

peak caused by loss of interlayer water occurs in all cases between 140 and 160°. Where present, the notch on recovery is attributed to the presence of calcium in the lattice. High temperature exotherms are not recorded because of difficulties encountered with the apparatus when temperatures were raised much above 800°.

Each sample was X-rayed before and after treatment with ethylene glycol, with the glycolated materials giving basal spacings slightly less than the accepted value of 17 Å. (11, 12). It was shown by Mackenzie (12) that this spacing would be reduced to lower values when insufficient ethylene glycol was present to complete the complex formation. However, before discarding the data, in question, a detailed study of the tracings was undertaken by Dr. L. B. Halferdahl.¹ While several of the clays showed quartz and/or gypsum peaks he was able to classify each of the samples as bentonite containing montmorillonite as the chief clay mineral. This finding, together with the evidence gathered

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from the differential thermal studies, was considered as sufficient to confirm the identity of the clays under study.

Further laboratory data designed to assist in evaluation of these clays as possible pharmaceutical agents will be reported in part II of this investigation.

REFERENCES

- (1) Keele, J., *Geol. Surv. Can. Mem. No. 66*, 1915, 4.
- (2) Ellis, S. C., *Can. Dept. Mines, Mines Branch, Memorandum Series 3*, 1921.
- (3) Ries, H., and Keele, J., *Geol. Surv. Can. Mem. No. 25*, 1913, 26.
- (4) *Ibid.*, 1913, 73.
- (5) Spence, H. S., *Can. Dept. Mines, Mines Branch, No. 626*, 1924, 35 pp.
- (6) Spence, H. S., and Light, M., *ibid.*, No. 723, 1931, 34 pp.
- (7) Byrne, P. J. S., "Bentonite in Alberta," Research Council of Alberta, Rept. No. 71, 1955.
- (8) Berkowitz, N., *Fuel*, 34, 355(1957).
- (9) Routine procedure employed in laboratories of the Alberta Research Council, Edmonton, Alberta.
- (10) Brindley, G. W., "X-Ray Identification and Crystal Structures of Clay Minerals," The Mineralogical Society (Clay Minerals Group), London, 1951, p. 118.
- (11) Bradley, W. G., *J. Am. Chem. Soc.*, 67, 975(1945).
- (12) Mackenzie, R. C., *Trans. Faraday Soc.*, 44, 368(1948).

Pharmaceutical Investigation of Selected Alberta Bentonites II

Limit Tests and Mechanical Analysis

By ARTHUR J. ANDERSON† and ELMER M. PLEIN

A collection of bentonite samples from known Alberta deposits was examined. Limit tests as described in the B.P. and U.S.P. were completed on each. Additional procedures were undertaken to assist in evaluation of physical properties of the clays. On the basis of this work, one sample was shown to be of pharmaceutical quality, with a second sample from the same commercially important deposit being excluded from this category on a minor technicality only.

TWENTY-NINE SAMPLES of bentonite taken from deposits throughout Alberta were examined in the course of this work. All clays were identified as bentonite by qualified mineralogists, with verification by differential thermal and X-ray techniques being made on a selected group of interesting samples (1).

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A laboratory study of the collected materials was then made to determine the presence of reserves of pharmaceutical grade bentonite in the province. A rigorous chemical analysis was not undertaken since pharmaceutical requirements were based mainly upon the inherent physical properties of the clays. However, certain chemical procedures were completed to aid in characterization.

EXPERIMENTAL

All samples were dried at 90°, reduced to a fine powder (200 mesh) by passage through a laboratory hammer mill, and then mixed well to obtain a uni-

form blend. The materials were then stored in suitable closed glass, metal, or polythene containers.

After preliminary testing of several bentonites, a supply of Volclay B.C. grade¹ was chosen as most suitable for use as a control clay in this study.

