

Alteration of Three Turkish Bentonites by Treatment with Na_2CO_3 and H_2SO_4

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In this study, fine fractions of bentonites from the Çankırı and Kütahya regions were treated with Na_2CO_3 and H_2SO_4 . The resulting materials were analysed by X-ray diffraction (XRD), thermogravimetric and differential thermal analyses (TGA, DTA) and infrared (IR) spectroscopy. Surface areas of the samples were also measured. The results showed that structural changes were observed by treatment with Na_2CO_3 and H_2SO_4 . These changes showed differences depending on exchangeable cations, clay type and the ratio of additives.

Key Words: Bentonite, soda activation, acid activation.

Introduction

Smectite clays are widely used in a variety of industrial applications. In order to develop the surface and rheological properties of bentonites, they are treated with some inorganic chemicals. These are Na_2CO_3 and acids (HCl , H_2SO_4)¹⁻². Natural clays contain inorganic exchange cations such as Na^+ , Mg^{+2} and Ca^{+2} that are strongly hydrated in the presence of water. Na_2CO_3 treatment of bentonite depends on essentially on an ion exchange reaction; ions in the bentonite are replaced by alkali ions. Na_2CO_3 treatment creates an active bentonite with a high swelling capacity and increased plasticity for using especially as drilling muds³. When bentonite is treated with acid, the exchangeable ions are replaced by H^- ions. During this process, the crystal structure of the bentonite is altered by the leaching of Al^{+3} , Fe^{+2} and Mg^{+2} ions and the specific surface area and porosity are increased. Acid treated bentonites are used as adsorbents and catalysts².

The structural changes in bentonites have been studied by scientists under different conditions. IR spectroscopy in conjunction with X-ray diffraction and other techniques has been extensively applied to investigate the structural changes of layer silicates⁴⁻⁶.

In the present work, three bentonites (Çankırı sodium bentonite (ÇNa-B), Çankırı calcium bentonite (ÇCa-B) and Kütahya calcium bentonite (KCa-B)) were treated with Na_2CO_3 and H_2SO_4 . The treated bentonites were then studied by XRD measurements, thermal analyses and IR spectroscopy.

Materials and Methods

Fractions smaller than $75\mu\text{m}$ of white-coloured Çankırı sodium bentonite (Cation exchange capacity (CEC): 85meq/100 g clay), Çankırı calcium bentonite (CEC: 47meq/100 g clay), and Kütahya calcium bentonite (CEC: 65meq/100 g clay), were used in the study. For sieve analysis, the 4187/ASTM-E11-70 standard analysis was applied. The chemical analyses of the bentonites are given in Table 1. The samples were analysed for Na^+ flame photometer (JENWAY PFP7) and for other elements by atomic absorption spectroscopy (Unicom 939 AAS). The cation exchange capacity (CEC) of the original bentonites was determined by the methylene blue test ⁷. The X-ray powder diagrams of the original and the treated samples, prepared as random powder material, were obtained via powder diffractometer (Rikagu D-max 2200). Montmorillonite was the main mineral in the samples. Minor amounts of quartz, α -cristobalite and albite were also identified in the raw materials. The specific surface areas of the original and treated bentonites were determined by micropore analysis equipment (ASAP 2000). Differential thermal analyses were obtained with thermal analyzer (Shimadzu-50) using a heating rate of $10^\circ\text{C}/\text{min}$. The infrared spectra of the samples were acquired with a spectrometer (8300 FTIR, Shimadzu).

Table 1. Chemical analyses of the original bentonites

Sample	MgO	Al ₂ O ₃	SiO ₂	CaO	Fe ₂ O ₃	SO ₃	K ₂ O	Na ₂ O	TiO ₂	KK*
ÇNa-B	0.85	15.50	70.74	0.46	2.23	0.17	0.24	2.12	0.00	6.53
ÇCa-B	7.13	9.36	34.90	14.40	3.21	0.10	2.11	2.73	0.28	22.30
KCa-B	1.40	14.00	68.20	2.82	0.90	-	1.70	0.70	0.10	9.10

