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Calcium bentonite vs sodium bentonite: The potential of calcium bentonite for soil foundation

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ABSTRACT

Bentonite is a favourable candidate as a sealing material in the deep geological repository to safe storage of highly radioactive nuclear waste in several countries. The high swelling characteristic made bentonite famously type of clay that extracted from smectite group with the main mineral is montmorillonite that has a double diffusion layer. The benefits of sodium bentonite like Wyoming bentonite has proven in the industry. Research on modifying the properties of calcium bentonite to high swelling clay like sodium bentonite for it be able to benefit the industry has been done. Most of the research attempted to improve the workability of calcium bentonite as an alternative material for replacing sodium bentonite in construction industry; however, very little is known about using raw calcium bentonite to improve weak soil subgrades. This paper highlighted the usage of calcium bentonite adapted in construction industry especially in soil stabilization activity and some experimental analysis has been made on the type of calcium bentonite found in British Columbia mine.

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1. Introduction

There is a growing body of literature that recognizes the importance of soil stabilization by chemical additives. Many chemical additives, such as lime, cement, fly ash, calcium carbide residue, or liquid polymer have been used to improve problematic soils [7–10,11–14,15,36]. The chemical additives usually act as agents that have diverse compositions and can modify the micro and physicochemical properties of the soil structure. Many studies have inspected the additive effects on clay like kaolin, bentonite (calcium and sodium montmorillonite), and sandy soils [6,38,16]. Tingle and Santoni [16] investigated the effectiveness of additives on pure minerals treated with polymer emulsion, and their results show that calcium montmorillonite has a better improvement in strength compared to sodium montmorillonite and kaolinite after 7 days curing. A similar study found that early curing age was able to promote the strengthening of the soil by applying <10% of non-traditional additives to bentonite and kaolin clay soils (Latifi et al., 2016a).

Bentonite is a clay mineral particle with two silica tetrahedral sheets and one aluminium octahedral sheet. The main mineral

group in bentonite clay is smectite group and the main mineral is montmorillonite which has a double diffusion layer. Two types of main ion exchanger that generally differentiates between sodium and calcium montmorillonite are Na^+ and Ca^+ ions, respectively. The high tendency of water absorption from Na^+ ion in sodium montmorillonite makes it prone to absorb as much water as it can, and this can be called the high swelling bentonite. On the other hand, the Ca^+ ion that also has a high Mg^+ ion in the calcium montmorillonite are less susceptible to water absorption and has been called a less swelling bentonite. The less swelling clay characteristic makes it as a suitable candidate for cementing agents for subgrade soil. Recent study by Marsh et al. [37] was comparing the effect of main mineral observed in the soil and the author found that between kaolinite, illite and montmorillonite, only montmorillonite was strongly effected by alkaline activator. This results in the formation of geopolymer product. Bentonite was found to has a significant fine aluminosilicate particle that may dissolve and its likely to polymerize when they get contact with the alkaline solution [17].

The presence of high calcium component from polymerization process can reinforce the treated material and the observed result was an appearance of the calcium alumina silicate hydrate (C-(A)-S-H) gel [3,13]. Duxson et al. [21] justified as the calcium provides

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extra nucleation sites for precipitation of dissolved species. A study by Mingyu [17] proved that the bentonite only acts as a filler to Fly Ash-based with NaOH and CaO as an activator. The treated soil was more compact, but no improvement was found in the composition and microstructures of the material. However, a recent study reported the substitution of 8% of $MgCl_2$ into bentonite could improve its compressive strength and N₂. BET data found the cementitious products have filled up the micropores among the soil particles and reduced external surface area of stabilized soil [6]. This paper highlighted the usage of calcium bentonite adapted in construction industry especially in soil stabilization activity and some experimental analysis has been made on the type of calcium bentonite found in British Columbia mine.

2. Calcium bentonite vs sodium bentonite

Bentonites are characterized based on their exchangeable cations like sodium and calcium, the swelling index and their pH. Moreno and Peinado [22] sorted bentonite into three categories which are sodium bentonite, calcium bentonite and activated sodium-calcium bentonite. First, the natural sodium bentonite has moderate to high swelling index due to a balance population of exchangeable ions between sodium and calcium with pH recorded around 9. Second is the natural calcium bentonite that is categorized as low swelling index with <0.5% swelling. Supported by study conducted in Muhammad and Siddiqua [3] that reported the cation exchange capacity (CEC) of the calcium bentonite with the value of 50 meq/100 g, which is lower than high swelling type bentonite with the range of 80–85 meq/100 g. The exchangeable sodium ion is weak, however, its dominant by calcium and magnesium ions that has high proportion of exchangeable ions and pH is in neutral state. The final type is activated calcium bentonite that has extensive swelling index than sodium bentonite with pH between 9 and 10. The exchangeable ion of this type of bentonite is relatively high for both calcium and sodium ions.

