



The improvement of gelling property of bentonites using their physico–chemical and mineralogical characteristics

Bentonitlerin jelleşme özelliğinin fiziko–kimyasal ve mineralojik özellikleri kullanılarak iyileştirilmesi

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ABSTRACT

In this study, the physical, chemical, and mineralogical properties of three commercial bentonite samples (Turkey) were determined using physical, chemical, XRD, TG–DTA and IR analysis methods. Experimental results show that the studied samples contain smectite as the dominant clay mineral and considering the tetrahedral layer charges (Çankırı >Ordu >Reşadiye), Reşadiye sample was found to resemble an ideal montmorillonite, Çankırı sample a beidellitic montmorillonite and Ordu sample having an intermediate character. The octahedral iron content of the Çankırı sample also was found to be highest and that of the Ordu sample was the lowest. The critical coagulation concentration, sedimentation volume, gelling coefficient, glycerol surface area and cation exchange capacity tests were done in order to reveal the physico–chemical characteristics of the samples. Considering these characterisations, Çankırı sample was found suitable for the improvement of its rheological properties. MgCl₂·6H₂O was used as an inorganic additive and the effect of pH and reagent concentration on the rheological properties was investigated. It was found that the gelling and swelling properties were improved by 30% and 34%, respectively.

Key words: Bentonite, gelling coefficient, sedimentation volume, smectite.

ÖZ

Bu çalışmada, fiziksel, kimyasal, XRD, TG–DTA ve IR analiz yöntemleri kullanılarak üç ticari bentonit (Türkiye) örneğinin fiziksel, kimyasal ve mineralojik özellikleri belirlenmiştir. Deneysel sonuçlar; kullanılan bentonit örneklerinin baskın olarak smektit içerdiğini ve terahedral tabaka yükü göz önüne alındığında (Çankırı >Ordu >Reşadiye), Reşadiye örneğinin ideal montmorillonite, Çankırı örneğinin beyidellitik montmorillonite ve Ordu örneğinin de ara karakterdeki montmorillonite benzediğini göstermiştir. Ayrıca, Çankırı örneğindeki oktahedral demir içeriğinin en fazla ve Ordu örneğindeki oktahedral demirin de en az olduğu bulunmuştur. Örneklerin fiziko–kimyasal özelliklerini belirlemek amacıyla kritik koagülasyon konsantrasyonu, çökelti hacmi, jelleşme katsayısı, gliserol yüzey alanı ve kation değişim kapasitesi deneyleri yapılmıştır. Bu tanımlamalar dikkate alınarak, reolojik özelliklerinin iyileştirilmesi için en uygun örneğin Çankırı örneği olduğu anlaşılmıştır. Anorganik katkı maddesi olarak MgCl₂·6H₂O kullanılarak, pH ve reaktif derişiminin reolojik özelliklere olan etkileri incelenmiştir. Jelleşme ve şişme özelliklerinde sırasıyla %30 ve %34 iyileştirme sağlanabileceği anlaşılmıştır.

Anahtar kelimeler: Bentonit, jelleşme katsayısı, çökelti hacmi, smektit.

INTRODUCTION

Montmorillonite and beidellite are the principal constituents of bentonite deposits resulted from

various alteration and weathering processes of alkaline rocks. While montmorillonite represents Mg for Al octahedrally substituted end–member of the dioctahedral smectites, beidellite repre-

sents Al for Si tetrahedrally substituted end-member (Grim, 1968). As montmorillonite and beidellite have the highest occurrence, bentonites having intermediate chemical and mineralogical compositions can be formed (Lim and Jackson, 1986; Çoban and Ece, 1999). Due to random interstratifications, some of their properties (gelling, swelling, cation exchange, etc.) may alter and so detailed physico-chemical and mineralogical identification of the samples are required in order to evaluate and to improve their properties, which have crucial importance in drilling, foundry, bleaching, clarification and pelletizing industries (Murray, 1999).

