OKLAHOMA
GEOLOGY
NOTES

Cover Picture

North Fork of Salt Creek Canyon

In this southeastward view of the North Fork of Salt Creek Canyon, the Shimer Gypsum is shown capping the northeastern (left) wall, with the Nescatunga and Medicine Lodge gypsum beds forming ledges below. These three units are members of the Permian Blaine Formation and produce, or have produced, a major part of the gypsum and anhydrite from this area. Both the Blaine and the Cloud Chief (also Permian) contain vast reserves of high-purity gypsum and anhydrite quarried primarily for use in construction materials.

This photograph is from Oklahoma Geological Survey Guide Book X, *Common Minerals, Rocks, and Fossils of Oklahoma*, by W. E. Ham and N. M. Curtis, Jr., and was taken from the top of the Blaine escarpment in Blaine County (sec. 23, T. 18 N., R. 12 W.). The Ferguson Salt Plain, covered with precipitates from salt-saturated solutions from springs in the underlying Flowerpot Shale, lies between 200 and 250 feet below this escarpment.

—P. W. W.

ABSTRACTS OF OKLAHOMA GEOLOGY PAPERS GIVEN AT MID-CONTINENT A. A. P. G. MEETING

September 28 and 29

Seven of the nineteen papers presented September 28 and 29 at the Mid-Continent Regional Meeting of the A. A. P. G. in Wichita, Kansas, dealt either directly or indirectly with Oklahoma geology. With the exception of that by F. H. Manley, Jr., the abstracts of those papers, printed here, also appeared in the August issue of the A. A. P. G. Bulletin.

Permission of the authors and of N. C. Smith, Executive Director of the A. A. P. G., to publish this material is gratefully acknowledged, as is the cooperation of G. W. Pike, convention co-chairman, who provided copies of the abstracts.

Early Paleozoic Overlap, Southern Mid-Continent

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Cambrian volcanics and Precambrian basement rocks produced an irregular topography in the Mid-Continent during intermittent Late Cambrian-Early Ordovician inundations. Large islands remained until Roubidouxian time; highest peaks persisted until Mississippian. The Early Paleozoic sequence is thickest in interisland channels of northeastern Oklahoma and in the more rapidly and uniformly subsiding basinal area of southern Oklahoma.

Dresbachian transgression, spreading westward, northward, and possibly southward, failed to reach most of Kansas and northern Oklahoma. During Franconian time, only southern Oklahoma and Missouri received sediments; Trempealeauan inundation covered all but central Kansas and the islands of northeastern Oklahoma. Sandstone and carbonate comprise the Cambrian.

Following post-Cambrian regression, Ordovician seas spread a blanket of carbonate over most of Oklahoma and Kansas. Sandstone is most abundant at the base of the Gasconade in eastern Oklahoma. It is also common in Roubidouxian rocks.

Paleogeographic maps and a worm's eye view map illustrate the intermittent nature of the transgressions and emphasize the inherent problems of time correlation.

Some Interesting Aspects of Carbonate Oil Accumulation in the Mid-Continent Area

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Close sample studies are necessary to evaluate properly the porosity and permeability characteristics of carbonate reservoirs. The depositional porosity fabric and resultant permeability are varied in

carbonates and may range from highly porous, impermeable chalks to somewhat less porous, but highly permeable, intergranular porosity present in carbonate banks, which may be composed of pellets, oölites or admixtures of fragmental debris. The presence of fossil cavities, calcispheres, and occasional reefoid deposits may modify the overall fabric. In addition to these depositional characteristics, tectonism can alter the basic porosity-permeability relationships through fracturing, recrystalization and/or tectonic dolomitization.

Cases are known where several of these various types of porosity are present in a single deposit and influence log analysis in either a negative or positive manner. A nonpermeable chalk or calcisphere porosity carrying high water saturation may produce oil if the fracture fabric or associated intergranular permeability is oil-bearing. Likewise, the reverse may be true if non-producible oil is trapped in the high porosity-low permeability deposits and the more permeable fracture and/or intergranular porosity is water-bearing.