Bentonite was found to contain significant fine aluminosilicate particles that may dissolve, and are likely to polymerize when they come in contact with the alkaline solution [17]. Also, previous studies have shown that heat curing in temperatures <100 °C for 24 h can expedite a polymerization process of achieving acceptable strengths in brief periods of time [18]. The high tendency of water absorption from Na^+ ions in sodium montmorillonite makes it prone to absorbing relatively large amounts of water, resulting in high swelling bentonite. Due to these properties, sodium bentonite is a favourable candidate as a sealing material in the deep geological repository to safe storage of highly radioactive nuclear waste [19,20]. On the other hand, calcium montmorillonite, which contains Ca^+ ions as well as high Mg^+ ions, is less susceptible to water absorption, and is known as a low swelling bentonite. The low swelling clay characteristic makes it a good candidate for cementing agents for subgrade soil. Research has also been done on modifying the properties of calcium bentonite to sodium bentonite, to benefit the industry [23]. The modification of calcium bentonite, by using a phosphate dispersant, was proven to effectively replace the sodium bentonite application for cutoff walls [24]. Basically, a study has shown the relative contributions of sodium bentonite like Wyoming bentonite to the industry. Many researches have proven the benefits of sodium bentonite in soil foundation. Research on modifying the properties of calcium bentonite to high swelling clay like sodium bentonite for it be able to benefit the industry has been done [23]. Most of the research attempted to improve the workability of calcium bentonite as an alternative material for replacing sodium bentonite in construction industry; however, very little is known about using raw calcium bentonite to improve weak soil subgrades.

3. Application in research and industry

3.1. Calcium bentonite as an activator for soil

Following the addition of calcium bentonite in the soil, few chemical additives, such as alkaline activator or salt stabilizers, were needed as a substitution for creating a strong chemical bonding between soil particles. The geopolymeric binder is comprised of agglomeration of nanocrystalline zeolite compacted by an amorphous gel phase. The amorphous gel phase consists of a transformation of an X-ray amorphous to semicrystalline or polycrystalline. These crystalline products can only be observed after a long reaction time and vary in degree of crystallinity, which is divided into four degrees: highly crystalline, nanocrystalline, polycrystalline, and amorphous. The crystallinity within the geopolymeric binder phase is usually observed around 5 nm particulates, limiting XRD detection [27]. However, studies show that the geopolymers are largely featureless 'hump' centered at approximately $27-29^\circ 2\theta$ [25]. This geopolymer was called an amorphous aluminosilicate gel which is a primary binder phase in the geopolymeric system. The hump becomes a central determination of geopolymer binder since the gel has no crystal shape; hence, it would not show a discrete XRD diagram such as those clearly observed for the crystalline pattern. This was because the exact boundary between crystalline and amorphous materials for XRD is very difficult to quantify. Theoretically, an alkaline activator consists of a ratio of sodium silicate and sodium hydroxide applied to an aluminosilicate material to dissolve silica and alumina in the soil, as recently discussed by various studies [2,10,28]. Destruction of the original silica and alumina-rich in raw material requires a high concentration of hydroxyl (OH^-) ions in the alkaline medium, which is necessary for polymerization processes to occur [26]. During the dissolution phase, these tend to balance the excessive negative charges and later modify the Si and Al coordination [10]. The process continues with precipitation and crystallization. The precipitation and reorganization phase results in a custom ordered three-dimensional chain linked structure (i.e. Si-O-Al and Si-O-Si bonds) that is more stable. This three-dimensional matrix attaches to the un-reacted particles and produces a robust new structure [29]. Meanwhile, the alkaline cations will act as building blocks of the structure. The dissolved Al-Si complex tends to diffuse from any solid surface during the continuous nucleation trigger process. This process is a step in the formation of a new structure via self-organization. In the polymeric system, nucleation trigger occurs through a replacement of water in the hydration shells of cations by small aluminates or silicates species. The nucleation of a solid face can be induced under high concentration of silicate-hydrate and alumina-hydrate into concentrated alkali activated solution at high rate of nucleation. This happens when the degree of supersaturation and number of nucleation trigger is very high. However, less nucleation can be developed close to the particle when the system cannot activate a high alkali solution under high levels of silicate-hydrate and alumina-hydrate. When the nucleation is absent in such proximity to the particle surfaces, a weak geopolymeric matrix will be bonded between the particles [27]. In such exposure, a hydroxide-activated system is likely to generate rapid nucleation in these regions, resulting in lower mechanical strength development of the product developing than with a silicate-activated system.

