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

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Abstract

Deep geological disposal systems for high-level radioactive waste employ a multi-barrier approach, combining natural and engineered barriers like bentonite. Bentonite is used as a buffer and backfill material due to its negatively charged surfaces with a high cation exchange capacity (CEC), which enhances radioactive metal ions absorption via cation exchange. In this study, four different methods for measuring the CEC of bentonite were investigated, focusing on factors such as cost, time, complexity, precision, clay affinity, and suitability of calcareous soil. The Cu-triethylenetetramine (Cu-tri) method was identified as the most suitable approach due to its high precision, low interference on calcareous soil, and high affinity for clay minerals.

High-level waste repository

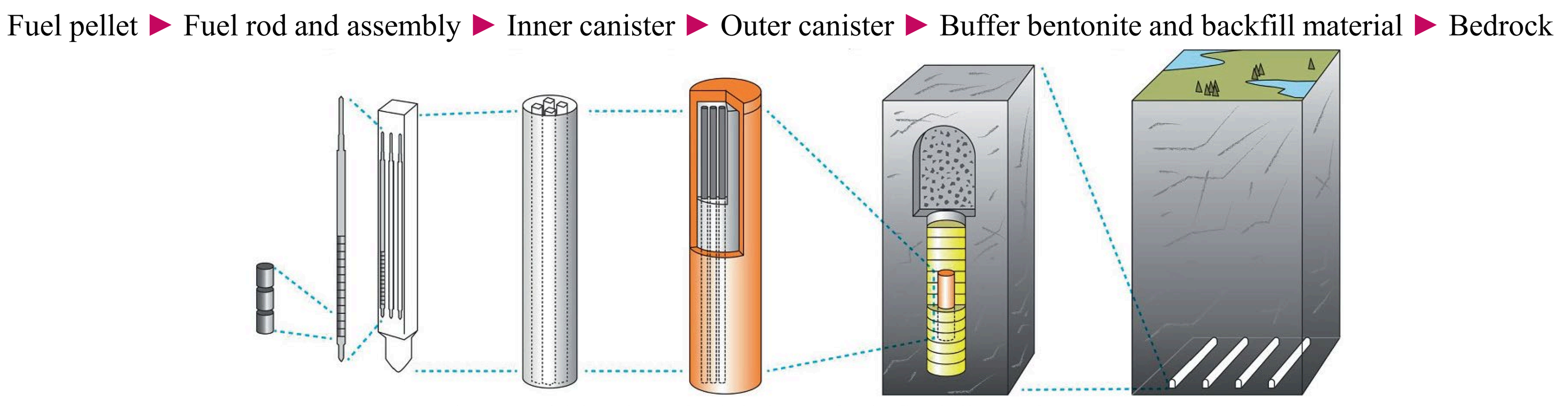

Fig 1. Multi-barrier principle in Posiva's final disposal concept

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].

