INFLUENCE OF ACETIC ACID ON STRUCTURAL CHANGE AND SHEAR STRENGTH OF CLAYS*

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Abstract– This paper presents shear strength test results and structural changes in clay soils with acetic acid. Two different clay soils were used, kaolinite and another containing montmorillonite with a mixed mineralogy, while pure water and various contents of acetic acid (20%, 40%, 60% and 80%) were used as pore fluids. Clay-pore fluid slurries prepared with a water content of twice the liquid limit of each acetic acid content were consolidated under a 100 kPa pre-consolidation pressure. Direct shear tests were conducted on samples taken from pre-consolidated mixtures in order to determine changes in shear strength. Additionally, optical microscope images and scanning electron photomicrographs were obtained in order to observe structural changes under the influence of acetic acid.

According to the experimental results, significant increases occurred in peak shear strength and shear strength parameter values in both clays in parallel with increasing acetic acid content. These increases were higher in the clay with montmorillonite; in particular, there were substantial changes in the internal friction angle. Increasing liquid limit values with increasing acetic acid contents in kaolinite resulted in a substantial decrease in the other clay. The optical microscope images and scanning electron photomicrographs indicated that lumpy formations occurred in both clays with the addition of acetic acid, and their structures began to resemble that of a silt and fine sand form.

Keywords– Clay, acetic acid, shear strength, kaolinite, montmorillonite

I. INTRODUCTION

Today, many sites have become contaminated with various organic fluids such as acetic acid. It is possible for fluids to seep into the soil, particularly in solid waste storage units, industrial buildings, mines and their waste repositories, where organic fluids are in contact with the ground. The variation of pore fluid properties in soil has a major effect on soil behaviour. This effect is a function of pore fluid properties and soil mineralogy [1]. In particular, clay soils are highly affected by changes in pore fluids, due to their particle surface forces and all of their engineering properties becoming altered. Determining changes in the engineering properties of soils is important for understanding and taking precautions according to the behaviors of these soils when used as foundation soil or infill soil.

The effects of organic fluids on clays have been investigated by many researchers [2-4]; it was reported that the behavior of montmorillonite was dependent on changes in diffuse double layer repulsive forces, whereas the behavior of kaolinite was less affected by these forces. Mitchell [5] attributed the insignificance of the diffuse double layer theory in kaolinite to the large particle size of kaolinite. The behavior of kaolinite under the influence of organic fluids is controlled by van der Waals attractive forces [6]. Clays tend to flocculate and behave almost as if they were silt soil in the presence of organic fluids,

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which have a lower dielectric constant than water, in accordance with the change in van der Waals attractive force and diffuse double layer repulsive force between clay particles [7].

One of the most common organic fluids in geotechnical engineering applications is acetic acid, due both to its formation and being an intermediate product. Although it is a weak acid, acetic acid has a significant effect on the behavior of clays due to its low dielectric constant and its interaction with some minerals within the clay. Various researchers have used acetic acid in their studies in order to represent organic fluids [8-11].

Some researchers [12, 13] explained that the variation in the diffuse double layer thickness affected the Atterberg Limits. Kaya and Fang [14] associated the decrease in the liquid limit (LL) values of the soils with the net increase in the attractive forces due to a considerable decrease in the repulsive forces between the particles and the collapse of the diffuse double layer. Sridharan et al. [15] reported that the LL values of montmorillonite consistently increased with an increase in the dielectric constant of the pore fluid, whereas those of kaolinite decreased. The experiments performed on kaolinite by the former researchers showed that the LL values increased with increasing acetic acid contents and the decreasing dielectric constant of the pore fluid [8, 11, 16]. A study of Georgia Kaolinite obtained LL values of 58% for pure water and 80% for acetic acid [17].