3.2. Calcium bentonite for geopolymer

Studies by Granizo et al. [30], Yip and Deventer [31] and Kragten et al. [32] mentioned the effect of Ca^{2+} on geopolymerization. It is possible that C-S-H compounds and $Ca(OH)_2$ precipitate in the geopolymer system. In fact, the formation of C-S-H interferes and

affects the formation of geopolymeric matrix [33]. This interference may result in retarding the primary driving force for nucleation and crystal growth. Instead of achieving a reaction with an alkaline activator, forming a geopolymer product, the production of cementitious product such as C-S-H, C-A-H, C-(A)-S-H or M-S-H were likely to occur as a result of pozzolanic reactions. The hypothesis of stabilization mechanism is proposed such as the illustration in Fig. 1. The potential of the cementitious product from calcium and magnesium elements is due to the similarity of the size of both elements with regards to lyotropic series (refer to Fig. 2), which might be received from the raw soil and additive sources. The elements are needed to alter the electrolyte concentration of the pore fluid in clay soil that can result in increased flocculation and decreased the spacing between soil particles [16]. The pozzolanic reactions take place over curing time, which results in the formation of cementitious product.

The addition of calcium bentonite as catalyst in activating process has been studied in Muhammad and Siddiqua [3]. Overall, this study supports the idea that a mixture of bentonite magnesium-alkalinization additive is able to improve the strength of silty sand especially after it was heat treated at 60 °C in 24 h. The formation of the new binder from bentonite (source of reactive silica and alumina), magnesium chloride (source of magnesium) and alkaline activator (providing more reactive silica and high pH) leads to a binder/cementitious coating for a silty sand structure. In the mixture, the amorphous part which can be dissolved in alkaline environment came from the bentonite. In nature, most alumina-silicate substances are crystalline like quartz. Therefore, their precipitation in any chemical reaction is difficult. However, the heat treatment process allows the loss of constituent water that leads to re-coordination of aluminium and oxygen ions, which then transforms the structure from crystalline to amorphous. Thus, the tested additive can be used for stabilizing the silty sand. Future research will focus on modifying the processing method for the heated additive, such that it may be easily applied in situ to raw subgrade soils.

4. Characteristics of calcium bentonite

Around 30 million ton of raw calcium bentonite reserved was estimated in a mine located in Kamloops, British Columbia (BC),

Canada was never been studied or used as cementing agents for road subgrade soil in BC. It is rarely found this type of clay soil can alter and contribute to the greater strength of fine-grained soil. Few tests have been conducted on this raw sample for characterisation study of calcium bentonite.

4.1. Cation exchange capacity (CEC)

The methylene blue index (MBI) test follows from ASTM C837 standard was used to evaluate the CEC of calcium bentonite. The test able to measure the clay ability to absorb the methylene blue dye which correlates to its CEC. The MBI test involves methylene blue dye in small increments, then spotting the solution on a filter paper. Once a blue halo appears around the spot, the end point is reached means there is excess methylene blue that is not absorbed by the clay. Once the end point is reached the volume of methylene blue die added to achieve a halo (V) is known and the Methylene Blue Index (MBI) can be calculated with the formula $MBI = 0.5 (V)$. As to compared, the V for the calcium bentonite was 100 mL and the sodium bentonite was 170 mL and the MBI for both were 50 meq/100 g and 85 meq/100 g of clay, respectively. This value is equivalent to $CEC = 0.051 \text{ eq}/100 \text{ g}$ for the calcium bentonite, which is determine as low cation exchange capacity [3,14]. Fig. 3 shows the drops of methylene blue on the filter paper and the blue halo spots that used to determine the MBI.

