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The characterization of Na_2CO_3 Activated Kütahya Bentonite

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A calcium bentonite from Kütahya region (Turkey) was activated with Na_2CO_3 at various ratios (1, 2, 2.5, 5, 10, 15g / 100 g bentonite). Due to ion exchange, the original Ca-bentonite was converted to Na-bentonite by Na_2CO_3 when the Na_2CO_3 /bentonite ratio was 2.5% (2.5 g Na_2CO_3 /100 g bentonite, A2.5). Na-bentonite (A2.5) obtained by soda activation was treated with 3 g CaCl_2 / 100 g bentonite and converted to Ca-bentonite again. The products were investigated by chemical analysis, X-ray diffraction and micropore analysis. It was observed that the cation exchange capacity (CEC) did not change until the soda ratio was 2.5 %. After this value the CEC decreased rapidly. The main montmorillonite hkl diffraction reflections were changed by Na_2CO_3 and CaCl_2 treatments. This showed that ion exchange was realized. It was observed that the specific surface area decreased from $49.34 \text{ m}^2 \text{ g}^{-1}$ to $29.92 \text{ m}^2 \text{ g}^{-1}$ by Na_2CO_3 and increased from $29.92 \text{ m}^2 \text{ g}^{-1}$ to $70.34 \text{ m}^2 \text{ g}^{-1}$ by CaCl_2 . In addition, it was determined that Na_2CO_3 activated Kütahya Ca-bentonite can be used as drilling mud.

Key Words: Bentonite, montmorillonite, surface properties, CEC, drilling muds.

Introduction

Scientific interest in bentonite is related to a wide range of applications, such as dispersions including drilling fluids and cements, paints, cosmetic etc. In particular, experience with drilling in the major oil producing countries has shown bentonite clay as the chief raw material that should be added in the preparation of drilling fluids. Its suspension has excellent colloidal properties. Many of its technical uses are based on the strong viscosity increase after the addition of soda and thixotropic properties (Miano and Rabaioli, 1994; Brandenburg and Lagaly, 1988, Singlh and Sharma, 1991).

Detailed studies have been carried out on bentonite suspensions, their coagulation by different salts, pH, rheological properties, surface area, cation exchange capacity, particle size and electrolyte concentration 4,5,6,7. Results from these studies indicate that the physical and rheological properties of bentonites are affected by the Na/Ca ratio and the CEC. Fahn (1973) investigated different raw bentonites and the products obtained after HCl and Na_2CO_3 treatments. He found certain reversible changes after the treatments. Acid treated samples show high $S_i\text{O}_2$ and low $R_2\text{O}_3$ contents, a high specific surface area and increased micropore

volume and bleaching ability. The samples treated with Na₂CO₃ were more like raw bentonite, with a lower SiO₂ and a higher R₂O₃ content, and low specific surface area, volume of micropores and bleaching ability. Komadel et al. (1990) found similar results.

In this study, we investigated the influence of Na₂CO₃ and CaCl₂ on some physicochemical and adsorption properties and determined whether Kütahya bentonite can be used as a drilling mud.

Experimental

Fractions smaller than 36 μm of white Kütahya Ca-bentonite (Ca-B) were used. The total reserve of this bentonite area is estimated to be about 1 million tons (The Mineral Research and Exploration Report, 1972, 1996). A chemical analysis of the bentonite is given in Table 1. The X-ray powder diagrams of the original and the activated samples, prepared as random powder material, were obtained with a Philips Powder Diffractometer, model PW 1730 CuKα radiation (40kV, 20 mA).

Table 1. Chemical analysis of Ca-Bentonite samples

(%)	Al ₂ O ₃	SiO ₂	K ₂ O	Fe ₂ O ₃	CaO	MnO	TiO ₂	P ₂ O ₅	Na ₂ O	MgO	A.Z.*	Others
Ca-B	14.00	68.20	1.70	0.90	2.82	0.20	0.10	0.10	0.70	1.40	9.10	0.78
Ca-B1	19.98	62.90	0.59	1.26	2.38	-	-	-	0.61	0.47	11.3	0.51

* weight loss at 1000° C

Ca- bentonite was activated with Na₂CO₃ at various mass ratios (soda ratio:0.5, 2, 2.5, 5 % labelled A0.5, A2, A2.5, A5) (Yıldız, 1997). For the samples activated at various Na₂CO₃ ratios, the CEC was determined by the methylene blue¹². Na- bentonite (Na-B) obtained by Na₂CO₃ activation (A2.5) was treated by 3 g CaCl₂/100 g bentonite to convert to Ca-bentonite (Ca-B1). The sediment was dried in an oven at 105° C.

