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Research Article

Effect of Calcium and Sodium Ratios in Bentonite on Swelling

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ABSTRACT

This article investigates the effects of calcium and sodium ratios on the swelling capacity of calcium bentonite samples collected from different locations. Bentonite, with its properties such as swelling capacity, cation exchange capacity (CEC), and adsorption ability, is widely used in many industrial applications ranging from drilling muds to environmental barriers. However, chemical and mineralogical variations resulting from geological formation processes can influence the performance of bentonite. Turkey holds a significant share of the world's bentonite reserves, with high-quality bentonite deposits particularly located along the Ordu-Giresun-Trabzon line. In this study, 11 bentonite samples collected from Ordu Province were analyzed using X-ray Fluorescence (XRF) to determine their calcium and sodium contents, and swelling tests were performed in accordance with ASTM D5890 standards. The findings reveal that calcium and sodium ratios alone are not decisive in determining swelling capacity. When compared with similar studies in the literature, it is understood that factors such as mineralogy, particle size distribution, and CEC play a more dominant role.

1. Introduction

Bentonite is a natural material composed of swelling clay minerals, primarily montmorillonite. According to 2023 data, global bentonite production is approximately 18 million tons, with the largest producers being the USA, China, India, Greece, and Turkey. With an annual production of about 1.2–1.5 million tons, Turkey ranks among the top five producers. Bentonites are classified into three main groups based on their swelling capacity: Sodium Bentonite (high swelling, Wyoming type), Sodium-Calcium Bentonite (moderate swelling), and Calcium Bentonite (low swelling). The industrial significance of bentonite is directly related to its swelling capacity and CEC values. Although calcium bentonites generally have low swelling capacities, these values can be improved through sodium activation.

In the literature, many factors influencing the swelling capacity of bentonites have been identified. These include mineralogy, particle size, CEC value, environmental conditions, and particularly the type of exchangeable interlayer cations. The presence of sodium ions is generally associated with high swelling capacity, whereas calcium ions are linked to lower swelling values. Due to their low permeability, sodium bentonites play an important role in environmental engineering [4]. It has also been emphasized in various studies that a decrease in calcium content generally enhances swelling behaviour [5]. The aim of this study is to determine the effect of calcium and sodium content on the swelling capacity of calcium bentonites obtained from different deposits in Ordu Province.

1.2. Bentonite History

Bentonite is a clay mineral dominated by montmorillonite, characterized by high swelling capacity and unique physicochemical properties. Widely used in many industries around the world, bentonite has been scientifically defined since the nineteenth century and is today regarded as a strategic mineral. The history of bentonite extends from its geological formation processes to its wide range of modern applications.

The use of bentonite-type clays dates back to ancient times, where they were employed for various purposes. In Ancient Egypt, they were preferred in mummification processes due to their oil and liquid absorption properties [3]. Archaeological findings from Mesopotamian civilizations indicate their use in ceramic production and as a building material. Bentonite was also consumed for medicinal purposes, particularly in the treatment of digestive system disorders, where it was known as a "healing clay" [13]

The term "bentonite" was first introduced in 1898 to describe clays obtained from the Fort Benton area in Wyoming, USA (Knight, 1898). These clays exhibited remarkable swelling behavior and extraordinary plasticity when in contact with water, which distinguished them from other clays and led to their scientific classification as a separate group.

From the beginning of the twentieth century, bentonite started to be used in a wide range of industrial applications driven by the industrial revolution and increasing technological demands. It found applications as a binder in the foundry industry, as a viscosity-enhancing and flow-stabilizing material in drilling fluids for petroleum and natural gas, as a soil conditioner and animal feed additive in agriculture, and as a clarifying agent in wine and beer production [14]. After the Second World War, bentonite became recognized as a strategically important mineral, particularly in the metallurgy and energy sectors.

