

1-1-2018

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Influence of leachate on the Oligocene-Miocene clays of the İstanbul area, Turkey

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Received: 18.09.2017 • Accepted/Published Online: 27.11.2017 • Final Version: 08.01.2018

Abstract: Oligo-Miocene clay outcrops on the European side (west and northwest part) of İstanbul were analysed. Formerly, a landfill and sanitary landfill were built on the clay. Mineral liners of the current and extending parts of the İstanbul landfill consist of these clays, since they include a considerable amount of smectite, illite, and kaolinite. With this feature, these clays are also an important candidate for the buffer material of repositories for nuclear wastes of newly planned nuclear power plants. In this context, one Miocene and two Oligocene clay samples were subjected to leachate under low stress using an odometer device during a period of 30 days, 180 days, and 360 days to understand the chemical and mineralogical transformations and subsequent changes in the clay structure. The results of this work and our ongoing other research revealed that İstanbul clays are mostly illite/smectite mixed-layer minerals. Illites considerably increased while the illite/smectite mixed-layer minerals decreased in the first 15–30 days. The kinetics of the three clays was studied to understand the reasons for the illite increase. Increase of the activation energy over time may be attributed to the successive intercalation of illite lattice layers as alteration of mixed-layer illite-smectite clays. Mineral dissolution, however, is still the primary mechanism for illitization when the low activation energy is considered. With these findings, the utilization of İstanbul clays is questionable for clay barriers of landfills or sealing material of hazardous wastes.

Key words: Illite/smectite mixed-layer mineral, clay structure, landfill leachate, clay barrier, activation energy

1. Introduction

Clays are the crucial element of the barrier of a sanitary landfill or buffer of nuclear waste in deep geological repositories. Although the mineral liners are generally supplemented with nonpermeable polymeric membranes, they are still the essential part of leachate barriers. However, in most of the standards, the type of the required clay mineral is not defined. There are some approaches indicating that illites and kaolinites are better, since they maintain stability during leachate exposure. On the other hand, some approaches recommend using smectites to increase the adsorption and attenuation, which can also cause changes in the clay structure and subsequently increase the permeability. For instance, Rowe (1987) noted that leachate caused agglomeration in a clay barrier and increased its permeability approximately 1000 times. Campbell et al. (1983), King (1993), and Peters (1993) said that leachate may affect the clay liner at different levels. Quigley et al. (1987) stated that any mineralogical change affected the permeability. All this research does not refer to clay mineralogy. On the other hand, in their mineralogy-based works, Batchelder and Joseph (1996) and Batchelder et al. (1998a, 1998b) indicated that leachate caused

disintegration of the smectites and mixed-layer minerals through cation exchange. They also expressed that illites break off from mixed-layer minerals, which can be called illitization, and colloidal content was increased due to the high ion content. Similarly, Joseph et al. (2003) mentioned the mineral break up and structural disintegration due to leachate and added that the occurrence of capillary cracks and increase of permeation rates could be caused by preferring single-valence cations (especially $K^+ + NH_4^+$), which led a decrease in the interlayer distance of smectite minerals.

A large amount of work was carried out to understand the mineralogical and geochemical changes (e.g., K contents) related to increasing temperature (Eberl and Hower, 1976; Eberl et al., 1986; Pytte, 1982; Pytte and Reynolds, 1989; Bauer and Velde, 1993; Huang et al., 1993; Pusch and Madsen, 1995; Cuadros and Linares, 1996). However, apart from these works, Öztoprak and Pisirici (2011) briefly showed that leachate can also vary the mineralogy of smectite, including clays. They used three different Oligo-Miocene-aged İstanbul clays, which included either smectite-rich or smectite/illite (I/S) mixed-layer minerals. In their work, micro- and macrostructural

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changes of clays were observed early after 30 days (1 month) of leachate exposure time.

This paper is an extension of the work of Oztoprak and Pisirici (2011) and presents the results of the latter clay samples, which were exposed to leachate during 180 days (6 months) and 360 days (12 months). In this work, the effect of exposure duration of leachate was studied by comparing the variation of index properties, chemical content, mineral content, mineral types, and structure of clays. In addition to this, the kinetics of İstanbul clays were studied and the obtained results were adopted for leachate-smectite or I/S mixed-layer minerals interaction. The aim of this study was to determine whether the İstanbul clays would stay stable or lose their integrity during the leachate exposure.