*Weight loss at 1000°C

Na₂CO₃ Treatment

Three bentonite samples (KCa-B, ÇCa-B and ÇNa-B) were activated with Na₂CO₃ at various mass ratios (soda ratio: 0.5, 2, 2.5, 5, 10, 15, 20% labelled as S0.5, S2, S2.5, S5, S10, S20 for KCa-B, ÇS1, ÇS2.5, ÇS5, ÇS10, ÇS20 for ÇCa-B and SS1, SS2.5, SS5, SS10, SS20 for ÇNa-B). Bentonite and Na₂CO₃ were added to 800 ml boiling water and the dispersion was left boiling for 1 h. After dilution with water the dispersion was allowed to settle in a large bottle for 48 h and the supernatant suspension was separated by decantation. The sediment was again dispersed in water, the supernatant was again decanted and this procedure was repeated until bentonite was no longer dispersed in the supernatant. The supernatants were collected, concentrated by evaporation and dried in an oven at 105°C .⁸

H₂SO₄ Treatment

The bentonite samples (ÇCa-B, ÇNa-B and KCa-B) dried at 105°C were treated with H₂SO₄ solutions at 98°C for 5 h in a three-neck glass flask. H₂SO₄ concentrations were prepared as 0.5, 1, 1.5, 2, 3, 4 M. A reflux condenser was attached to prevent loss of acid and water. Agitation was achieved by a magnetic stirrer. The ratio of the mass of clay to the volume of acid solution was $1\text{g}/10\text{cm}^3$. The clay was filtered and washed free of sulphates. Treated samples were dried at 105°C and stored in bottles for analyses (Acid ratio: 0.5, 1, 1.5, 2, 3, 4 M labelled as, A0.5, A1, A1.5, A2, A3, A4 for ÇCa-B and B0.5, B1, B1.5, B2, B3, B4 for KCa-B and, C1, C1.5, C2, C3, C4 for ÇNa-B)

Results and Discussion

Basal spacing ($d(001)$), and the BET surface areas of the original and treated bentonites are presented in Table 2.

Table 2. Properties of original and treated bentonites

Bentonite	$d(001)$ (Å)	BET(m^2g^{-1})
KCa-B	15.00	54.97
ÇCa-B	14.50	73.14
ÇNa-B	12.00	63.00
S0.5	14.50	50.60
S2	12.60	45.83
S2.5	12.10	29.92
S5	12.10	26.51
S10	12.50	26.89
S15	12.70	23.60
S20	12.90	23.11
ÇS1	14.01	66.31
ÇS2.5	13.57	58.17
ÇS5	13.01	43.48
ÇS10	12.99	33.63
ÇS20	13.23	31.21
SS1	12.21	58.13
SS2.5	12.07	55.14
SS5	11.98	54.08
SS10	12.13	53.66
SS20	12.32	53.41
A0.5	14.41	111.56
A1	14.48	217.86
A1.5	14.42	252.95
A2	-	251.31
A3	-	246.15
A4	-	119.76
B0.5	14.49	83.60
B1	14.39	114.80
B1.5	14.28	159.60
B2	14.31	190.45
B3	-	139.50
B4	-	92.60
C1	12.43	73.06
C1.5	11.64	95.71
C2	11.96	110.15
C3	11.24	125.63
C4	-	98.61

The X-ray diffraction basal spacings $d(001)$ of the original bentonites were between 12 and 15 Å (Table 2). $d(001)$ basal spacings decreased by Na_2CO_3 activation for KCa-B from 15 to 12.1 Å. This showed that Na^+ ions replaced Ca^{+2} ions in the interlayer and formed Na-bentonite.⁷ As seen in Table 2, $d(001)$ of Na_2CO_3 activated KCa-B reached basal spacings of an original Na-bentonite (ÇNa-B, 12 Å) at 2.5 Na_2CO_3

ratio. The changes in the basal spacings for Na₂CO₃ treated ÇCa-B samples are similar to KCa-B. However, a marked change was not observed in the basal spacings of Na₂CO₃ treated ÇNa-B.

The basal spacings of untreated (KCa-B, 15.00 Å, ÇCa-B, 14.50 Å, ÇNa-B, 12.00 Å) and H₂SO₄ treated samples, prepared as random powder material, are also given in Table 2. The main basal spacings belonging to montmorillonite disappeared after 1.5 M H₂SO₄ treatment for ÇCa-B, 2 M H₂SO₄ for KCa-B and 3 M H₂SO₄ for ÇNa-B depending on the decomposition of the structure. ÇCa-B is more soluble than ÇNa-B and KCa-B due to its rich magnesium content.