Edge-to-edge (EE), edge-to-face (EF) and face-to-face (FF) interactions (van Olphen, 1963) are very important and practical for understanding the stability and rheological characteristics of clay suspensions. These type of particle interactions are intimately related to the electrical charges on the basal planes and the edge surfaces. The electrical charges vary in magnitude and sign depending on suspension pH, suspension electrolyte concentration, electrolyte type and the presence of special complexing anions (van Olphen, 1963; Heath and Tadros, 1983; Benna et al., 1999). In alkaline suspensions, EF type interactions are not favourable due to the repulsion of negative surfaces, but an EE type or a band-like interaction favors due to the high negative potential on the high surface area basal planes of the particles (Luckham and Rossi, 1999). Durán et al. (2000), using theoretical considerations, found that at $\text{pH} < 7$ the EF interactions and at $\text{pH} > 7$ the EE interactions are dominant and at $3 < \text{pH} < 10$ the FF interactions are practically impossible. Special complexing anions, such as polymetaphosphates, are added to the clay suspensions to greatly reduce the Bingham yield stress by disrupting the EE or EF type associations and specific adsorption of the anion to the clay edge surface makes the edge charge more negative as showed by Oster et al. (1980). Accordingly, the Bingham yield value of the suspension should increase if the potential on the edges is changed from negative to positive in alkaline pH values and the mechanism of the improvement in gelling property of bentonites due to formation of positively charged edge surfaces by use of inorganic additives was explained by Obut (2001).

Although the mineralogical and petrographical studies on some of the Turkish bentonite deposits, such as Çankırı, Tokat, Ayvacık, and Ordu have been done (Türkmenoğlu and Aker, 1990; Gümüşer ve Yalçın, 1998; Çoban and Ece, 1999; Çelik et al., 1999), their physical characterisation related to gelling and swelling properties are not correlated in detail with their mineralogical properties. The aim of this study is to determine some physical, chemical, and mineralogical properties of three commercial bentonite samples so as to be able to improve some of their properties by inorganic additives. In this respect; Çankırı sample was found suitable for improvement of the gelling coefficient and the sedimentation volume properties, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was tested as an inorganic additive, and the effect of reagent concentration and pH on the rheological properties was studied.

EXPERIMENTAL STUDY

Materials

The Çankırı, Reşadiye and Ordu bentonite samples were supplied by Karakaya Bentonit A.Ş. which are marketed as foundry sand binder, drilling mud additive and bleaching earth, respectively and these marketed samples were named as original samples. Original, $-2\mu\text{m}$ separated fractions, methylene blue (Hoechst), glycerol (Prolabo), Merck grade reagents (NaCl, LiCl, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, HCl, NaOH, ethylene glycol) and distilled water were used in the experiments.

Methods

Original clay samples were used as received from the supplier. Purified clay fractions were prepared by first removing carbonates and organic matter, and then collecting clay fraction by centrifugation as described in Jackson (1964) for use in only ethylene glycolated and heated XRD analysis for identification of the existing clay mineral type. $-2\mu\text{m}$ fractions used in all other experiments were prepared only by decantation obeying Stokes' law.

XRD patterns of random powder, ethylene glycolated, heated (300°C) and Li-250 treated (Lim and Jackson, 1986) specimens were obtained using Philips PW 1140 X-ray diffractome-

ter with $\text{CuK}\alpha$ radiation. Chemical analysis of the original and $-2\mu\text{m}$ fractions were carried out using Philips PW 1480 X-ray spectrometer, and carbon contents of the original samples were determined using Leco 1000 model analyzer. The amount of exchanged Na in cation exchange capacity measurements for original samples were done using Varian Spectra AA-5 atomic absorption spectrometer. Thermal behavior of the original samples were identified using Rigaku 2.22E2 model TG-DTA thermal analyzer with $10^\circ\text{C}/\text{min}$ heating rate, and infrared spectra of the $-2\mu\text{m}$ fractions were determined using Nicolet 520 FT-IR spectrometer with KBr disc method.

pH (6% wt/vol), critical coagulation concentration with NaCl (3% wt/vol), methylene blue index (ASTM, 1992), cation exchange capacity (Bain and Smith, 1994), measured and theoretical glycerol surface areas (Jackson, 1964; Güven, 1992), gelling coefficient (TS 5360, 1996) and sedimentation volume (1.4g sample/100ml water) values of the original samples were also determined.

In the improvement studies conducted on the $-2\mu\text{m}$ fractions of the Çankırı sample which is the most invaluable one, suspensions containing 4g sample and 190ml distilled water ($\sim 2\%$ wt/vol) were prepared by vigorous mixing for 5 minutes and then the required amount of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was added to the suspension. During the magnetic stirring of suspension, the desired pH values (8, 9, 10, 10.5, 11 and 12) were adjusted using HCl or NaOH solutions with concentrations between 0.005–0.1 M. After 1 hour stirring at the desired pH value, the suspensions were dried at $105 \pm 5^\circ\text{C}$ and used in sedimentation volume and gelling coefficient tests.