The specific surface areas of the original Ca-B, the Na₂CO₃ and the CaCl₂ activated samples were determined by ASAP 2000 micropore analysis. For determination of performance as a drilling mud, the TS977 (1992) standard test was applied.

Results and Discussion

The X-ray diffraction patterns of original and Na₂CO₃ activated samples are illustrated in Figure 1. Montmorillonite was the main mineral; however, minor amounts of quartz, α-chyrstoballite and albite were also identified by XRD. These inorganic nonclay impurities were removed by centrifuge after soda activation. As seen from the activated sample patterns, the peaks of quartz and albite minerals mostly disappeared; however, it was not possible to remove α-chyrstoballite from the mixture. This was because α-chyrstoballite was finely dispersed in the sample. The main montmorillonite hkl diffraction reflections are present in all samples. Lower d(001) values were found for the Na-B obtained by soda activation at 2.5 g Na₂CO₃/100 g bentonite (about 12.1Å) than in the original Ca-B (15.04 Å). These results show that original Kütahya bentonite was converted to Na-B. In addition, maximum rheological properties were observed for Na-B (A2.5)¹¹. Sarıkaya et al (1994) found similar results.

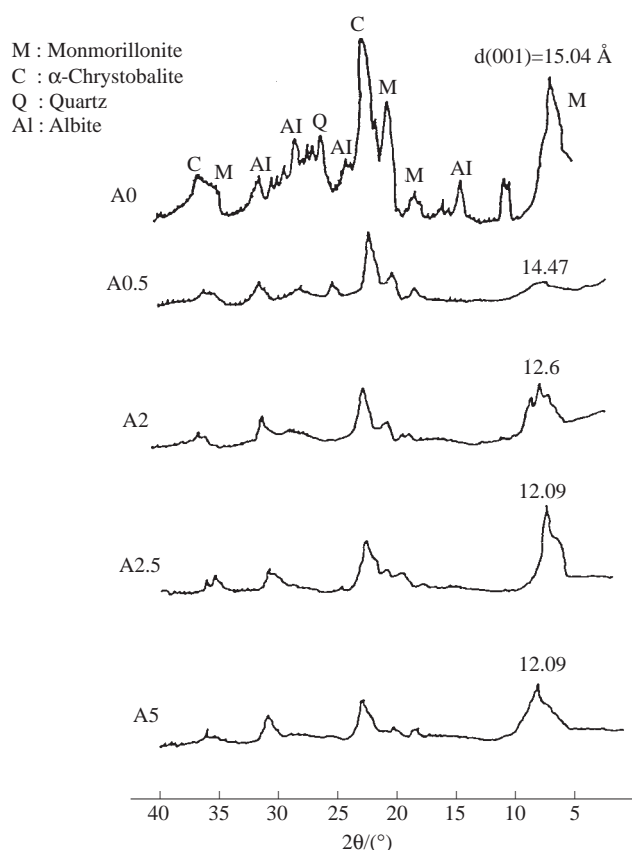


Figure 1. X-ray diffraction patterns of original and Na₂CO₃ activated samples

Afterwards, the Na-B obtained by soda activation was treated by CaCl₂ and converted to Ca-B1. The X-ray diffraction patterns of the original Ca-B, Na-B and Ca-B1 are illustrated in Figure 2. The d(001) values in the Na-B sample (about 12.09 Å) was lower than in the original Ca-B (15.04 Å), and it was observed that the d(001) value increased from 12.09 to 14.74 Å by CaCl₂ treatment. This showed that the Na-B can be converted by CaCl₂ to Ca-B1. In the activated samples, the peaks of quartz and albite mostly disappeared. Hence it is possible to obtain purer Ca-B1 than the original. Chemical analysis of Ca-B and Ca-B1 are presented in Table 1. In the original Ca-B, the percentage of SiO₂ was 68.20%, while in the activated (Ca-B1) sample the percentage of SiO₂ was 62.90%. The decrease in percentage was an expected result after the removal of the free SiO₂ by Na₂CO₃ treatment. The percentage of CaO in the original Ca-B was 2.82%, and this value decreased to 0.92% by Na₂CO₃ activation and increased to 2.38% by CaCl₂ treatment (Ca-B1) (Table 1). In the Na-B, the percentage of Na₂O was 3.20%. This value decreased by about 0.61 % in the Ca-B1 sample. This showed that 80% of Na⁺ ions in the sample exchanged with Ca⁺² ions.