2. Material and tests

2.1. Origin and characterization of used clays

Lithologic units from the Paleozoic into the Tertiary and Quaternary periods are located in the İstanbul region. Engineering practices and problems (e.g., construction, excavation, landslides, use for filling and coating) are particularly associated with the Upper Oligocene-lower Miocene formations. These are mainly the Danişmen Formation (Gürpınar member Tdg, Ağaçlı member Tda, Süloğlu member Tds), Çekmece Formation (Bakırköy member Tçb, Güngören member Tçg), and İstanbul Formation (Ti). Figure 1 depicts the extension of all these formations in the vicinity of İstanbul. These similarly aged formations include similar clays and sometimes it is too difficult to distinguish them by means of micro and engineering properties. Especially in the western part of İstanbul, the Gürpınar, Güngören, and Bakırköy clays are smectitic and mostly high-plasticity clays. Therefore, the clays used were picked from the Danişmen Formation (Gürpınar member) and the Çekmece Formation (Güngören member). According to Oktay et al. (1992), the age of this formation is Upper Oligocene – Lower Miocene in the vicinity of İstanbul. Oktay et al. (1992) indicated that upper levels of the Gürpınar member (Tdg) consist of claystone with limestone bearing *Congerina* fossils, marl, rarely conglomerate, siltstone, and sandstone alternations and were deposited in a deep-sea fan and delta plain environment in the vicinity of the Karaburun region (north of İstanbul) and the river-lake environment in the region of Gürpınar (west of İstanbul).

The Güngören member (Tçg) consists of generally green-colored clays and marls, dirty white-colored limestone interlayers with *Mactra*, and sand lenses. Arıç (1955) lithologically differentiated clays and marls within the formation and Sayar (1976) first named the formation. Clayey limestone-clay stratification becomes more frequent towards the Bakırköy Formation, which overlies

the Güngören member. Clay parts are greenish-blue in colored, smooth-irregular, and thinly layered. They often include sand lenses. According to the *Mactra* and helix, teeth, and spines of vertebrates, the age of formation was defined as upper Miocene (Sarmasien) by Arıç (1955), and it precipitated in a lake environment that included very fine-grained terrigenous material.

In this research, one clay sample from the Güngören member (clay G1) and two different clay samples from the Gürpınar member (clay G2 and clay G3) were used to determine the effects of the landfill leachate. The location of samples can be seen in Figure 1. These clays were selected on purpose, since they belonged to typical formations either used as barrier material at the Göktürk and Kemberburgaz landfill sites or as foundation soil at the Göktürk sanitary landfill site, as shown in Figure 1.

Several tests were carried out on the soil samples prior to and after exposure to leachate for determining particle size distribution, Atterberg limits, specific gravity, chemical composition, mineral content, cation exchange capacity, and existing cations. All three clay samples include mostly clays and are classified as CH type clays. Clay G1 contains 72% clay, 26.7% silt, and 1.3% sand, with liquid limit LL = 70% and plasticity index PI = 46%. Clay G2 contains 59% clay, 32.4% silt, and 7.6% sand, with LL = 60% and PI = 38%. Clay G3 contains 85% clay, 14.3% silt, and 0.2%, with LL = 99% and PI = 65%. According to the XRD analyses, the clay parts of the three samples are composed of I/S mixed-layer minerals, illite, kaolinite, and chlorite. Mixed-layer minerals were defined by finding the corresponding positions given in Table 1, borrowed from the extensive data of Meunier (2005).

The percentage of the minerals in the clay part was obtained by the areas of first peaks using the indices of Weaver (1960) and Kübler (1984) belonging to the XRD imprints of orientated and then ethylene-glycolated samples (Figure 2). According to this, the clay part of G1 was determined as 82% I/S mixed-layer mineral, 10% illite, and 8% kaolinite. The nonclay part of clay G1 contains quartz, calcite, and feldspar minerals. Clay G2 was determined to have 95% I/S mixed-layer mineral, 3.3% kaolinite, 1.7% illite, and chlorite in very small amounts. The nonclay part of clay G1 contains feldspar, quartz, and albite minerals. The clay part of G3 was determined as 80% I/S mixed-layer mineral, 12% illite, and 8% kaolinite. The nonclay part of clay G3 contains quartz, feldspar, and calcite minerals.