The presence of these varied porosity fabrics can be recognized in samples, and a method of logging and estimating the importance of the different types is suggested. Utilization of well-sample data coordinated with realistic log analysis can lead to successful completion in zones which might be overlooked in a cursory log analysis. Examples of these sedimentary types from the Mid-Continent area are discussed and illustrated.

Use of Clay Mineralogy in Determining Source of Basin Sands

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In some areas, the usual methods of geological interpretation of possible source areas using conventional subsurface techniques, petrography, bulk mineralogy and conventional heavy-mineral studies have yielded inconclusive results. A relatively new method is the utilization of clay-sized material, in particular the clay minerals and clay-mineral assemblages, present in shale, carbonate, and sandstone samples. This is of special interest to petroleum exploration because the usual kind of subsurface sample retrieved, while not of sufficient quantity or quality for standard studies, yields an abundant supply of readily identifiable clay minerals and other clay-sized material which, with supporting subsurface information, can unravel some of the most complex provenance studies.

Clay-mineral assemblages not only aid in determining source areas, but they also can be used reliably to help correlate, zone, and interpret the depositional history of sedimentary sequences. Such is the case in the Lower Cretaceous Trinity Group, southern Oklahoma. Approximately 95 percent of the 200-mile exposure trend of the Trinity Group, consisting of bedded to poorly indurated clays, loosely cemented fine to coarse sands, conglomerates, both coarse and fine, and locally, marl and limestone, contains no persistent marker units or diagnostic fossils. In this study, interpretation of the clay-mineral

assemblages and distribution and provenance clay petrology indicate that the areal and stratigraphic distribution of the clay minerals (1) is related to their paleogeographic positions in the original basin of deposition, (2) reflects variations in contributions from various source areas, (3) indicates that the clay minerals are primarily detrital in nature, and (4) can be used to determine the source of basin sands. Further clay-mineral studies, supported by gravel orientation studies and subsurface information, also indicate (1) the nearshore site of active sedimentation transgressed northwestward with a northwestward sea advance; (2) the rocks at the base of the Trinity Group become younger toward the northwest by successive onlap; (3) the general shoreline trend during deposition of the Trinity Group was southwest-northeast, not east-west as generally considered.

The assumption that the clay minerals are primarily detrital in origin and are related to their original paleogeographic position in a basin reflecting the composition of the source area is a practical working hypothesis on a "first-approximation" basis. This assumption is practical for all clay-mineral studies for all basin sands unless there is evidence (such as diagenesis, size sorting, etc.) to the contrary.

Stratigraphic Applications of Dipmeter Data in the Mid-Continent

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Dipmeter techniques recently developed to solve Mid-Continent stratigraphic problems use short-correlation-interval dip computations and a statistical approach to interpretation. These techniques extend dipmeter interpretation methods first introduced in Tertiary formations along the Gulf Coast.

Paleozoic sands, as in the Pennsylvanian section of the Anadarko basin, often are deposited on surfaces of low dip and low topographic relief. Lithologic unit boundaries usually are nearly parallel, providing little information with which to predict the direction of improved sand development. Here, cross-stratification anomalies produce most of the dips computed.

To detect cross-bedding and describe its orientation within thin sedimentary units, correlation intervals must be short, yielding computed dips for every few feet of hole. Correlations are influenced by many factors, including the attitude of the underlying surface at the time of deposition and subsequent tilting. Many of the dips computed are due to current-bedding, and indicate the direction of sediment transport.

Random variations in sedimentation tend to confuse a superficial study of the data. To emphasize trends and minimize random events, statistical methods are used. Azimuth frequency diagrams and modified Schmidt plots reveal the direction of sediment transport, the direction of interval thickening, and present structural dip. These methods produce greater accuracy and confidence in orienting and extrapolating sand isopachs.

The Depositional Environments of the Spiro Sands in the Arkoma Basin

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Isopach maps, electric log cross-sections and Kodachrome slides of the Spiro sands in Wilburton, Kinta, and Milton-Cartersville fields are used to illustrate the author's interpretation of the depositional environment of these sands in the Arkoma basin.

At least three sands, differing genetically and in age, have all been termed the Spiro sand in the Arkoma basin.

In the Wilburton field, the Spiro sand appears to be a marine facies of the Wapanucka lime and possibly Morrowan in age.