The change in the cation exchange capacity (CEC) by Na₂CO₃ ratios is illustrated in Figure 3. The CEC of the original Ca-B sample was 29 meq/100 g bentonite (Yıldız 1997). The CEC was low because of nonclay impurities. It was thought that the ion exchange did not affect the CEC. The curve in Figure 3 could be extrapolated and the CEC of the original Ca-B would be determined as 78 meq/100 g bentonite. This value was also the same for the Na-B sample. The CEC did not change until the soda ratio was 2.5%, after which it decreased sharply. This change can be generally explained as follows: As known, some isomorphous substitutions of the Al⁺³ by Fe⁺³ on the tetrahedral sheet and Mg⁺² on the octahedral sheet occur on the

surface of the bentonite particle. If these substitutions take place, a net negative charge develops. This charge is then balanced by adsorbed cations. When the soda ratio increased, the net negative charge was balanced by Na⁺. Thus, the interlayer excess negative charge decreased and the CEC also decreased.

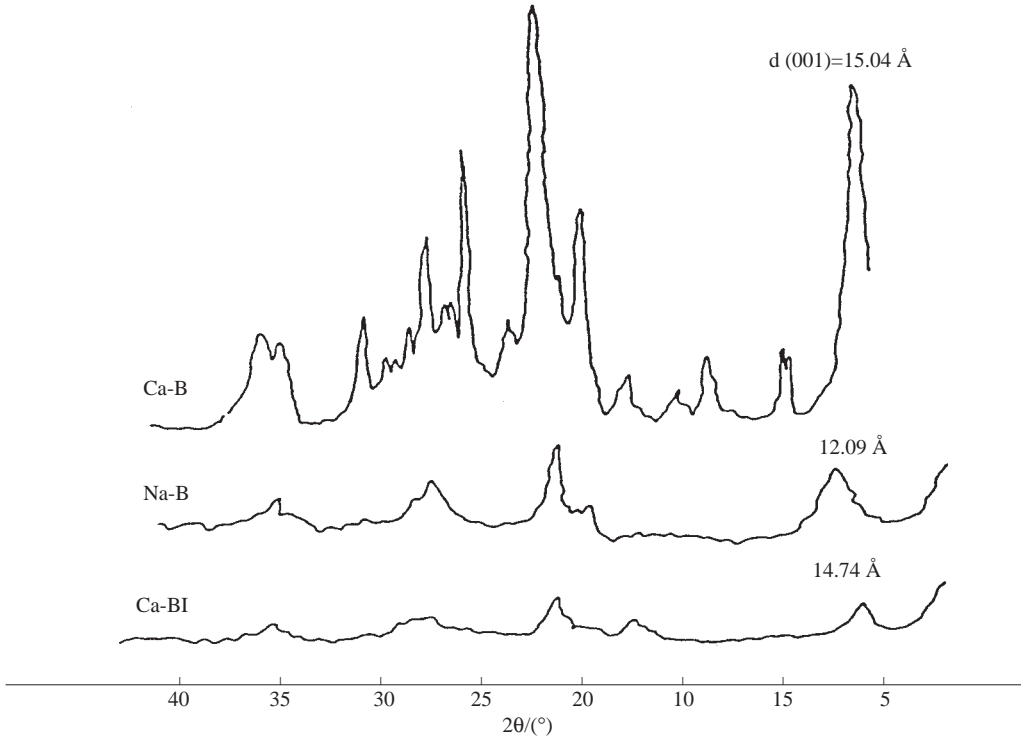


Figure 2. X-ray diffraction patterns of the original and the activated samples

Nitrogen adsorption isotherms of the original bentonite and activated samples are shown in Figure 4. The specific surface areas were determined from nitrogen adsorption isotherms by using data up to P/P₀ = 0.3. The specific surface area, the micropore area, the micropore volume and the average pore diameter of the sample are given in Table 2. The surface area (BET) of the original sample (Ca-B) was 49.34 m²g⁻¹. After the soda treatment this value decreased from 49.34 m²g⁻¹ to 29.92 m²g⁻¹. As known, the distance of the interlayer was 15.04 Å, and after treatment by Na₂CO₃ it decreased to 12.09 Å. Ca⁺² ions were exchanged by Na⁺ ions and this caused a decrease in the micropore area, such that the surface area of the Na-B was lower than that of the Ca-B. By treatment on Na-B with CaCl₂ (Ca-B1), the surface area increased from 29.92 m²g⁻¹ to 70.34m²g⁻¹. The higher surface area was obtained because of the removal of nonclay impurities by the Na₂CO₃ activation.