The BET surface areas of the original KCa-B, ÇCa-B and ÇNa-B were respectively 54.97 m²g⁻¹, 73.14 m²g⁻¹ and 63.00 m²g⁻¹, (Table 2). The BET surface area of the KCa-B decreased with Na₂CO₃ activation from 54.97 m²g⁻¹ to 23.11 m²g⁻¹. Ca⁺² ions were exchanged by Na⁺ ions and this caused a decrease in the micropore area and low BET surface areas for Na₂CO₃ treated samples. Similarly, the BET surface area of ÇCa-B decreased with treatment (from 73.14 to 31.21 m²g⁻¹). The BET surface areas of Na₂CO₃ treated ÇNa-B samples also decreased slightly depending on the adsorption of Na⁺ ions.

The change in BET surface areas for H₂SO₄ treated samples is also shown in Table 2. For the samples treated with 1.5 M H₂SO₄ (ÇCa-B), 2M H₂SO₄ (KCa-B) and 3M H₂SO₄ (ÇNa-B) the value of specific surface area reached a maximum (for ÇCa-B, 252.95 m²g⁻¹, for KCa-B, 190.45 m²g⁻¹ and for ÇNa-B, 125.63 m²g⁻¹) and then decreased (for ÇCa-B 119.76 m²g⁻¹, for KCa-B, 92.60 m²g⁻¹ and 98.61 m²g⁻¹). This indicates that the observed chemical and structural changes after treatment with higher acid concentrations caused an alteration of the morphology and consequently the surface properties of the samples.

The DTA plots for Na₂CO₃ treated Kütahya calcium bentonite (KCa-B) are shown in Figure 1. Original KCa-B shows a low-temperature endothermic peak at about 100-200°C, a medium-small endothermic peak at about 750°C and a small S-shaped endothermic-exothermic peak system at about 890-950°C. These peaks are due to the loss of sorbed moisture, dehydroxylation and structural changes, respectively. Through Na₂CO₃ treatment (A0, A0.5, A1, A2) the samples give a large-low temperature endothermic peak at between 75 and 125 °C, a large endothermic peak at about 450-700 °C and an endothermic peak at about 950°C. The peak at 950°C showed ion exchange in the bentonite. By increasing the Na₂CO₃ ratio (A5, A15, A20), the endothermic peak 450-700°C becomes very small. This may be a result of excess Na⁺ ions affecting the energy with which the hydroxyl groups are bound to in the lattice. Therefore, the intensity of the dehydroxylation peak changed. The DTA curves for original and Na₂CO₃ treated ÇCa-B are given in Figure 2. The curves showed considerable water loss at low temperatures (100 to 200°C). The amount of this water, which occurs mostly as interlayer water between the silicate sheets, is contingent upon the nature of the adsorbed ions. Loss of OH⁻ water occurs between 600°C and 700°C. A marked endothermic-exothermic reaction was observed at about 900-1000°C. Enstatite, mullite or anorthite may develop at about 1000°C, in addition to the β-quartz, probably depending on the amount of magnesium present and possibly also on the amount of exchangeable Ca⁺². Na₂CO₃ treated ÇCa-B samples showed changes similar to KCa-B. The DTA curves corresponding to original and Na₂CO₃ treated ÇNa-B are presented in Figure 3. The original sample showed water loss at low temperature (first endothermic peak), an endothermic peak due to loss of OH lattice water, beginning at about 650°C, ending at about 750°C and an endothermic peak at about 800-900°C correlated with the destruction of the lattice. By Na₂CO₃ treatment, the intensity of the dehydroxylation peak showed some changes depending on the changing energy of the hydroxyl groups.

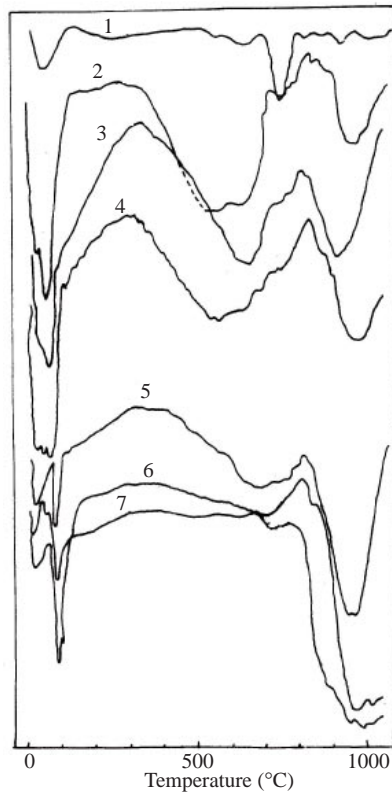


Figure 1. DTA of original and Na_2CO_3 treated KCa-B: 1: Original, 2: S0.5, 3: S1, 4: S2.5, 5: S5, 6: S10, 7: S20