RESULTS AND DISCUSSION

X-ray Diffraction Analysis

Random powder diffraction patterns (Figure 1) show that the original and the $-2\mu\text{m}$ fractions contain smectite as the dominant clay mineral with the associated impurities of quartz, feldspar, dolomite, kaolinite, illite, cristobalite, and zeolite. Although $-2\mu\text{m}$ fractions contain these impurities, the maximum semi-quantitatively estimated total amount of these impurities using XRD patterns are not higher than 25%. On the

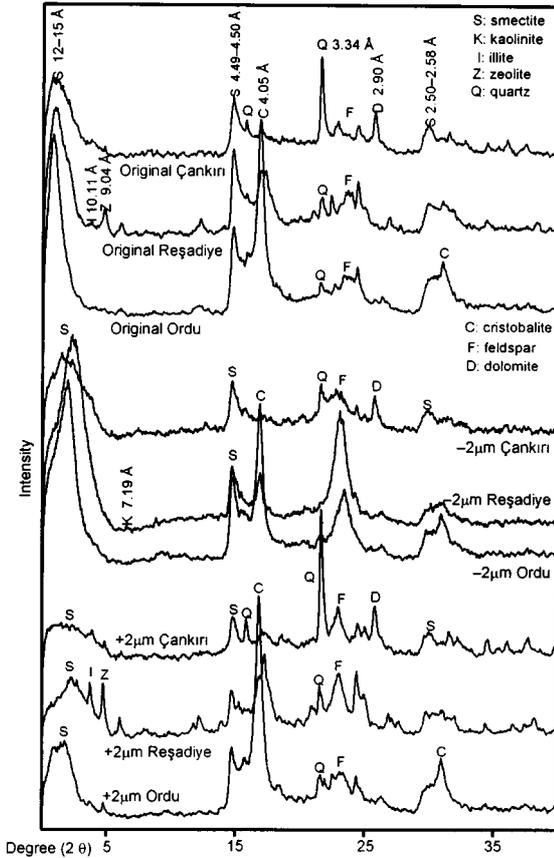


Figure 1. XRD patterns of the original and the $-2\mu\text{m}$ fraction

Şekil 1. Orijinal ve $-2\mu\text{m}$ 'lik fraksiyonun XRD desenleri

other hand, $+2\mu\text{m}$ fractions contain low amounts of smectite and very high amounts of the above mentioned impurities. $d_{(001)}$ values of the samples show that the $-2\mu\text{m}$ fractions of the Ordu and Reşadiye samples contain Na^+ ($d_{(001)}=12.5\text{Å}$) and $-2\mu\text{m}$ fraction of the Çankırı sample contains Na^+ and Ca^{2+} ($d_{(001)}=12.1\text{Å}$ and 15.2Å) as the main exchangeable cations.

The patterns of heated and ethylene glycolated samples (Figure 2) confirm that the dominant clay mineral in the three samples is smectite, due to the increase of basal spacing to 17.3Å – 18.0Å (Grim, 1968; Borchardt, 1989). Octahedral characters of the samples were determined from $d_{(060)}$ values that were 1.512, 1.503 and 1.499Å for the Çankırı, Reşadiye and Ordu samples, respectively. Since all these $d_{(060)}$ values are in the range of 1.49 – 1.52Å , the smectites in the samples can be characterized

as dioctahedral in character (Moore and Reynolds, 1989). The $d_{(060)}$ value also has an increasing tendency with the increase of the Fe content of octahedral layer, as found by Russell and Clark (1978), and accordingly, octahedral Fe content of the smectites in the samples is highest for the Çankırı sample, intermediate for the Reşadiye and lowest for the Ordu sample. On the other hand, Li-250 treatment (Figure 2) shows that the Reşadiye and Çankırı samples have the lowest and the highest tetrahedral charges, respectively.

High K_2O content of the Çankırı sample can be attributed to the presence of illite which is determined as a separate phase rather than a mixed layer type from ethylene glycolated pattern as described by Moore and Reynolds (1989). On

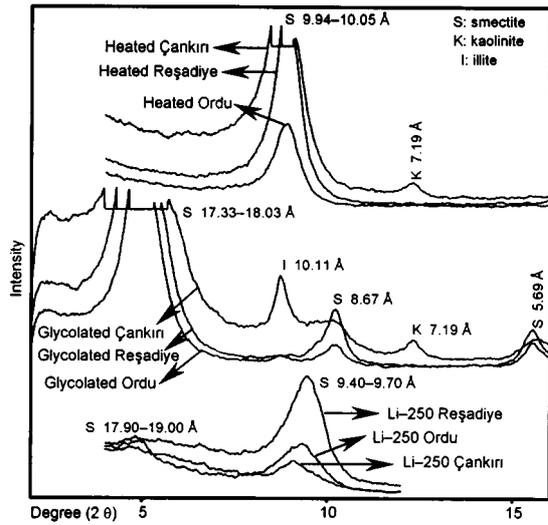


Figure 2. XRD patterns of the treated clay samples
Şekil 2. İşlenmiş kil örneklerinin XRD desenleri

the other hand, considering the findings of Çoban and Ece (1999) for iron(III)-rich beidellitic montmorillonite, it may be concluded that the Çankırı sample contains this type of smectite related with the peaks of 4.42 Å, 4.00 Å, and 3.53 Å.

