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The effect of structural properties of Ankara clay on the electrokinetic properties

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Research Article

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Ankara clay, Electrokinetic, SEM, EDS, Zeta potential.

ABSTRACT

The aim of this study is to investigate the effect of structural properties of soil known as Ankara clay, which contains different properties, on its electrokinetic behavior. For this purpose, the 8 disturbed samples from Ankara clay were collected from the different locations of Yüzüncüyıl and Karakusunlar areas, which were observed to contain no excess gravel and carbonate concretions. The electrokinetic behavior of these collected samples were evaluated by using the results of plastic limit, liquid limit, methylene blue, swelling, XRD, XRF, SEM, EDS and BET measurements and analyses as well as zeta potential tests. By these experimental studies, it has been determined that Ankara clay exhibits electrokinetic behavior in line with the whole rock composition since it contains different clay minerals. The monovalent and divalent electrolytes such as NaCl and $CaCl_2$, respectively, increase the zeta potential of Ankara clay negatively. However, in the analyses, it was determined that $FeCl_3$ trivalent electrolyte is the electrolytes determining the zeta potential, tend to convert zeta potential of clays from negative to positive depending on the concentration, and this could be the case with increased concentration.

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1. Introduction

Natural clay minerals are formed by the degradation of the primary minerals forming the rocks by long being exposed to atmospheric conditions and/or alteration by the effect of hydrothermal solutions. When these processes are considered, it is clearly seen that parameters such as the type of primary mineral (bedrock ion content), temperature and pH are very important in the formation behavior of clay minerals. Unlike gravel, sand and silt size soils that are deposited by the effect of gravity, the electrokinetic properties of these minerals come to the fore due to the effect of electrical forces in the formation behavior of clays in the phyllosilicate group. As mentioned in the study of Önalp (2013), the determination of these electrokinetic characteristics of clays is very important in mining applications and projects due to this formation model. The basic structural units in clay minerals are "tetrahedric layer" and "octahedric layer", and the bonding of these basic structural units to each other by forming different layer structures causes the formation of different clay minerals (eg kaolinite, illite, montmorillonite) and therefore exhibit different physico-mechanical behaviors. Therefore, the clays are under the influence of chemical bonding (eg, Van der Waals) forces that form on their surfaces and generate their electrokinetic properties. The crystalline O and OH ions in kaolin mineral of 1: 1 layer type are bonded to each other by H bond and have a low ion-exchange capacity and therefore a low layer charge (x-0). The basic structural units in clay minerals are "tetrahedric layer" and "octahedric layer", and the bonding of these basic structural units

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to each other by forming different layer structures causes the formation of different clay minerals (eg kaolinite, illite, montmorillonite) and therefore exhibit different physico - mechanical behaviors. Therefore, the clays are under the influence of chemical bonding (eg, Van der Waals) forces that form on their surfaces and generate their electrokinetic properties. The crystalline O and OH ions in kaolin mineral of 1: 1 layer type are bonded to each other by H bond and have a low ion - exchange capacity and therefore a low layer charge (x~0). On the other hand, the adjacent interlayer bond in the smectite mineral that has 2: 1 layer structure is the weak Van der Waals bond and has high ion exchange capacity and therefore has a high layer load (x - 0.6) (Moore and Reynolds, 1997).

Angle and Hamza (1989) examined the zeta potentials of the clay mixtures they had prepared in ratios of 70% kaolin and 30% smectite, and stated that H+ and OH- ions had dominant roles in the zeta potential value. Zhao et al. (1989) studied the adsorption velocity and the capacity of polyethylene glycol polymer in different molecular weight of montmorillonite type clays. These researchers determined that the adsorption capacity of clays containing different exchangeable cations was different. Ross et al. (1998) stated in their study by adding sodium electrolyte on montmorillonite clay minerals that thixotropy changes with the electrolyte concentration depending on the surface charges. Benna et al. (1999) investigated rheological and electrokinetic measurements together using three different montmorillonite samples. Besides, the issue of interaction of clay with polymers, surfactants and salts has been extensively studied (Chang et al., 1992; Ece et al., 1999; Alemdar et al., 2000; Pal and Vanjara, 2001; Bergaya and Lagaly, 2001; Güngör et al., 2001; Yalçın et al., 2002; Janek and Lagaly, 2003).

In the evaluation of zeta potentials and electrokinetic behavior of clays until today, certain clay types or samples that are mixed in certain proportions have been used. It was detected that studies consisting of natural clayey soils where swelling and non - swelling clay minerals (smectite and kaolin) coexist in different proportions were found to be quite limited. Therefore, it was needed to investigate its electrokinetic properties, since it contained clay minerals with different crystal structures, which present a complex structure. In order to solve this limitation, the reddish brown, brown clayey units, which contain pebbles in places and lime concretions in their upper parts defined as the "Ankara clay" by Birand (1978) were used. In addition, due to engineering problems such as swelling and settlement observed in the center of Ankara city (Çetinkaya, 1978; Furtun, 1989; Çokça, 1991; Ergüler, 2001; Ergüler and Ulusay, 2003; Avşar, 2003; Avşar et al., 2005; Özgüven, 2014), it was determined that the zeta potential and electrokinetic behavior of the Ankara clay used was not investigated in many studies. Ankara clay causes serious foundation problems with shrinkage in engineering structures as a result of swelling or loss of water depending on the changing water content. Since the behavior of the mineral group constituting Ankara clay is so different that they are called opposite to each other, it is very important to determine the mineral types and thus to reveal the index properties of clayey soils in sense of understanding their mechanical behaviors. On the other hand, it can find wide usage areas such as adsorbents and viscosity because of these properties. Due to its high surface area, especially the activated filtration is also used in paint and paper industry as it shows swelling in water (Akın and Çelik, 1995). Although there have carried out many studies on the mineralogical properties of Ankara clay (Aras et al., 1991; Koçyiğit and Türkmenoğlu, 1991; Met et al., 2005; Sezer et al., 2003), the determination of the physico - chemical properties and Atterberg properties of this clay will contribute to the prevention of damages that may occur during the planning and design phase and afterwards presenting a foresight about the behavior of clay is thought that engineering studies.

Considering the limitations and requirements presented above in summary, the zeta potential and electrokinetic properties of Ankara clay with different physico - mechanical behavior such as kaolinite, illite and smectite (Met et al., 2005) were investigated. For this purpose, the field and sampling studies were carried out in Yüzüncüyıl and Karakusunlar regions. For the determination of parameters such as physical, chemical and mineralogical properties of the samples taken, the Atterberg limits, porosity, methylene blue, swelling, XRD, SEM, Brunauer, Emmett and Teller (BET) gas adsorption method and zeta potential experiments were performed to determine the electrokinetic behavior. The results obtained in these experimental studies were analyzed and interpreted within the scope of this study.