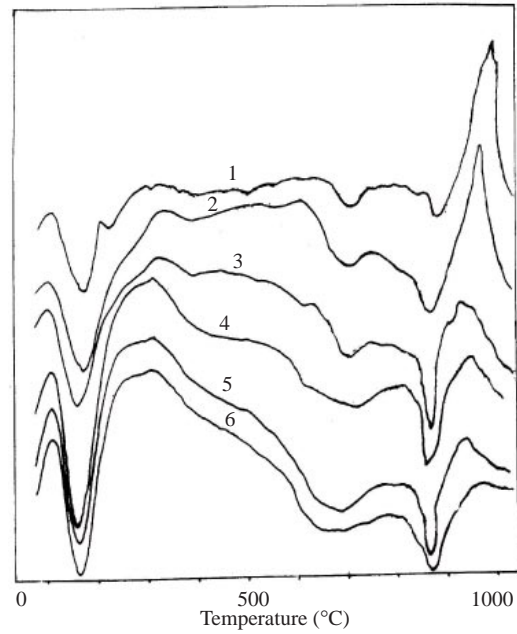


Figure 2. DTA of original and Na_2CO_3 treated ÇCa-B: 1: Original, 2: ÇS1, 3: ÇS2.5, 4: ÇS5, 5: ÇS10, 6: ÇS20

TG curves for Na_2CO_3 treated KCa-B bentonite are illustrated in Figure 4. Curves showed a gradual continuous weight loss between 25 and 125°C. Weight loss for the original sample, between

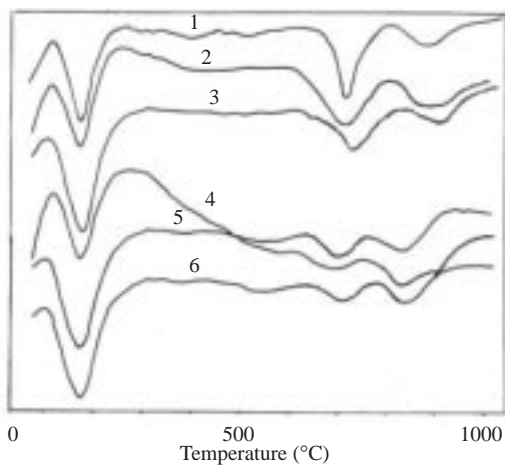


Figure 3. DTA of original and Na_2CO_3 treated ÇNa-B: 1: Original, 2: SS1, 3: SS2.5, 4: SS5, 5: SS10, 6: SS20

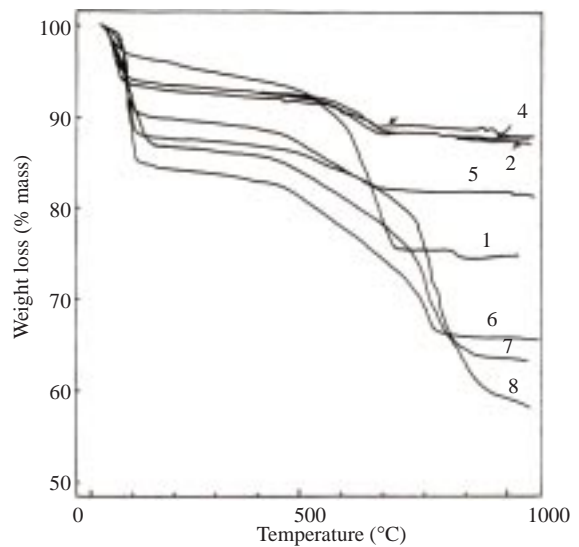


Figure 4. TG of original and Na_2CO_3 treated KCa-B; 1: Original 2: S0.5, 3: S1, 4: S2, 5: S2.5, 6: S5, 7: S10, 8: S20