Such characteristics as geometry of the sandstone bodies, sedimentary structures, composition, nature of the boundaries and other features, lead the author to believe that in the Kinta and Milton-Cartersville areas the Spiro sands were deposited in an environment likely to produce channel, as well as transgressive, unconformity sand deposits.

Application of Trend Analysis to Pre-Morrow Surface, Southeastern Hugoton Embayment Area

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Trend analysis is a technique used to distinguish between trends, such as regional dip or thickening, which may influence a whole region under consideration, and small-scale effects (anomalies) which are locally influential. Insofar as oil and gas fields are nearly always associated with anomalies or departures from the regional trend, whether governed by structural, thickness or lithologic factors, trend analysis should prove to be an important prospecting tool.

The electronic computer has permitted the application of trend analysis and numerous other techniques to large areas by the oil industry. A procedure involving the computer has obvious advantages in that it provides a degree of rigor that more elementary methods lack and reduces considerably the amount of time involved in computation.

Application of the technique to the pre-Morrow surface in the southeastern part of the Hugoton embayment using few control wells reveals objectively the combined topographic and structural relief that existed prior to Pennsylvanian deposition. With few exceptions, Morrow sandstones, and hence production, are found empirically to be related to the flanks of structures or in depressions.

A Basis for Red Fork Sand Exploration in Northwest Oklahoma

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The Red Fork Sand produces oil and gas over a large area of north-central Oklahoma. There are indications that several oil fields

comparable to the Burbank field (0.5 billion barrels) can be found in northwestern Oklahoma during the next few years by using available well control for detailed reconstruction of the depositional environments of the Red Fork Sandstone.

The Red Fork Sand was deposited west of the Nemaha ridge during "Cherokee" (Desmoinesian) time in a large embayment called the Enid embayment. There were two early phases of offshore bar deposition, followed by a brief period when the sea receded from the area and channel sands were deposited. Using this interpretation, several unusual problems can be explained.

The Oakdale field in southeastern Woods County has oil reserves of over 20 million barrels from the Red Fork Sand. The sand in this field is in two separate linear bands. The Southwest Wakita field in Grant County produces from two fairly distinct Red Fork Sand bodies that correlate with the sand at Oakdale. The Wakita trend in Grant County produces from a thin Red Fork Sand slightly higher stratigraphically than that at Oakdale and Southwest Wakita. In the Cheyenne Valley field in Major County, the Red Fork is interpreted as being a channel deposit, and it is higher stratigraphically than in the previously mentioned fields. This channel-type deposit is productive and fairly widespread over the Enid embayment, and it has several distinguishing characteristics.

By reconstructing the depositional environment of the Red Fork Sandstone and by interpreting this interval as representing three fairly distinct phases, the Red Fork is seen to be a reservoir with great potential in the Anadarko basin. There are several good indications where major producing areas are located, and they can be found by basing an exploration program on detailed reconstruction of depositional environments to explain the problems that arise, and to make interpretations necessary to find prospective Red Fork Sand trends.

Determination of Cation-Exchange Capacity by Continuous Titration

Raymond L. Kerns, Jr.*

INTRODUCTION

The surface chemical properties of clays are of great interest to clay mineralogists, and numerous studies on clay surface chemistry have been conducted in order to characterize, identify, classify, and better understand the properties of clay minerals. Some of the more economically and industrially oriented uses of clay materials are directly related to these properties. One of the more striking manifestations of the surface chemistry of a clay is its cation-exchange capacity, that is, the degree to which some of the chemically bonded ions may be removed or reversibly exchanged by treatment with various reagents.

