# BASELINE STUDIES OF THE CLAY MINERALS SOCIETY SOURCE CLAYS: CATION EXCHANGE CAPACITY MEASUREMENTS BY THE AMMONIA-ELECTRODE METHOD

D. BORDEN AND R. F. GIESE

Department of Geology, State University of New York at Buffalo, Buffalo, New York 14260, USA

## INTRODUCTION

The cation exchange capacity (CEC) of fine-grained materials, and especially clay minerals, is a fundamental property of these materials, and can be determined routinely. A search of the recent literature illustrates the great interest of this property to researchers. For example, a search of the GeoRef database for references to ''cation exchange capacity'' for the years 1980 to 1999 yields 2559 citations.

Methods of measurement are based on a determination of the quantity of a particular exchangeable cation, by a variety of means, expressed per 100 g of dry clay. These methods are principally chemical and spectroscopic. The present study describes the results of measurements made primarily on Source Clay minerals using a particularly simple, reliable and inexpensive method developed by Busenberg and Clemency (1973).

## METHODOLOGY

The method, in common with other procedures, involves the saturation of exchangeable cation sites with a chemical species, in the present case, ammonium cations. The ammonium-exchanged clay is dispersed in an alkaline solution of sodium hydroxide that releases the ammonium as dissolved ammonia gas. A specific-ion electrode then detects the signal from the ammonia dissolved in solution. Comparison of the signal from the unknown solution with a series of solutions containing known concentrations of ammonia yields the ammonia concentration and thus the cation exchange capacity.

## INSTRUMENTATION

The ammonia ion-selective electrode used was the HNU Systems Inc. model ISE-10-10-00 with a new ammonia membrane cap. The electrode was connected to an Orion Research Inc. model 720A pH/ISE Meter. Ammonia standards were made by diluting freshly prepared 0.1 M ammonium chloride. A Labconco Freeze Dryer 4.5 Model 77500 was used in the preparation of the clay samples for CEC analysis. All centrifugation was performed on an IEC Centra-8 centrifuge. A constant magnetic stirring rate was obtained by connecting a Fisher Stirrer Model 120MR to a Su-

perior Electric Co. Powerstat Variable transformer (Type 3pn116B) set such that there was maximum stirring with no vortex. Complete mixing during various washes was assisted by using a VWR VAR1-WHIRL test-tube mixer set at the maximum fast speed. Reagent solutions were adjusted to pH 7.00 as monitored by a Sensorex combination pH electrode (Model S200C). Additions of either dilute ammonium hydroxide or acetic acid were added drop-wise as necessary.

## SAMPLE PREPARATION

Seven clays (Table 1) from the Source Clays collection of the Clay Minerals Society (synthetic mica-montmorillonite (Syn-1) was not included in this study) were used as supplied (*i.e.* with the fine size-fractions collected using centrifugation and then freeze dried). Details of the preparation of the Source Clays are described elsewhere in this volume. The non-Source Clay samples, BP Mineral Colloid, Laponite RD, and Laponite RDS (all from Southern Clay Products, Gonzales, Texas) were used directly from the original shipping container. Triplicate 2.0 g samples were ammoniated with a solution (pH 7.00) of 1 M ammonium acetate ($NH_4Ac$) for three days. After the supernatant liquid was decanted, the samples were ammoniated again for 3 d with a 1 M $NH_4Ac$ solution. The ammoniated clay was collected, using centrifugation for 10 min at 3000 rpm, and then each sample was washed with 20 mL of 1 M $NH_4Ac$ five times. This was followed by four washes using 20 mL aliquots of 1 M $NH_4Cl$ (adjusted to pH 7.00) and one wash using a 20 mL aliquot of 0.25 M $NH_4Cl$ (adjusted to pH 7.00). The samples were then washed with methanol until a negative silver nitrate test for residual chloride ions was obtained, followed by an additional methanol wash. The ammoniated clay samples were covered with a clean tissue held in place with a rubber band and allowed to air-dry without heating. Once the samples were dry, any clumps were broken apart with a glass stirring rod.

Samples were weighed into clean 150 mL Pyrex beakers; the sample weights were selected to keep the final ammonia concentrations between $10^{-4}$ and $10^{-1}$ M, which is the range covered by the standard solutions. The weights varied between 100 mg for the mont-

Table 1. Summary of the CEC measurements (meq/100 g) of the Source Clay minerals, along with Laponite and Mineral Colloid BP samples.

| Type | Identity | CEC | Standard deviation |
|------|----------|-----|--------------------|
| Laponite | RD | 47 | 4 |
| | RDS | 91 | 4 |
| Kaolinite | KGa-1b | 3.0 | 0.1 |
| | KGa-2 | 3.7 | 0.1 |
| Palygorskite | PFl-1 | 17.5 | 0.2 |
| Montmorillonite | SHCa-1 | 66 | 4 |
| | SWy-2 | 85 | 3 |
| | BP | 84 | 3 |
| | STx-1 | 89 | 2 |
| | SAz-1 | 123 | 3 |

morillonite clay samples and 400 mg for kaolinite and palygorskite.

After the Orion 720A was calibrated with standard $NH_4Cl$ solutions of various concentrations and repetitive experiments showed that the pH/ISE meter-electrode drift was minimal, 50.0 mL of deionized water were pipetted into a sample beaker containing the clay and a 1.27 cm (0.5 in) Teflon-coated magnetic stirring bar. After the electrode was immersed in the solution and tapped firmly to dislodge any air bubbles trapped on the ammonia membrane, the magnetic stirrer was started and 0.5 mL of 10 M NaOH was added with a push-button pipette. The readings of the electrode potential (in mV) were recorded at 30 s intervals until a constant reading was obtained.

To minimize the drift of the pH/ISE meter/electrode, each set of measurements of the six replicates of each standard clay was initiated with a measurement of the $NH_4Cl$ standards and the set was terminated by a similar measurement of the $NH_4Cl$ standards. The measurements of the initial $NH_4Cl$ standards were used to calculate the CEC for the first two clay samples. The average of the standards data for the initial and final standard $NH_4Cl$ experiments was used to calculate the CEC of the middle two samples and the final standard $NH_4Cl$ measurements were used to calculate the CEC of the last two samples.

## RESULTS

The concentrations of ammonia in the exchange positions of each clay sample were obtained from the equation:

$$CEC = \frac{50c}{w \times 10^{-5}}$$

where $c$ is the measured concentration of ammonia in mol/L, 50 is the volume of water added to the dry clay sample, $w$ is the weight of the dry clay sample, and $10^{-5}$ is a conversion factor (Busenberg and Clemency, 1973). The values reported here are based on the measurement of six replicates except for the Laponite samples, where only two replicates were examined. It is not clear why the standard deviations of the Laponite samples are larger than the standard clay samples.

## REFERENCES

Busenberg, E. and Clemency, C.V. (1973) Determination of the cation exchange capacity of clays and soils using an ammonia electrode. *Clays and Clay Minerals,* **21,** 213–217.

E-mail of corresponding author: glgclay@acsu.buffalo.edu