2. Introduction and Geology of the Study Area

The settlement area of Ankara City is located between the North Anatolian Region, which has a rugged mountainous and forested morphological structure, and the arid Konya Plain. Considering the purpose of the study, Yüzüncüyıl and Karakusunlar regions were selected as the study area. This region, which generally has a slightly sloping topography, varies between 848 and 1000 m above sea level. A continental climate prevails in Ankara and its surroundings, similar to the Central Anatolia Region and the rainfalls are intensively observed in winter, spring and autumn. The dry months, which significantly affect the behavior of Ankara clay in the region, are known as June - July - August - September.

As emphasized in previous studies (Chaput, 1931; Erol, 1976; Kasapoğlu, 1980), Lower Paleozoic epimetamorphic schists form the bedrock of geological units outcropping in Ankara and its surroundings. These basic metamorphic units are overlain by the geological units such as greenish - brown and schist interbedded greywackes and metagreywackes which unconformably contain Permo - Carboniferous and Triassic limestone blocks. Liassic red basal conglomerate containing pebbles with granitic mineralogical composition, sandstone, siltstone and fossil calcarenites, and Dogger, Malm and Lower Cretaceous, yellowish - white, ammonitic limestones, siliceous - sandy - clayey limestones, platy and nodular limestones in the upper layers overly these mixed series (Chaput, 1931; Kasapoğlu, 1980; Ergüler, 2001). These units are the overlain by the ophiolitic melange (serpentinite, radiolarite, spilite, basalt, diabase, limestone, sandstone, mudstone, marl, flint and gabbro). The ophiolitic melange is then overlain by a Lower - Upper Cretaceous flysch series containing conglomerate, sandstone, siltstone, marl and olistostromes (Chaput, 1931; Kasapoğlu, 1980; Ergüler, 2001). In the study area, there are conglomerates, sandstone, siltstone, red - green marl and limestones in the Paleocene period, fossilliferous sandy limestones in the Eocene period and sedimentary units formed in lagoon and evaporitic environments in the Oligocene period. As mentioned in previous studies, the rocks such as Miocene siliceous - clayey lacustrine limestones, marls, claystones, conglomerates, andesites, basalts, agglomerates and tuffs are found overly Oligocene units (Chaput, 1931; Kasapoğlu, 1980; Ergüler, 2001). Miocene units are overlain by Upper Pliocene units defined as fluvial and lake deposits (Chaput, 1931; Kasapoğlu, 1980). These Upper Pliocene units with an average thickness of 200 meters in the middle of the basin are composed of pebbly, sandy, silty and clayey levels (Erol, 1976). The typical brown - red clayey formations found in the upper parts of these units, occasionally containing gravel and lime concretions, were named as "Ankara clay" by Birand (1978). Aras (1991), emphasized that these reddish - brown sediments were formed in an alluvial fan environment by making detailed sedimentological evaluation and analysis of these Upper Pliocene sediments. In addition, the same researcher stated that the Ankara clay was formed as a result of the degradation of rocks such as andesite, schist and graywacke in the origin - bedrock study.

3. Material and Method

For the purpose of this study, the Yüzüncüyıl and Karakusunlar regions, where fluvial clayey deposits known as the Ankara clay are heavily exposed, were selected as the study area, and the disturbed samples were taken to be used in pre - planned laboratory experiments in 8 different locations, taking into account the construction excavations and road cuts (Figure 1). A typical cross section in locations where sampling is carried out is presented in Figure 2, and detailed information about the experiments performed on collected samples is explained below.

The particle size of sediments forming clayey units provides preliminary information about the content of possible clay minerals. Considering the effect of the clay particle size ratio on the physicochemical and physicochemical behavior of these units, the particle size distribution graphics of samples were determined by the analyses performed using the method proposed by ASTM (1994) consisting of three different stages such as dry coarse sieve, hydrometer and dry fine sieve. Atterberg limits are frequently used to evaluate the swelling behavior of clayey units and determine the swelling parameters by empirical approaches. Considering the importance of Atterberg limits in determining the behavior of clayey units, the Atterberg limits of the samples collected were similarly determined by considering the standards recommended by ASTM (1994).

The methylene blue test is based on the replacement of methylene blue cations with exchangeable cations

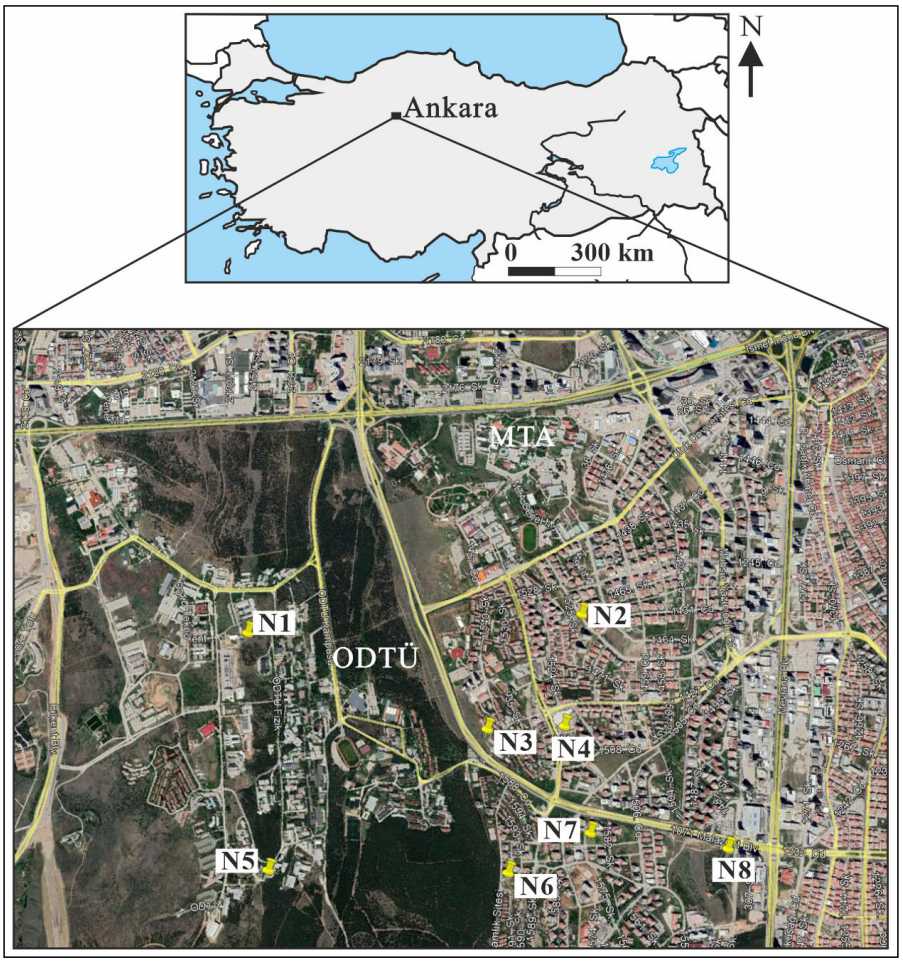

Figure 1- Study area and locations where Ankara clay samples were taken.

