Transactions of the Korean Nuclear Society Spring Meeting
Jeju, Korea, May 9-10, 2024

Review of Test Methods for the Cation Exchange Capacity of Bentonite Buffer in a High-Level Waste Repository

Yunjin Choi [a], Byoungkwan Kim [b], Seokju Hong [b], Seokyoung Oh [b], Hyunmin Ma [b], Wooyong Um [b]*
[a]*Nuclear Environmental Technology Institute (NETI),*
Pohang University of Science and Technology (POSTECH), Pohang, Gyeongbuk 790–784, Republic of Korea
[b]*Division of Advanced Nuclear Engineering (DANE),*
Pohang University of Science and Technology (POSTECH), Pohang, Republic of Korea, 37673
**Corresponding author: wooyongum@postech.ac.kr*

***Keywords :** bentonite buffer, montmorillonite, isomorphous substitution, cation exchange capacity

1. Introduction

Since high-level radioactive waste generates a lot of heat due to radioactive decay, studies on its disposal are actively underway. Among them, a deep geological disposal system is considered as one of the preferred methods in many countries. Especially, multi barrier system is constituted of natural barriers and engineered barriers including canister, buffer and backfill [1].

Bentonite is the most commonly used material for engineering buffer and backfill materials. Bentonite contains a large amount of montmorillonite which has one octahedral sheet of alumina between two tetrahedral sheets of silica. Through isomorphous substitution occurring in this structure, the surface of bentonite is negatively charged and the surrounding cations are attracted to make it electrically neutral [2]. These charge-compensating cations can be replaced by other cations present in the aqueous solution, which is called cation exchange.

There are several standard methods for measuring cation exchange capacity (CEC), and those methods are slightly different [3-6]. In this study, we investigated and compared major four methods for measuring CEC. We considered the characteristics (pros and cons) of each method to implement the most suitable one for the conditions. Thus, we evaluated the limitations of these testing methods and their applicability to the various conditions.

2. Standard CEC test methods

2.1 Ammonium acetate method (EPA 9080)

This method is the most widely used one to determine the CEC, but not appropriate for calcareous soils (or soils with high Ca content) that readily dissolve in ammonium acetate solution, because the release of calcium carbonate limits the saturation of exchange sites by the ammonium ions. This may affect the results and cause the lower cation exchange capacity. Therefore, this experimental method may not be suitable for Korea in which Ca-bentonite is primarily studied to use. General procedure is shown below.

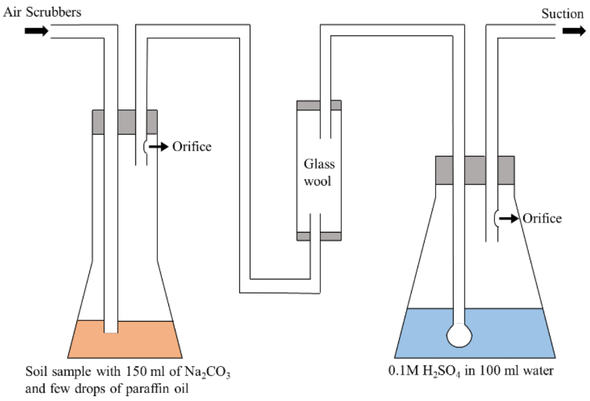

Fig. 1. Diagram of aeration unit for determination of absorbed ammonium

(i) Place 10 g of air-dried soil with particles smaller than 2 mm into a 500 ml Erlenmeyer flask and add 250 ml of neutral 1M NH_4OAc.
(ii) Shake the flask and allow it to stand overnight.
(iii) Use a 55 mm Buchner funnel to suction only the soil, taking care not to let it dry or crack.
(iv) Leach the soil with neutral NH_4OAc reagent until no calcium is detected in the effluent solution.
(v) Leach the soil four times with neutral 1 M NH_4OAc, followed by leaching with 0.25 M NH_4Cl.
(vi) Rinse the electrolyte using 150 to 200 ml of 99 % isopropyl alcohol. Once the chloride test in the leachate (using 0.1 M $AgNO_3$) becomes negligible, allow the soil to drain thoroughly.
(vii) Place an excess of 0.1 M standard H_2SO_4 in the 500 ml Erlenmeyer flask on the aeration apparatus.
(viii) Add 10 drops of methyl red indicator and add sufficient distilled water to make the total volume approximately 100 ml. Then, connect the flask to the apparatus.
(ix) Place the soil sample saturated with ammonium into the 800 ml Kjeldahl flask located in the flow line just before the Erlenmeyer flask with the standard acid.
(x) Add 150 ml of Na_2CO_3 solution and a few drops of paraffin oil into the flask, then connect it to the apparatus.
(xi) Turn on the suction at the end of the apparatus and set the airflow to 450 to 500 liters per hour.
(xii) Aerate for 17 hours (Fig. 1). Titrate the remaining acid in the absorption solutions using standard 0.1 M

NaOH solution until the color changes from red to yellow.
(xiii) Calculate adsorbed ammonium content from titration values.

2.2 Barium chloride method (ISO 11260)

This method is using barium instead of ammonium, but also subject to the interference of calcium present in calcite or gypsum in the sample. The formation of barium carbonate can reduce the accuracy of CEC. It is also affected by the presence of any soluble salts, providing values for exchangeable cations higher than the actual ones. By measuring the electrical conductivity of the soil sample, the presence of salts can be observed. General approach of this method is shown below.