Volk and Jackson (1964) demonstrated that clay minerals have several definite types of surface sites to which ions may become attached with varying degrees of tenacity. Some of these sites are on the crystallite edge and others in the so-called interlayer positions; some may accommodate positively charged ions, others, anionic constituents. The source of the charges which supply the bonding energy are not peculiar to clay minerals or colloidal sized particles. These unsatisfied structural charges are due to broken bonds at the crystal surface, vacancies or defects in the lattice, charge deficiencies resulting from the isomorphous substitution of ions with different charges, and/or exposed H^+ ions of lattice hydroxyls. These are properties of macroscopic and microscopic sized materials as well as those of sub-microscopic and colloidal sized particles. The effect of these properties is enhanced, however, by the extremely small size of clay-mineral particles, that is, by the increased ratio of total surface area to volume, which accompanies a reduction in particle size. However, simple physical reduction of clay particle size does not necessarily produce a direct linear increase in surface chemical reactivity. Other factors such as the accessibility of interlayer sites must also be considered. Surface properties do become more significant, though, when dealing with clay-sized particles rather than with more coarsely crystalline substances.

Table I contains data on the variations of cation-exchange capacities of a kaolinite (Harman and Fraulini, 1940) and three illites (Grim and Bray, 1936) as a function of the particle size. It is clearly illustrated that a decrease in the particle size of these materials results in an increased cation-exchange capacity.

There have been several methods devised for measuring the total cation-exchange capacity of clay minerals, among them the titration technique presented in the following pages. After converting the clay to an H^+ form, it is then titrated with a standardized base, and pH readings are taken after successive additions of reagent. The cation-exchange capacity is then extrapolated from a titration curve plotted

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from the resulting data. The advantages and disadvantages of the technique are also discussed.

TABLE I.—VARIATION OF CATION-EXCHANGE CAPACITY
AS A FUNCTION OF PARTICLE SIZE

| | ILLITE[†] | | KAOLINITE[††] | |
	ESD[*]	CEC[**]	ESD[*]	CEC[**]
Sample 1	0.1 -1.0	18.5	10 -20	2.4
	0.06-0.10	21.6	5 -10	2.6
	0.06	33.0	2 - 4	3.6
			0.5 - 1	3.8
Sample 2	0.1 -1.0	13.0	0.25- 0.50	3.9
	0.06-0.10	20.0	0.25- 0.10	5.4
	0.06	27.5	0.10- 0.05	9.5
Sample 3	0.1 -1.0	20.0		
	0.06-0.10	30.0		
	0.06	41.7		

† Grim and Bray, 1936.
†† Harman and Fraulini, 1940.
* Equivalent spherical diameter in microns.
** Cation-exchange capacity in milliequivalents per 100 gms dry clay.

THE TITRATION METHOD

Sample preparation.—The cation-exchange information most useful to the clay mineralogist is obtained from size-fractioned samples, or at least from particle-size classes small enough to eliminate non-clay constituents. For commercial clay petrological or soil information it is sometimes desirable to determine the CEC of bulk samples. Because wet sieving is a necessary part of the procedure outlined here, bulk samples should be crushed to 325 mesh. Previously size-fractioned samples which contain particles less than 43 microns ESD (equivalent spherical diameter) need not be so finely powdered. In this case, 80 mesh is sufficient. Cation-exchange capacities are usually reported as milliequivalents per 100 gms of oven-dried clay (meq/100 gms dry basis). Samples are usually oven-dried between 105 and 120 °C, as temperatures in this range are probably sufficient to drive off the absorbed water from most clay minerals. Differential-thermal-analysis curves indicate that part of the interlayer water of vermiculite and Mg-interlayered montmorillonite may be retained to slightly over 200 °C. In order to keep sample treatment as consistent as possible, all clay samples should be dried at the same temperature, and a temperature of 220 °C is suggested.

The cation-exchange capacity of a clay may be reduced after heat treatment, and although temperatures affecting the CEC are usually greater than 200 °C, it is better to weigh air-dried clay samples for cation-exchange work. The weight of the oven-dried sample may be used after weight losses have been determined at 200 °C on separate cuttings of the same sample.

Cation-exchange experiments should be conducted with the greatest precision possible so that data on different materials may be directly compared. Some of the factors that affect CEC and the shape of the titration curve are the sample concentration or weight-percent of clay in suspension and the type of base used in the titration. The same clay material will ordinarily have different exchange capacities with bases of different cations. The base (usually sodium hydroxide) and the same clay suspension concentration should be used for all samples. Gains in volume during titration should also be consistently maintained. The cation-exchange capacities of montmorillonites and vermiculites are more sensitive to concentration variations than are the illites, kaolinites, and other clay minerals.