Thermal Analysis

Differential thermal analysis (DTA) and thermal gravimetric analysis (TG) data for original samples are given in Table 1. The DTA curves are characteristic for smectite minerals (Greene-Kelly, 1957), namely, a large endothermic peak between 80–150°C, a smaller endotherm between 500–700°C and an endo-exothermic inversion between 800–1000°C. These peaks correspond to the loss of adsorbed water, dehydroxilation and the structural changes, respectively. Absence of any exotherm in the DTA curves around 300°C is an indication that the original samples do not contain organic contaminants in appreciable quantities (Özkan and Ross, 1979) as verified by the carbon analysis results of 1%, 0.6% and 0.3% for the Çankırı, Reşadiye and Ordu samples, respectively.

Although the second endothermic peak was obtained around 650°C for Reşadiye and Ordu samples, the Çankırı sample has an endotherm around 500°C due to high Fe content in its octahedral layer (MacKenzie, 1970). Accordingly, among the studied samples, the Çankırı sample has the highest amount of octahedral iron in its structure. The endotherm around 500°C for the Çankırı sample may also be explained in terms of the possible low crystallinity sequence of the original samples (Özkan and Ross, 1979). The endothermic peak around 700°C

Table 1. The DTA-TG data for the original samples
Çizelge 1. Orijinal örneklerin DTA-TG verileri

Sample	DTA data			TG data	
	1 st peak (°C)	2 nd peak (°C)	3 rd peak (°C)	Temp. range (°C)	Weight loss (%)
Çankırı	88	495	799 (exo)	20–195 342–830	8.2 6.8
Reşadiye	88	669	848 (endo)	20–257 605–910	8.7 3.9
Ordu	93	654	886–924 (endo-exo)	20–300 577–990	9.2 2.3

may be related to the carbonate mineral content of the Çankırı sample (Smykatz–Kloss, 1974).

Infrared Analysis

Infrared spectra of $-2\mu\text{m}$ fractions are given in Figure 3. The Reşadiye sample has no or very low Si substitution for Al in its tetrahedral layer, since there is no band absorption near 3660 cm^{-1} . But, the Çankırı and Ordu samples have noticeable absorption considering ideal montmorillonite and unnoticeable absorption with respect to ideal beidellite (Borchardt, 1989). These results well correlate with the results of Li–250 tests.

Main O–H stretching absorptions occur at 3636 , 3634 , and 3627 cm^{-1} for the Ordu, Reşadiye and Çankırı samples, respectively. This sequence, as stated by Köster et al. (1999), is related to the amount of Fe in octahedral layers of the samples. The amount of octahedral Fe in the samples according to the IR analysis is highest for the Çankırı, intermediate for the Reşadiye, and lowest for the Ordu sample, which is in good agreement with the XRD and the DTA results. Considering also the band absorption between $877\text{--}890\text{ cm}^{-1}$ for octahedral Al–Fe–OH, octahedral Fe content of the samples is determined to follow the above sequence (Bishop et al., 1994).

The IR absorption caused by the structural O–H and Fe–OH bands at 3560 and 820 cm^{-1} ,

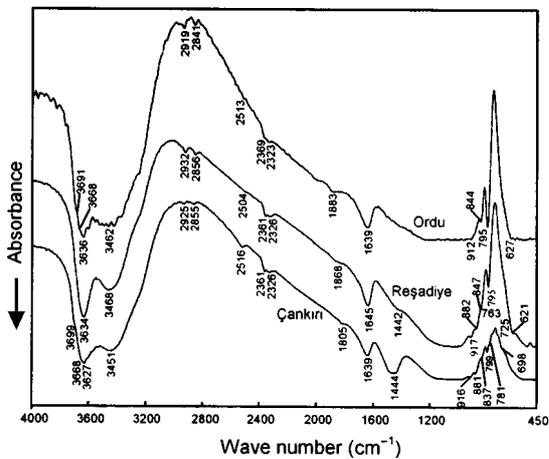


Figure 3. IR spectra of the original samples
Şekil 3. Orijinal örneklerin IR desenleri

respectively are characteristic for nontronites (Borchardt, 1989). The absence of such bands is an indication that none of the samples is nontronite. As stated by Klopogge et al. (1999), natural beidellites have strong absorption bands at 698 , 779 and 799 cm^{-1} . Only Çankırı sample has weak absorptions at 698 , 781 and 799 cm^{-1} , which may show that the sample has high beidellitic character or contains beidellite as mixed layer.