Many researchers have studied changes in the strength behavior of clay soils brought about by organic fluids [18-24], especially in recent years. The results have shown significant variations, as both the nature and geometry of clay particles in clay-fluid systems are extremely changeable; characteristics of pore fluids are very different and sample preparation systems can greatly influence results. Sridharan et al. [23] stated that the shear strength behavior of kaolinite under the influence of organic fluids differed greatly from that of montmorillonite and that, while the undrained shear strength value increased in kaolinite, it decreased in montmorillonite. In tests of compressed kaolinite using water and various organic fluids, Moore and Mitchell [25] found that shear strength changed significantly with the decreasing dielectric constant of pore fluids, which was in harmony with the change in attractive force. In tests on kaolinite, Yildiz [8] found that, while there was no change in shear strength behavior up to 50% acetic acid content, there was a decrease in strength beyond that point. Likewise, in triaxial compression tests on kaolinite, Anandarajah and Zhao [9] obtained higher peak shear strengths using acetic acid, which had a very small dielectric constant, instead of water.

Almost all previous studies reported strength changes in clays under organic fluids relative to cohesion (c) and internal friction angle values (φ). Al-Yaqout et al. [22] conducted direct shear tests within the scope of a geotechnical study on the Al-Adan solid waste store in Kuwait. They reported that the effective φ value varied between 26.7° and 50°, while cohesion varied between 7.43 kPa and 35 kPa. In triaxial compression tests of samples taken from urban solid waste landfills, Zhan et al. [24] found that cohesion fell from 23.3 kPa to 0 kPa, but the φ value rose from 9.9° to 26°. Soule and Burns [18] found that the φ value increased from φ = 7° to φ = 34-37° in bentonites that were treated with ammonium cations.

The present study examined how changes in pore fluids affect the behavior of clays using two clay soils differing mineralogy and acetic acid contents. Atterberg limit tests were carried out, then direct shear tests were performed in order to determine changes in shear strength. Optical microscope images (OM) and scanning electron photomicrographs (SEM) were also obtained to observe structural changes in the clays.

2. EXPERIMENTAL PROCEDURE

a) Materials

Two different clays were used in the experimental study. The first was kaolinite, which was obtained from
Bozüyük (Turkey); the other clay was taken from a field in Aksaray City (Turkey) and called Aksaray clay. X-ray diffraction (XRD) was used to determine the clay mineral contents (ASTM 1972) [26] (Table 1). The geotechnical and physical properties of the clays are given in Table 2.

Table 1. XRD results of the clays

<table>
<thead>
<tr>
<th>Clays</th>
<th>All rock analysisa</th>
<th>By mass (%)</th>
<th>Clay mineralb</th>
<th>By mass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>Clay</td>
<td>80.0</td>
<td>Kaolinite</td>
<td>91.0</td>
</tr>
<tr>
<td></td>
<td>Quartz</td>
<td>16.0</td>
<td>Illite</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>Feldspar</td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aksaray clay</td>
<td>Clay</td>
<td>41.0</td>
<td>Montmorillonite</td>
<td>49.0</td>
</tr>
<tr>
<td></td>
<td>Dolomite</td>
<td>30.0</td>
<td>Sepiolite</td>
<td>33.0</td>
</tr>
<tr>
<td></td>
<td>Calcite</td>
<td>24.0</td>
<td>Kaolinite</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td>Quartz</td>
<td>2.0</td>
<td>Illite</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>Feldspar</td>
<td>3.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a: According to ASTM (1972) Catalogue [26]
b: According to Grim [27], Brindley [28] and Wilson [29]

According to the XRD pattern, the behavior of the first clay was directed by the kaolinite mineral and the behavior of the Aksaray clay was determined by montmorillonite, which formed 49% of this clay. Moreover, large amounts of calcite and dolomite minerals within the Aksaray clay played an extremely important role in the behavior of the clay due to their special reactions with acetic acid.

Pure water and acetic acid, which can dissolve in water in any percentage, were used as pore fluids in the study. The chemical formula of acetic acid is CH₃CO₂H and its dielectric constant ($\varepsilon_0=6.2$) is much lower than that of water ($\varepsilon_0=80.4$) [33]. Acetic acid tends to enter into chemical reactions with the clay. In the experiments, acetic acid was added to pure water in proportions of 20%, 40%, 60% and 80%.

b) Methods

In the experimental study, the two clays were dried at 105°C and pulverized. Then, Atterberg limit tests were conducted at different contents of acetic acid and the Casagrande Test was applied according to ASTM D4318-95b Standard Test [34].