Chemical analysis of the soil samples was characterized by X-ray fluorescence (XRF). The results of the chemical analysis, which are compatible with the results of XRD analysis, will be discussed later. The cation exchange capacity (CEC) was calculated by designating Na⁺ cations using the method of Bache (1976). According to this

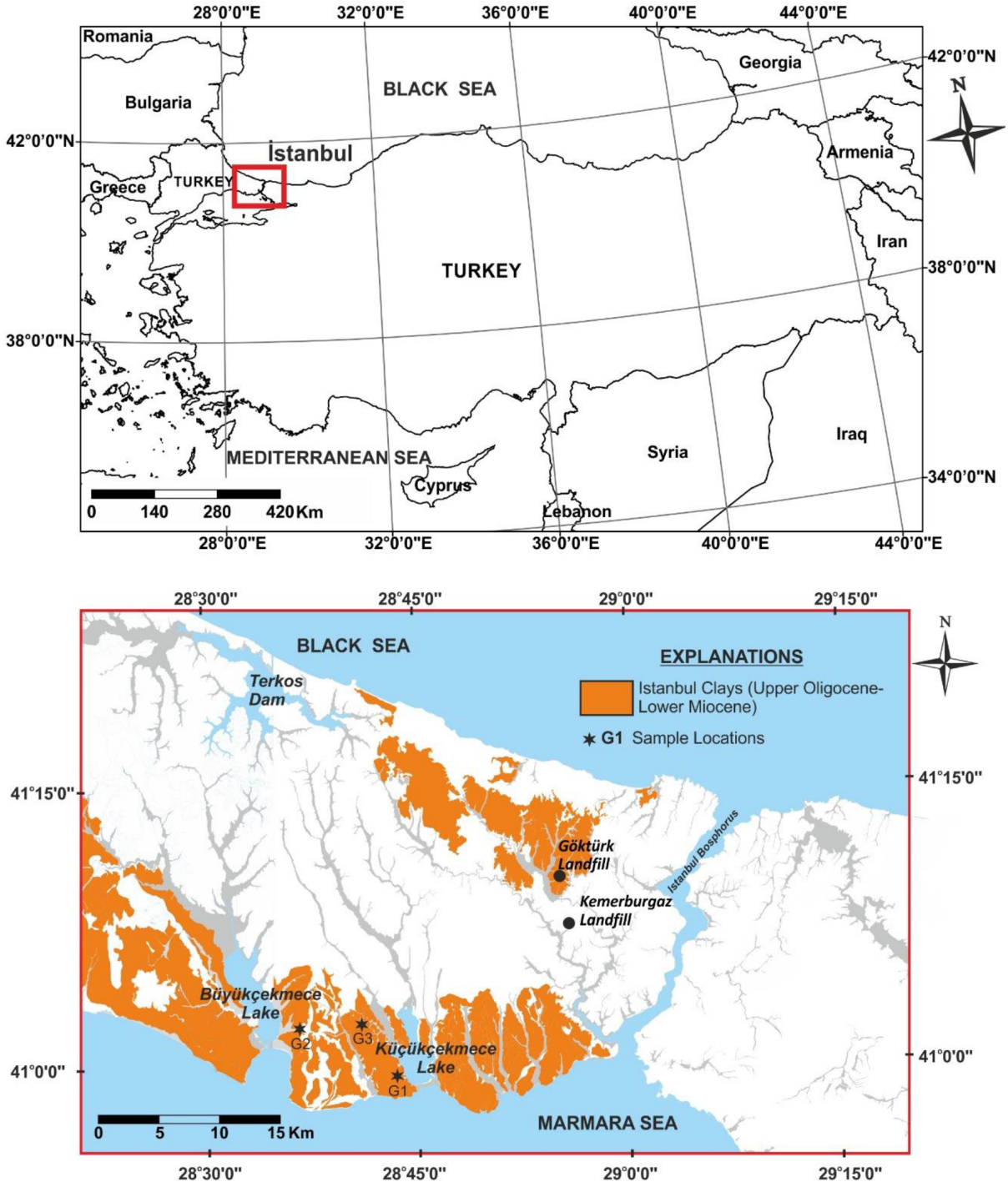


Figure 1. Oligo-Miocene clays in the vicinity of İstanbul.