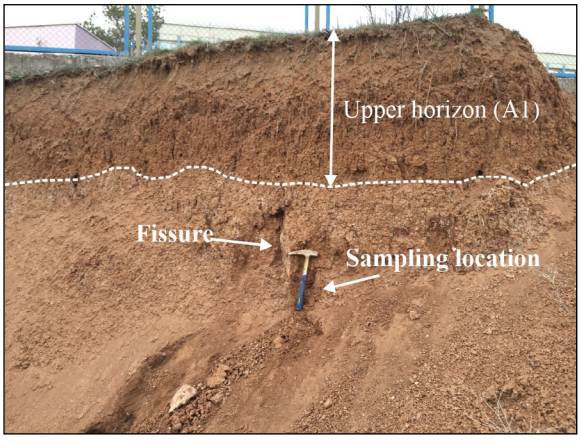

Figure 2- The outcrop where the sampling is made in which the studied clay as a result of the construction foundation excavations is typically observed and sections where plant roots are not present (sample N1; latitude 39.897020° and longitude 32.778787°; look direction NE).

of the clay. Methylene blue is adsorbed as much as the amount of exchangeable cations of the clays during the experimental application phase. After the saturation is reached, the added methylene blue ions are released in the dispersion. Based on the concentration in which methylene blue ions are released, the amount of methylene blue adsorbed by the clay mineral is determined and the cation exchange capacity (CEC) is calculated from the amount of charge they carry. In this study, methylene blue experiments of the samples were carried out in accordance with ASTM C837 (2019) standards.

Many experimental methods have been proposed to determine the swelling parameters of clays. In order to determine the swelling properties of samples collected within the scope of this study, TS 10252 (1992) which is very practical approach was preferred. The samples, which were taken in this swelling behavior determination approach, were powdered until they

reached the size of a particle under 100 microns, then, were poured into the measuring cylinder with a capacity of 100 ml without causing sample loss by taking 2 g from these samples . This prepared water - sample mixture was then left to sedimentation for 24 hours and the resulting volumetric change was determined and recorded.

The BET approach is one of the most used methods in clay definition and classification, as the surface area values vary according to clay types. The BET analysis was used to determine the parameters of surface area, pore volume and pore radius of the collected samples. For this purpose, the surface area and pore size analyzer (Nova 2200e Quantachrome Instruments) was used. For these experiments, 0.2 - 0.5 g of sample was prepared and placed in the chamber of the device. The cell was weighed and placed in the nitrogen container section by filling the liquid nitrogen container with gas to the previously determined level. The desired analysis was drawn considering the pressure sensors, pH, relative pressure graph, adsorption and desorption parameters. During the experiment, the adsorbent pressure in the equilibrium approaches the saturation and the pores are completely filled with the adsorbent. The total pore volume was determined by calculating the adsorbent density with filled pores in the sample.

X - ray diffraction analyses (XRD) were performed in two separate stages, as whole rock (WR) and clay fraction (≤2 μm particle size). For whole rock analyses, the directly powdered Ankara clay samples were used. For clay fraction analyses, a certain amount of powder was put into sample beakers, and then samples were filled with distilled water and mixed in micronized mixers until a homogeneous mixture was obtained. Considering the Stokes' law, the components remaining in suspension were soaked with a pipette and poured on three different glasses. After each glass was dried at room temperature, one sample was made ready for normal shooting, the other one was made ready for retarded shooting kept in ethylene glycol for 2 hours and the remaining sample was made ready for shooting by being kept in an oven at 550° C for 2 hours. The clay fraction shots were carried out in 4 - 30° shooting range. In order to determine the content of exchanging cations (for example, Na^{+}, K^{+}, Ca^{++} and Mg^{++}) in selected samples, the major element analyses of the samples were carried out using the Panalytical Axios XRF Spectrometer device with a relative error margin of ± 3 with 98% accuracy in MTA laboratories. The samples taken for XRF analysis were placed in meter cups and dried in an oven at 105° C for 3 hours. Then, the samples taken from the oven were transferred to the desiccator to cool down and their masses were recorded by weighing after being kept at room temperature for one hour. 3 g of this dry sample was taken and the mixture was prepared by adding 0.9 g of cellulose. In addition to XRD and XRF analyzes of the samples taken from the study area, the scanning electron microscopy (SEM) - EDS analyzes were carried out to take close - up images of the clayey parts, make morphological evaluations and reveal the chemical composition of certain points.

All samples were subjected to size reduction and nano size distribution was obtained before the zeta potential determination. The particle size distributions of the powdered samples were determined by laser. For electrokinetic measurements of clay samples collected within the scope of this study, the pH adjustment was made with NaOH and HCl by taking 1 ml of stock solution. Only the pure water was used in the preparation of samples. The zeta potentials were calculated by measuring movement velocities of the clay particles in the prepared samples at different pH values. In Zeta potential measurements, the Malvern Zetasizer Nano Z device, which can automatically calculate the zeta potential value and considers the voltage and particle velocity, was used. In measurements, approximately 20 readings were taken for each sample whose pH value was adjusted to vary between 3 - 11, and the mean and standard deviation of zeta potential values determined by the device were recorded.

4. Discussion

The engineering problems such as the need for clay raw materials due to the increasing need in ceramic and food industries in our country and the environmental pollution after mining activities clearly reveal the importance of using clay minerals. Today, the electrochemical treatment approach of clay and similar natural materials is widely and effectively used in the treatment of heavy metal pollution of natural resources such as soil contamination after mining activities. In this study, which was carried out by considering the importance of clay minerals today and covering the electrochemical properties of clay, Ankara clay was directly preferred instead of

using kaolin and bentonite or a mixture of these clays prepared in certain proportions like in previous studies. The results obtained from the experiments performed within scope of this study and the evaluations made regarding these results are presented below.

4.1. Physicochemical and Physicomechanical Properties of Ankara Clay

The method proposed by ASTM (1994) to form the particle size distribution curves of unconsolidated soil materials and the results of experiments consisting of three different stages used was combined and presented in Figure 3. Using the graphics given in Figure 3, the clay particle size ratio values of the samples were calculated and presented in Table 1. As can be clearly seen in Figure 3 and Table 1, the clay particle size ratio of these samples is high, varying between 28% and 58% with an average value of about 44%. The results obtained in the Atterberg limit tests are also presented in Table 1. As seen in Table 1, it is seen that a significant portion of the samples taken from Ankara clay are above 50% of the liquid limit values and therefore these clayey units are rich in swelling clay mineral types.