4.2. Atterberg limit test

Atterberg limit test was performed through determination of Plasticity index (PI) value from the difference of liquid limit (LL) and plastic limit (PL). These limits are used to describe moisture behaviour and moisture sensitivity of different soils. The LL is the moisture content that defines when the soil changes from a plastic to viscous state. Meanwhile, the PL is the moisture content that defines when the soil changes from a semi-solid to a plastic state. A wet method preparation was used to performed PI test in accordance with ASTM D4318. First, the multi-point test by Casagrande method was carried out to determine the LL. Then the hand rolling method was used when determining the PL.

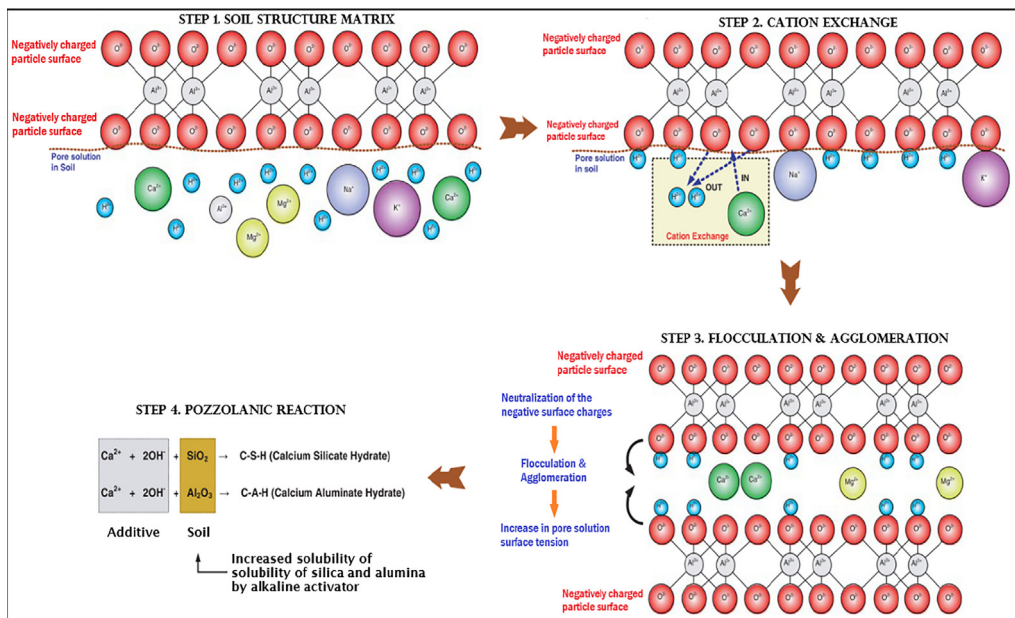


Fig. 1. Proposed stabilization mechanism (Source: Shon et al. [35]).

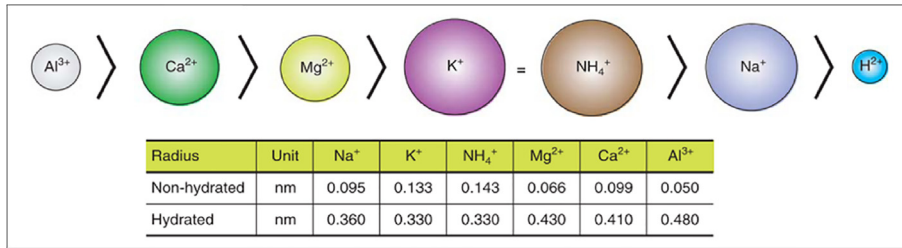


Fig. 2. Lyotropic series (Source: Shon et al. [35]).

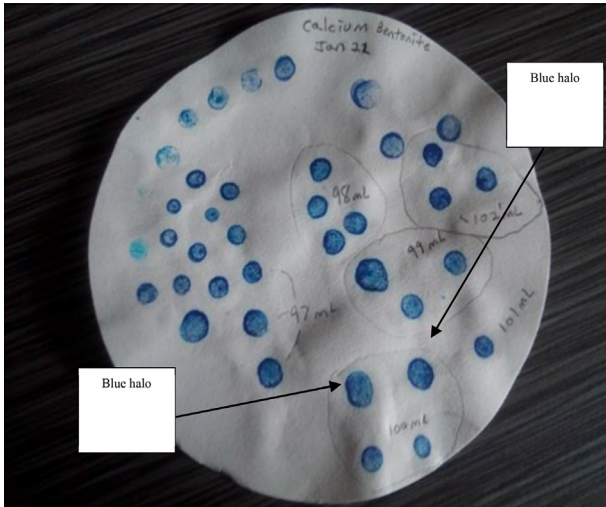


Fig. 3. Methylene blue test.