Cation exchange

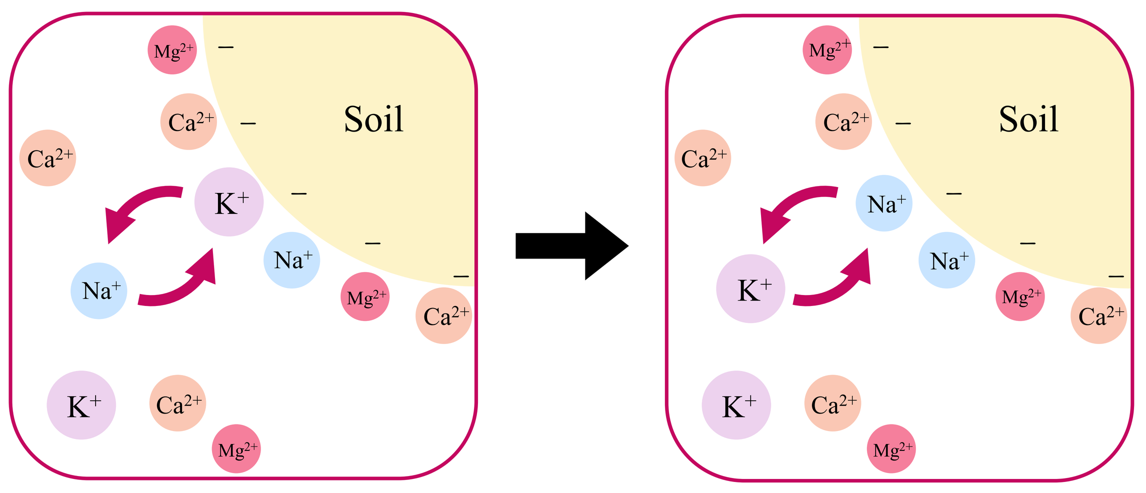

Fig 2. Process of cation exchange occurring in the soil

Bentonite is the most commonly used material for the 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.

Ammonium acetate method (EPA 9080)

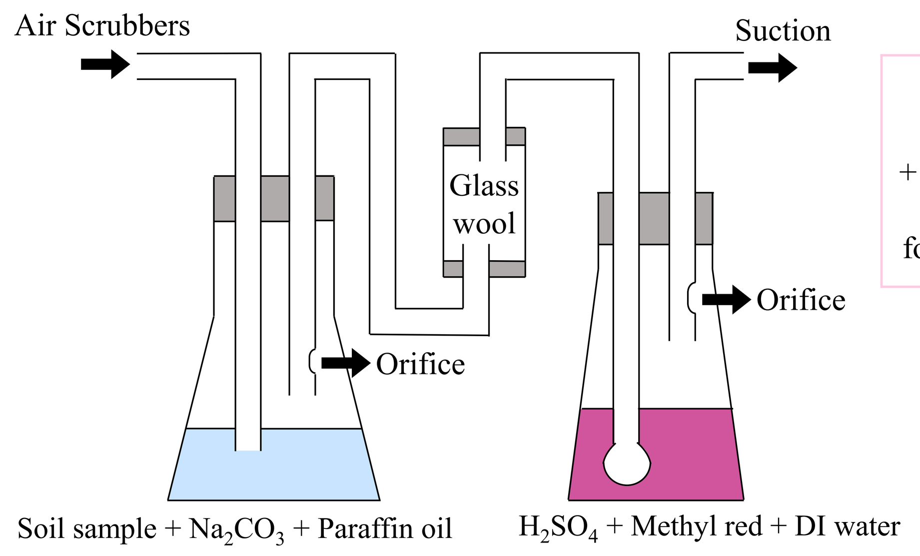

Fig 3. Diagram of aeration unit for determination of absorbed ammonium

- Due to its low hydration energy, NH_4^+ can penetrate the interlayers of clay, leading to the collapse of clay layers. Additionally, NH_4^+ is trapped between silicate sheets and excluded in cation exchange reactions. This can lead to errors in measuring the accurate CEC.