The parameters such as physical properties, surface areas and cation exchange capacity of clayey units, which are generally rich in clay minerals, are controlled by the clay mineralogical composition (Fityus et al., 2000). The methylene blue test is widely used in calculating the amount of exchangeable cations of reactive clays (Çokça and Birand, 1993*a*). Methylene blue dye ($C_{16}H_{18}N_3SCl$) is a large polar organic molecule that adsorbs on the negatively charged surfaces of clay minerals and has a high solubility in water (Yitik, 2006). The CEC values obtained from the methylene blue tests carried out

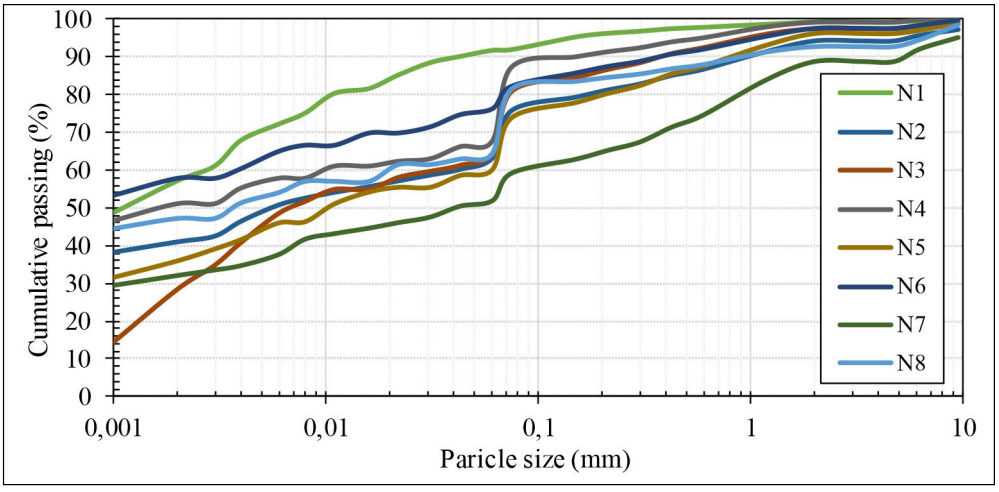

Figure 3- Particle size distribution graphics of the samples.

Table 1- Clay fraction, plastic limit, liquid limit, cation exchange capacity, swelling volume and gelation coefficient values of the samples.

Sample No.	Sample Coordinates		Clay (%)	PL (%)	LL (%)	CEC (meq/100 g)	Swelling Vol. (ml)	Gelation Coeff.
	Lat.	Long.						
N1	39.897020°	32.778787°	57	56	87	4	6	≥8.3
N2	39.897934°	32.800484°	41	31	59	25	2	≥8.3
N3	39.892238°	32.794312°	28	25	50	21	2	≥8.3
N4	39.892390°	32.799248°	51	25	41	48	12	≥8.3
N5	39.885446°	32.780462°	36	38	52	35	10	≥8.3
N6	39.885338°	32.795573°	58	45	72	48	10	≥8.3
N7	39.887212°	32.800795°	32	28	48	24	4	≥8.3
N8	39.886515°	32.809324°	47	23	65	33	8	≥8.3

PL: plastic limit, LL: liquid limit, CEC: cation exchange capacity.

in accordance with ASTM C837 (2019) standards are given in Table 1. As seen in Table 1, the cation exchange capacity values of the samples vary between 4 meq / 100g and 48 meq / 100g with an average value of approximately 30 meq / 100g. These results are consistent with the results obtained from the methylene blue experiments previously performed on Ankara clay (Çokça and Birand, 1993*b*; Ergüler, 2001; Sezer et al., 2003; Met et al., 2005). The CEC values, swelling, plasticity and etc. are important indicators in terms of physical properties. Therefore, the higher these values, the higher the swelling and gelation behavior of the relevant clay sample.

The swelling volume values obtained using the TS 10252 (1992) approach are presented in Table 1. As can be seen in this table, the highest swelling behavior was detected in sample N4. In addition, it was determined that the clay particle size percentage of the sample N4 was detected as 51% compared to the other samples. The gelation coefficients of eight separate samples taken were made according to the TS 5360 (1996) standard, and it was concluded that the samples would not show gelation, since the results obtained (Table 1) were higher or equal than 8.3.

Surface area is an important factor controlling the surface properties and thus the electrokinetic behavior of clay minerals and many approaches have been proposed to determine this parameter of clays. The basic method for measuring surface area from the gas adsorption approach based on the relationship between the volume of gas applied to the samples used in the test and the applied pressure has been widely used in previous studies. As also stated by Santamarina et al. (2002), the surface areas of high surface area materials such as clay minerals can be determined precisely using the BET gas adsorption method. The measured BET surface area of materials that have a microscale hollow texture is calculated from the combination of the adsorption on the surface of the relevant particle and the condensation in micropores (Michot and Villieras, 2006). Considering these evaluations emphasized in previous studies the BET analysis was used in determining the surface area, pore volume and pore radius parameters of the collected samples. Within the scope of this study, the results of detailed BET analysis performed on Ankara clay are given in Table 2. For Ankara clay, it has been determined that the graphs of BET analysis are the most suitable and explanatory type of isotherm since it is linear.

Table 2- Surface area, pore volume and pore radius values of samples taken from Ankara clay.

Parameter	Method	N1	N2	N3	N4	N5	N6	N7	N8
Surface area (m^2/g)	MultiPoint BET	82.800	90.840	59.730	115.100	61.290	89.130	56.680	117.300
	BJH^a	24.020	26.460	19.910	33.340	22.290	34.220	19.360	31.740
	BJH^d	44.170	51.730	35.290	63.820	41.220	61.090	37.390	62.240
	DH^a	24.510	27.020	20.330	34.050	22.760	34.950	19.770	32.420
	DH^d	44.950	52.680	35.940	65.010	42.050	62.300	38.080	63.430
	t^d	55.510	63.980	44.630	81.760	50.340	67.920	49.110	80.990
	t^m	27.290	26.860	15.090	33.380	10.940	21.220	7.567	36.280
Pore Volume (cc/g)	BJH^a	0.071	0.065	0.055	0.074	0.058	0.068	0.048	0.069
	BJH^d	0.079	0.075	0.060	0.087	0.061	0.074	0.053	0.081
	DH^a	0.069	0.063	0.054	0.073	0.057	0.067	0.047	0.068
	DH^d	0.077	0.073	0.059	0.085	0.060	0.072	0.052	0.079
	t^m	0.013	0.013	0.007	0.017	0.005	0.011	0.004	0.019
Pore Radius (µm)	BJH^a	3.357	3.366	3.367	3.384	0.002	0.002	0.002	0.002
	BJH^d	3.769	3.766	3.763	3.755	0.002	0.002	0.002	0.002
	DH^a	3.357	3.366	3.367	3.384	0.002	0.002	0.002	0.002
	DH^d	3.769	3.766	3.763	3.755	0.002	0.002	0.002	0.019