Although the direct shear test is mostly performed on sands rather than clays, it was thought that direct shear tests would be more appropriate for determining the shear strength of clays due to the tendency of clays to turn into a silt and fine sand form in the presence of acetic acid. In order to prepare direct shear test samples, slurries prepared with a water content twice the liquid limit ($w=2LL$) (in Table 3) of each acetic acid content were pre-consolidated by placing them into a cell 220 mm in diameter and...
200 mm in height, designed to allow fluids to exit from both the top and the bottom. The specimens obtained from the pre-consolidated slurry, using a gradual load increase up to 100 kPa, (12.5, 25.0, 37.5, 50.0, 62.5, 75.0, 87.5, 100.0 kPa), were used for the direct shear tests.

Table 3. The Atterberg limit test results of clays

<table>
<thead>
<tr>
<th>Clays</th>
<th>Liquid limit (LL) (According to the weight) (%)</th>
<th>Plasticity index (PI) (According to the weight) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>LL</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PI</td>
<td></td>
</tr>
<tr>
<td>Aksaray clay</td>
<td>LL</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PI</td>
<td></td>
</tr>
</tbody>
</table>

After pre-consolidation of the slurries, at least three samples were taken in rings with circular sections of 62.5 mm internal diameter and 20 mm in height. Direct shear tests were conducted according to the ASTM D-3080 Standard Test [35]. Vertical pressures of 32.6, 65.2 and 130.5 kPa were applied to each sample, respectively. The samples were cut at a horizontal speed of 1 mm/min.

For the OM investigation, amounts of 5% (m/m) clay were dispersed in the acetic acid/water mixtures. The suspensions were prepared in 10 ml glass tubes and shaken for approximately 2 min. Then, one or two drops were taken from the suspensions, dripped onto a glass surface and photographic images were immediately taken using an optical microscope (×100 magnification). For the SEM images, parts of the samples that were used in the experiments with different acetic acid contents were dried and images were produced using a ZEISS EVO SEM at 20.00 kV and a beam current of 53 pA in the Konya Technocity at Selcuk University. The SEM images were taken at ×2500 magnification and a 10 mm working distance, which enabled visualization of the general pore distributions and fabrics as well as the pore geometries.

3. TEST RESULTS

a) Kaolinite

The kaolinite presented a plastic property for the various acetic acid contents, and the liquid limit and plastic limit tests were easily performed. In general, increasing acetic acid contents led to increasing LL values, although the plasticity index values (PI) did not increase by much (Table 3). The maximum shear strength values and corrected failure envelopes for kaolinite obtained from the direct shear tests are shown in Fig. 1. Maximum shear strength values were obtained in parallel with the increasing acetic acid contents. Values obtained for the 80% acetic acid content were on average 2.5 times higher than those for pure water. Likewise, an increase was observed in the cohesion and the $\phi$ values in parallel with increasing acetic acid contents (Table 4). Increases in the maximum shear strength values and shear strength parameters were attributed to the following:

The two fundamental physico-chemical factors that cause structural and shear strength changes in clay particles are the van der Waals attractive and diffuse double layer repulsive forces. The behavior of kaolinite is controlled by van der Waals attractive forces between the particles [6]. Diffuse double layer repulsive forces are minimal in kaolinitic soils in comparison to montmorillonitic soils [4]. Zhao [17] calculated the change in physico-chemical forces of kaolinite particles for nine organic fluids with different dielectric constant values [33], as shown in Fig. 2, in the event that the distances between particles for the kaolinite are 0.003$\mu$m and 0.001$\mu$m, respectively. According to Fig. 2, if the dielectric constant of a pore fluid decreases, the net force between the clay particles will be an attractive force. In this study, the dielectric constants of pore fluids decreased with increasing acetic acid contents. So
accordingly, in kaolinite, the highest attractive force between the particles should be for the sampled with 80% acetic acid content (from Fig. 2) because the net attractive force between the clay particles increases due to the decreasing dielectric constant of the pore fluid [14]. Thus, the particles formed clusters through a flocculation process and began to demonstrate increased resistance. The strength values obtained in the direct shear tests were in concordance with this change.