Table 2. Surface properties of bentonite samples

Properties	Bentonite samples		
	Ca-B	Na-B	Ca-B1
BET surface area /m ² g ⁻¹	49.34	29.92	70.34
Micropore area/ m ² g ⁻¹	2.42	4.14	7.36
Micropore volume/10-3 cm ³ g ⁻¹	0.63	1.74	2.86
Average pore diameter (BET)/ Å	91.12	179.02	118.92

Cumulative adsorption pore areas of the original and the activated samples are shown in Figure 5. These curves show that the original and activated samples had wide pore size distribution with mean pore

diameters of 20-500 Å for mesopores and of below 20 Å for micropores. Ca-B1 had a greater increase of pore area for micropores than for mesopores. In Na-B, the increase of pore area for micro and meso pores is slower than original Ca-B and Ca-B1 (Figure 5). The micropore areas and the average pore diameter are given in Table 2. For Ca-B1, Na-B and Ca-B, the micropore areas were 2.42 m²g⁻¹, 4.14 m²g⁻¹ and 7.36 m²g⁻¹ and the average pore diameter values were 91.12Å, 179.02Å and 118.92Å respectively (Table 2). Na-B had the greatest average pore diameter and the smallest surface area.

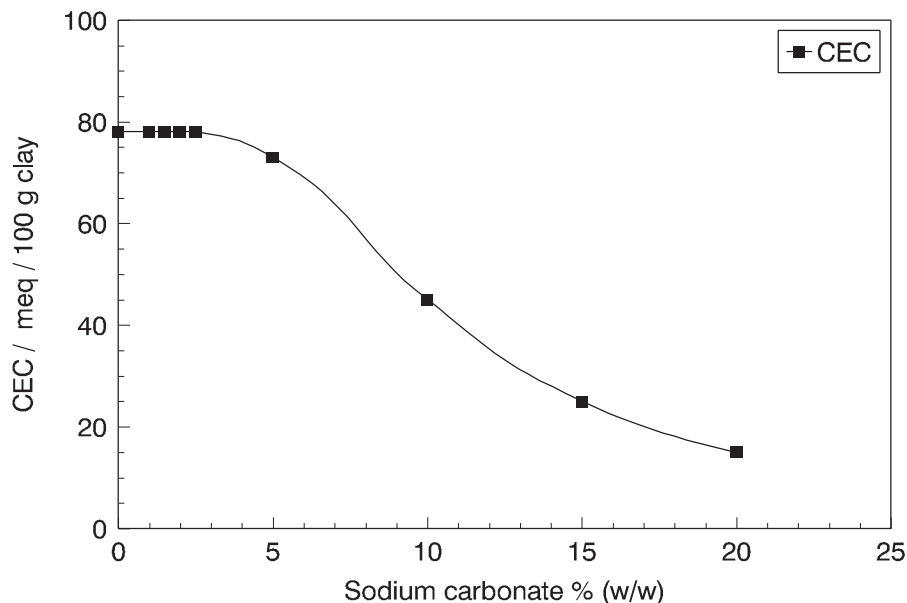


Figure 3. Plot of the CEC versus sodium carbonate % (O:29 meq/100g bentonite for original Ca-B (Yıldız,1997))