BJH^a: BJH cumulative adsorption; BJH^d: BJH cumulative desorption; DH^a: DH cumulative adsorption; DH^d: DH cumulative desorption; t^d: t-method outer; t^m: t-method micro poreb

4.2. Mineralogical and Chemical Analysis of Ankara Clay

The physico - mechanical behavior of clays versus the change in water content is controlled by the clay mineral type and crystal structure that it contains (Yegorov, 1997). The case that geological units rich in clay minerals to be rich in swelling clay minerals results in increase in plasticity, swelling capacity and compressibility properties (Terzaghi and Peck, 1967). Considering these results obtained in previous studies, XRD analyses were carried out in order to determine the mineralogical composition of the samples. , samples are analyzed in the range of 20 - 70°C 2Θ using nickel filter and copper radiation, and the results obtained are interpreted in accordance with ASTM (1972) standards in qualitative XRD analyzes as a standard. The information obtained from these graphs prepared as a result of XRD analyses was determined qualitatively considering the criteria suggested by ASTM (1972) and presented in Table 3, the data obtained from the diffractograms in this chart are ranked according to the intensity of reflection, and this mineral ranking does not represent any quantitative value. When the normal shooting of clay fraction diffractograms given in Figure 4 is examined, the presence of 14 Å reflection of the smectite mineral is observed. This situation indicates that the exchangeable cation of the smectite group mineral of Ankara clay samples is rich in Ca^{++}.

In addition to the mineralogical composition of clays, physicochemical properties directly affect some engineering properties such as swelling behavior and shear strength of soils (Ergüler, 2001). The values of major elements obtained from the analyses made in the XRF spectrometer are presented in Table 4. Considering the results given in Table 4, it is understood that CaO percentage in Ankara clay are quite high with values varying between 6.7% to 21.2% due to carbonate nodules observed at shallow depths while Na_2O percentage is generally lower than other

Table 3- Minerals detected in the samples as a result of XRD analyses.

Sample No.	Detected minerals
N1	Quartz, Calcite, Smectite, Plagioclase, Chlorite, Kaolinite, Serpentine, Mica
N2	Quartz, Calcite, Smectite, Chlorite, Kaolinite, Mica, İllite
N3	Calcite, Quartz, Plagioclase, Chlorite, Smectite, Mica, İllite, Kaolinite
N4	Quartz, Calcite, Plagioclase, Smectite, Mica, İllite, Chlorite, Kaolinite
N5	Quartz, Calcite, Smectite, Plagioclase, Chlorite, Kaolinite, Mica, İllite
N6	Quartz, Calcite, Smectite, Plagioclase, Chlorite, Kaolinite, Mica, İllite
N7	Quartz, Plagioclase, Montmorillonite, Chlorite, Kaolinite, Mica, İllite, Amorphous material
N8	Calcite, Quartz, Montmorillonite, Plagioclase, Mica, İllite, Serpentine, Chlorite

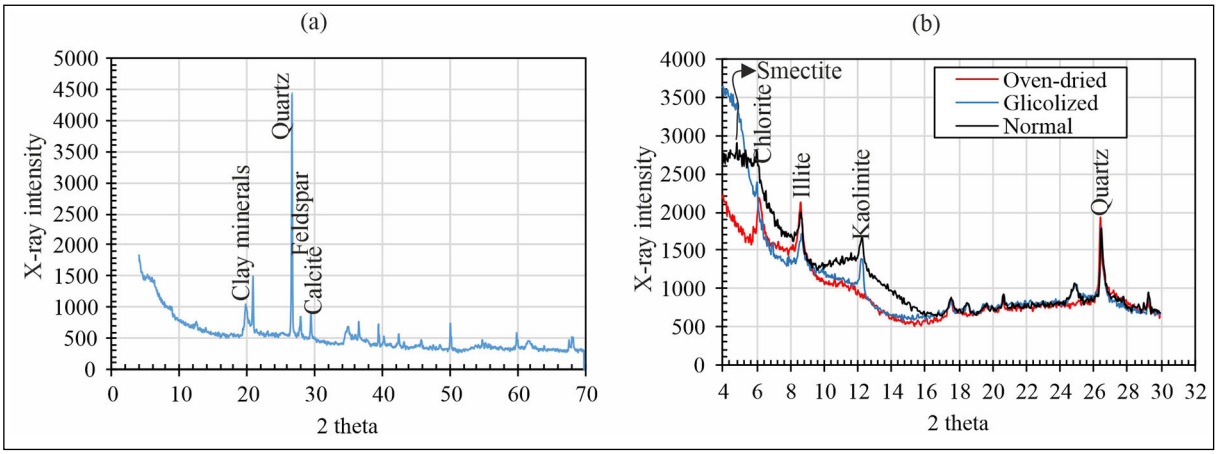

Figure 4- Diffractogram of the whole rock stage of XRD analysis of the sample N4 a) and the diffractograms belonging to the clay fraction of the same sample b).

Table 4- Percentages of major elements obtained from chemical analyses performed on samples (LOI: Loss on Ignition).

Sample No	LOI (%)	Al_2O_3 (%)	BaO (%)	CaO (%)	Cr_2O_3 (%)	Fe_2O_3 (%)	K_2O_3 (%)	MgO (%)	Na_2O (%)	SO_3 (%)	SiO_2 (%)	TiO_2 (%)
N1	14.2	16.9	0.07	10.3	0.02	5.9	1.9	3.9	0.6	0.18	45.3	0.7
N2	13.3	16.9	0.03	9.6	0.02	5.9	1.9	3.0	0.3	0.09	48.3	0.7
N3	19.5	11.7	0.05	21.2	0.02	4.4	1.1	2.8	0.4	0.13	38.1	0.6
N4	10.2	19.1	0.04	3.2	0.02	6.5	2.1	3.2	0.4	0.09	54.4	0.8
N5	16.1	12.9	0.04	15.8	0.02	4.7	1.2	2.7	0.4	0.15	45.5	0.5
N6	11.6	17.4	0.05	6.7	0.02	5.8	1.6	3.0	0.2	0.09	52.8	0.7
N7	13.4	13.7	0.04	13.6	0.02	5.1	1.7	2.7	0.6	0.08	48.5	0.6
N8	19.4	12.7	0.03	19.0	0.02	4.7	1.5	3.0	0.4	0.24	38.4	0.6

major elements with a value varying between 0.2 - 0.6. Abduljauwad (1993) stated that K_2O_3 indicated the presence of illite mineral, while SiO_2, Al_2O_3, Fe_2O_3, MgO and CaO indicated the presence of smectite mineral. When looking at the total percentages of all major elements proposed by Abduljauwad (1993) for smectite, it is concluded that smectite mineral is more than other clay minerals in the studied samples, and this result is consistent with the results obtained in X - ray diffraction analysis.