Very weak absorption at 3699 and 3691 cm^{-1} may be related to the presence of trace amounts of kaolinite in Çankırı and Ordu samples, respectively. The absorption bands near 1444 and 1442 cm^{-1} indicate the presence of carbonate minerals which show typical absorption band at 1450 cm^{-1} as found by Huang and Kerr (1960).

The absorption bands in the infrared spectra of all samples at 3450 and $1630\text{--}1650\text{ cm}^{-1}$ are related to the H–O–H stretching and bending vibrations that can be removed upon heating to 200°C as stated by Grim (1968). Related absorption values found for the samples were $3468/1645\text{ cm}^{-1}$, $3462/1639\text{ cm}^{-1}$ and $3451/1639\text{ cm}^{-1}$ for the Reşadiye, Ordu and Çankırı samples, respectively.

Chemical Analysis

Chemical compositions of original and $-2\mu\text{m}$ fractions are given in Table 2. This table shows that the amount of total iron is lower than that of ideal or natural nontronites (Russell and Clark, 1978; Köster et al., 1999). The decrease in SiO_2 and increase in Al_2O_3 and MgO contents of $-2\mu\text{m}$ fractions show an increase in smectite content with respect to the original samples.

Physico–Chemical Tests

The test results related to the physico–chemical properties of the studied smectite samples are given in Table 3. As the Reşadiye sample has the lowest tetrahedral charge and contains sodium as the dominant exchangeable cation, the critical coagulation concentration value with NaCl (CCC_{NaCl}), as expected, has the highest value. Since tetrahedrally charged clays have lower critical coagulation concentration values than the octahedrally charged clays (Hetzl and

Table 2. Chemical compositions of the original and the $-2\mu\text{m}$ fractions
Çizelge 2. Orijinal ve $-2\mu\text{m}$ 'luk fraksiyonların kimyasal bileşimleri

Weight %	Çankırı		Reşadiye		Ordu	
	Original	$-2\mu\text{m}$	Original	$-2\mu\text{m}$	Original	$-2\mu\text{m}$
SiO ₂	52.51	51.64	59.70	60.20	68.05	65.29
Al ₂ O ₃	15.72	17.30	16.55	18.66	14.36	16.19
$\Sigma\text{Fe}_2\text{O}_3$	6.30	7.51	3.74	4.73	1.94	2.40
MnO	0.11	0.08	0.11	0.03	0.07	0.03
MgO	3.56	3.82	1.70	2.20	2.52	2.60
CaO	4.10	2.73	3.16	1.07	1.61	0.88
Na ₂ O	1.94	2.11	2.33	2.59	1.68	2.24
K ₂ O	2.10	2.17	1.14	0.51	1.01	0.50
TiO ₂	0.72	0.77	0.34	0.35	0.22	0.23
P ₂ O ₅	0.13	0.13	0.15	0.03	0.03	0.01
Cr	0.0173	0.0190	0.0006	0.0032	0.0004	0.0039
Zr	0.0099	0.0109	0.0165	0.0106	0.0033	0.0029
LOI*	10.27	10.83	8.74	8.29	6.20	8.09
Total	97.49	99.12	97.68	98.67	97.69	98.47

*LOI: Loss on ignition.

Doner, 1993), the results of CCC_{NaCl} tests related with Ordu and Çankırı samples are also in good agreement in this respect, that the Ordu sample (Na type) has a higher value than the Çankırı sample.

The methylene blue index (M.B.I.) value is lowest for the Çankırı sample and highest for the Ordu sample. The M.B.I. experiment was done at pH ~3 and at this pH value the released octahedral cations, mainly Fe³⁺ and Mg²⁺, compete with the positively charged methylene blue cation for the exchange sites on the clay plates thus reducing the M.B.I. value. Since the Çankırı sample has the highest amounts of iron and magnesium in its structure (see Table 2), the

measured index for the Çankırı sample has the lowest value and for the Ordu sample the situation is reversed.

The glycerol surface area (G.S.A.) values are also related to the tetrahedral charge of the bentonites and increasing tetrahedral charges cause lower measured glycerol surface areas. According to G.S.A._{measured} results, Çankırı sample has the highest tetrahedral charge while the Reşadiye sample has the lowest supporting the results of IR analysis and Li-250 tests.