Table 4. Shear strength parameters of the kaolinite for various acetic acid contents

<table>
<thead>
<tr>
<th>Acetic acid content (%)</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cohesion (c) (kPa)</td>
<td>9.44</td>
<td>13.53</td>
<td>19.50</td>
<td>23.00</td>
<td>23.72</td>
</tr>
<tr>
<td>Internal friction angle (\phi)</td>
<td>3.66</td>
<td>4.97</td>
<td>5.59</td>
<td>5.96</td>
<td>8.25</td>
</tr>
</tbody>
</table>

Fig. 1. The results of direct shear tests of the kaolinite for various acetic acid contents

**b) Aksaray clay**

Both the LL and PI values of Aksaray clay decreased with increasing acetic acid content and the decreasing dielectric constant of pore fluid (Table 3). The liquid and plastic limit tests were difficult to apply, as the clay particles turned into a silt and fine sand form due to excessive lumping during the tests, especially at higher acetic acid contents. In Aksaray clay, just as in the case of kaolinite, the maximum shear strengths increased in accordance with the increasing acetic acid contents (Fig. 3). These increases began to be more obvious, especially with the 40% acetic acid content. The values obtained for the 80% acetic acid content were three times higher than for pure water. Whereas the Aksaray clay had both
increased cohesion and $\phi$ values, the changes became more conspicuous, especially in the $\phi$ values (Table 5). The changes in maximum shear strengths and shear strength parameters were attributed to the following:

The clay fraction of Aksaray clay mostly consists of montmorillonite mineral. The behavior of montmorillonite clays depends on the diffuse double layer repulsive force rather than the van der Waals attractive force. Theoretically, the diffuse double layer thickness in montmorillonite is 40 times greater than that of the thickness of the clay mineral [36]. A decrease in the thickness of the diffuse double layer caused by organic fluids reduces electrical repulsive forces, and this causes flocculation in the clay [37]. Chen [6] investigated the interaction energy with changes in the dielectric constant of pore fluid between particles of montmorillonite clay minerals using organic fluids (Fig. 4). The attraction energy ($E_{\text{att}}$) between the particles in montmorillonite showed very small values and was almost negligible in comparison to the repulsive energy ($E_{\text{rep}}$). The total net interaction energy ($E_{\text{tot}}$) depends on the change in repulsive energy.

<table>
<thead>
<tr>
<th>Acetic acid content (%)</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cohesion ($c$) (kPa)</td>
<td>22.09</td>
<td>25.08</td>
<td>25.85</td>
<td>29.67</td>
<td>30.16</td>
</tr>
<tr>
<td>Internal friction angle ($\phi$)</td>
<td>2.52</td>
<td>4.15</td>
<td>11.86</td>
<td>20.44</td>
<td>24.84</td>
</tr>
</tbody>
</table>

In the case of the pore fluid being acetic acid, the diffuse double layer between the clay particles collapsed together with a decrease in the dielectric constant, and repulsive forces decreased. The net force that occurred between the particles due to the decrease in the repulsive forces between particles increased in such a way that the attractive force became more dominant. As a consequence of this change, the clay particles underwent flocculation by approaching each other and the permeability of the clay increased. The water content of the clay decreased with the increase in permeability. The clay demonstrated higher resistance to external forces due to the low water content, flocculation of the particles and the more effective mechanical contacts between the particles. Thus, the clay demonstrated behavior almost similar to that of over-consolidated clay [38].