All results obtained in SEM - EDS analyzes are presented in Table 5. When the SEM images of all samples taken from eight locations within the scope of this study and the EDS analysis results given in Table 5 were examined in order to determine the textural and chemical properties of Ankara clay, no trace of sodium was found in any sample except for the sample N1. It is seen that the sample N2 has more oxygen and relatively less in magnesium than other locations. In general, when the amount of elements in all locations is evaluated in terms of +1, +2 and +3 ion

Table 5- The weight and element percentage amounts of Ankara clay samples obtained from EDS analyses.

Element	Evaluation based on weight							
	N1	N2	N3	N4	N5	N6	N7	N8
O K (%)	43.68	53.86	45.69	33.15	55.56	39.41	49.53	42.92
NaK (%)	1.72	-	-	-	-	-	-	-
MgK (%)	4.01	1.76	2.43	2.15	1.22	2.69	3.35	3.52
AlK (%)	12.62	5.73	9.89	11.31	2.18	14.65	13.48	12.69
SiK (%)	26.70	35.40	28.53	43.71	3.57	29.17	24.85	28.45
K K (%)	2.14	0.80	1.40	2.71	-	2.23	2.12	1.94
CaK (%)	2.74	0.40	6.95	0.62	36.29	3.56	2.48	3.65
TiK (%)	0.21	-	0.27	-	-	-	0.32	1.05
FeK (%)	6.19	2.06	4.85	6.35	1.17	8.29	3.88	5.78
Element	Evaluation based on element							
	N1	N2	N3	N4	N5	N6	N7	N8
O K (%)	59.01	67.62	61.55	47.80	74.55	55.36	64.37	58.62
NaK (%)	1.61	-	-	-		-	-	-
MgK (%)	3.56	1.45	2.15	2.04	1.09	2.49	2.86	3.16
AlK (%)	10.11	4.26	7.90	9.67	1.74	12.20	10.39	10.28
SiK (%)	20.55	25.32	21.89	35.90	2.73	23.34	18.39	22.13
K K (%)	1.18	0.41	0.77	1.60		1.28	1.12	1.08
CaK (%)	1.48	0.20	3.74	0.36	19.44	2.00	1.29	1.99
TiK (%)	0.10	-	0.12	-		-	0.14	0.48
FeK (%)	2.39	0.74	1.87	2.62	0.45	3.33	1.44	2.26

distribution, a close distribution with respect to each other is observed. Considering the Table 1, the lowest and highest values in terms of swelling potential were determined in samples N3 and N4, respectively. In addition, considering the percentage of clay particle size of these samples, it was seen that the samples N4 and N3 had quite different values from each other. Besides, while the ratio of clay fraction of the sample N4 that have high swelling is 51%, the ratio of the clay fraction of the sample N3 with a lower swelling potential is found to be 28%. The results of typical SEM images and EDS analyses of these two locations are given in Figure 5. As can be clearly seen in Figure 5, the SEM image of the sample N4 with a relatively higher swelling volume is detected as more leafy mineral (Figure 5b), however the SEM image of the sample N3 with the lowest swelling volume shows a more granular texture (Figure 5a). Considering the shooting of point where EDS analyzes are made in Figure 5a and the obtained element percentages, it is understood that there is a mineral at this point and it is the clay mineral according to the SEM image given in Figure 5b.

4.3. Electrokinetic Properties of Ankara Clay

The zeta potential (ζ) is defined as the electrical potential that occurs at the boundary surface between the negatively charged colloidal particle and the environment surrounding this particle. The value of this potential varies depending on the amount of surface charge, the type of colloid, pH of the medium and the electrical properties of the solvent. Zeta potential is used to evaluate many important properties such as electrokinetics of colloidal systems with negatively charged surfaces such as clay minerals and determine the electrical charge or potential of particles.

The particle size distribution curves of the powdered samples to be used in Zeta potential experiments are presented in Figure 6. The zeta potential vs pH change graphs obtained from the samples as a result of these experimental activities are presented in Figure 7. As can be seen in the graphs of change in Figure 7, there occurs a decrease in the zeta potential values in all samples depending on certain functions due to increasing ambient pH. When the

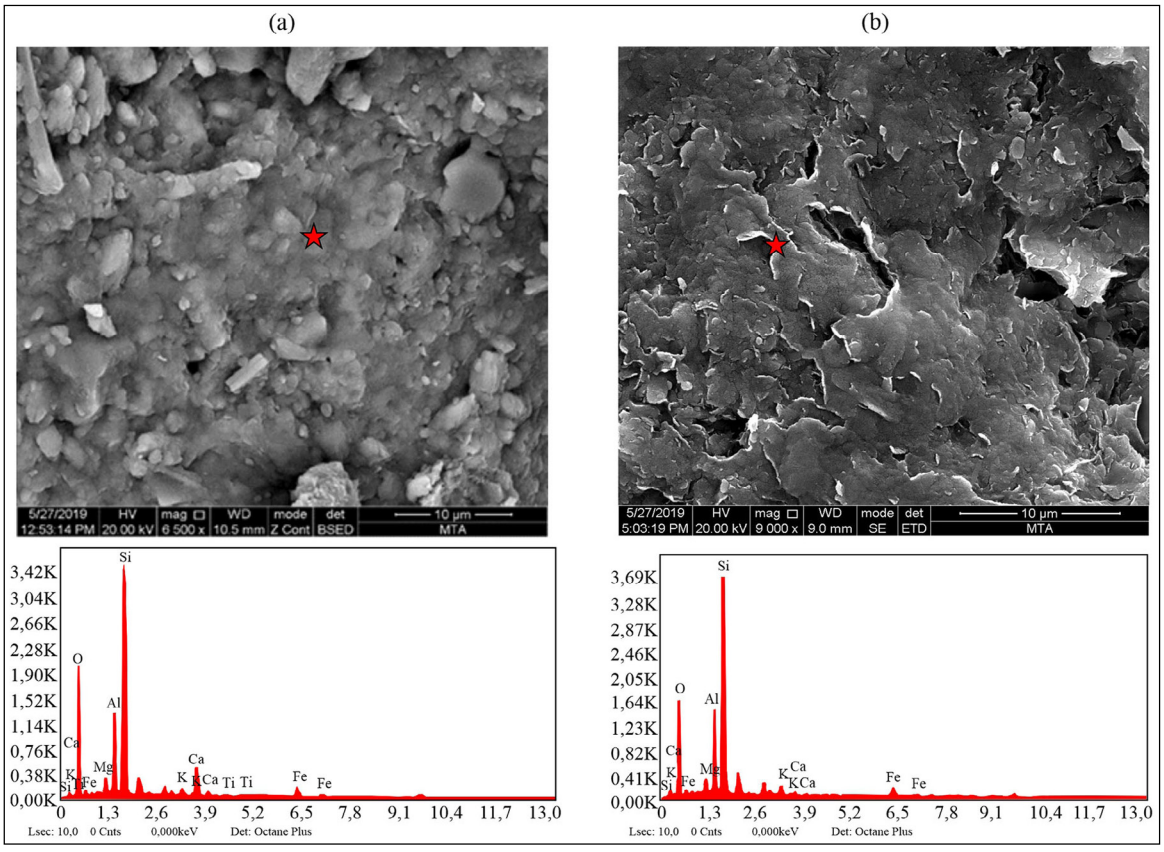

Figure 5- a) SEM image and EDS graph of the sample N3 that has the lowest swelling potential, b) SEM image and EDS graph of the sample N4 that has the highest swelling potential.