25 and 500°C, was lower than the treated samples. This phenomenon may be explained only with an exchangeable cation of high hydration energy. The hydration energy of Ca^{2+} cations is smaller than that of Na^+ cations. For samples A10, A15, A20 weight loss was higher than A0-A5 after 650°C depending on excess Na_2CO_3 . The total weight loss was about 23% for original KCa-B. But in the soda activated samples, weight loss varied from 9% to 17% for S1-S5 samples and 32% and 41% for S10-S20 samples. The total weight loss of original ÇCa-B was about 22%; however, weight losses of Na_2CO_3 treated samples varied between 20% and 30%. Similarly, the total weight loss of ÇNa-B increased from 17% to 23% via Na_2CO_3 treatment. It was noted in the treated samples that the weight loss corresponding to the physisorbed water and of the first water molecules bound to the sodium cation increased with Na_2CO_3 treatment. In addition, the weight loss due to the destruction of the structure also increased.

The IR spectra belonging to original and Na_2CO_3 treated (KCa-B) bentonites are presented in Figure 5 for the range 4000-400 cm^{-1} . The spectra are sensitive both to structural and compositional variations in the minerals. For the original and treated samples, OH^- groups showed absorption of high frequencies of 3500 to 3700 cm^{-1} , whereas the adsorbed water showed absorption at lower frequencies, 3400 cm^{-1} , and another band between 1500 and 1600 cm^{-1} corresponding to the deformation vibration of water. Displacement of the OH^- stretching vibration to lower frequencies associated with band broadening in the samples is due to hydrogen bonding. For original samples, the band at about 900 cm^{-1} indicated the influence of iron in the structure. Frequencies between 1150 and 400 cm^{-1} are lattice vibrations. Absorption in the 1150-960 cm^{-1} region resulted from Si-O stretching vibrations. Bands in the 960 to 550 cm^{-1} region are due to R-O-H vibrations. Because of its iron and aluminium content, an absorption band at 850 cm^{-1} was shown in the original samples (hydroxyl groups shared between ferric iron and aluminium in the octahedral layer). The strong absorption in the region below 550 cm^{-1} originated principally from in-plane vibrations of the octahedral ions and their adjacent oxygen layers. These vibration couples were seen because of metal-oxygen stretching or silicon-oxygen bending. As seen in Figure 5, between the original and Na_2CO_3 treated samples some changes were seen in the absorption bands. Vibration peaks at about 850 cm^{-1} (AlMgOH) and 524 cm^{-1} (Al-O-Si) increase after Na_2CO_3 treatments. The absorption band at 850 cm^{-1} showed a small shift toward higher frequencies. The contents of Al and Mg have increased as well as the intensities 850 cm^{-1} and 524 cm^{-1} after removal of the free SiO_2 by Na_2CO_3 treatments. In the IR spectra of Na_2CO_3 treated ÇCa-B, similar changes were also observed (Figure 6). The intensity of the peak at about 1150 cm^{-1} resulting from Si-O stretching vibrations decreased depending on removal of the free SiO_2 by treatment. The IR spectra of Na_2CO_3 treated ÇNa-B are given in Figure 7. A marked change is not observed at bands between 400 and 960 cm^{-1} . The intensity of the band at about 1500 cm^{-1} (deformation vibration of water) increased with Na_2CO_3 treatment.

In Figures 8-11, changes in DTA and TG curves after treatment with different concentrations of H_2SO_4 (0-4 M) for KCa-B, ÇCa-B and ÇNa-B are shown. The first low temperature endothermic peak is due to the loss of sorbed moisture (Figures 8-10). The second endothermic peak (shoulder at 180 °C) is due to exchangeable Ca^{+2} ions in the ÇCa-B (Figure 9). The higher acid concentration (3M H_2SO_4) caused the removal of Ca^{+2} ions, consequently the peak at 180°C disappeared. The acid treatment carried out at 1-4M concentrations were observed to cause a breakdown in the crystal structure between 900 and 1000 °C, as the peaks belonging to bentonite disappeared in this temperature range (Figures 8-10).