The necessary sample weight is controlled by the experimental system, and the volume of base that may be added, by the size of the buret being used. A 5-ml microburet permitting direct reading to 0.01 ml and estimation to 0.001 ml is satisfactory; a single titration run should be completed without refilling the buret.

A 1-2 gm clay sample dispersed in 500 ml of distilled water provides a suspension that is dilute enough (0.20 to 0.40% by weight) to assure noninterference of the clay particles. Assuming a theoretical or average CEC for a particular clay mineral, and a volume of 2.5 ml of base added to reach the end point, a functional normality (N) may be calculated from the formula:

$$N = \frac{C\,W}{100\,V} \qquad (Eq.\ 1)$$

where C is the cation-exchange capacity in meq/100 gm dry clay, W is the sample weight in grams, and V is the volume of standard base to be added. With the above conditions of sample weight (1 gm) and volume (2.5 ml), and assuming an average CEC of 100 meq/100 gms for montmorillonite, a normality for the base of 0.4N is obtained. For illites with a theoretical CEC of 25 meq/100 gms dry clay, a 0.1N NaOH standard solution is ideal. Table II lists experimental conditions for measuring the CEC of various clays. The range of cation-

TABLE II.—DATA FOR CATION-EXCHANGE TITRATION SYSTEMS

	CEC[*]	CEC (THEORETICAL AVERAGE)	DRY SAMPLE WEIGHT (GMS)	VOLUME (ML)	NORMALITY
Montmorillonite and vermiculite	80-150	100	1	2.50	0.4
Endellite, 4H$_2$O (Halloysite, 4H$_2$O)	40- 50	45	2	2.25	0.4
Illite and chlorite	10- 40	25	1	2.50	0.1
Sepiolite-attapulgite -palygorskite	20- 30	25	1	2.50	0.1
Kaolinite	3- 15	9	2	1.80	0.1
Halloysite, 2H$_2$O	5- 10	7	2	1.40	0.1

[*]From Grim, 1953 (p. 129); in meq/100 gms dry clay at pH 7.

exchange capacities, average values, sample weight, and volume of base required to reach the theoretical end point are included.

The carefully weighed samples should be dispersed in about 250 ml of distilled water in a 1-liter erlenmeyer flask. This is best accomplished with a 15-minute treatment in an ultrasonic generator tank. If the clay tends to clump, as some montmorillonites do, prolonged agitation with a mechanical shaker may be more effective.

Conversion to hydrogen form.—After the clay is thoroughly dispersed, a suitable acid reagent must be added to remove all exchangeable cations from the clay. Dowex 50W-X4 resin in the H^+ ionic form is ideal for this purpose. A resin weight of 10 times the theoretical amount necessary to completely exchange the clay should be added to the dispersed clay in the flask. Care should be taken not to lose any of the suspension which may have splashed onto the rubber stopper or the neck of the container; a wash bottle filled with distilled water is useful for rinsing this material back into the flask. The Dowex resin has an exchange capacity of 5.4 meq/gm dry basis. The resin is ordinarily in the wet form, however, and has a moisture content of 67.1%. Therefore, the exchange capacity of the wet resin is 1.8 meq/gm. The average CEC of montmorillonite is 100 meq/100 gms (1 meq/gm) dry basis, so about 6 gms of resin should be added to a 1 gm sample of montmorillonite. About 1.5 gms of resin will efficiently strip 1 gm samples of illite which have an average CEC of 25 meq/100 gms dry basis.

The suspension-resin mixture should be shaken slowly for about 4 hours, after which the suspension may be separated from the resin by sieving into 1-liter beakers. A 325 mesh wet sieve is small enough to catch the Dowex 50W-X4 resin. Wet-screen analyses report 99.5% of the resin beads are caught on a 70 mesh screen. The sieves and beakers should be thoroughly cleaned and rinsed with distilled water several times before using. After pouring the suspension through the screen, remove any remaining clay from the resin and sieve with a wash bottle. The flask should be rinsed several times with 50 ml of distilled water and this material also poured through the screen; the total volume should be increased to the necessary amount (500 ml is suggested) by adding distilled water. Care should be taken to avoid losing any of the clay.