Additionally, the excessive strength increase obtained under the effect of acetic acid can be explained by the reaction of 30% dolomite (CaMg(CO$_3$)$_2$) and 24% calcite (CaCO$_3$) in the clay with the acetic acid. As a result of the treatment of calcite with acetic acid, calcium acetate (Ca(CH$_3$CO$_2$)$_2$), and the treatment of dolomite with acetic acid, calcium acetate (Ca(CH$_3$CO$_2$)$_2$) or magnesium acetate (Mg(CH$_3$CO$_2$)$_2$) compounds were formed (Eqs. (1, 2)) [39].
Influence of acetic acid on structural chance and…

\[
\begin{align*}
\text{CaCO}_3 + 2 \text{CH}_3\text{COOH} &= \text{Ca(CH}_3\text{CO}_2)_2 + \text{H}_2\text{O} + \text{CO}_2 \\
\text{MgCO}_3 + 2 \text{CH}_3\text{COOH} &= \text{Mg(CH}_3\text{CO}_2)_2 + \text{H}_2\text{O} + \text{CO}_2
\end{align*}
\] (1) (2)

\[\text{Dielectric constant of pore fluid, } \varepsilon_0\]

\[\text{E}_{\text{rep}} / K T \times 10^5\]

\[\text{E}_{\text{att}} / K T \times 10^5\]

\[\text{E}_{\text{tot}} / K T \times 10^5\]

Fig. 4. Variation of interaction energy in montmorillonite with dielectric constants of pore fluids[6]
  a) repulsive energy, b) attractive energy, c) total energy

The behaviors of these compounds can be better understood by analysis of their open structures (Fig. 5a, 5b). The open structure of these compounds clearly shows that there are unbonded minus (-) loads on one edge of the oxygen (O) atoms that are bonded to the carbon (C) atoms. Metals such as iron (Fe), aluminum (Al), sodium (Na) and potassium (K) are bonded to these edges in unbonded oxygen atoms. This relationship continues in a chain. Due to these chains, the structure becomes more resistant to external forces [40].

Fig. 5. Open structural display of the calcium acetate (Ca(CH₃CO₂)₂) and magnesium acetate (Mg(CH₃CO₂)₂) formations in the chemical reactions, a) Calcium acetate (Ca(CH₃CO₂)₂), b) Magnesium acetate (Mg(CH₃CO₂)₂)

4. DISCUSSION OF RESULTS

The increase in maximum shear strength in the presence of acetic acid was lower in kaolinite than in Aksaray clay (Fig. 1, 3); however, the increase in cohesion was higher in kaolinite than in Aksaray clay.
This phenomenon can be accounted for by the fact that the kaolinite turned to gel as a result of the effect of acetic acid. Kaolinite minerals are composed of alumina silicate at a ratio of 1:1, which can decompose by entering into a reaction with acid under the appropriate conditions. Due to the formation of gel-like silica aluminium hydroxide as a result of the reaction between kaolinite and acetic acid, filtration became difficult, the filtration speed decreased and viscosity increased. As a consequence of this reaction, it became difficult for the excess fluid within the slurry that was subjected to pre-consolidation to flow out, and the initial water content of the samples used for the direct shear tests increased. Thus, the increase in the shear strengths became limited. Due to gelification, the viscosity between the particles increased and therefore the cohesion values demonstrated a more conspicuous increase.

Both kaolinite and Aksaray clay showed increases in $\phi$ values with increasing acetic acid content. When an external force was applied to both clays, which tended to acquire a silt and fine sand form in the presence of organic fluids, the mechanical contacts between particles increased and the friction resistance that occurs as a result of the contact caused when particles are forced to displace, increased. Changes in the $\phi$ value of the clay became far more obvious than changes in cohesion, especially for Aksaray clay. The $\phi$ value was 24.84° for the 80% acetic acid content, which was 9.86 times greater than that of the value obtained for pure water; this increase in $\phi$ value is very important for shear strength. Likewise, Olgun and Yıldız [10] carried out undrained-unconsolidated triaxial compression tests (UU) on Aksaray clay, using samples pre-consolidated with different acetic acid contents, to analyze changes in shear strength. It was found that cohesion values did not vary with increasing acetic acid content, whereas the $\phi$ values increased from 3.97° to 14.71°. In this case, the theory proposed by Schmertmann [19] that the rigidity and the increase in resistance in the presence of organic fluids are due to $\phi$ value rather than cohesion was verified for Aksaray clay. However, it should be noted that excessive increases in the $\phi$ value of Aksaray clay are related to the reactions of calcite and dolomite with acetic acid, as well as a decrease in the dielectric constant of pore fluid (Eqs. (1) and (2)).