Arsenic.—Since the B.P. (2) bentonite monograph contains a section limiting the maximum allowable arsenic content to not more than 8 p.p.m., it was felt that such data should be included in this study. For this purpose the quantitative procedure as detailed in the U.S.P. (3) was employed.

Nine Alberta clays, representative of deposits found in widely scattered areas of the province, were selected for this determination. Of these, seven clays yielded negative results, one a bare trace of color, and one a concentration of 1 p.p.m. of arsenic.

On the basis of the results obtained from the above sampling it was concluded that further testing was not indicated.

Alkalinity.—The B.P. states that a 2% w/v suspension of bentonite in distilled water should record a pH of 9.00–10.50. The U.S.P. requires a slightly narrower range of 9.00–10.00 for a 1 in 50 aqueous suspension.

Procedure

Two grams of clay was added in small portions to about 75 ml. deionized distilled water in a 100-ml. graduated cylinder. After all of the clay had been added and had settled to the bottom of the cylinder, more deionized water was added to the 100-ml. mark. The contents were then transferred to a Pyrex beaker containing a Teflon-coated stirring bar, and the assembly was placed on a magnetic stirrer. The contents were stirred at a rapid, uniform speed, and readings were taken with a Beckman Zeromatic pH meter using a calomel-glass electrode pair. The data are presented in Table I.

TABLE I.—pH VALUES OF ALBERTA BENTONITE AQUEOUS SUSPENSIONS^a

Sample ^b	Mean	Range	Sample	Mean	Range
1	9.20	0.40	16	9.60	0.00
1A	8.87	0.20	21	9.15	0.00
3	8.93	0.12	23	9.70	0.00
4	9.35	0.10	24	9.83	0.05
5	9.27	0.05	25	9.70	0.00
6	9.75	0.02	26	9.49	0.02
7	8.54 ^c	0.01	27	9.80	0.00
8	8.05 ^c	0.10	28	9.00	0.00
9	8.80	0.00	29	9.50	0.00
10	9.03	0.20	30	9.22	0.05
11	8.60 ^c	0.00	31	9.18	0.05
12	8.00 ^c	0.15	32	9.37	0.05
15	8.62 ^c	0.05			

^a 2.0% w/v. ^b As indicated, certain samples were, for various reasons, discarded as unsuitable for laboratory testing. All clays were determined in triplicate with the exception of samples 8 and 23; in these two instances, duplicate readings only were recorded. ^c Considered as indicative of substandard bed.

Swelling Power.—To be acceptable as a pharmaceutical agent, a bentonite must show pronounced swelling ability upon hydration. The U.S.P.

monograph describes a simple test designed to evaluate the swelling power of bentonite in distilled water. Readings are taken after 2 hours. The B.P. monograph sets a similar standard of quality. However, in this test the distilled water is replaced by a 1% sodium lauryl sulfate solution. The presence of the wetting agent assists materially in reducing the time needed to wet the powder. Furthermore, while the clay in this instance must also swell to the same apparent volume as before (24 ml.), the time required to do so is not specified.

The B.P. procedure was employed throughout in this determination. Clays were hydrated overnight and apparent volumes were read the next morning. Precautions were taken in each case to prevent loss of liquid through evaporation.

Six native bentonites were found to meet the official requirements of the test. However, a comparison of these values with those presented in Table 1 revealed little correlation between degree of alkalinity and swelling power. It was felt that this discrepancy could be due, in part at least, to excessive quantities of inert material in the native clays. Accordingly, a method for the removal of such substances was devised. This consisted of preparing 1 L. of a 4% (w/v) suspension of each clay sample in distilled water.² After sedimentation for 24 hours, the supernatant colloidal dispersion was removed by decantation and evaporated to dryness in an oven. The residue was then reduced to a 200-mesh powder and the B.P. test was employed, as before, to determine swelling power for each of the purified clays. Each sample was run in triplicate and the values averaged.