method, CEC values of clays G1, G2, and G3 are obtained as 51, 54.4, and 69.8 mEq/100 g, respectively. These CEC values (50–70 mEq/100 g) correspond to illite-smectite mixed-layer clays. Exchangeable cations (ECs) of clays were obtained using the method of Chapman (1965). Na⁺, K⁺, Ca⁺², Mg⁺², Fe, and Al⁺³ cations were removed from

the clays and the amounts of the removed cations were found in units of mEq/100 g by using inductive coupling plasma/mass spectrometry (ICP/MS). The ammonium (NH₄⁺) content was calculated separately by combustion method, which is the direct measurement of total nitrogen (N) content. In this work, 20 mg of sample was oxidized in

Table 1. Position of peaks of essential mixed-layer clay minerals classified in decreasing interlayer spacing values of 001 planes (prepared from the extensive data of Meunier, 2005).

Position (Å)	Mineral
16–18.5	Smectite-rich R0 mixed-layer minerals (EG)
16.5–17.5	Smectite (EG)
14.5–16	C/S R1 (EG)
13.7–15	C/S R1 (Nat.)
14–15	Smectite or smectite-rich R0 mixed-layer mineral (Nat.)
14–14.35	Chlorite
12.9–13	Smectite with 1 water layer
12–12.45	Smectite with 1 water layer (Nat.)
10.2–14.35	I/S R1 (Nat.)
10–10.1	Illite
9.9–10.7	I/S R ³ 1 > 90% illite (Nat.)
9.9–10.3	I/S R ³ 1 > 90% illite (EG)
7.20–8.50	K/ S R0 (EG)
7.10–8.50	C/S R0 (EG)
7.5–8.2	C/S R1 (EG)
7.00–9.00	M/C (>30% chlorite)
7.20–7.36	Serpentine
7.13–7.20	Kaolinite
7.00–7.14	Chlorite
Nat., “Natural” sample	EG, Ethylene glycol-saturated sample
R0, Randomly ordered	R1, Ordered mixed-layer mineral
I/S, Illite/smectite mixed layer	C/S, Chlorite/smectite mixed layer
M/C, Mica/chlorite mixed layer	K/S, Kaolinite/smectite mixed layer

a furnace at 1000 °C and an infrared detector determined N content. Before leachate exposure, ECs of all clays were between 62 and 65 mEq/100 g, and this result reveals that smectite minerals of the I/S mixed-layer minerals are Ca-smectite.

2.2. Characteristics of landfill leachate

Landfill leachate was taken from the Kemberburgaz landfill site, which is out of operation. As seen from Table 2, leachate reflects the country characteristics with high alkalinity and ion contents. The pH values were above 7.0 at the beginning of the research. The pH value of leachate was 7.6 when it first arrived at the laboratory but increased to 8.3 and approximately 9.0 after 6 months and 1 year, respectively, at laboratory temperature of 23–24 °C.

2.3. Sample preparation and test procedures

To understand and compare the effect of the leachate on İstanbul clays, two different undisturbed samples

and one disturbed sample were utilized: 1) undisturbed Güngören clay: clay G1; 2) undisturbed Gürpınar clay: clay G2; 3) reconstituted Gürpınar clay: clay G3. To prepare the reconstituted samples of G3 clay, material was pulverized and later passed through a #200 sieve. Afterward, the material was compacted using water with standard Proctor compaction energy at the optimum water content. Compacted samples were left to cure for 30 days so that they could gain structure. They were not allowed to lose moisture during curing.

Clay samples were put into a 50-mm ring odometer apparatus. Clays were exposed to free swelling under pressure of 5 kPa inside the leachate for 30 days, 180 days, and 360 days in the odometer. XRD, XRF, and ESEM analyses were carried out by using the leachate-exposed samples in the odometer. On the other hand, witness samples, which were kept in similar conditions with main samples, were utilized to increase the sample amount in order to carry out the index tests.