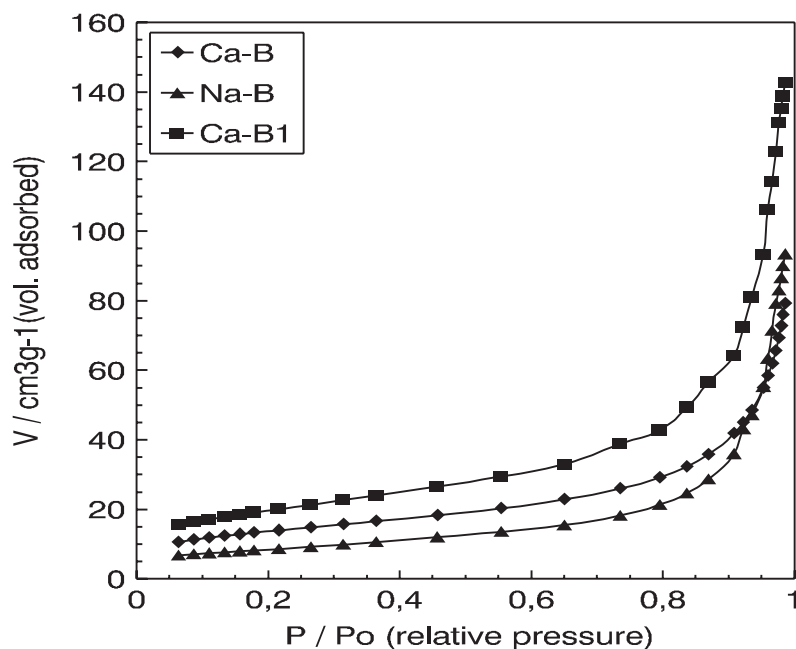


Figure 4. Nitrogen adsorption isotherms of the original and the activated samples.

The pore size distributions of the original and the activated samples are illustrated in Figure 6. Ca-B1 had a greater mesopore volume than Na-B and Ca-B. This change of the pore structure was the result of

the removal of impurities from the bentonite and the exchange of cations.

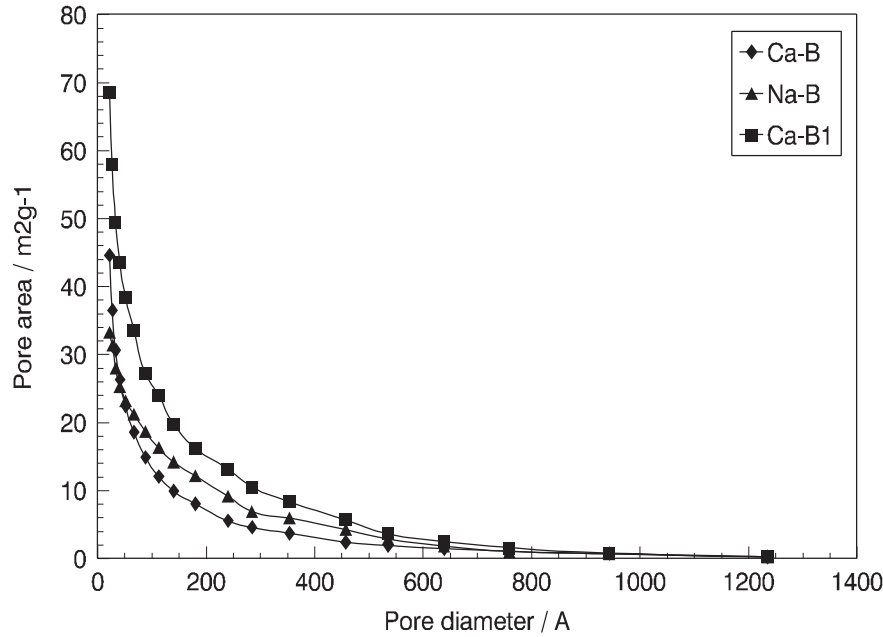


Figure 5. Cumulative adsorption pore area of the original and the activated samples.