(i) Place 2.5 g of air-dried soil with particles smaller than 2 mm into a 50 ml polyethylene centrifuge tube.
(ii) Add approximately 30 ml (with a tolerance of ± 0.1 ml) of 0.1M $BaCl_2$ solution to the tube.
(iii) Shake the tube for 1 hour, then centrifuge at 3000 g for 10 minutes.
(iv) Transfer the supernatant liquid to a 100 ml flask.
(v) Add 30 ml of 0.1 M $BaCl_2$ solution, then repeat this process twice, adding the supernatant liquid to the flask each time.
(vi) Fill the flask with 0.1 M $BaCl_2$ solution to the volume.
(vii) Place 30 ml of a 0.0025 M $BaCl_2$ solution into the soil cake and shake for one day. (If 2.5 ml of solution remains in the soil cake, the barium concentration will be about 0.01 M)
(viii) Centrifuge at 3000 g for 10 minutes and decant the supernatant liquid.
(ix) Add 30 ml (with a tolerance of ± 0.1 ml) of 0.02 M $MgSO_4$ solution to the sample substituted with Ba^{2+} and shake it overnight.
(x) Centrifuge at 3000 g for 10 minutes, then decant the supernatant liquid through coarse filter paper into a conical flask.
(xi) All the barium present in the solution or adsorbed will precipitate as insoluble barium sulfate and exchangeable ions will be immediately replaced by magnesium.
(xii) Measure the concentration of Mg^{2+} with ICP-AES.

2.3 Methylene blue method (ASTM C837)

This method can measure CEC in a short time and does not require expensive equipment. However, since the light blue halo is visually detected, it is difficult to clearly observe if faint colors appear. In addition, this method proceeds via molecular aggregation between organic dye and planar molecular, which can lead to the formation of dimers and higher species of methylene blue. Consequently, it leads to non-adsorption on an equimolar basis, which can result in inaccuracies in CEC measurements [5]. General approach of this method is shown below.

(i) Place 2 g of dried soil in a 600 ml beaker.
(ii) Add 300 ml of distilled water to the beaker and mix it until the clay is uniformly dispersed.
(iii) Add sulfuric acid and stir until the pH of the slurry is within the range of 2.5 to 3.8.
(iv) With the slurry remaining under the mixer, fill the buret with the methylene blue solution.
(v) Add 5 ml of the solution to the slurry and stir for 1-2 minutes.
(vi) Place a drop of the slurry on the edge of the filter paper.
(vii) Observe the appearance of the drop on the filter paper. The light blue halo around the drop signals that the end point has been reached.
(viii) Add the solution slowly to the slurry in 1.0-mL increments, stirring for 1-2 minutes after each addition. Continue until reaching the end point.

2.4 Cu-triethylenetetramine method (SKB TR-16-14)

In this method, the Cu-tri complex can be quantified by a spectrophotometer because it shows a very strong blue color. In addition, since cation exchange occurs in a short time, the result can be confirmed within 30 minutes. General approach of this method is shown below.

(i) Dry the bentonite sample in an oven at 40 °C to become less plastic.
(ii) Grind it using a ball mill at 200 rpm for 10 minutes.
(iii) Mix the ground bentonite (400 mg ± 10 mg) with 33 ml of deionized water and disperse on a vibrating table for 30 minutes.
(iv) Undergo ultrasonic treatment for approximately 15 minutes.
(v) Add 7 ml solution of 45 mM Cu-tri to achieve equilibrium with the copper solution.
(vi) Disperse the sample on the vibrating table for another 30 minutes.
(vii) Centrifuge it at 3000 RCF (relative centrifugal force) for 5 minutes.
(viii) Measure the spectrophotometer at 583 nm (absorption maximum) using a double-beam spectrophotometer.

3. Conclusions

Standard test methods for measuring CEC differ for each regulation. Ammonium acetate method and barium chloride method have difficulties in measuring accurate CEC because of calcareous soils that can be dissolved easily. Therefore, they are not appropriate in Korea because of Ca-bentonite primarily studied to use.

Excluding the aforementioned methods, we find the Cu-tri method to be more dependable in contrast to the methylene blue method, which experiences more interference in the formation of dimers and higher species. Here, we suggest Cu-tri method for measuring CEC of Ca-bentonite which will be used as a buffer in a high-level waste repository.

ACKNOWLEDGEMENT

This work was supported by the Institute for Korea Spent Nuclear Fuel (iKSNF) and Korea Foundation of Nuclear Safety(KOFONS) grant funded by the Korea government(Nuclear Safety and Security Commission, NSSC)(RS-2021-KN066110)

REFERENCES

[1] Smith, P., P. de Preter, and S. Voinis. "safety of deep geological repositories." NEA News 21 (2003): 1.

[2] Meyer, D., and J. J. Howard. Evaluation of clays and clay minerals for application to repository sealing. No. ONWI-486. D'Appolonia Consulting Engineers, Inc., Pittsburgh, PA (USA); Pennsylvania State Univ., University Park (USA), 1983.

[3] EPA METHOD 9080. Cation-exchange capacity of soils (ammonium acetate). 1986.

[4] QUALITY, ISO Soil. Determination of Effective Cation Exchange Capacity and Base Saturation Level Using Barium Chloride Solution. 2018.

[5] Bujdák, Juraj. "Hybrid systems based on organic dyes and clay minerals: Fundamentals and potential applications." Clay Minerals 50.5 (2015): 549-571.

[6] ASTM C837-09. Standard test method for methylene blue index of clay. 2014.

[7] SVENSSON, Daniel, et al. Developing strategies for acquisition and control of bentonite for a high level radioactive waste repository. Svensk Kärnbränslehantering AB, Swedish Nuclear Fuel and Waste Management Company, 2017.