

Pharmaceutical Investigation of Selected Alberta Bentonites III. Cation Exchange Determination

By ARTHUR J. ANDERSON† and ELMER M. PLEIN

Previously reported data established that anomalous behavior of Alberta bentonites could not be explained on the basis of official limit tests. Results of a cation exchange study of these clays are discussed.

TO EVALUATE the acceptability of Alberta bentonites as pharmaceutical agents, a study of the various known deposits of the material was undertaken. Details regarding identification procedures and limit tests were reported earlier (1, 2).

Since the anomalous behavior of the clays could not be explained on the basis of the data obtained from the official limit tests, it was felt that a knowledge of the cation exchange capacities of the respective clays might provide a better basis for explaining the apparent lack of uniform quality found among the samples collected.

Clay minerals possess to a varying degree the ability to adsorb cations and to retain these in an exchangeable state (3-5). This ability is claimed to be the result of unbalanced lattices and is expressed in milliequivalents (meq.) of cation per 100 Gm. of clay. Increasing valency of the cation and decreasing hydration of the particle facilitates this exchange.

Various methods for determining the cation-exchange capacity of soils have been reported (5-12). The continued search for a satisfactory method served only to emphasize the difficulties inherent in such a determination. Even less accuracy has been found in the determination of the specific exchangeable cations (13).

EXPERIMENTAL

The procedure employed in this study was taken from the "Methods Book, Soils Survey Laboratories," University of Alberta (14), and was essentially a modified version of the ammonium acetate method of Schollenberger and Simon (12). In general, neutral ammonium acetate solution was used to displace the original adsorbed cations from the clays by a process of leaching. The leachates were retained for determination of the specific cations removed in the leaching process. The capacity of the clays to adsorb ammonium ions under controlled conditions was then determined by a Kjeldahl technique employing titration of 4% boric acid solution with standard sulfuric acid. Values obtained are presented in Table I.

In considering the ammonium acetate leachates obtained from the cation exchange procedure, it appeared that analytical procedures designed to yield quantitative values for sodium, potassium, calcium, and magnesium should be sufficient for the purposes of this study. The four cations mentioned were considered to exert the most significant effects on hydration properties of bentonites. Advantage

was taken of the flame photometer analytical method for all four of the cations mentioned (Table II).

A Beckman spectrophotometer, model DU, with an acetylene and oxygen burner was employed in the determination of these exchanged cations. Sensitivity of the flame signal response was enhanced through use of a model 9200 photomultiplier unit. Interference effects were lessened by means of a flooding technique as employed by the Alberta Soils Survey Laboratories (14, 15).

RESULTS

Per cent transmittance of sodium, potassium, calcium, and magnesium was read at 589 m μ , 769 m μ , 422.5 m μ , and 285.2 m μ , respectively. The values for each ion were referred to a standard curve for that ion and translated into meq./L. This latter value was then converted into meq. per 100 Gm. of oven-dry clay through

$$\text{meq./100 Gm. oven-dry clay} = \frac{F(\text{meq./L.}-\text{blank}) 25}{W}$$

where F = dilution factor for the leachate necessary to bring transmittance values within the range covered by the standard curve, and W = weight of oven-dry sample.

Ideally, the sum of the exchanged cations should equal the cation exchange capacity for each clay studied. However, due to a number of factors, such as errors inherent in the procedures employed plus the presence of soluble salts extracted during the leaching process, such an agreement is rarely obtained. In Table III such differences are attributed to the presence of soluble salts only.

On this basis, the clays from the Rosalind beds (Samples 1A, 3, 21, and 28) showed very little soluble salt content, with exchangeable potassium also very low. Sample 32, while also a product of

TABLE I.—CATION-EXCHANGE CAPACITY OF
SELECTED ALBERTA BENTONITES

Bentonite Sample No.	Cation Exchanges (av.)	Range
29 (Control) ^b	82.53	0.99
1A	64.27	1.02
3	59.17	0.22
4	54.76	0.55
6	66.10	0.16
9	61.15	0.45
21	75.06	0.39
25	58.87	0.27
28	66.65	1.15
30	66.47	1.22
31	66.08	0.86
32	51.08	1.24

^a Reported in meq. NaOH per 100 Gm. oven-dry clay.
^b Volclay B. C. grade, received from the American Colloid Co., Merchandise Mart Plaza, Chicago 54, Ill.