Turkey is among the leading countries in terms of bentonite reserves, with studies estimating that it possesses more than 250 million tons of bentonite [15]. Major deposits are located in Ordu-Ünye, Tokat-Reşadiye, Çankırı, Edirne-Keşan, Çanakkale-Çan, and Kütahya. Bentonite production in Turkey began in the mid-twentieth century and gained significant momentum after the 1980s, both for domestic use and export. Today, Turkey is one of the world's leading producers and exporters of bentonite.

In modern times, bentonite has an exceptionally wide range of applications. It is used in petroleum and natural gas drilling, in the foundry industry, in iron and steel production through pelletizing, in cement and ceramic industries, in the clarification of wine, beer, and fruit juices, in wastewater treatment and environmental engineering, in cat litter production, and in pharmaceutical and cosmetic industries. With such diverse uses, bentonite has remained not only a material of historical significance but also a strategic mineral for modern industry. The physical form of a calcium bentonite sample collected from the Ordu region is shown in Figure 1.

1.3. Mineralogical and Chemical Properties

Bentonite exhibits exceptional swelling capacity due to the presence of the montmorillonite mineral. Montmorillonite is a 2:1 layered aluminosilicate mineral with exchangeable cations in its interlayers, which govern its interaction with water and, consequently, its swelling behavior. Sodium bentonites, in particular, demonstrate high swelling and dispersion properties due to the pre presence of Na^+ ions, while calcium bentonites show lower swelling and generally lower plasticity.

Clays are classified as swelling (smectite) or non-swelling (mica) based on their hydration behavior. Smectites can swell even by adsorbing atmospheric moisture, whereas non-swelling clays typically contain non-hydrated K^+ or divalent cations, limiting their interaction with water [8]. The swelling and dispersion capacity depends on the type, amount, and distribution of cations between montmorillonite layers [10]

Stone minerals in bentonite samples, such as quartz, feldspar, and biotite, reduce the montmorillonite content and consequently decrease the swelling capacity. These minerals fill the voids between montmorillonite crystals, altering the crystal and pore structure. As a result, pore volume decreases, total surface area is reduced, and water absorption and swelling capacity are negatively affected [9]

Chemical analyses are critical for evaluating the industrial potential of bentonite. X-Ray Fluorescence (XRF) and Inductively Coupled Plasma (ICP) analyses provide information about elemental composition, particularly Na/Ca and Si/Al ratios, as well as heavy metal content. These data are essential for assessing both swelling behavior and environmental safety [6]

In addition to mineralogical and chemical characteristics, surface area, pore distribution, and particle size influence water retention and rheological properties. An increased BET surface area enhances water adsorption and swelling capacity. Smaller particle sizes improve rheological properties and result in more homogeneous behavior in practical applications [11]

Table 1 presents the average results of analyses conducted on bentonite samples collected from the Fatsa district of Ordu province.

Table 1. Physical properties of bentonite

Properties	Value/Range
Color	White, Gray, Greenish
Density	1,5-2,4 g/cm³
Bulk Density	0,8-1,0 g/cm³
Grain Size	%90 < 2 µm
Specific Surface Area	600-800 cm²
Moisture (H2O)	%20 - 30
Swelling Index	8-18 mL / 2 g
Cation Exchance Capacity	30-70 meg/100 g
Porosity	High
Plasticity	Medium

Figure 1. The physical appearance of bentonite

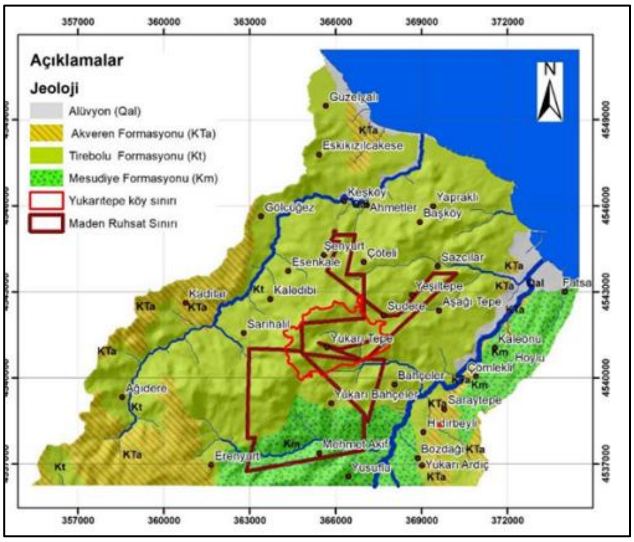

Figure 2. The geological map of the Ordu (Akbaş was simplified from (2011).