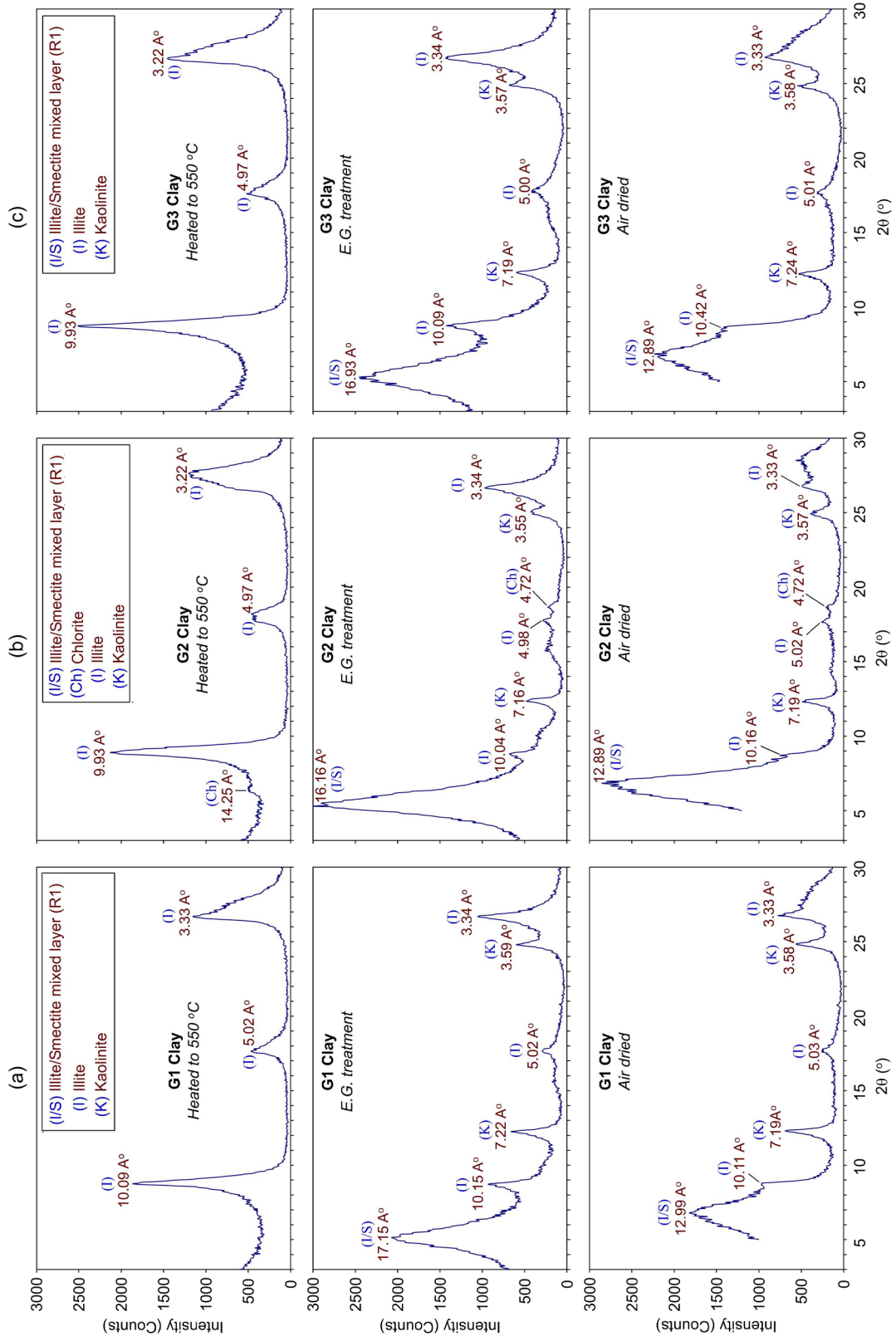


Figure 2. XRD patterns obtained from oriented clay parts of: a) clay G1, b) clay G2, c) clay G3.

Table 2. Chemical composition of landfill leachate used in this research.

Parameter	LC	tw
Chemical oxygen demand, COD	10,370	-
Dissolved COD	9800	-
Total dissolved solids, TDS	15,400	-
Volatile TDS	3413	-
Total hardness (as CaCO ₃)	2500	-
Alkalinity (as CaCO ₃)	22,300	-
pH	7.6	7.2
Sulfate, SO ₄	270	2.53
Chloride, Cl	2700	4.26
Kjeldahl nitrogen, N	2200	-
Nitrate, NO ₃	7.2	-
Ammonium, NH ₄	2500	-
Calcium, Ca	385	49
Magnesium, Mg	660	12
Sodium, Na	2152	24
Potassium, K	1450	3.3
Ferrous, Fe	13.5	0.01
Total phosphate, P	26	-
Manganese, Mn	542	-
Copper, Cu	62.5	-
Chromium, Cr	7.65	-
Nickel, Ni	3.6	-
Mercury, Hg	5.4	-
All values in mg/L except pH		

