sample weights were 5 g; solution volumes were 17 ml]

	E1	E2	E3	E4	E5	E6
Ammonium	unheated				acidulated, fine ground	100 °C
solution: dwell time	20 min.	30 min.	40 min.	60 min.	25 min.	40 min.
hkl	Relative intensities, in percent (units)					
020	76(62)	93(72)	85(70)	79(68)	86(55)	81(67)
200	33(27)	32(25)	34(28)	29(25)	26(17)	31(26)
$20\bar{1}$	12(19)	17(13)	16(13)	15(13)	14(9)	17(14)
111	22(18)	26(20)	22(18)	17(15)	18(12)	23(19)
400, 330	100(82)	100(77)	100(82)	100(86)	100(64)	100(83)
$22\bar{2}$	30(25)	28(22)	28(23)	26(22)	27(17)	29(24)
621, 530, 260	20(16) Gypsum	18(14) Gyspum	15(12) Gypsum	17(15) Gypsum	16(10) Gypsum	16(13) ----
	Intensity ratios (units)					
020/$N\bar{X}^{\#}$ =	3.39	3.73	3.55	3.85	3.83	3.41
400/$N\bar{X}$ =	4.48	3.99	4.16	4.67	4.47	4.22

#, $N\bar{X}$ = Sum (200 + $20\bar{1}$ + 111)/3, intensity units

Table 8.--X-ray diffraction data for unheated and 100 °C treated clinoptilolite-bearing Rockyford Ash Member that was Na- and K-exchanged in hydroxide solutions at 20 °C

[All samples were plus 10 mesh-minus 6 mm material. G1 was immersed in 0.1 molar NaOH solution for 80 min.; G5B was treated likewise before immersion in 0.5 molar KOH solution. Prior to K-exchange all samples were air dried, except G6 that was heated at 100 °C]

		-----5 g in 15 ml of 0.5 M KOH-----				5 g in 20 ml of 0.25 M KOH	
	G1 80 min.	G5A 0.1M NaOH	G5B	G2	G3	G4	G6
dwell time (min.)	0	40	80	60	3,960	unheated 120	100 °C 120
hkl		Relative intensities, in percent (units)					
020	55(37)	58(24)	52(32)	62(34)	64(34)	52(33)	55(35)
200	33(22)	36(15)	35(22)	36(20)	38(20)	35(22)	34(22)
$20\bar{1}$	13(9)	15(6)	10(6)	11(6)	9(5)	10(6)	9(6)
111	33(22)	29(12)	29(18)	27(15)	30(16)	25(16)	26(17)
400, 300	100(67)	100(41)	100(62)	100(55)	100(53)	100(63)	100(64)
$\bar{2}22$	33(22)	34(14)	34(21)	35(19)	30(16)	25(16)	33(21)
151, 350	37(25)	41(17)	52(32)	44(24)	42(22)	41(26)	47(30)
$62\bar{1}$, 530, 260	19(13)	17(7)	23(14)	22(12)	21(11)	24(15)	22(14)
			Intensity ratios (units)				
$020/\overline{NX}$[#] =	2.09	2.18	2.09	2.49	2.49	2.25	2.19
$400/\overline{NX}$ =	3.79	3.73	4.04	4.02	3.88	4.30	4.00

[#], $\overline{NX}$ = Sum (200 + $20\bar{1}$ + 111)/3, intensity units

Table 9.--X-ray diffraction data for ammoniated clinoptilolite-bearing Rockyford Ash Member

[Samples were immersed in a 1 normal NH_4 OH solution. All samples were plus 10 mesh minus 6 mm. All were put in solutions at 20 °C, except 4H, for which both samples and solution were held at 50 °C. All were dried at 100 °C prior to X-ray analysis]

	1H	2H	3H	4H	5H	6H
Pretreatment:	20 °C	20 °C	20 °C	50 °C	20 °C	100°
Ammonium solution dwell time: (minutes)	30	60	960	30	1,170	1,080
hkl	Relative intensities, in percent (units)					
020	99(66)	73(55)	81(61)	64(46)	66(52)	79(57)
200	43(29)	37(28)	39(29)	35(25)	30(23)	36(26)
$20\bar{1}$	18(12)	19(14)	15(11)	15(11)	14(11)	15(11)
111	33(22)	35(26)	32(24)	33(24)	27(21)	32(23)
400, 330	100(67)	100(75)	100(75)	100(72)	100(77)	100(72)
$22\bar{2}$	33(22)	28(21)	33(25)	29(21)	31(24)	32(22)
151, 350	42(28)	31(23)	36(27)	39(28)	44(34)	38(27)
$62\bar{1}$, 530 260	25(17)	21(16)	24(18)	22(16)	22(17)	24(17)
	Intensity ratios (units)					
$020/\overline{NX}^{\#}$ =	3.14	2.43	2.86	2.30	2.84	2.85
$400/\overline{NX}$ =	3.19	3.31	3.52	3.60	4.20	3.60