Titration.—Cation-exchange data may be obtained by titrating the hydrogen-clay suspension, prepared in preceding steps, with a standard base. The method requires measurement of the initial pH of the H^+-clay suspension followed by the addition of a predetermined amount of standard base, stirring time to allow for equilibration, and measurement of the resulting pH. Titration is continued through the end point of the reaction (at a pH around 7) and until the titration curve begins to level off (usually around a pH of 9 to 11).

The size of the titration aliquot added each time depends on the normality of the suspension, the standard base used, the amount of sample, and the expected CEC of the clay. To obtain a detailed titration curve, a minimum of 12 measurements should be made before a pH of 7 is reached. For montmorillonites and illites titrated under the

experimental conditions outlined in table II, an aliquot of 0.2 to 0.25 ml is small enough. When a 5-ml microburet is used, this ordinarily amounts to the successive addition of 4 to 6 drops of base. This is somewhat variable and should be established for each buret.

After the addition of each titration aliquot a minimum equilibration time of 20 minutes should be allowed before a pH reading is taken. The suspension may be stirred while waiting with a magnetic stirring plate and stirring rods immersed in the clay suspension. The rods should be washed off and rinsed with distilled water before being put into the suspension. This equilibration time is not extremely long if three samples are processed at the same time.

Buret readings should be taken immediately before and after the addition of base and recorded on a data sheet. This serves as a check for base which might have been lost by leaking of the buret. The time that each titration step was performed should also be recorded. Table III is a sample data tabulation of a CEC titration of a 0.05-1.0 micron ESD sample of bentonite, API sample 25 from Upton, Wyoming (Kerr and others, 1950).

Cation-exchange capacity in meq/100 gms dry clay for each successive step may be computed by the formula:

$$CEC = \frac{NV}{W} \times 100 \qquad (Eq.\ 2)$$

where N is the normality of the base being used, V is the cumulative volume of base added in milliliters, and W is the dry sample weight in grams.

Experimental considerations.—The significance of data obtained using any cation-exchange capacity technique depends upon the reproducibility of the method. This is directly related to the experimental design, limitations of the method, and the techniques of the analyst. Acceptable data should not be expected if the various steps of sample preparation, titration, and pH measurements are not performed with precision. Sample weight and weight-loss determinations should be as accurate as possible. Extreme care should be taken so that none of the clay sample is lost during dispersion and stripping. The bead of liquid that usually remains on the tip of the buret after titration should be added to the suspension by rinsing the tip with a small amount of distilled water. The suspension remaining on the pH meter electrodes should also be washed back into the beaker after each reading has been made. The total gain in volume of the suspension should be consistent throughout the experiment and the final volume should always be the same. Titrations should be carried well beyond a pH of 7 to permit extrapolation of the CEC from the resulting curve.

The calibration of the pH meter should be checked occasionally. If the meter is allowed to warm up for several hours before titration is begun, drift will be minimal, even through longer experiments. The pH meter is calibrated to a pH of 7 of the standard buffer solution at 25 °C. Temperature of the clay suspension should be measured periodically so that proper adjustment of the pH meter can be made, as pH varies slightly with temperature changes. There will ordinarily be a

temperature increase of a few degrees during the experiment from stirring the sample.

Presentation of data.—Data obtained from titration is usually plotted graphically with pH on the ordinate and values for the CEC in meq/100 gms dry basis along the abscissa. The cation-exchange capacity of the 0.05-1.0 micron bentonite from Upton, Wyoming, (table III) is presented graphically in figure 1. Cation-exchange data for the 0.05-1.0 micron bentonite, API sample 20, from Lorena, Mississippi, is also included. These analyses were performed in triplicate and the CEC interpreted from the curves at a pH of 7. These data are listed in table IV and compared with values from the literature for these clays.