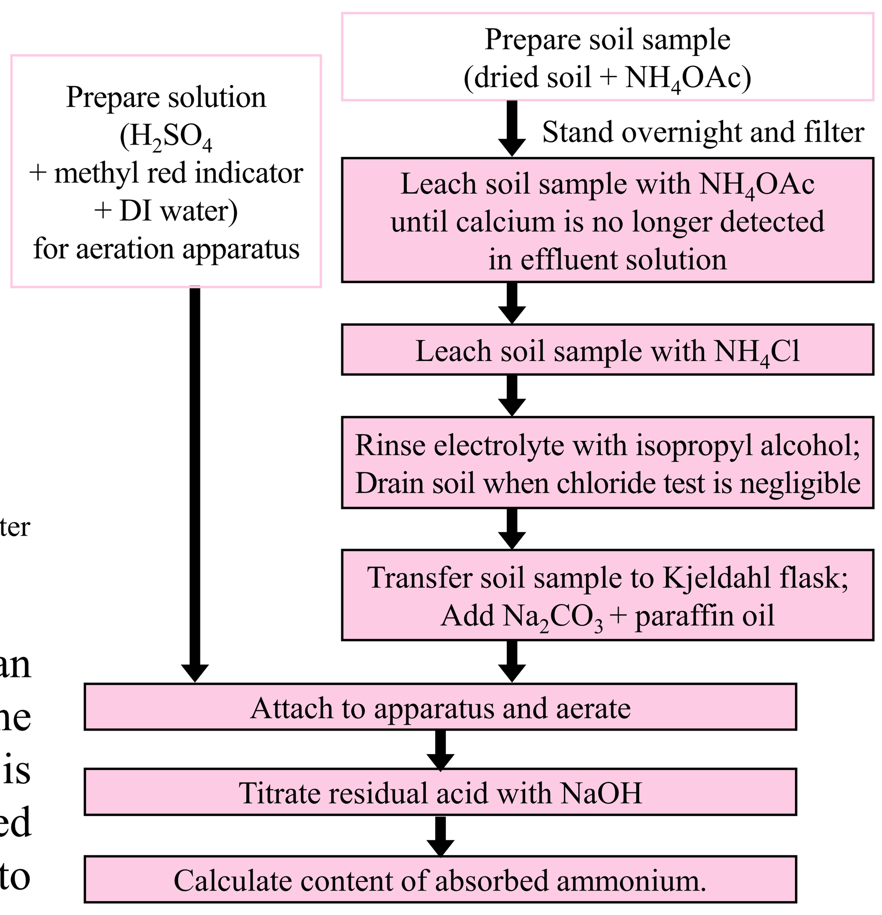

Fig 4. Flow chart of ammonium acetate method

Methylene blue method (ASTM C837)