LC, Landfill leachate of Kemberburgaz (Göktürk) site
tw, Tap water

3. Results and discussion

3.1. Mineralogy and structure of clays

The effect of leachate on the microstructure and index properties of clays is clearly evolved with time when the numbers are examined in Table 3. The XRD patterns of three clays have also considerably changed after leachate exposure even after 1 month (Figure 3). In particular, the intensity of I/S peaks decreased while the intensity of illite peaks increased. In addition to this, the asymmetric shape of I/S mixed-layer peaks became noticeable after leachate exposure. The interlayer distances of I/S, C/S, and S decreased within the first month but increased during the following 11 months. As seen in interlayer distances of EG-treated samples in Table 3, the increase is from 16.99 Å to 17.46 Å for clay G1, from 16.16 Å to 16.99 Å for clay

G2, and from 16.93 Å to 17.60 Å for clay G3 during 1 year of leachate exposure. Interlayer spacing of air-dried I/S minerals decreased from 12.99 Å to 12.53 Å for clay G1 and from 12.89 Å to 12.62 Å for clay G2. No change was observed in clay G3. The achieved I/S peaks revealed that clays transformed into smectite-rich minerals (S) and discrete illite according to the positions of the peak data of Meunier (2005) in Table 1.

Leachate exposure increased the ECs but decreased the CEC and hence lowered the specific surface. When the amounts of ECs presented in Table 3 are examined, it is seen that clays exchanged NH₄⁺, Na⁺, and K⁺ instead of Ca⁺² and Mg⁺². The highest increase in the amounts was observed in NH₄⁺ and Na⁺ ions; K⁺ ions followed them. However, a decrease was observed in the Mg⁺² ion amount whereas no significant change was observed in the amount of Ca⁺² ions for the clays exposed to the leachate. The decrease in the distance between the I/S layers in G1 and G2 can be attributed to the increase in the NH₄⁺ and Na⁺ ions, while no change in G3 can be identified with the increase in the Ca⁺² ions. Nonetheless, it would not be erroneous to think that the exchange of cations had a role in the change of the interlayer distance and structure.

The amounts of I/S or smectite decreased while the amount of illite increased. Considerable change was observed in a month of leachate exposure. As seen from Table 3, during 12 months of leachate exposure, the amount of the I/S mixed layer in clay G1 decreased from 82% to 64.2%, while the amount of illite increased from 10% to 25.4% and the amount of kaolinite increased from 8% to 10.4%. The amount of the I/S mixed layer in clay G2 decreased from 94.5% to 83.7%, while the amount of illite increased from 1.7% to 5.8% and the amount of chlorite increased from 3.8% to 10.5%. The amount of the I/S mixed layer in clay G3 decreased from 80.0% to 59.8%, while the amount of illite increased from 12% to 29% and the amount of kaolinite increased from 8.0% to 11.2%.

The chemical composition of the clay samples can also be seen in Table 3. The amount of SiO₂ and Al₂O₃ noticeably decreased in all three samples with the effect of the leachate, while the amount of CaO increased in the samples. This can be interpreted as evidence that some amount of tetrahedral and octahedral structure was partly destroyed and carbonate structures increased with the effect of the leachate.

The ESEM images in Figures 4–6 demonstrate the initial condition and structure before leachate exposure and how the texture is affected after the leachate exposure just for 1 month. The effect of the leachate is clearly observed in snapshots and ESEM images of all clays. Collapses, disintegrations, and cracks were observed in all clay samples. In addition to this, a considerable increase occurred in colloidal content after applying a hydrometer test on the exposed samples (Figure 7a). According to the

Table 3. Characteristics of clays before and after exposure to leachate.