1.4. Geological Formation of Bentonite

The geological formation of bentonite primarily occurs through the alteration of volcanic ash and tuff. In this process, the development of the montmorillonite mineral is facilitated under the influence of temperature, pressure, and groundwater, with the transformation completing over geological timescales of millions of years. Bentonite deposits in Turkey are particularly associated with Neogene-aged volcanic rocks, providing a fundamental framework for understanding the formation mechanisms of bentonite in the region. The geological modeling map for the Ordu region is given in Figure 2.

The mineralogical and chemical properties of bentonite include montmorillonite content, cation exchange capacity (CEC), swelling capacity, and rheological behavior. Furthermore, the differences between calcium bentonite (Ca-bentonite) and sodium bentonite (Na-bentonite) are of significant importance for industrial applications.

The industrial applications of bentonite in Turkey are diverse. Drilling mud production accounts for the largest share of its usage, while other applications include the foundry industry, clarification in wine, fruit juice, and beer production, cement additives, wastewater treatment, and use in the cosmetic and pharmaceutical sectors. Notably, cat litter production represents one of the main areas in which Turkey holds a strong position in exports.

Future perspectives indicate the increasing importance of bentonite in environmental engineering applications, such as waste containment and impermeable barriers, as well as its potential use in innovative fields like nanotechnology and drug delivery systems. Comparative analysis with the literature shows that the findings of this study are consistent with previous research by [6] and [14] supporting existing knowledge regarding the geological, mineralogical, and industrial characteristics of bentonite deposits in Turkey.

1.5. Bentonit Reserves in Turkey and Regional Variations

Bentonite is one of the most abundant industrial minerals in Turkey, occurring in significant reserves due to the country's geological diversity. The deposits are mainly associated with Neogene-aged volcanic rocks. According to recent studies, Turkey hosts approximately 250–300 million tons of proven bentonite reserves [12]. A considerable portion of these reserves is characterized by a high montmorillonite content, which provides a competitive advantage in international markets.

Bentonite deposits in Turkey are concentrated in several regions, including the Central Black Sea (Ordu, Tokat, Çorum, Amasya), Central Anatolia (Ankara, Eskişehir, Kütahya), Aegean (Balıkesir, Çanakkale), Marmara (Edirne, Tekirdağ), and Southeastern Anatolia (Diyarbakır, Batman). Among these, the Ordu-Ünye, Tokat-Reşadiye, and Çankırı areas are particularly significant for sodium bentonite, while calcium bentonite deposits are more common in the Balıkesir and Çanakkale regions. The geological map of the Ordu region is shown in Figure 2.

Turkey is among the leading countries in bentonite production, with an annual output of approximately 1.5–2 million tons. On the other hand, the largest producers continue to be America, India, China and Türkiye, respectively. A substantial share of the produced bentonite is consumed domestically, particularly in drilling, foundry, iron and steel, and cat litter industries, while a notable portion is exported. The main export markets include European countries, the Middle East, and the Russian Federation.

The evaluation of bentonite reserves requires not only the assessment of quantity but also the mineralogical characteristics and cation exchange capacity. Sodium bentonites in Turkey are widely preferred in drilling and waste containment applications due to their high swelling capacity and rheological properties, whereas calcium bentonites are mainly utilized in the iron-steel industry and cat litter production.