NATIONAL[®] Standard sodium bentonite was reported the value of LL, PL and PI were 644, 31 and 613, respectively. Meanwhile, the values obtained from the calcium bentonite were 209, 21 and 188 for LL, PL and PI, respectively. In Ahonen et al. [1] released the required LL values for high-grade sodium bentonite should be $\geq 250\%$ and for high grade calcium bentonite was $\geq 80\%$. The different in values between studied calcium bentonite and reported in Ahonen et al. [1] because the author mentioned the most reasonable method to determine the plastic properties of bentonite with fall cone test due to difficulties of handling the mixture using the Casagrande LL device.

4.3. Swelling index test

Swell potential is one of the most important properties of bentonite for drilling fluids, and for geotechnical and environmental engineering applications. However, swelling soils especially for soil foundation should be under control because it can cause serious engineering problem. The percentage of volumetric swell of soil depends on several factors such as type of fine materials, Atterberg limits, dry density, permeability and soil access to source of water intrusions. Fig. 4 demonstrated the difference of swelling potential between calcium bentonite and sodium bentonite at the same method of preparation in accordance with ASTM D5890. This method also called free swell test. A 2 g dried sample and finely ground bentonite is dispersed into a 100 mL cylinder in 0.1 g increments. Each increment takes at least 10 min to allow full hydration and settlement of the bentonite. This step continues until the 2 g sample has been added to the cylinder. The cylinder then covered and protected from disturbance for 16–24 h until the reading is consistent. The sodium bentonite tested in this study has an average at 35 mL/2g and similar reported in Naka et al. [34]. However, as can be seen in Fig. 4(a), the average swelling index for calcium bentonite at 12 mL/2g. Although the increase is significant, the average swell index of the calcium bentonite is less than half of the sodium bentonite. This significant result can be explained by the present of cation concentration in the mineral. As expected in both sodium bentonite and calcium bentonite have the existences of the Na⁺, Ca⁺ and Mg⁺ cations that effected the cation exchange capacity, Atterberg limits and swell potential. Study by Bradshaw et al. [9] shows an equivalent effect of the presence of high Na⁺ increase the swell index while high Ca⁺ has low swelling index (refer Table 1). Even if the presence of high Mg⁺ in the clay mineral will reduce the swell potential. This can be supported by the EDS analysis observed for the calcium bentonite sample that shows in Fig. 5. The percentage weight of Na, Ca and Mg were

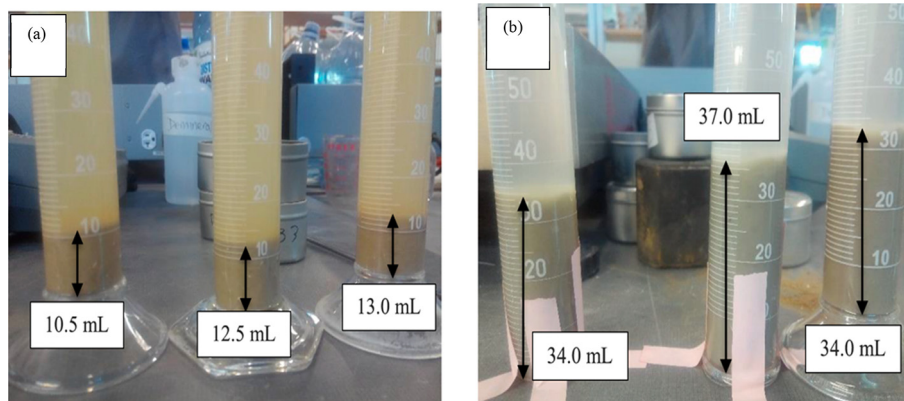


Fig. 4. Comparison of swelling index test (a) calcium bentonite, and (b) sodium bentonite.

Table 1
Effects of cation concentration in swell index (Source: Bradshaw et al. [9]).