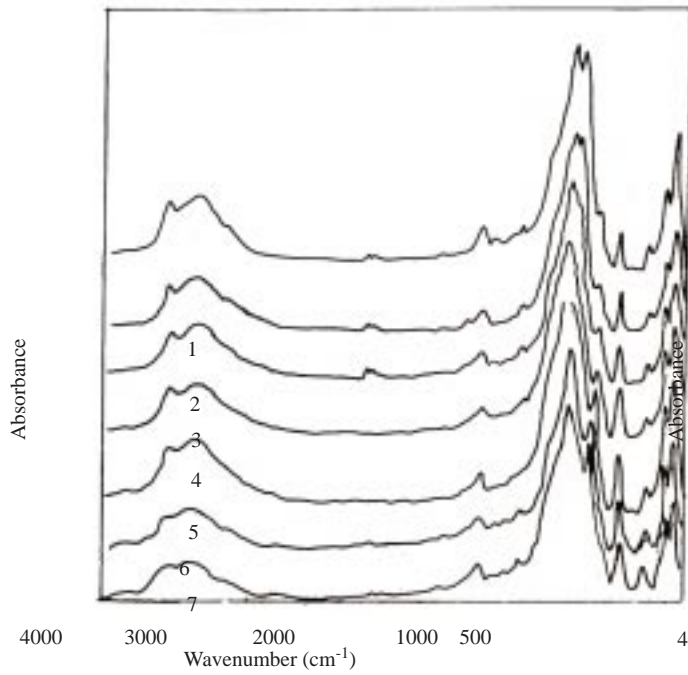


Figure 5. IR spectra of original and Na_2CO_3 treated KCa-B: 1: Original, 2: S0.5, 3: S1, 4: S2.5, 5: S5, 6: S10, 7: S20

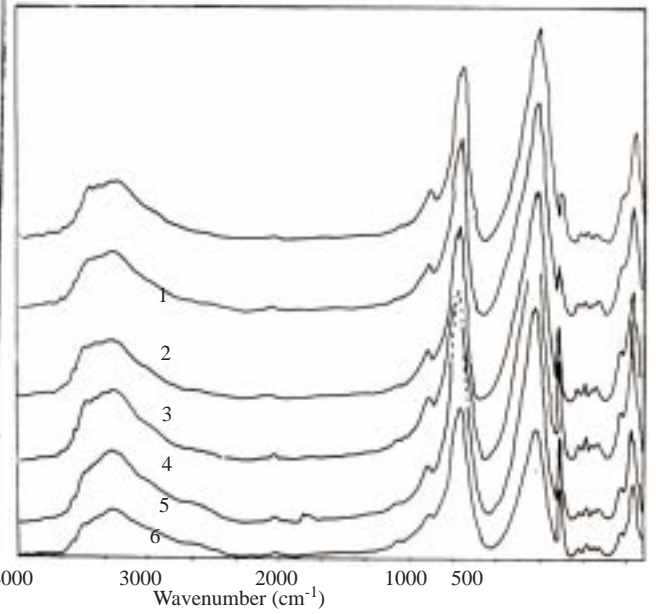


Figure 6. IR spectra of original and Na_2CO_3 treated ÇCa-B: 1: Original, 2: ÇS1, 3: ÇS2.5, 4: ÇS5, 5: ÇS10, 6: ÇS20

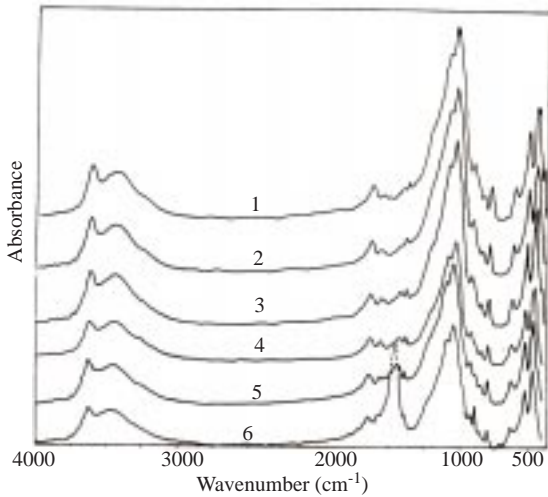


Figure 7. IR spectra of original and Na_2CO_3 treated ÇNa-B: 1: Original, 2: SS1, 3: SS2.5, 4: SS5, 5: SS10, 6: SS20