The total CEC may be taken at one of several points along the curve, the specific choice depending upon the analyst. Because of the popularity of the ammonium acetate isotherm technique, the exchange

TABLE III.—DATA SHEET FOR CATION-EXCHANGE TITRATIONS*

TIME	NO.	INITIAL	FINAL	INCREMENT (ML)	PH	CUMULATIVE VOLUME (ML)	CEC†
	1	0.141	0.141	0	3.18	0	0
8:15 a.m.	2	0.141	0.267	0.126	3.29	0.126	4.88
8:40	3	0.321	0.434	0.113	3.31	0.239	9.26
9:05	4	0.434	0.571	0.137	3.39	0.376	14.56
9:25	5	0.571	0.704	0.133	3.42	0.509	19.71
9:44	6	0.704	0.833	0.129	3.48	0.638	24.71
10:10	7	0.833	0.955	0.122	3.52	0.760	29.44
10:35	8	0.955	1.099	0.144	3.60	0.904	35.01
11:00	9	1.099	1.220	0.121	3.70	1.025	39.71
11:25	10	1.220	1.350	0.130	3.80	1.155	44.74
11:50	11	1.350	1.478	0.128	3.90	1.283	49.70
12:15 p.m.	12	1.478	1.610	0.132	4.03	1.415	54.81
12:40	13	1.610	1.730	0.120	4.20	1.535	59.47
1:05	14	1.730	1.865	0.135	4.40	1.670	64.69
1:30	15	1.865	2.000	0.135	4.81	1.805	69.92
1:50	16	2.000	2.132	0.132	5.40	1.937	75.04
2:15	17	2.132	2.268	0.136	5.87	2.073	80.31
2:40	18	2.268	2.391	0.123	6.20	2.196	85.01
3:05	19	2.391	2.525	0.134	6.57	2.330	90.26
3:30	20	2.525	2.653	0.128	7.01	2.458	95.21
3:55	21	2.653	2.785	0.132	7.79	2.590	100.3
4:20	22	2.785	2.923	0.138	8.95	2.728	105.7
4:40	23	2.923	3.051	0.128	9.35	2.856	110.6
5:00	24	3.051	3.185	0.134	9.70	2.990	115.8

Plus 4 more titrations to pH 10.5

* Sample: bentonite, Upton, Wyoming, API 25b; .05-1.0 ESD; normality of base — 0.3938N NaOH; sample weight (air dried) = 1.000 gm; weight loss at 220 °C = 7.58%.
† Meq/100 gms at 220 °C, oven-dried basis.

TABLE IV.—CATION-EXCHANGE CAPACITIES FOR TWO
API MONTMORILLONITES (BENTONITES)

		API 20 (LORENA, MISS.)	API 25B (UPTON, WYO.)
CEC[1]:	Titration 1	117	96
	Titration 2	114	94
	Titration 3	116	98
	Mean	116±2	96±2
	Maximum deviation	1.3%	2.1%
CEC[2]:	API value	117	95
Deviation of experimental CEC value from API value		1.0% low	2.1% high

[1] Milliequivalents of NaOH per 100 gms of clay, oven dried at 220 °C.
[2] From Kerr and others (1950). Values determined by ammonium acetate isotherm method; milliequivalents per 100 gms of clay, oven dried at 105 °C.

capacity at pH 7 (point A, fig. 1) is frequently reported. Others reason that the reaction is complete at a point in the vicinity of B in figure 1, where a steep rise in the curve results from the addition of nonreacting base, but this point is difficult to define precisely on some titration curves. Still others, more familiar with titration curves for strong acids and bases, choose the inflection point of the curve (point C). This point is easily defined but is not accurate for the end point of a reaction involving a weakly acidic H^+ clay with a strong base. The slope of the curve is too small and variable for the inflection point to indicate the completion of the reaction (near point B). The curve position chosen is necessary information, however, and should be reported with the total CEC for the particular material.

For comparison, it is best to report the CEC of some standard sample which was measured with this same technique; a sample of the Wyoming bentonite is probably best for this experiment, because there is abundant published data on this material. There are undoubtedly purer materials which might be used, however.

Titration curves may also provide useful information on different types of surface reactions of a clay related to the different reacting sites on the particles. Jonas (1963) has demonstrated that there are at least two different reactions which may be observed in closely controlled cation-exchange measurements of H^+ montmorillonites. One is due to the acid nature of the edge sites, and the other is a result of interlayer exchange positions. The edge sites are completely exchanged at a lower pH than the interlayer sites and are responsible for a larger part of the total CEC as particle size decreases. This property probably accounts for the midrange hump (point D) in the titration curves of figure 1.