For Aksaray clay, the change in the $\phi$ value caused the clay to behave almost like a silt and fine sand. According to Table 6, which shows typical $\phi$ values for different soils [41], Aksaray clay had $\phi$ values similar to loose silt or silty sand at 60% acetic acid content and similar to hard silt or silty sand at 80% acetic acid content. Similarly, Ratnaweera and Meegoda [20] reported that, in the presence of organic fluids, their clay soil samples exhibited behavior similar to that of granular soils.

Table 6. Typical values of internal friction angle for different soils [41]

<table>
<thead>
<tr>
<th>Soil class</th>
<th>Internal friction angle ($\phi^\circ$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hard, well graded, coarse sand</td>
<td>37 - 60</td>
</tr>
<tr>
<td>Hard, uniform graded fine sand</td>
<td>33 - 45</td>
</tr>
<tr>
<td>Loose dry sand</td>
<td>28 - 34</td>
</tr>
<tr>
<td>Loose silt or silty sand</td>
<td>20 - 22</td>
</tr>
<tr>
<td>Hard silt or silty sand</td>
<td>25 - 30</td>
</tr>
</tbody>
</table>

According to the liquid limit test results, whereas the LL values in kaolinite increased slightly with increasing acetic acid contents, the effect of acetic acid on the LL value was limited. Kaolinite is affected by external factors less than other clay minerals (illite, montmorillonite) due to kaolinite’s powerful hydrogen bonds and the thinner diffuse double layer with respect to its dimensions [36]. However, some increase in the LL values resulted from the gelification process and water molecules, which were in the buffer zone between the particles in different acetic acid contents that were pulled through the particle surface [17]. On the other hand, the LL values in Aksaray clay demonstrated a substantial decrease with
increasing acetic acid contents. This situation is related to the thickness of the diffuse double layer around the clay particles. The diffuse double layer thickness of the montmorillonite is proportionally much greater than for the other clay minerals. The diffuse double layer thickness is directly proportional to the square root of the dielectric constant of the pore fluid [42]. Consequently, the diffuse double layer thickness decreased with the decreasing dielectric constant of the pore fluid in the tests. In other words, the amount of fluid around the clay particles and the LL values of the clay decreased considerably with the decreasing diffuse double layer thickness.

Despite the increase in LL values in kaolinite, the shear strength parameters, especially the cohesion values, increased slightly due to van der Waals attractive forces. In other words, the shear strength parameters changed in direct proportion to the increasing LL values. Unlike kaolinite, the LL values in Aksaray clay decreased quite significantly due to flocculation of particles. Therefore, the shear strength parameters, and in particular the φ values, increased significantly. Specifically, the shear strength parameters showed changes that were inversely proportional to the decreasing LL values.

According to the OM images, it was observed that the particles in both clays were separate and there was no visible interaction among the particles in the presence of pure water (Fig. 6). It was clearly observed that clustering and flocculation of particles increased in accordance with increasing acetic acid content. The increase in clustering and flocculation manifests itself more conspicuously in Aksaray clay than in kaolinite. For example, while a ball-like and totally clustered structure was observed in Aksaray clay at 80% acetic acid content, it was observed that there were particles in kaolinite that were partially clustered and indistinct and still tended to cluster. The finding that images in kaolinite were indistinct can be interpreted as being a result of gelification in the structure of kaolinite, caused by acetic acid [40].

The degree of flocculation and the sizes of the clusters that formed in the OM images were in parallel with the results obtained from the shear strength experiments. The behavior of the clays that resembled silt and fine sand also underwent changes in this manner [43]. For example, in Aksaray clay, greater shear strength and φ values were obtained in the 80% acetic acid content than in the 40% acetic acid content, and the amount of clustering and flocculation were also in concordance with this change (Fig. 6e and 6f).