In conclusion, Turkey possesses strategically important bentonite reserves. Sustainable exploitation, transformation into value-added products, and effective utilization in international markets will significantly contribute to the country's economy. In addition, Türkiye has an important place in bentonite production compared to others (Figure 3).

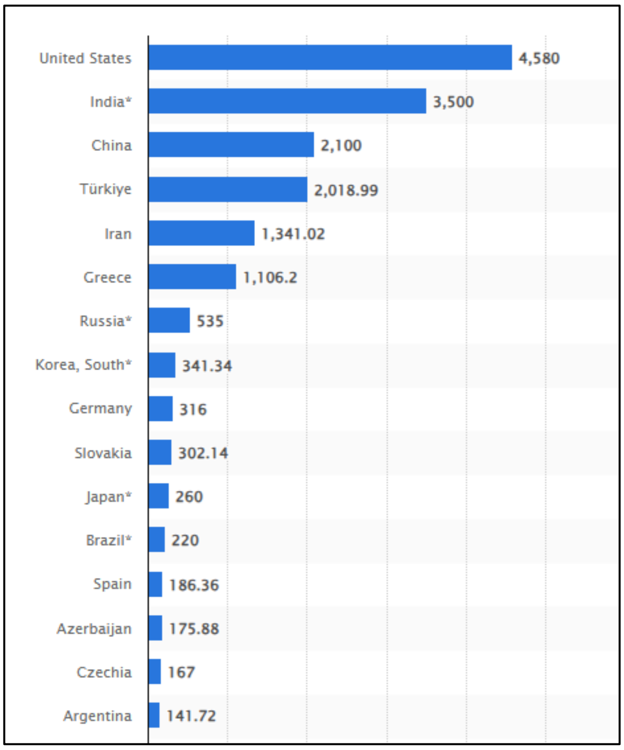

Figure 3. Global bentonite production volume by country (2022). Published by Madhumitha Jaganmohan, 2024

1.5.1. Industrial Applications of Calcium Bentonite

Despite its low swelling capacity, calcium bentonite is utilized in many industrial fields thanks to its high adsorption capacity. It is used as a binder in the foundry industry, as a rheological stabilizer in drilling muds, and in agriculture to enhance the water retention capacity of soils. In addition, it is applied in environmental remediation, as an additive in animal feed, and in drug delivery systems. Through sodium activation, its swelling capacity can be increased, enabling adaptation to a wider range of applications.

1.5.2. Sodium Activation and Its Effect on Swelling Capacity

Studies and experiments have shown that by applying sodium carbonate activation to existing Ca-bentonite samples, the commercial value of low-performance bentonites can be enhanced.

1.6. Swelling Test in Bentonite

The swelling capacity of bentonites is primarily determined by the montmorillonite mineral and the exchangeable cations (Na^+, Ca^{2+}, Li^+) in the interlayers. Water molecules interact with these cations and penetrate between the crystal layers, resulting in volumetric expansion. Sodium bentonites are particularly favored in industrial applications due to their high swelling capacity, whereas calcium bentonites exhibit lower swelling. Laboratory evaluation of bentonite swelling can be conducted using various methods. The Casagrande method involves exposing bentonite powder to water for a defined period and measuring the volume increase in ml/g, while the free swell test provides a more precise and rapid assessment. Rheological tests also determine viscosity and swelling behavior, providing valuable information for drilling mud applications. Swelling capacity is influenced by montmorillonite content, stone mineral proportion, particle size, porosity, pH, and ionic strength of the environment. High montmorillonite content, low stone ratio, smaller particle size, and higher porosity enhance water absorption and swelling, whereas higher Ca^{2+} concentration or ionic strength may restrict swelling. Therefore, swelling test results are critical for evaluating the performance of bentonite in drilling mud, waste containment barriers, and geotechnical engineering applications [8],[3],[10],[14]

2. Materials and Methods

2.1. Sample Collection

In this study, 11 samples were collected from different bentonite deposits within the borders of Ordu Province. After on-site crushing and homogenization, the samples were transported to the laboratory. To increase the representativeness of each sample, subsamples taken from different points were combined to prepare composite samples.