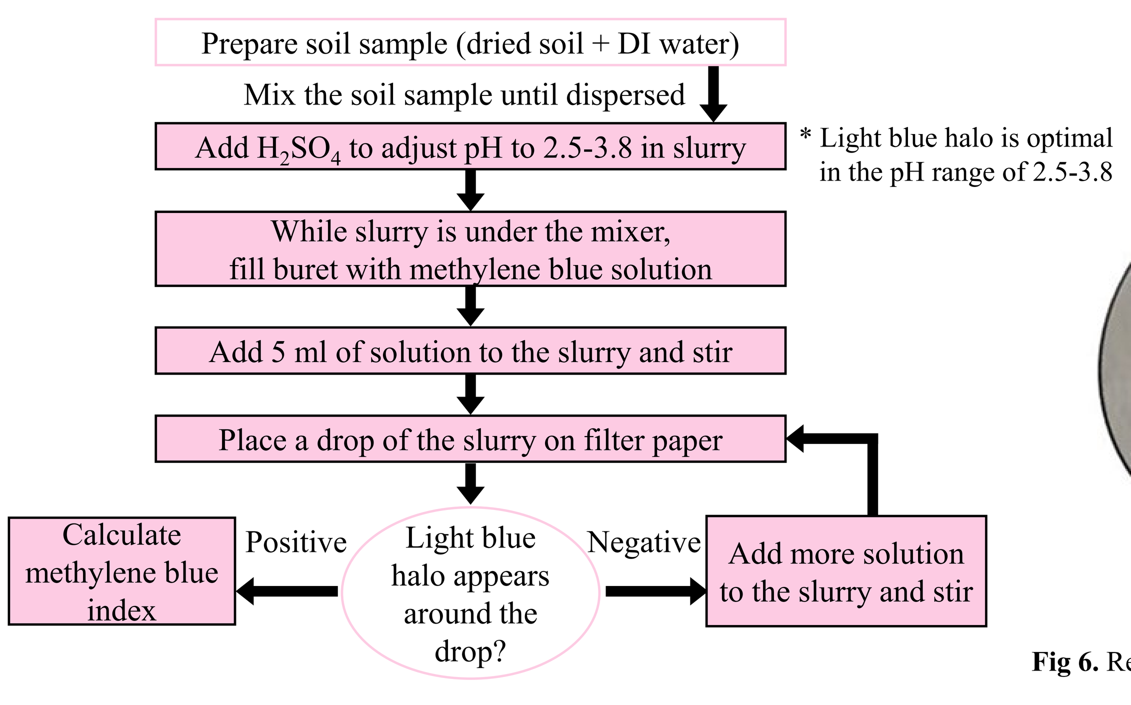

Fig 5. Flow chart of methylene blue method

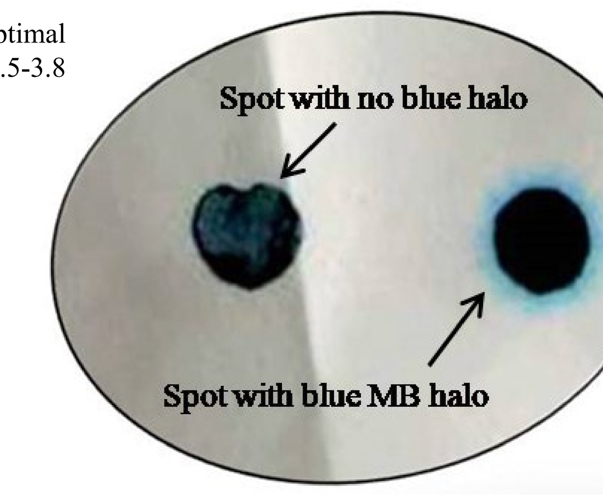

Fig 6. Representation of the spots (with and without MB halo)

- Methylene blue method involves the aggregation of organic dye and planar molecules, which can lead to the formation of dimers and higher species of methylene blue. As a result, it may cause non-equimolar adsorption, leading to inaccuracies in CEC measurements.
- Relying on visually detecting a light blue halo, it can be difficult to determine the endpoint clearly when faint colors appear.

Barium chloride method (ISO 11260)

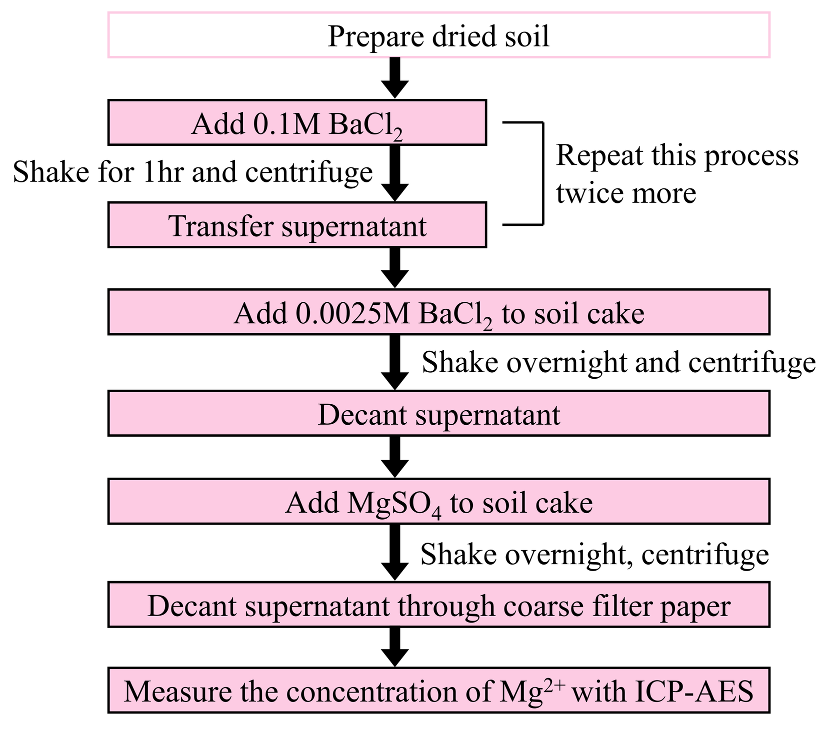

Fig 7. Flow chart of barium chloride method

- **Calculate CEC with concentration of Ba^{2+}**

$BaCl_2$ can dissolve $CaCO_3$ in bentonite, leading to the precipitation of $BaCO_3$. Consequently, this may result in a higher measured CEC.