The sedimentation volume and the gelling coefficient values of $-2\mu\text{m}$ fractions were determined as 11.5–12.8, 25.2–18.2 and 19.9–16.7 for the Çankırı, Reşadiye and Ordu samples, respectively. It may be stated that $-2\mu\text{m}$ fractions of the Reşadiye and Ordu samples are sodium type since, their sedimentation volume and gelling coefficient values are very high compared to the Çankırı sample which is a Na/Ca type mineral. The sedimentation volume and gelling coefficient values of the Reşadiye sample are higher than those of the Ordu sample and this may be related to the high tetrahedral charge that reduces particle swelling and layer separation. The sedimentation volume and gelling coefficient values of the original samples are low and can not be compared due to high amounts and variable impurity contents of them.

Table 3. Some physico-chemical properties of the original samples

Çizelge 3. Orijinal örneklerin bazı fiziko-kimyasal özellikleri

Property	Çankırı	Reşadiye	Ordu
pH	10.1	9.9	9.8
CCC_{NaCl} (me/l)	14.3	23.7	16.0
C.E.C. (meq/100g)	47.7	69.9	57.7
M.B.I. (meq/100g)	52.7	65.0	72.2
G.C.	12.3	11.8	10.0
S.V.	7.0	8.0	5.7
G.S.A. _{measured} (m ² /g)	482	741	602
G.S.A. _{theoretical} (m ² /g)	762	753	749

The Improvement Studies

The effect of pH on the sedimentation volume (S.V.) and the gelling coefficient (G.C.) values (without inorganic additive) on $-2\mu\text{m}$ fractions of the Çankırı sample were determined and the results are given in Figure 4. The S.V. and the G.C. values of the $-2\mu\text{m}$ fractions at natural pH of 10.25 were 11.5 and 12.8, respectively. Considering these values, increase of pH from 10.25 to 10.50 gives the maximum values of the S.V. and the G.C. of 12.2 and 13.3, respectively. This increase can be attributed to the sodium cation added for pH regulation. But this does not explain the fact of the lowering of these values at higher pH values. As the S.V. and the G.C. reach their maximum values at pH=10.5 this may be related to the release of magnesium cation from the interlayers or from the structure of the clay sample as stated by Chen *et al.* (1990). In order to support this claim, magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) was decided to be used as the inorganic additive.

The minimum and maximum amounts of added magnesium chloride were determined considering the critical coagulation concentration (CCC) value of the sample with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (1.90 meq/liter). The S.V. and the G.C. test results of the $-2\mu\text{m}$ fractions treated at the minimum and the maximum amounts of the inorganic additive are given in Figure 5. The S.V. and the G.C. values were increased with respect to the original values when %1.45 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ $\{[\text{Mg}]=1.5 \cdot 10^{-3} \text{ M}\}$ was used and the highest values obtained

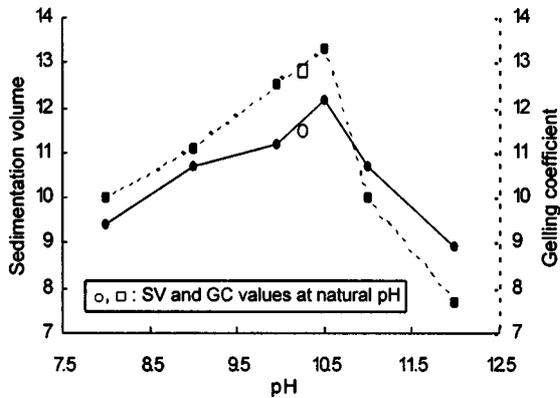


Figure 4. The S.V. and the G.C. values of the $-2\mu\text{m}$ fraction

Şekil 4. $-2\mu\text{m}$ 'lik fraksiyonun S.V. ve G.C. değerleri

were 15.4 and 16.7, respectively at pH=10. Since the CCC value was exceeded with addition of 27.46% $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, the S.V. and the G.C. values were very low as seen from Figure 5. Since the observed increasing and decreasing tendency in the S.V. and the G.C. values could be related with the change of potentials on the edge and basal surfaces of the clay platelets, zeta potential measurements were done on the $-2\mu\text{m}$ fraction (without inorganic additive) and $-2\mu\text{m}$ fraction treated with %1.45 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. The results of these measurements related with the pH–logarithmic concentration diagram for a total magnesium concentration of $1.0 \cdot 10^{-4} \text{ M}$ and $1.5 \cdot 10^{-3} \text{ M}$ are given in Figures 6 and 7, respectively. As seen from these figures, the concentration of the MgOH^+ reaches its maximum value at pH values around 10.5 and 10, respectively, when the zeta potential values become about 7–10 mV more positive.