2.2. Chemical Analysis

The chemical composition analysis was carried out using an XRF device. After drying the samples at 105 °C for 24 hours, they were sieved to pass through a 75 µm mesh and then prepared for XRF analysis. The calibration of the device was performed using standard reference materials provided by the manufacturer.

2.3. Particle Size Control

To maintain consistency throughout the study, all bentonite samples were standardized to a uniform particle size prior to testing. Maintaining a consistent particle size minimized variability in swelling behavior and other physicochemical properties, enabling more accurate and reliable comparisons among different samples.

2.4. Swelling Test

The swelling capacity was measured in accordance with ASTM D5890 standard. Two grams of bentonite sample were slowly added over 1–2 hours into a 100 mL graduated cylinder containing distilled water, and after a 24-hour waiting period, the swelling volume was measured in millimeters. The experiments were performed in triplicate, and the average values were used (Figure 4).

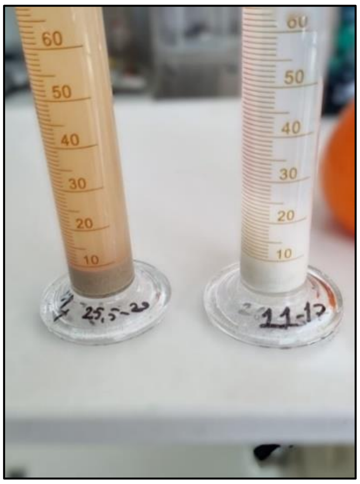

Figure 4. Swelling test

3. Findings and Discussion

Table 2 presents the CaO and Na_2O contents of the bentonite samples along with their swelling capacities. Statistical analysis (Pearson correlation) revealed a correlation coefficient of $r = -0.05$ between CaO content and swelling capacity, and $r = 0.4$ between Na_2O content and swelling capacity. These values are not statistically significant.

This indicates that the swelling capacity of bentonite cannot be explained solely by its calcium and sodium content. Similar to the findings in the literature [Gürbüz & Ece, 2005], factors such as mineralogy, particle size distribution, CEC value, and pH have been reported to exert a stronger influence on swelling. In particular, bentonites with a high percentage of montmorillonite may exhibit high swelling capacities even when their calcium content is low (Figure 5).

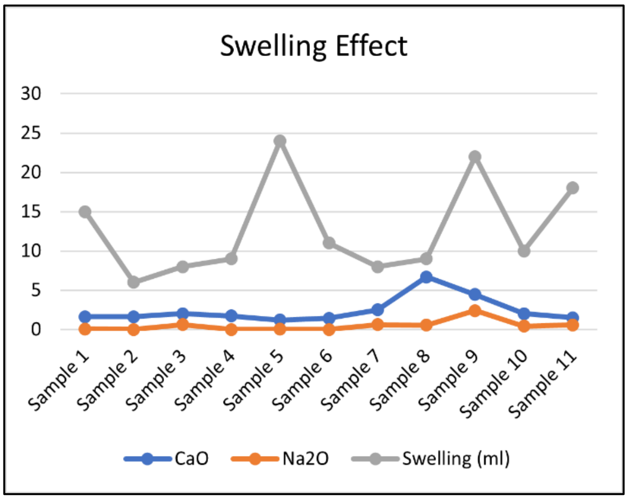

Figure 5. Swelling effect

The results also show that geological formation processes have a significant effect on the chemical composition and mineralogy of bentonites. The bentonites in the Ordu region were formed through the weathering of volcanic ash and tuffs, and mineralogical differences were observed among different locations. Therefore, site-based quality classification is of importance for industrial applications.