Apparent swelling volumes for each clay, before and after purification by water sedimentation, were compiled. These are presented in Fig. 1. Sample 7 could not be purified by this method since the total sample settled as "dead clay."

Mechanical Analysis.—During the preparation of bentonite dispersions it was observed that a marked difference in sand and silt content existed among the various samples. Since the presence of such inert material was considered undesirable in a pharmaceutical clay, a quantitative determination of sand, silt, and clay fractions of each sample was undertaken.

The U.S.D.A.³ size limits for sand, silt, and clay fractions were employed (4). On this basis, 50 μ was taken as the dividing line between very fine sand and coarse silt. The lower limit for silt was set at 2 μ , and clay was considered to consist of all particles of diameters less than 2 μ .

Olmstead, Alexander, and Middleton (5) studied the application of the pipet method to mechanical analysis and developed an improved technique with a single pipet that was adapted by the Soils Laboratories of the U.S.D.A. Lyon and Buckman (6) suggested that the average surface soil could be considered to have a density of 2.65. Steele and Bradfield (7) later employed this factor to calculate sedimentation times at 25°. From this work it was determined that particles having a diameter of 2 μ and a density of 2.65 would require 41 minutes, 32 seconds at 25° to fall 1 cm. in a water medium.

² Because of their relatively high viscosity at this concentration, samples 1A, 21, 28, and 29 were further diluted to 2 L. to allow for satisfactory sedimentation.

³ United States Department of Agriculture.

¹ Received from the American Colloid Co., Merchandise Mart Plaza, Chicago 54, Ill.

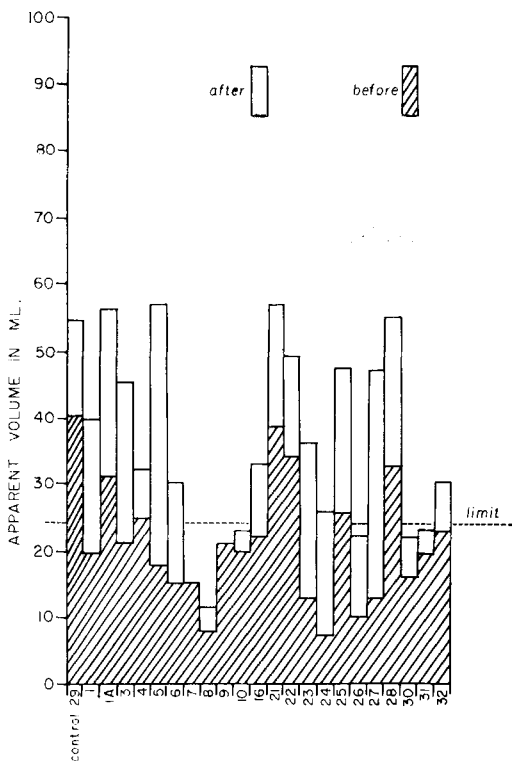


Fig. 1.—Swelling power of Alberta bentonites before and after purification by water sedimentation (2).

Procedure⁴

With the aid of a Waring Blendor, a 10-Gm. sample of air-dry clay was mixed to a smooth dispersion in 200 ml. of distilled water. The mixture was then transferred, with rinsings, to a 400-ml. electrolytic beaker, covered, and allowed to hydrate for 24 hours.

After hydration, 10 ml. of dispersing agent⁵ was added to the system and the contents of the beaker were again transferred to a blending cup and stirred briskly for 20 minutes.

The dispersed sample was then washed onto a 300-mesh sieve,⁶ the silt and clay passing through into a 1-L. graduated cylinder. Washing of the sieve contents was continued until the volume in the cylinder totaled 800 ml. Further washings were not collected, but the procedure was continued until the sand (and some coarse silt) was freed of any last traces of clay. Contents of the sieve were then washed into a tared aluminum dish, evaporated to dryness at 90°, and then dried to constant weight at 105°.