CONCLUSIONS

In this study, the physico–chemical characteristics of three bentonite samples were determined using critical coagulation concentration, sedimentation volume, gelling coefficient, glycerol surface area and cation exchange capacity tests. The type and origin of tetrahedral charge, the amount of octahedral iron and the type of exchangeable cation in the samples were determined by mineralogical identification and then

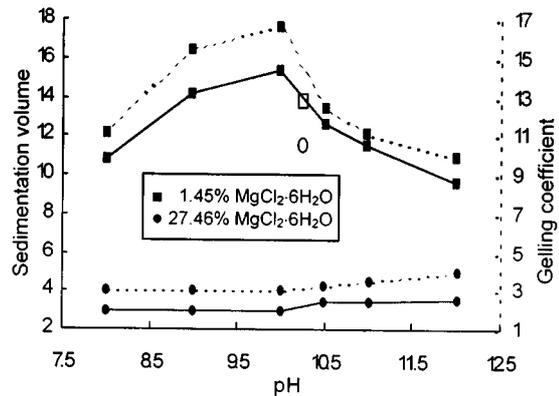


Figure 5. The S.V. and the G.C. values of the $-2\mu\text{m}$ fraction for 1.45% $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 27.46% $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ additions.

Şekil 5. $-2\mu\text{m}$ 'lik fraksiyonun 1.45% $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ve 27.46% $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ilavelerindeki S.V. ve G.C. değerleri.

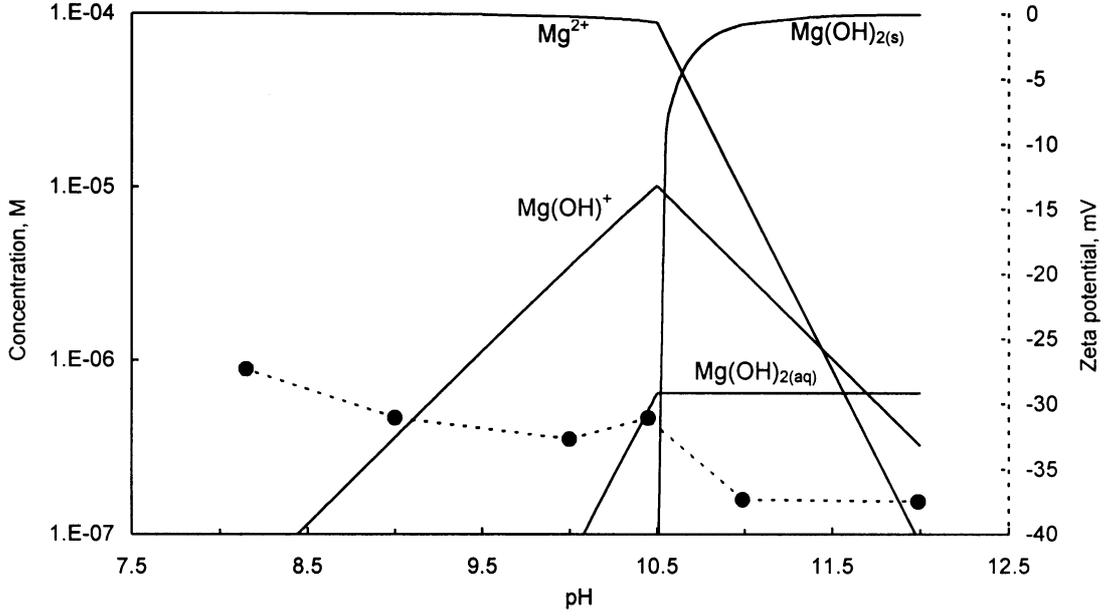


Figure 6. Zeta potential values for $-2\mu\text{m}$ fraction and the pH-logarithmic concentration diagram for $1.0 \cdot 10^{-4}$ M Mg concentration

Şekil 6. $-2\mu\text{m}$ 'lik fraksiyonun zeta potansiyel değerleri ve $1.0 \cdot 10^{-4}$ M Mg derişimi için pH-logaritmik derişim diyagramı