Subgrade	Final water content (%)	Swell index (ml/2g)	Bound cation concentrations (cmol ⁺ /kg)			
			Na	Ca	Mg	K
None (new GCL)	N/A	28.0	32.1	20.2	6.8	0.1
Torpedo sand	75.1	21.5	31.5	19.3	6.6	1.0
	75.7	20.5	27.4	20.1	6.9	1.0
Cedar Rapids clay	59.2	20.0	32.9	19.7	7.0	<0.001 ^a
	64.4	21.0	29.7	22.2	5.5	0.9
Boardman silt	61.9	20.5	32.0	19.9	7.0	<0.001 ^a
	73.9	19.0	28.2	23.1	8.7	0.2
Red Wing clay	67.3	21.5	31.9	19.8	6.8	0.9
	66.1	19.5	23.4	28.7	8.4	1.0

^a Less-than symbol indicates lower than method detection limit.

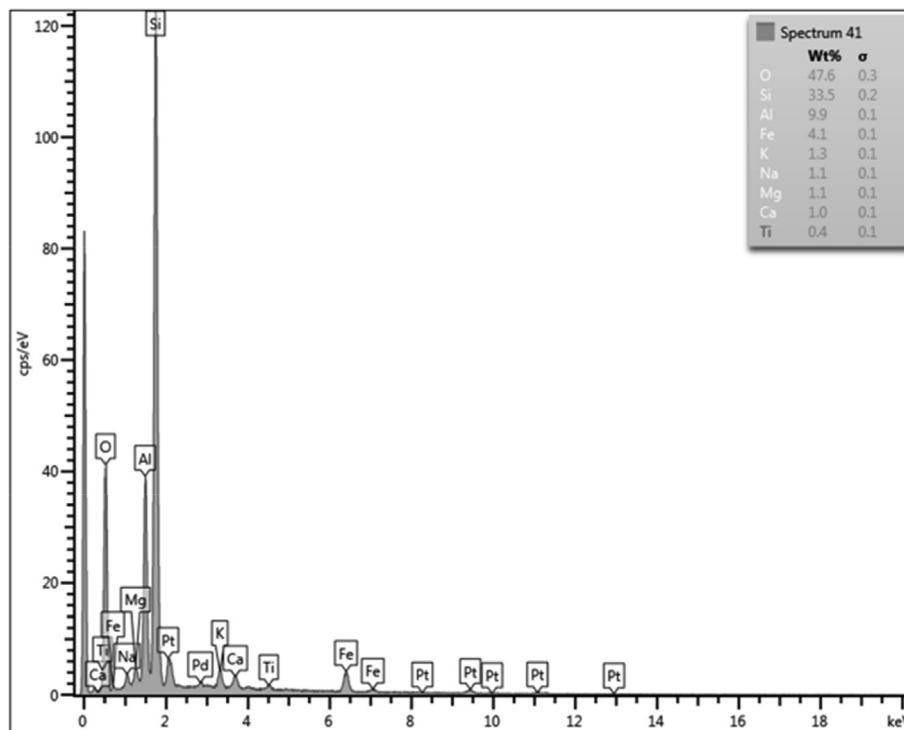


Fig. 5. Chemical composition of calcium bentonite.

Table 2
Relations between Atterberg limits and swelling potential (). Source: [4–5]

Liquid Limit (%)	Plastic Limit (%)	Swelling index
<50	<25	Low
50–60	25–35	Marginal
>60	>35	High

equals means the Na was not a dominant cation concentration which result in low swelling index for this studied calcium bentonite. In Table 2, Pitts [4] and Kalantari [5] also mentioned the value of PL below 25% is categorized as low swelling potential which significant with the results obtained for the calcium bentonite.

5. Conclusion

The present review shows the calcium bentonite has a potential use as a soil stabilizer by chemical stabilization method. Further

discussion on the results from classification study of the calcium bentonite that obtained from the Bentonite mine in British Columbia, Canada were presented. This type of bentonite also known as a calcium bentonite that has major potential research opportunity by modifying the physicochemical properties of weak soil. The presence of Ca and Mg cations in the calcium bentonite are significantly changing the behavior of swelling index in the soil. Bentonite has shifted the way of clay soil characteristic as a problematic soil. The physicochemical characteristics as well as the mineralogy and morphological characters of this soil can improvise and modifies. As a result, this type of material can be used to replace the traditional method like replacing problematic soil with high bulk density soil and installation of expansive ready-made or constructed material on-site. Future research will focus on modifying the processing method for the heated additive, such that it may be easily applied in situ to raw soils.

CRedit authorship contribution statement

Nurmunira Muhammad: Conceptualization, Methodology, Investigation, Validation, Data curation, Writing - original draft.

Sumi Siddiqua: Supervision, Conceptualization, Methodology, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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