The silt and clay suspension was then made up to 1 L. with more distilled water, mixed well, and

the cylinder placed in a suitable water bath at 25°. Sedimentation was calculated for 2- μ particles at 25° using the 2.65 density factor as recommended by Steele and Bradfield.

A 25-ml. automatic pipet with a filling time of 12 sec. was employed to obtain the clay aliquot at a depth of 8 cm. Filling of the pipet was accomplished by means of a controlled vacuum, and the contents were then transferred to a tared moisture dish. One rinse from the pipet was added and the dish was then placed in an oven at 90° until dry. Heating to constant weight was done at 105°.

All determinations were made at least in duplicate and reported in per cent on the basis of oven dry weight of the sample. In calculating the weight of clay obtained from the pipet aliquot, a correction factor was introduced to account for the weight of dispersing agent contained. The per cent of silt content was obtained by subtracting the sum of the percentages of sand and clay from 100. Values obtained are reported in Table II.

TABLE II.—PHYSICAL ANALYSIS OF ALBERTA BENTONITES

Sample ^a	Mean Sand Content, %	Range	Mean Clay Content, %	Range	Silt Content, % (By Difference)
1	1.52	0.03	82.17	0.07	16.31
1A	1.67	0.09	92.56	1.13	5.77
3	1.96	0.08	89.08	0.21	8.96
4	0.72	0.03	84.80	0.94	14.48
5	11.23	1.30	51.42	1.98	37.35
6	Trace	..	67.99	0.86	32.01
7	3.79	0.26	75.39	0.58	20.82
8	3.63	0.15	50.08	2.68	46.29
9	0.72	0.02	83.78	0.16	15.50
10	1.37	0.07	87.33	1.80	11.30
21	0.75	0.02	94.73	2.04	4.52
23	3.65	0.02	65.75	1.15	30.60
24	9.46	0.23	40.64	1.95	49.90
25	0.88	0.03	71.19	0.29	27.93
26	10.48	0.16	48.46	0.45	41.06
27	45.10	0.10	43.85	1.49	11.05
28	1.69	0.06	91.06	1.62	7.25
29	Nil	..	95.56	1.22	4.44
30	2.38	0.18	78.55	0.04	19.07
31	2.30	0.05	80.55	1.28	17.15
32	Nil	..	88.48	1.23	11.52

^a Samples 29 and 32 were received as "grit free" powders due to their method of preparation.

Gel Formation.—Suspensions of swelling-type bentonite in suitable concentration will set to a gel, sometimes in a matter of seconds. Magnesium oxide has been shown to augment this effect significantly. An explanation of the phenomenon was later advanced by Hauser and Hirshon (8).

Both the B.P. and U.S.P. bentonite monographs contain provisions designed to set a minimum gel-forming standard for such clays. The test procedures are identical except for minor differences in wording. No more than 2 ml. of clear supernatant liquid should separate from the gel proper by the end of the test period.

For convenience, the B.P. procedure was followed in this study. Samples were prepared in triplicate, the results being averaged and presented in graphic form in Fig. 2.

⁴ Based on the procedure employed in the Soils Laboratory, Research Council of Alberta, Edmonton, Alberta.

⁵ Sodium hexametaphosphate, 35.70 Gm., and 7.94 Gm. of sodium carbonate per L. The sodium carbonate was employed as an alkaline buffer to prevent hydrolysis of the metaphosphate back to the *ortho* form.

⁶ While the U.S.D.A. has set 50 μ as the lower limit of size for sand, a 300-mesh screen is usually employed for this purpose. Calibration of the screen used showed an average opening of 47.87 μ , indicating that at least a portion of the coarsest silt could be expected to remain in the sand fraction.