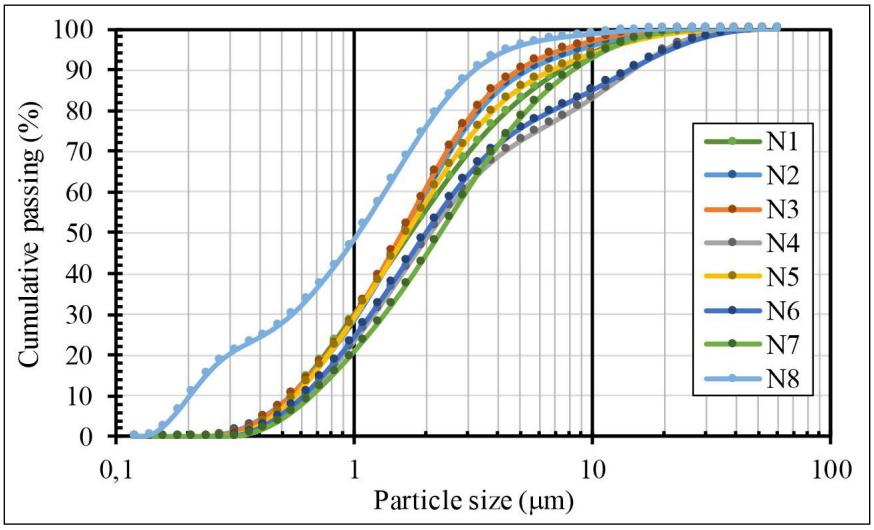

Figure 6- Particle size distribution curves determined by using laser of the samples prepared for zeta potential measurements.

results of zeta potential experiments performe for all samples are taken into consideration, pH values of the clay samples, which also show swelling behavior, vary between 2.03 and 12.10, and the measured zeta potential values vary between -3.56 mV and -51.8 with an average value such as -16.17 mV. Similar results were also obtained in the study conducted by Akın and Çelik (1995) consisting of the electrokinetic behavior of montmorillonitic clay minerals. These researchers emphasized that although they decreased the pH value of the environment to 3, the zeta potentials of the clay mineral they studied remained at negative values and that the zero load point (syn) of the montmorillonite mineral could not be determined. Akın and Çelik (1995) emphasized that they detected similar results for Ünye and Kırka borax montmorillonite minerals. Dikmen et al. (2011) determined the zero load points of Ahırözü and Üçbaşlı kaolin at pH ~4.2 and pH ~3.2, respectively using kaolin type clay in their study. The results obtained from these studies show that the zero load point of clays such as montmorillonite and Ankara clay with swelling capacity could not be found.

In addition to the different ambient pH values of the samples, it was thought that measuring the zeta potentials of the clay solutions in different electrolyte environments by taking the electrolyte type and concentrations into consideration would be useful in understanding the electrokinetic properties of these clayey samples. For this purpose, zeta potential experiments were carried out in single (NaCl), double ($CaCl_2$) and triple ($FeCl_3$) valent electrolyte solutions in concentrations of 0.1 mol L^{-1}, 0.01 mol L^{-1}, 0.001 mol L^{-1} and 0.0001 mol L^{-1}. The results obtained in the experiments performed using pure water at 25° C are presented in Figure 8. As seen in Figure 8, zeta potential values present different exchange functions depending on the type of electrolyte and there occurs a decrease in zeta potential values depending on the increase in concentration. It is seen that the effect of trivalent cations is higher in the decreasing behavior of zeta potential of these clayey units. While cations with +3 ions change zeta potentials from negative to positive in pure clay minerals depending on the concentration, there is only a tendency in Ankara clay and continued at staying in negative value. It was determined that Ankara clay did not have any isoelectric point. While monovalent cations make the zeta potential more and more negative, the exchange of divalent (Ca^{+2}, etc.) cations present in the crystal structure and the univalent (Na^{+}, etc.) cations in the solution has led to the development of a positive charge deficiency on the surface (Dikmen et al., 2011). Dikmen et al. (2011) emphasized that it is expected that the ratio of mineral to water and the intra surface will be replaced by equivalent amounts of cations in order to maintain total electroneutrality since the ion exchange process is basically a stoichiometric reaction. It is also possible that this situation, which is expected in theory, may not be fully realized, and thus, this observed situation caused the clay surface to have a more negative structure.