[#], $\overline{NX}$ = Sum (200 + $20\bar{1}$ + 111)/3, intensity units

Table 10.--X-ray diffraction data for 20 °C dried and 100 °C dried and ammoniated clinoptilolite-bearing Rockyford Ash Member

[All samples were treated with a 4 molar ammonium hydroxide solution for indicated periods of time. Sample 1KK was treated with 0.5 molar KOH solution after NH_4 OH treatment of sample 1K. All data are for 100° dried material]

	1K	2K	3K	4K	5K	1KK
Treatment:	20 °C	20 °C	100 °C	100 °C	100 °C	100 °C
solution dwell time: (minutes)	45	25	25	30	25	60
grain size:	coarse (+10m-6mm)	-60 m	coarse (+10m-6mm)	-60 m	35-60 m	-60 m
hkl	Relative intensities, percent (units)					
020	76(53)	81(67)	64(50)	75(62)	82(42)	51(34)
200	34(24)	36(30)	42(33)	33(27)	39(20)	39(26)
$20\bar{1}$	14(10)	14(12)	17(13)	15(12)	16(8)	10(7)
111	31(22)	31(26)	36(28)	33(27)	33(17)	33(22)
400, 330	100(70)	100(83)	100(78)	100(82)	100(51)	100(67)
$22\bar{2}$	33(23)	31(26)	32(25)	30(25)	27(14)	36(24)
151, 350	37(26)	38(32)	47(37)	30(25)	37(19)	37(25)
$62\bar{1}$, 530 260	21(15)	22(18)	24(19)	20(16)	20(10)	18(12)
	Intensity ratios (units)					
$020/N\bar{X}^{\#}$ =	2.84	2.96	1.87	2.82	2.80	1.85
$400/N\bar{X}$ =	3.75	3.66	3.16	3.72	3.40	3.66

$^{\#}$, $N\bar{X}$ = Sum (200 + $20\bar{1}$ + 111)3, intensity units

Table 11 has the X-ray diffraction data for material treated with hydrochloric acid solution; one of the acidulated samples was used for ammonium exchange in ammonium sulfate solution, and another was used for sodium exchange in sodium hydroxide solution. Hydrochloric acid treatment removed more calcium than potassium. From 7-30 percent of the potassium was removed, and 44-60 percent of the calcium was removed by hydrochloric acid treatment (table 4). The acidulated and ammonium-exchanged sample lost 38 percent of its original potassium content and 75 percent of its original calcium content. Analysis of the nitrogen content of this ammonium-exchanged sample by two methods gave 1.26 weight percent (Dumont method) and 1.27 weight percent (Kjeldahl method). This amount of nitrogen indicates the presence of about 1.62 weight percent of ammonium. The sodium-exchanged sample lost 16 percent of the original potassium and 39 percent of the original calcium (table 4). The ammonium-exchanged sample has enhanced 020 and 400 X-ray reflections, in comparison to the sodium-exchanged sample (table 11).

Table 12 shows the X-ray diffraction intensity data for ammonium-exchanged material treated with ammonium sulfate at 40 °C for three periods of time. Exchange of potassium ranged from 27-37 percent; more than 23-27 percent of the calcium was exchanged. The intensity of the 020 reflection is significantly greater for ammonium-exchanged material than for non-exchanged, sodium-exchanged, or potassium-exchanged material.

Table 13 gives the X-ray diffraction data for material treated with a 2.6 molar solution of ammonium chloride and a 2.4 molar solution of sodium chloride (7 g of material in 50 ml of solution) at 40 °C. For the ammonium-exchanged material, 37-40 percent of the original potassium was exchanged and 51-56 percent of the calcium was exchanged (table 4). For the sodium-exchanged material, 19-22 percent of the original potassium was exchanged and 36-37 percent of the calcium was exchanged (table 4). The relative intensity of the 020 reflection for the ammonium-exchanged material is substantially greater than that of the sodium-exchanged material (table 13, fig. 2).