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† Present address: Faculty of Pharmacy, University of Alberta, Edmonton, Alberta, Canada.

TABLE II.—DETERMINATION OF EXCHANGEABLE IONS IN LEACHATES BY FLAME SPECTROPHOTOMETER^a

Bentonite Sample	Na ⁺		K ⁺		Ca ⁺⁺		Mg ⁺⁺	
	589 m μ	Range	769 m μ	Range	422.5 m μ	Range	285.2 m μ	Range
29 (Control) ^b	50.90	2.39	2.12	0.35	56.57	2.62	13.57	0.31
1A	33.98	3.04	0.50	0.02	26.32	2.64	6.65	0.28
3	28.09	0.57	0.52	0.01	27.83	1.00	8.64	2.17
4	20.19	3.53	0.76	0.04	26.38	1.43	2.47	0.39
6	61.80	0.77	3.26	0.29	13.80	1.42	4.06	1.12
9	57.88	1.76	2.59	0.16	56.31	1.20	5.48	1.38
21	36.94	2.35	0.40	0.06	33.89	0.23	7.70	0.94
25	36.59	0.90	1.00	0.02	44.59	1.16	3.60	1.34
28	36.51	0.81	0.58	0.03	23.32	1.18	6.00	0.27
30	27.55	2.87	0.60	0.06	51.97	0.97	10.17	0.82
31	24.33	1.12	0.63	0.04	71.40	1.49	13.50	1.60
32	31.79	0.77	0.83	0.14	59.71	4.54	5.35	0.87

^a All values are presented as meq. per 100 Gm. oven-dry clay. ^b Volclay B. C. grade, received from the American Colloid Co., Merchandise Mart Plaza, Chicago 54, Ill.

TABLE III.—COMPILATION OF CATION-EXCHANGE CAPACITY AND EXCHANGEABLE ION DATA FOR SELECTED ALBERTA BENTONITES^a

Bentonite Sample No.	Exchanged Ions in Leachate				Exchanged Ions, Total	Cation-Exchange Capacity ^b	Soluble Salts in Clay
	Na ⁺	Ca ⁺⁺	K ⁺	Mg ⁺⁺			
29 ^c	50.90	56.57	2.12	13.57	123.16	82.53	40.63
1A	33.98	26.32	0.50	6.65	67.45	64.27	3.18
3	28.09	27.83	0.52	8.64	65.08	59.17	5.91
4	40.19	26.38	0.76	2.47	69.80	54.73	15.07
6	61.80	13.80	3.26	4.06	82.92	66.10	16.82
9	57.88	56.31	2.59	5.48	122.26	61.15	61.11
21	36.94	33.89	0.40	7.70	78.93	75.06	3.87
25	36.59	44.59	1.00	3.60	85.78	58.87	26.91
28	36.51	23.32	0.58	6.00	66.41	66.65	0.24 ^d
30	27.55	51.97	0.60	10.17	90.29	66.47	23.82
31	24.33	71.40	0.63	13.50	109.86	66.08	43.78
32	31.79	59.71	0.83	5.35	97.68	51.08	46.60

^a All values are presented as meq. per 100 Gm. of oven-dry clay. ^b From Table I. ^c Control: Volclay B. C. grade, received from the American Colloid Co., Merchandise Mart Plaza, Chicago 54, Ill. ^d Within the limits of error for these determinations this value may be considered as zero.

the Rosalind beds (1), had been collected from the stack at the plant in an effort to procure an air-floated commercial product free of "grit." As shown in the table, significant changes in cation values were found when compared with the "regular" Rosalind clays. A notable increase in calcium ion was found in the leachate, while a reduced cation exchange capacity was observed. On the other hand, Sample 9 with a lower swelling power and much lower gelling power than Sample 32 (2) was shown to possess a higher cation exchange capacity than the latter clay (Table III). Similar observations could be made for other samples presented, indicating that the information shown, while of interest to the clay investigation generally, was not in itself sufficient to account for the observed behavior of the clay samples studied.

This conclusion is in agreement with the findings of Foster (16) who reported that the degree of swelling of sodium montmorillonites was not correlated with cation-exchange capacity or with charge on the tetrahedral layers.

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