Advantages and disadvantages of the titration method.—A distinct advantage of the titration technique is that a reaction history of the material is provided after the data have been plotted. There is a definite
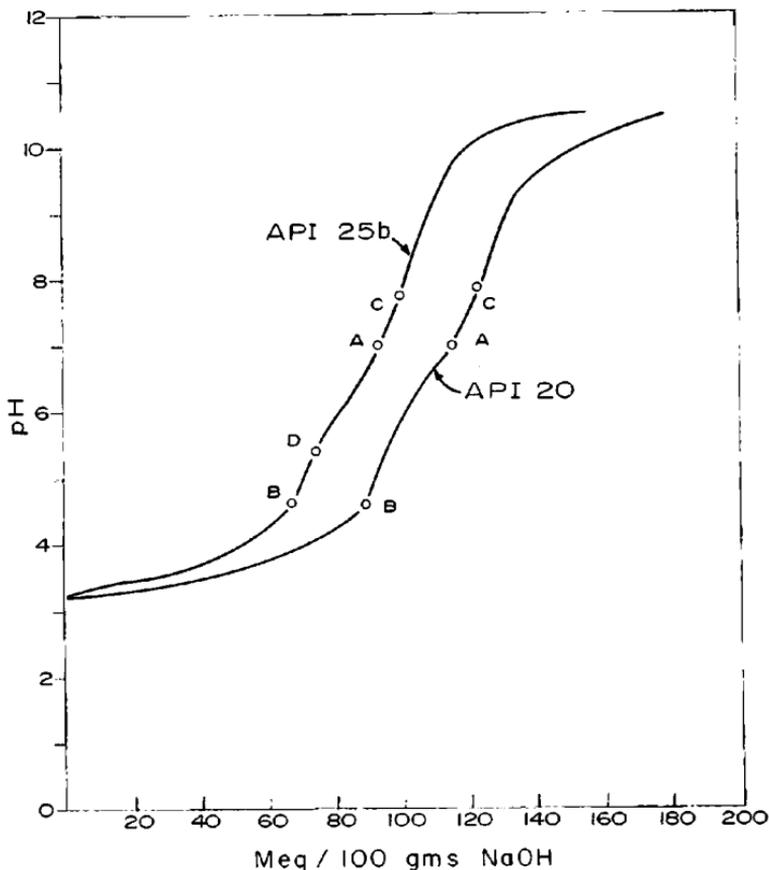
Figure 1. Cation-exchange capacity titration curves for two 0.05-1.0 micron ESD montmorillonites (bentonites): API 20 from Lorena, Mississippi, and API 25b from Upton, Wyoming.

disadvantage in that the exchange reaction takes place over a wide pH range, and though it is not known at this time what effect this has on the cation-exchange capacity, the effect is considered significant. The isotherm technique using ammonium acetate is carried out at a constant pH which effectively eliminates this factor.

The conversation of the clay to the H^+ form effectively removes all the surface cations, particularly when treatments are fairly rigorous. In the isotherm method, however, it is believed that K^+ ions are non-exchangable even in the case of expendable clays, and an extremely rigorous acid treatment of clays may result in an alteration of the structural lattice chemistry, such as selective removal of Al^{+3} ions

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from the tetrahedral layer. This would result in CEC data for a material that is structurally different from the original.

The titration method also provides information on the partial exchange capacities of the edge and interlayer-cation sites. However, for a detailed study of this sort, a large number of data points must be established. Longer equilibration times than ordinarily required for standard titration experiments may also be desirable. Due to the length of time involved in performing this experiment, it is more expedient to follow a revised program of sample treatment. A large number of samples of equal weight may be converted to the hydrogen form with some uniform stripping technique, after which the samples may be titrated with varying amounts of standard base and the total volume of suspension brought to the same level for all samples. These samples may then be allowed to equilibrate for as long a time as is convenient and pH readings made at some later date. The only disadvantage to this technique is that some of the samples remain for extended periods in an acid environment and others undergo a strong base treatment. The difference and significance of these extreme conditions are not fully known.

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