SEM photomicrographs of both kaolinite and Aksaray clay (Fig. 7) show that the fabrics had variable particle sizes, ranging from 1 to 30 µm in diameter. These particles were randomly distributed throughout the samples. Similar to the optical microscope images, the images obtained from the SEM were clearer in Aksaray clay than in kaolinite. There was no evidence of flocculation for pure water in either of the two clay types (Fig. 7a and 7e); however, ettringite formed when acetic acid was used. Large amounts of ettringite crystals are clearly visible in Figs. 7b, 7c and 7f. Conversely, the SEM images of the 80% acetic acid content in kaolinite and the 40% and 80% acetic acid contents in Aksaray clay only show a few ettringite crystals with the flocculation particles. Aluminium silicate hydrate (Al-S-H) gel formed between the particles and the ettringite rods joined together, resulting in increased strength in the kaolinite (Fig. 7d). On the other hand, a denser structure formed in Aksaray clay under the influence of acetic acid, especially at contents greater than 40%. Figures 7g and 7h show a greater portion of sand and silt size grains throughout the samples than in 7e and 7f, corresponding to the greater shear strength of Aksaray clay, especially with the increasing φ value. Larger pore spaces are shown in Figs. 7g and 7h, compared with the fabric in Fig. 7e. These large pore spaces are important for increasing permeability and decreasing LL values under the influence of acetic acid in Aksaray clay.
Fig. 6. Optical microscope images of two clays obtained for pure water, 40% and 80% acetic acid contents

Fig. 7. Scanning electron photomicrographs of two clays obtained for pure water, 20%, 40% and 80% acetic acid contents
5. CONCLUSION

The following conclusions may be drawn from this study;

(i) The shear strength values and structural changes of the clays under the influence of organic fluids were affected by the type of clay minerals and changes in the dielectric constant of the pore fluid.

(ii) The presence of acetic acid in Aksaray clay led to the collapse of the diffuse double layer particles and thus the LL and PI values of the clay decreased significantly. Conversely, the LL and PI values of kaolinite under the effect of acetic acid increased slightly due to gelification.

(iii) The increases in the shear strength of kaolinite were lower than those in Aksaray clay due to decomposition and gelification caused by acetic acid in the structure of kaolinite, which contains alumina silicate.
(iv) Besides a decrease in the diffuse double layer repulsive forces in Aksaray clay, the increases that occurred in the shear strength of Aksaray clay due to the chain-like formation caused by the reactions of calcite and dolomite with acetic acid were far more conspicuous than those in kaolinite.

(v) There were increases in the $\phi$ value of both clays in accordance with the increase in acetic acid contents. The increases were very prominent at acetic acid contents greater than 40%, especially in Aksaray clay, and the increases that occurred in shear strength resulted from changes in the $\phi$ value rather than changes in cohesion.

(vi) The increase in cohesion that occurred in kaolinite due to gelification of the structure was higher than that in Aksaray clay. The increases that occurred in the shear strength of kaolinite can be attributed to increases in cohesion; however, the $\phi$ value slightly influenced shear strength changes at acetic acid contents greater than 60%.

(vii) In kaolinite, both the LL and shear strength parameters, especially the cohesion values, increased with increasing acetic acid content. Conversely, in Aksaray clay, the shear strength parameters, especially the $\phi$ values, increased with increasing acetic acid content whereas the LL values decreased.

(viii) Although there was a tendency towards silt and fine sand structures in both kaolinite and Aksaray clay with increasing acetic acid contents, this was more evident in Aksaray clay. This change was quite clearly visible in the OM and SEM images obtained for both clays. The amount of flocculation of the particles shown in these images supported the changes in shear strength observed experimentally. This leads to the conclusion that the chemical composition of acetic acid is important for the long-term shear strength gain of stabilized clay, especially clay containing montmorillonite, calcite and dolomite.

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REFERENCES