SUMMARY

Ammonium Exchange

Prolonged treatment (68 h) of 20 °C dried material in ammonium sulfate solution at 20 °C resulted in a loss of 30 percent potassium and more than 38 percent of the calcium. The loss of calcium by exchange from zeolite is greater than 38 percent because X-ray diffraction shows that gypsum is present in the sample. Ammonium exchange of 20 °C dried material in ammonium sulfate solution at 60 °C exchanged as much as 25 percent of the potassium and more than 20 percent of the calcium (gypsum present). Pretreatment with sulfuric acid solution (20 m) prior to exchange in ammonium sulfate solution at 60 °C exchanged 38 percent of the potassium and more than 59 percent of the calcium (gypsum present); quantitative analyses indicated 1.37-1.39 weight percent of nitrogen in this ammonium-exchanged sample. Pretreatment with hydrochloric acid solution (20 m) prior to exchange in ammonium sulfate at 20 °C exchanged 38 percent of the potassium and 75 percent of the calcium; quantitative analysis showed 1.26-1.27 weight percent of nitrogen in this ammonium-exchanged sample. Exchange in ammonium chloride solutions at 40 °C removed about 40 percent of the potassium and 56 percent of the calcium. Based on the analysis of nitrogen in ammonium-exchanged material, it is estimated that the clinoptilolite-bearing Rockyford Ash Member examined in the present study has a maximum ammonium-exchange capacity of 2 weight percent, or 40 lbs per ton.

Table 11.--X-ray diffraction data for clinoptilolite-bearing Rockyford Ash Member

[All samples were treated at 100 $^{\circ}$C prior to solution treatment and prior to X-ray diffraction analysis. Acidulation treatment was a solution of H_2O:HCL of 5:1 by volume. Treatments with ammonium sulfate and sodium hydroxide for exchange were done on two fractions of acidulated sample 2HCL at 20 $^{\circ}$C]

Acidulation dwell time: (minutes)	30	50	90	4,165	50	50
grain size:	minus 60 mesh		plus 35 mesh, minus 12 mesh		minus 60 mesh	
exchange time: (minutes)					3,990 ammonium sulfate	5,340 sodium hydroxide
hkl	1HCl	2HCL	3HCL	4HCL		
	Relative intensities, percent (units)					
020	71(53)	69(46)	74(45)	94(49)	76(73)	85(45)
200	29(22)	22(15)	36(22)	37(19)	29(28)	43(23)
$20\bar{1}$	13(10)	18(12)	18(11)	21(11)	17(16)	21(11)
111	27(20)	30(29)	34(21)	31(16)	24(23)	32(17)
400, 330	100(75)	100(67)	100(61)	100(52)	100(96)	100(53)
$22\bar{2}$	27(20)	30(20)	44(27)	25(13)	19(18)	32(17)
151, 350	32(24)	30(20)	30(18)	31(16)	23(22)	40(21)
$62\bar{1}$, 530 260	16(12)	16(11)	20(12)	13(8)	13(12)	23(12)
	Intensity ratios (units)					
$020/N\bar{X}^{\#}$ =	3.06	2.94	2.50	3.20	3.27	2.65
$400/N\bar{X}$ =	4.33	4.27	3.39	3.39	4.30	3.12

$^{\#}$, $N\bar{X}$ = Sum (200 + $20\bar{1}$ + 111)/3, intensity units

Table 12.--X-ray diffraction data for ammonium-exchanged clinoptilolite-bearing Rockyford Ash Member

[Samples were dried at 40 °C, weighed and placed in a solution of 5 g $(NH_4)_2SO_4$ in 50 ml water at 40 °C. Samples were plus 10 mesh-6mm and weighed 5 grams. After treatment the samples were dried at 40 °C and weighed prior to X-ray diffraction analysis]

Solution dwell time: (minutes)	60	120	1,080
	M1	M2	M3
hkl	Relative intensities, percent (units)		
020	93(70)	97(73)	96(73)
200	36(27)	32(24)	34(26)
$20\bar{1}$	16(12)	17(13)	20(15)
111	21(16)	23(17)	21(16)
400, 330	100(75)	100(75)	100(76)
$22\bar{2}$	32(24)	31(23)	29(22)
151, 350	29(22)	33(25)	30(23)
$62\bar{1}$, 530 260	16(12)	15(11)	12(9)
	Gypsum present in all samples		
	Intensity ratios (units)		
$020/\bar{NX}^{\#}$ =	3.82	4.05	3.84
$400/\bar{NX}^{\#}$ =	4.10	4.16	4.00

$^{\#}$, $\bar{NX}$ = Sum $(200 + 20\bar{1} + 111)/3$, intensity units

Table 13.--X-ray diffraction data for ammonium- and sodium-exchanged clinoptilolite-bearing Rockyford Ash Member