- **Calculate CEC with concentration of Mg^{2+}**

In this method, $MgSO_4$ was utilized for leaching. By measuring the concentration of Mg^{2+} instead of Ba^{2+}, the interferences are avoided. Therefore, when using this method in Korea, where Ca-bentonite is primarily studied, it is essential to determine CEC based on the concentration of Mg^{2+}.

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

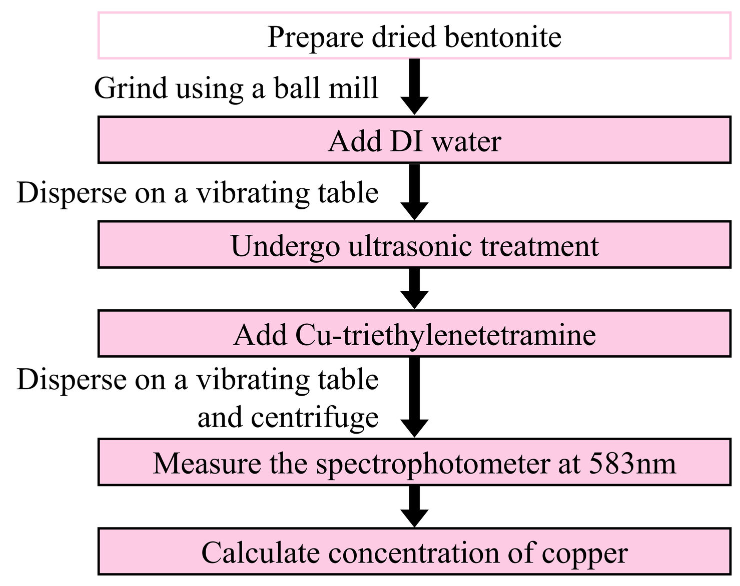

Fig 8. Flow chart of Cu-triethylenetetramine method

- Cu-triethylenetetramine complex has a high affinity for clay minerals, which is crucial for achieving complete ion exchange and obtaining reliable values of CEC.
- Cu-triethylenetetramine solution does not affect the dissolution of gypsum and calcareous materials. Therefore, it is particularly well-suited for use with Ca-bentonite, a clay type commonly studied in Korea.

Conclusions

Table 1. Comparison of four different methods for measuring CEC

	Ammonium acetate method	Methylene blue method	Barium chloride method	Cu-triethylenetetramine method
Time	Long	Short	Long	Moderate
Complexity	High	Very low	High	Low
Precision	Medium	Relatively low	High	High
Clay affinity	Relatively low	High	Relatively low	High
Calcareous soil	○	△	○	◎

- When comparing time, complexity, and clay affinity, the methylene blue method and the Cu-tri method were emerged as the most suitable options.
- However, in terms of precision, the methylene blue method relies on visually detecting a light blue halo as the endpoint, potentially leading to lower precision. Therefore, it is recommended to use the methylene blue method only as a preliminary or simplified approach.
- The three methods excluding the Cu-tri method have difficulties that arise in accurately measuring CEC due to the solution's tendency to dissolve calcareous soil. The presence of dissolved Ca^{2+} as a competitive ion can affect CEC measurement accuracy. Moreover, opting for the barium chloride method to measure Ba^{2+} concentration may result in $BaCO_3$ precipitation, leading to inaccurate CEC. Consequently, these methods are unsuitable for Korea, where Ca-bentonite is primarily studied.

References

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