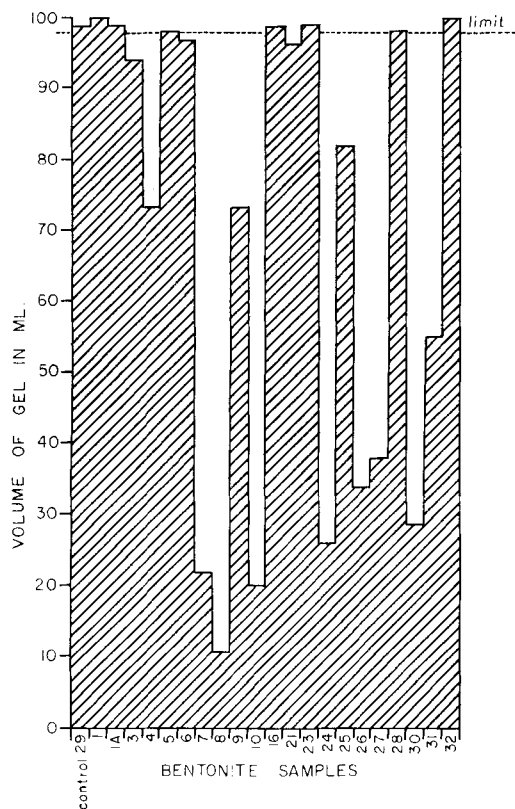


Fig. 2.—Gel formation of Alberta bentonites (2).

DISCUSSION

Alberta bentonites were found to be practically free of arsenic, making the clays suitable in this respect for use in medications to be taken internally. Alkalinity tests indicated that some samples were technically below standard. However, because the materials under test could not be considered as completely representative of each deposit, only five of the tabulated pH values were considered as probably indicative of substandard beds.

Swelling tests conducted on the clays indicate many are of the medium or low-swelling types. Six

clays met official standards, four of which are from the Rosalind lease.⁷ Preparation of clay concentrates by water sedimentation, with subsequent determination of swelling power of each, indicates that high-swelling fractions exist in a number of the known deposits. On that basis it would seem reasonable to anticipate that reserves of such high quality clay remain to be discovered in the province.

Twenty-one clays were examined for gel-forming ability. Seven of these were found to equal or exceed the official minimum requirements. It is interesting to note that of these, three clays had previously shown unsatisfactory swelling powers. Four of the seven samples which passed the gel-forming test were rich in clay content, but two of the seven were relatively poor in this respect. Such data only serve to accentuate the unpredictable nature of the native material.

On the basis of the official limit tests employed, only sample 28 was considered of pharmaceutical quality. Sample 1A, from the same beds was deficient in only one test, recording a pH of 8.87 instead of the required minimum of 9.00. Considering the method of collection, this deficiency could be considered a technicality.

While the B.P. "grit test" was not conducted on these materials, it is felt that the mechanical analysis procedure used was sufficiently stringent to afford an excellent indication of sand content to be found in the clays. Proper processing as a pharmaceutical grade bentonite would undoubtedly reduce this ingredient to a negligible quantity.

REFERENCES

- (1) Anderson, A. J., and Plein, E. M., *THIS JOURNAL*, **51**, 648(1962).
- (2) "British Pharmacopoeia," The Pharmaceutical Press, London, 1958.
- (3) "United States Pharmacopoeia," 15th rev. Mack Printing Co., Easton, Pa., 1955.
- (4) Kilmer, V. J., and Alexander, L. T., *Soil Sci.*, **68**, 15 (1949).
- (5) Olmstead, L. B., Alexander, L. T., and Middleton, H. E., *U. S. Dept. Agr., Tech. Bull. No. 170*, 1930.
- (6) Lyon, T. L., and Buckman, H. O., "The Nature and Properties of Soils," 4th ed., The MacMillan Co., New York, N. Y., 1943, p. 49.
- (7) Steele, J. G., and Bradfield, R., *Amer. Soil Survey Assoc.*, **15**, 88(1934).
- (8) Hauser, E. A., and Hirshon, S., *J. Phys. Chem.*, **43**, 1015(1939).

⁷ The Magcobar Mining Co. lease located at Rosalind, Alberta.