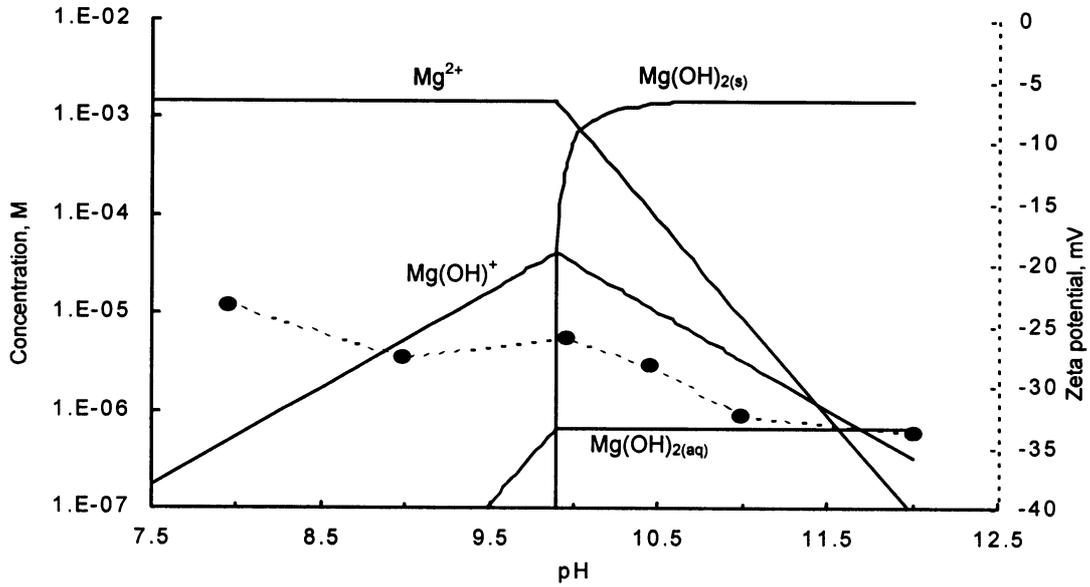


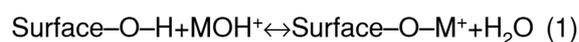
Figure 7. Zeta potential values for $-2\mu\text{m}$ fraction treated with 1.45% $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and the pH-logarithmic concentration diagram for $1.5 \cdot 10^{-3}$ M Mg concentration.

Şekil 7. 1.45% $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ile işlenmiş $-2\mu\text{m}$ 'lik fraksiyonun zeta potansiyel değerleri ve $1.5 \cdot 10^{-3}$ M Mg derişimi için pH-logaritmik derişim diyagramı.

relationships between the physico-chemical and mineralogical characteristics of the samples were correlated.

The maximum S.V. and the G.C. values, without any use of inorganic additive, were obtained at a pH of 10.50 which corresponded to the ma-

ximum concentration of MgOH^+ formed from the logarithmic concentration diagram drawn for a magnesium concentration of $1.0 \cdot 10^{-4}$ M estimated from the dissolution of magnesium from the structure of the sample. The validity of this result and the consideration was checked by introduction of Mg^{+2} ions into the medium using $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and adjusting the pH so as to control the amount of MgOH^+ formed. In this case, the maximum S.V. and the G.C. values were obtained at pH 10 which corresponded to maximum amounts of MgOH^+ formation at the logarithmic concentration diagram for a magnesium concentration of $1.5 \cdot 10^{-3}$ M. These conditions lead to the formation of positively charged edges and as verified from the zeta potential values, the potential becomes about 7–10 mV more positive around these pH values due to the adsorption of MgOH^+ on clay edges. The potential does not reverse in sign completely similar to findings of Fuerstenau (1975) for quartz, since the high surface area of negatively charged basal surfaces mask the positive potential. After treatment with %1.45 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 30% and 34% improvements in gelling and swelling properties were obtained, respectively and the mechanism of the improvement of the gelling and swelling properties can be explained by Equation 1.



When the amount of the MOH^+ specie is at its maximum value, the interaction with the edge surface of the clay platelet dominate to form a positively charged clay surface which favours the particle interactions and increases the gelling coefficient value of the clay.

The physico-chemical and mineralogical characteristics of the Reşadiye sample, currently used as a drilling mud additive, due to its high Na content and very low tetrahedral charge, seems suitable for direct treatment with quaternary ammonium cations to produce organoclays that are used for wastewater remediation (Jaynes and Boyd, 1991). Ordu sample, already being used for bleaching purposes, can further be processed by ion exchange methods to produce aluminum, iron, vanadium, titanium, niobium, tantalum, or zirconium type pillared clays suitable for molecular sorption and catalysis (Christiano et al., 1985; Tennakoon et al., 1986) or for

adsorption of organic contaminants (Wu et al., 2001) such as benzene, toluene, xylene, or phenol from polluted waters.

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