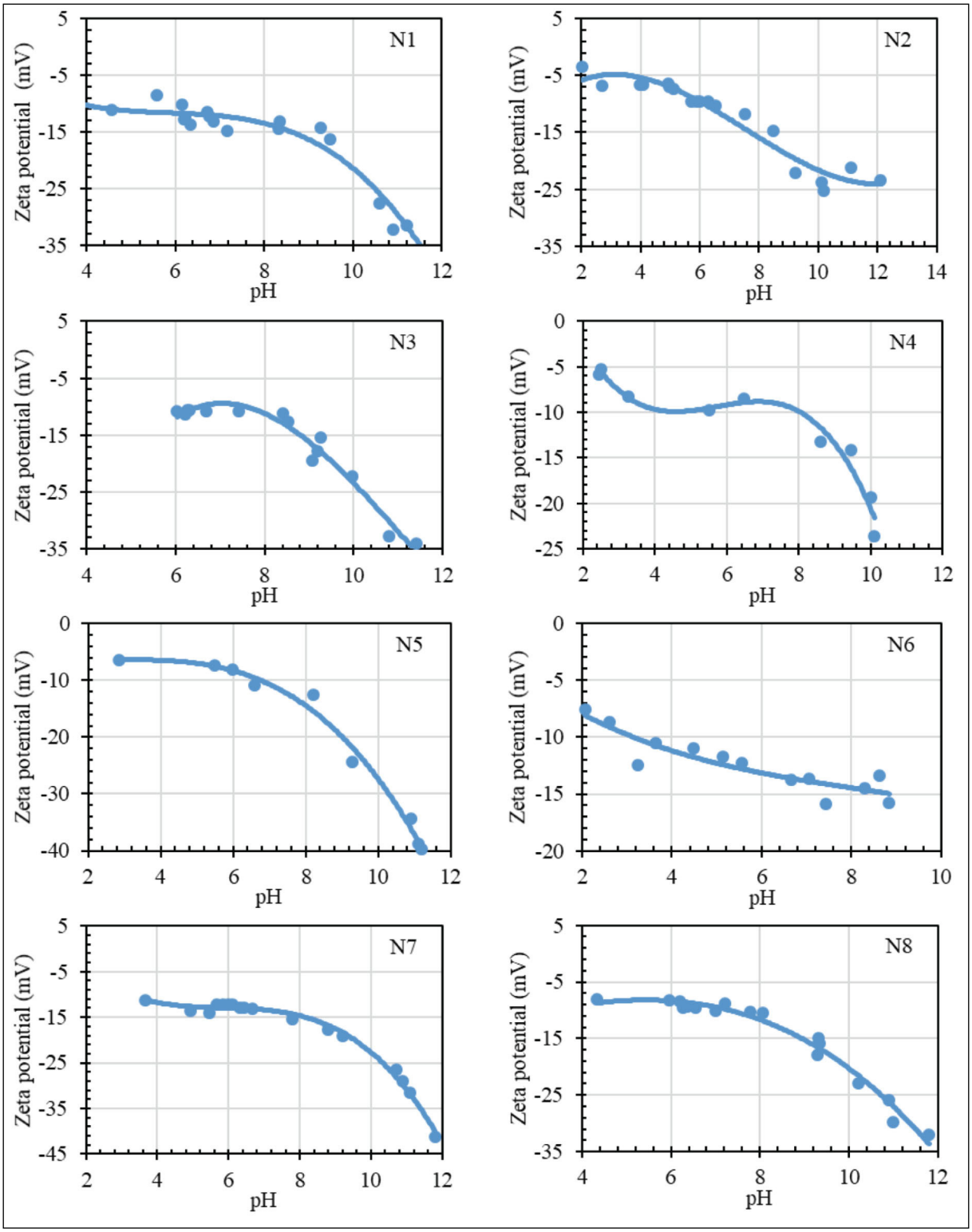

Figure 7- Zeta potential versus pH change graphs of the clay samples.

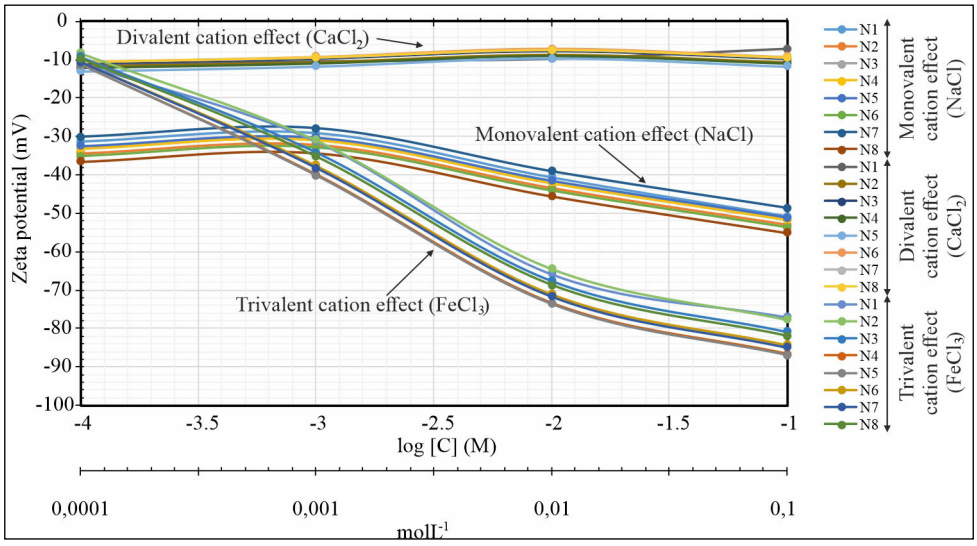

Figure 8- The concentration vs zeta potential variations of Ankara clay in single (NaCl), double ($CaCl_2$) and triple ($FeCl_3$) valence electrolyte solutions.

5. Conclusion

In this study, zeta potential measurements and the structural properties of Ankara clay were examined in detail in order to explain the electrokinetic mechanism. The results obtained are summarized below:

1. It was determined that the mineralogical composition of Ankara clay was generally formed by quartz, calcite, smectite, feldspar, kaolinite, illite and partially by chlorite, serpentine and mica minerals. The presence of swelling type clay minerals such as smectite in its mineralogical composition poses a problem for the light engineering structures of Ankara clay due to the swelling - shrinkage behavior of the region in rainy and dry periods up to a certain base depth.

2. The clay fraction content in Ankara clay reaches as high as 58% with an average value of 44%. The high ratio of clay fraction causes Ankara clay to have high Atterberg limits and therefore to show swelling behavior with the presence of swelling type clay minerals. In the analysis, it was understood that the clay fraction percentage and the liquid limit value are important indicators in understanding the swelling behavior and potential of Ankara clay. Similar swelling potential was also observed in the cation exchange capacity (CEC) results, which were determined in the methylene blue experiments of the samples and consistent with the results obtained in previous methylene blue experiments. Therefore, it was concluded that the CEC parameter was also an important input parameter in the estimation of physical properties of clays such as swelling and plasticity.

3. When MultiPoint BET method is taken as a basis, it was determined that the values of control surface area of the electrokinetic behavior of clay minerals varied between 57 m^2/g - 117 m^2/g with an average value of approximately 84 m^2/g for Ankara clay.

4. It was determined that the zeta potential values of Ankara clay samples, which also showed swelling behavior, varied between -51.8 mV and -3.56 mV with an average value of -16.17 mV, in the experiments performed under ambient pH values of 2.03 and 12.10. Considering the results obtained in all locations, the zeta potential values of all samples increase in negative values due to certain functions depending on the increasing ambient pH. Zero load point could not be determined in Ankara clay.

5. Using the samples taken to investigate the effect of electrolyte type and concentration on the electrokinetic properties of Ankara clay, Zeta potential experiments of single (NaCl), double ($CaCl_2$) and triple ($FeCl_3$) valued electrolyte solutions at concentrations of 0.001 mol L - 1 and 0.0001 mol L - 1 0.1 mol L - 1, 0.01 mol L - 1 were conducted. Monovalent and divalent electrolytes such as NaCl and $CaCl_2$ negatively increased the zeta potential of Ankara clay. However, it is considered that trivalent electrolyte

such as $FeCl_3$ is the electrolyte that determines the zeta potential and that the clay minerals tend to change their zeta potential from negative to positive depending on the concentration.

6. It was determined that Ankara clay, which was rich in different proportions of illite, kaolinite and montmorillonite clay minerals in addition to quartz, feldspar and calcite minerals, did not create any electrokinetic behavior similar with previous studies using minerals such as pure kaolin, montmorillonite, illite and sepiolite.

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