Table 2. The effect of components on swelling

SampleNo/ Component	CaO (%)	Na2O (%)	Swelling (ml)
Sample 1	1,64	0,09	15
Sample 2	1,63	<0,01	6
Sample 3	2,03	0,62	8
Sample 4	1,74	<0,01	9
Sample 5	1,22	0,05	24
Sample 6	1,44	<0,01	11
Sample 7	2,52	0,62	8
Sample 8	6,7	0,55	9
Sample 9	4,46	2,41	22
Sample 10	2,01	0,42	10
Sample 11	1,49	0,6	18

4. Result

This study revealed that calcium and sodium ratios alone do not have a significant effect on the swelling capacity of calcium bentonites collected from different locations. To better understand the industrial performance of bentonite, other parameters such as mineralogy, CEC, particle size, and modification techniques must also be considered.

From an industrial perspective, without sodium activation, the swelling performance of calcium bentonites may remain insufficient in drilling and foundry applications. Therefore, in raw material selection, not only chemical analysis but also mineralogical analysis and application-based tests should be evaluated together.

The study should be supported by tests such as determination of mineralogical structure using XRD, CEC measurements, investigation of the effect of particle size fractions on swelling capacity, organic modification, and geochemical origin analyses.

References

[1] A. Akbulut, *Bentonit*. Ankara, Türkiye: Maden Tetkik ve Arama Genel Müdürlüğü Yayını, 1996, 78 s.

[2] K. İpekoğlu, B. Kurşun, B. Bilge, ve B. Barış, "Türkiye bentonit potansiyeline genel bir bakış," in *2. Endüstriyel*

Hammaddeler Sempozyumu, İzmir, Türkiye, 1997, pp. 51–57.

[3] R. E. Grim, *Clay Mineralogy*. New York, NY, USA: McGraw-Hill, 1968.

[4] H. H. Murray, *Applied Clay Mineralogy*. Amsterdam, Hollanda: Elsevier, 2007.

[5] G. J. Churchman, W. P. Gates, ve B. K. G. Theng, “Clays and clay minerals for pollution control,” in *Handbook of Clay Science*, Amsterdam, Hollanda: Elsevier, 2002.

[6] A. Gürbüz ve İ. Ece, “The role of bentonite swelling capacity in environmental applications,” *J. Environ. Geol.*, vol. 47, no. 6, pp. 945–956, 2005.

[7] S. Ş. Erdinç, “Bentonitlerin metalurjik uygulamaları yönünden araştırılması ve Reşadiye bentonitlerinin bu açıdan incelenmesi,” Ph.D. diss., Jeoloji Müh. Böl., İstanbul Teknik Üniv., İstanbul, Türkiye, 1976.

[8] A. Alemdar, “Clay minerals and their properties,” *J. Turkish Geol.*, vol. 14, no. 2, pp. 23–34, 2001.

[9] M. F. Brigatti, E. Galán, ve B. K. G. Theng, “Structures and mineralogy of clays,” in *Handbook of Clay Science*, B. K. G. Theng ve M. F. Brigatti, Eds. Amsterdam, Hollanda: Elsevier, 2006, pp. 19–86.

[10] M. Sarıkaya et al., “Swelling behavior of smectite clays,” *Appl. Clay Sci.*, vol. 18, no. 2, pp. 67–78, 2001.

[11] J. Madejová, “FTIR techniques in clay mineral studies,” *Vibrational Spectrosc.*, vol. 31, no. 1, pp. 1–10, 2003.

[12] Maden Tetkik ve Arama Genel Müdürlüğü (MTA), *Türkiye Bentonit Potansiyeli Raporu*, Ankara, Türkiye, 2022.

[13] Carretero, M. I., & Pozo, Clay and non-clay minerals in the pharmaceutical industry. *Applied Clay Science, 46*(1), 73–80, 2009

[14] Murray, H. H. Traditional and new applications for kaolin, smectite, and palygorskite: A general overview. *Applied Clay Science, 17*(5–6), 207–221, 2000.

[15] Önal, M., & Sarıkaya, Y. Bentonite deposits of Turkey. *Applied Clay Science, 15*(1–2), 191–206, 1999.