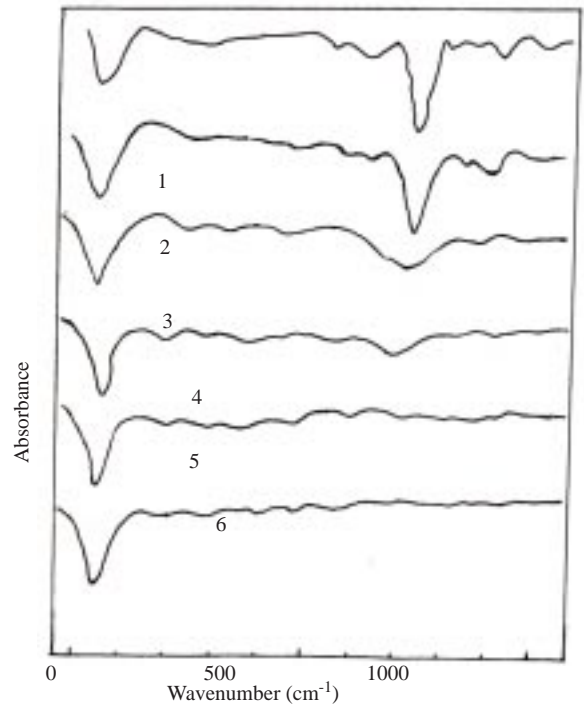


Figure 8. DTA of original and H_2SO_4 treated KCa-B: 1: Original, 2: B1, 3: B1.5, 4: B2, 5: B3, 6: B4

The TG curves corresponding to H_2SO_4 treated KCa-B are presented in Figure 11. While the weight loss was of about 23% for original KCa-B, it decreased by treatment (between 7% and 16%). Similarly, the total weight loss of original ÇCa-B was about 22% and 17% for original ÇNa-B. However, in the acid activated samples, weight loss varied from 8% to 12% for ÇCa-B and 11% to 16% for ÇNa-B. It was observed in TG

analysis that for treated samples weight loss is lower than for original bentonite because of decomposition. Dissolution of the octahedral sheets by acid treatment is shown in IR spectra for KCa-B (Figure 12). In the 1100-500 cm^{-1} region, AlMgOH vibrations at 850 cm^{-1} and Al-O-Si vibration at 524 cm^{-1} decrease after H_2SO_4 treatments ⁵. In the IR spectra of ÇCa-B, similar peaks and changes were also observed. The IR spectra of acid treated ÇNa-B are given in Figure 13. Similar to H_2SO_4 treated ÇCa-B and KCa-B, the intensity of the bands in the 960 to 550 cm^{-1} region due to R-OH vibrations decreased with treatment.

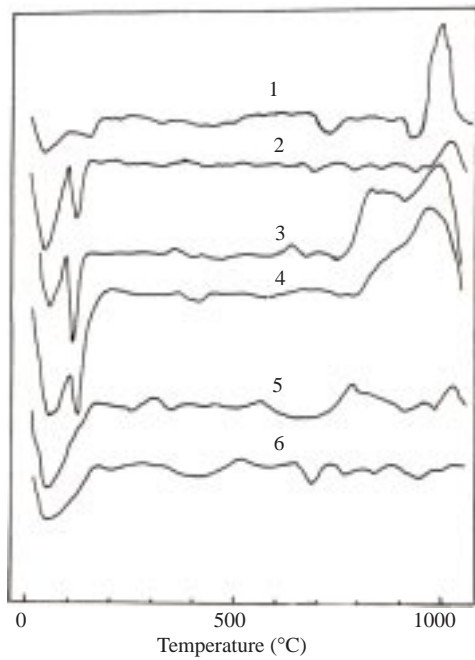


Figure 9. DTA of original and H_2SO_4 treated ÇCa-B: 1: Original, 2: A1, 3: A1.5, 4: A2, 5: A3, 6: A4

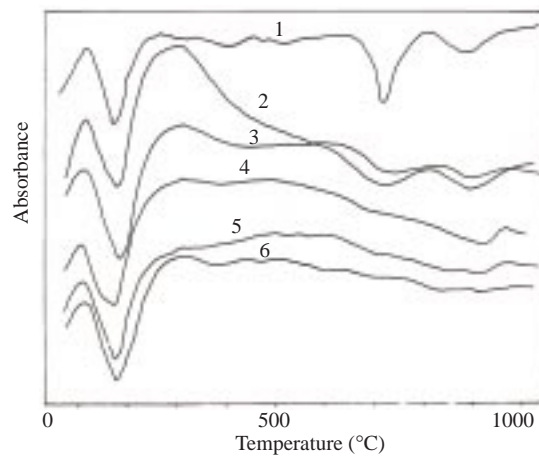


Figure 10. DTA of original and H_2SO_4 treated ÇNa-B: 1: Original, 2: C1, 3: C1.5, 4: C2, 5: C3, 6: C4