[Ammonium-exchanged samples were exposed to a solution of 7 g NH_4Cl in 50 ml H_2O at 40 °C; sodium-exchanged samples were exposed to a solution of 7 g of NaCl in 50 ml H_2O at 40 °C. Material was +35-12 mesh and samples were dried at 40 °C prior to X-ray analysis]

Treatment:	ammonium chloride		sodium chloride		40 °C only
dwell time: (minutes)	90	180	90	180	
	N1	N2	N3	N4	
hkl	Relative intensities, percent (units)				
020	86(65)	95(72)	81(48)	69(40)	70(45)
200	30(23)	33(25)	42(25)	40(23)	36(23)
$20\bar{1}$	17(13)	21(16)	19(11)	16(9)	17(11)
111	24(18)	25(19)	35(21)	33(19)	36(23)
400, 330	100(76)	100(76)	100(59)	100(58)	100(64)
$22\bar{2}$	32(24)	30(22)	35(21)	28(16)	31(20)
151, 350	28(21)	28(21)	37(22)	40(23)	42(27)
$62\bar{1}$, 530 260	14(11)	14(11)	20(12)	17(10)	22(14)
	Intensity ratios (units)				
$020/\overline{NX}^{\#}$ =	3.61	3.60	2.53	2.35	2.37
$400/\overline{NX}$ =	4.22	3.80	3.10	3.41	3.37

#, $\overline{NX}$ = Sum (200 + $20\bar{1}$ + 111)/3, intensity units

Ammonium exchange using ammonium hydroxide solutions is much less than those using ammonium sulfate solutions. Prolonged exposure (16 h) of the material to ammonium hydroxide solution exchanged less than 10 percent of the potassium and less than 25 percent of the calcium. Thus ammonium exchange is diminished at high pH.

Acidulation

Acidulation in strong hydrochloric acid solutions for a long period (3 d) exchanges as much as 30 percent of the potassium and 60 percent of the calcium. For short periods (30-90 m), less than 15 percent of the potassium is exchanged, whereas 45-50 percent of the calcium is exchanged.

Acidulation is strong sulfuric acid solutions for 22 d depleted the potassium content between 45-50 percent. Because gypsum was produced from the calcium exchange, the amount of calcium lost from the zeolite could not be determined. Short periods (20 m) of exposure to strong sulfuric acid solution exchanges as much as 30 percent of the potassium.

Potassium Exchange

Potassium exchange was done with potassium hydroxide solutions for short 40-120 m) and long (66 h) periods. Amounts of potassium were enhanced by as much as 125 percent. In general, the large amount of potassium exchanged did not do so at the expense of calcium; for air dried material the maximum amount of calcium exchanged was 15 percent. This demonstrates that the cation sites occupied by calcium were not potassium-exchangable sites, under the conditions of these experiments at 20 ^{o}C in strongly alkaline solutions. This relatively large amount of potassium-holding capacity, 2.5 weight percent or 50 pounds per ton, may be of interest in the application of a slow release potassium fertilizer.

X-ray Diffraction Results

The significant increase in the intensity of the clinoptilolite 020 reflection caused by ammonium exchange is demonstrated here, but the cause is not understood in the absence of single-crystal studies of ammonium-exchanged and non-exchanged clinoptilolite. However, the empirical observation of the effect may be useful in evaluating ammonium-exchange if other clinoptilolites respond in the same manner.

Ammonium-Exchange Capacity Measurements for Clinoptilolites

The maximum ammonium-exchange capacities of natural clinoptilolites, with or without pre-ammonium-exchange conditioning, are in the range of 1.0-2.3 milliequivalents per gram (or less than 230 meq/100 g) for material that contains 80 percent or more of clinoptilolite (Sheppard and Gude, 1982; Klieve and Semmens, 1980). This amounts to a maximum of 0.23 weight percent of ammonium or 2,300 parts per million. The clinoptilolite-bearing Rockyford Ash Member, that contains only 50-60 percent of clinoptilolite, contains 1.62-1.77 weight percent of ammonium after ammonium-exchange in ammonium sulfate solutions, based on quantitative analysis of nitrogen. It appears that the ammonia selective electrode measurement gives the value for the concentration of ammonia released in the Na-exchanged solution, but it does not measure the absolute amount of a ammonia derived from clinoptilolite. The value apparently represents the rate of ammonia release, and therefore the amount is proportional to the clinoptilolite concentration in the sample.

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