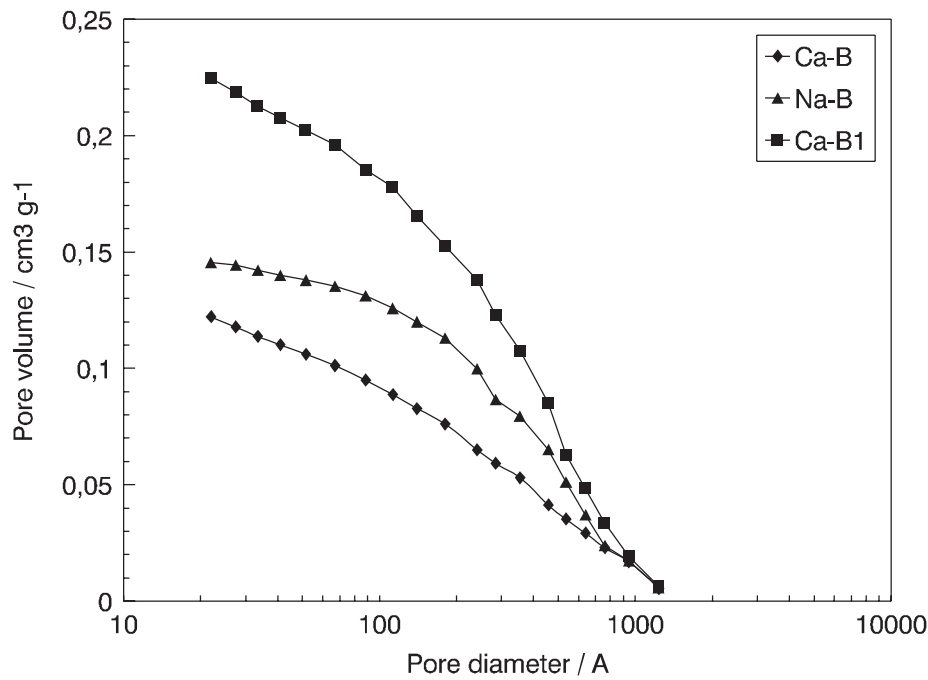


Figure 6. Cumulative pore volume distribution curves of the original and the activated samples

The use of Na-B as drilling mud was also investigated, and the TS977 (1992) standard test was applied. Rheological properties of the suspension with 22.5 g / 350 ml water were measured and the yield point (YP), plastic viscosity (PV) and apparent viscosity (AP) were determined respectively to be 6.72 Pa, 0.015 Pa s, and 0.022 Pa s (Table 3). For determination of the yielding capacity, the rheological properties were measured for three different bentonite concentrations (6g/100ml water, 5g/100ml water, 4g/100ml water).

Apparent viscosities of the suspensions varied from 0.019 to 0.009 Pa s (Table 3). From these measurements, the yielding capacity was determined as cited in TS977 standard. It was seen in Table 4 that when the yielding capacity for 24 hours was 14.4 m³ for the standard value, the determined value reached 19.2 m³. Screen analysis of the Na-B was also carried out. The standard maximum residue on the sieve was 2.5%, and the determined value was 0.78% for wet screen analysis. The standard minimum passing through the sieve was 98%, and the determined value was 100%. Maximum moisture and filtration for the standard were, respectively, 10 and 15, and they were 6.6 and 14 for the determined values. The determined values obtained for Na-B were similar to the standard values, so Na₂CO₃ activated Kütahya bentonite can be used as drilling mud.

Table 3. Rheological properties of Na-bentonite (A2.5)

GNa-B/100ml water	RPM Reading	Dial	YP/Pa	PV/Pa s	AV/ Pa s
22.5g/350ml water	600	44	6.72	0.015	0.022
	300	29			
6 g / 100 ml water	600	39	4.32	0.015	0.019
	300	24			
5 g / 100 ml water	600	28	0.96	0.013	0.014
	300	15			
4 g / 100 ml water	600	18	0.96	0.008	0.009
	300	10			

Table 4. The standard and the determined values of Na-bentonite (A2.5) for drilling fluids

Properties	Standard Value (TS977)	Determined value
Screen analysis		
Wet screen analysis 75µm 200 mesh) residue on sieve (K), %, maximum	2,5	0,78
Dry screen analysis 150µm (100 mesh) pass through sieve (G),%, minimum	98	100
Moisture (R), maximum	10	6,6
Filtration, L, maximum (S)	0.015	0.014
yielding capacity in 24 hours (yield), minimum	14.4 m ³	19.2 m ³
Suspension properties		
Direct-indicating viscometer viscometer Dial Reading at 600 rpm Pa, minimum	15,3	21.12
YP/PV, Pa/Pa s	21.12	446.4

Conclusions

Due to ion exchange, the original calcium bentonite (Ca-B) is converted to sodium bentonite (Na-B) by activation with Na₂CO₃, and the Na-B is also converted to calcium bentonite (Ca-B1) by treatment with CaCl₂. Depending on the Na₂CO₃ and CaCl₂ treatments, different chemical, analyses X-ray diffraction patterns and surface properties were observed. In Ca-B1, pore structure and adsorption properties were developed. The results showed that the cation exchange capacity (CEC) was affected by the Na₂CO₃ activation. In addition, it was found that Na-B obtained by Na₂CO₃ activation can be used as drilling mud.

Acknowledgment

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Nomenclature

Ca-B	Original calcium bentonite
Na-B	Sodium bentonite obtained by Na ₂ CO ₃ activation
Ca-B1	Calcium bentonite obtained from sodium bentonite (A2.5) by CaCl ₂
A0.5	0.5g Na ₂ CO ₃ /100 g bentonite
A2	2g Na ₂ CO ₃ /100 g bentonite
A2.5	2.5g Na ₂ CO ₃ /100 g bentonite
A5	5g Na ₂ CO ₃ /100 g bentonite
YP	Yield point, Pa
PV	Plastic viscosity, Pa s
AP	Apparent viscosity, Pa s

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