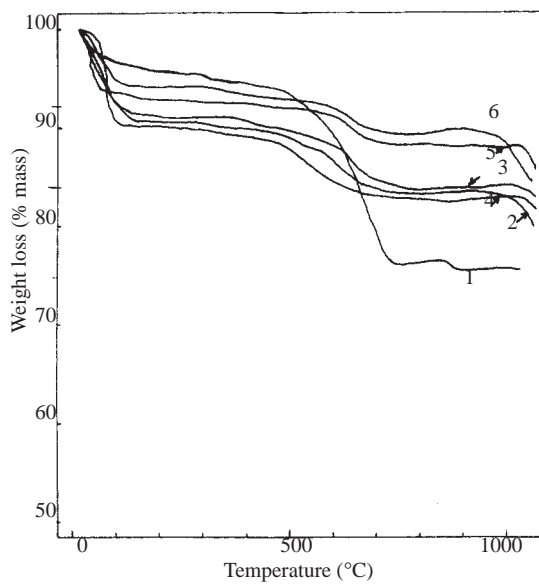


Figure 11. TG of original and H_2SO_4 treated KCa-B: 1: Original, 2: B1, 3: B1.5, 4: B2, 5: B3, 6: B4

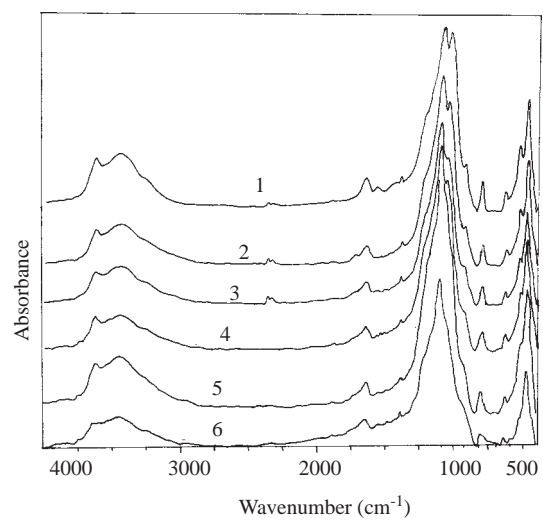


Figure 12. IR spectra of original and H_2SO_4 treated KCa-B: 1: Original, 2: B1, 3: B1.5, 4: B2, 5: B3, 6: B4

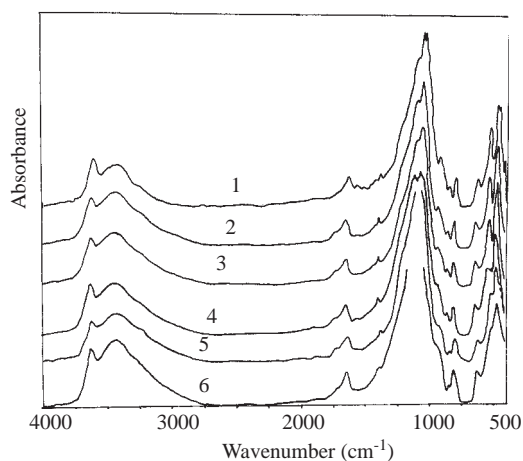


Figure 13. IR spectra of original and H₂SO₄ treated ÇNa-B: **1:** Original, **2:** C1 , **3:** C1.5, **4:** C2 , **5:** C3, **6:** C4

Conclusion

The analyses of treated samples with Na₂CO₃ and H₂SO₄ showed that the structure of bentonites completely changed following treatment. These changes were especially seen by X-ray diffraction, DTA and TG analyses and surface area measurements. It was observed that the structure changes depend on exchangeable cations, clay type and the ratio of the additive. It was concluded that a bentonite sample having certain required properties can be obtained by inorganic agent treatments.

Nomenclature

ÇNa-B: Çankırı sodium bentonite
ÇCa-B: Çankırı calcium bentonite
KCa-B: Kütahya calcium bentonite

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