Leachate exposure	No exposure (natural)			1 month of exposure			6 months of exposure			12 months of exposure		
	G1	G2	G3	G1	G2	G3	G1	G2	G3	G1	G2	G3
Clay name												
Particle size analysis (%)												
Sand	1.3	7.6	0.2	1.4	7.5	0.3	1.43	7.4	0.3	1.5	7.3	0.4
Silt	26.7	32.4	14.3	21.0	27.2	11.8	20.2	26.3	10.9	19.7	25.3	10.1
Clay (<0.002 mm)	72.0	59.0	85.0	77.6	65.3	87.9	78.4	67	88.9	78.8	67.4	89.5
Mineral content of clay part (%)												
I/S, C/S, or S-rich mixed layer	82	94.5	80	66.5	85.9	62.8	64.6	84	60.7	64.2	83.7	59.8
Illite	10	1.7	12	24.3	5.7	27.7	25.1	5.7	28.2	25.4	5.8	29
Chlorite	-	3.8	-	-	8.4	-	-	10.4	-	-	10.5	-
Kaolinite	8	-	8	9.2	-	9.5	10.2	-	11.1	10.4	-	11.2
Interlayer spacing of I/S or S after air drying (Å)	12.99	12.89	12.89	12.53	12.62	12.88	12.61	12.70	12.61	12.98	12.52	12.52
Interlayer spacing of I/S or S after EG treatment (Å)	16.99	16.16	16.93	16.36	15.77	16.67	17.13	16.87	17.06	17.46	16.99	17.60
Consistency limits												
Liquid limit, LL (%)	72	60	99	78	66	109	-	-	-	86	73	118
Plastic limit, PL (%)	26	22	34	31	27	40	-	-	-	42	36	49
Plasticity index, PI (%)	46	38	65	47	39	69	-	-	-	44	37	69
Specific gravity, Gs	2.75	2.72	2.78	2.67	2.67	2.74	-	-	-	2.66	2.66	2.72
Specific surface, SSA, cm ² /g	368	393	504	298	287	292	-	-	-	197	128	158
CEC (Na) (mEq/100 g)	51.0	54.4	69.8	41.2	39.7	40.4	32.7	38.7	30.8	27.2	17.7	21.8
Exchangeable cations (mEq/100 g)												
Calcium, Ca	55.81	52.69	51.97	55.9	50.2	55.17	38.03	37.98	37.69	40.92	37.39	36.53
Sodium, Na	0.89	0.046	1.88	6.37	5.13	7.2	18.83	9.34	16.01	38.00	41.72	48.43
Potassium, K	3.72	3.96	5.42	7.74	6.25	8.79	21.73	18.93	25.04	20.23	20.85	21.47
Ammonium, NH ₄	0.21	0.16	0.25	7.53	6.08	7.92	22.54	20.99	23.86	40.88	42.19	50.14
Magnesium, Mg	1.48	7.73	3.25	1.1	5.5	2.08	2.24	2.49	2.56	3.00	3.20	3.19
Aluminum, Al	0.047	0.033	0.067	0.06	0.05	0.07	0.05	0.04	0.06	0.034	0.022	0.058
Ferrous, Fe	0.059	0.05	0.048	0.28	0.28	0.26	0.13	0.24	0.076	0.023	0.014	0.043
Total	62.2	64.6	62.9	79.0	73.5	81.5	103.5	90.0	105.3	143.1	145.4	159.8
Chemical composition (%)												
SiO ₂	44.46	48.18	54.25	38.17	47.1	52.3	36.41	45.07	51.60	37.33	47.48	54.61
Al ₂ O ₃	14.32	14.7	16.78	11.77	13.98	15.41	10.93	13.65	15.50	10.84	13.62	15.70
CaO	12.59	7.87	2.86	15.97	8.33	3.56	17.10	8.69	2.46	18.21	8.52	3.80
Fe ₂ O ₃	4.9	7.59	6.38	4.65	6.89	6.6	5.46	7.00	6.52	4.99	7.37	6.89
K ₂ O	2.15	1.76	2.45	2.11	2.1	2.75	2.15	2.23	2.80	2.36	2.54	3.26
MgO	1.68	3.44	2.21	1.6	3.24	2.34	1.36	2.62	1.97	1.95	3.47	2.59
Na ₂ O	0.53	0.86	0.57	0.74	0.89	0.89	0.98	0.87	0.90	0.91	0.83	1.11
TiO ₂	0.57	0.78	0.71	0.47	0.79	0.71	0.45	0.74	0.71	0.46	0.77	0.72
MnO	0.07	0.14	0.032	0.045	0.14	0.063	0.04	0.12	0.06	0.04	0.13	0.05
Total	81.27	85.32	86.24	75.53	83.46	84.62	74.88	80.99	82.52	77.09	84.72	88.73

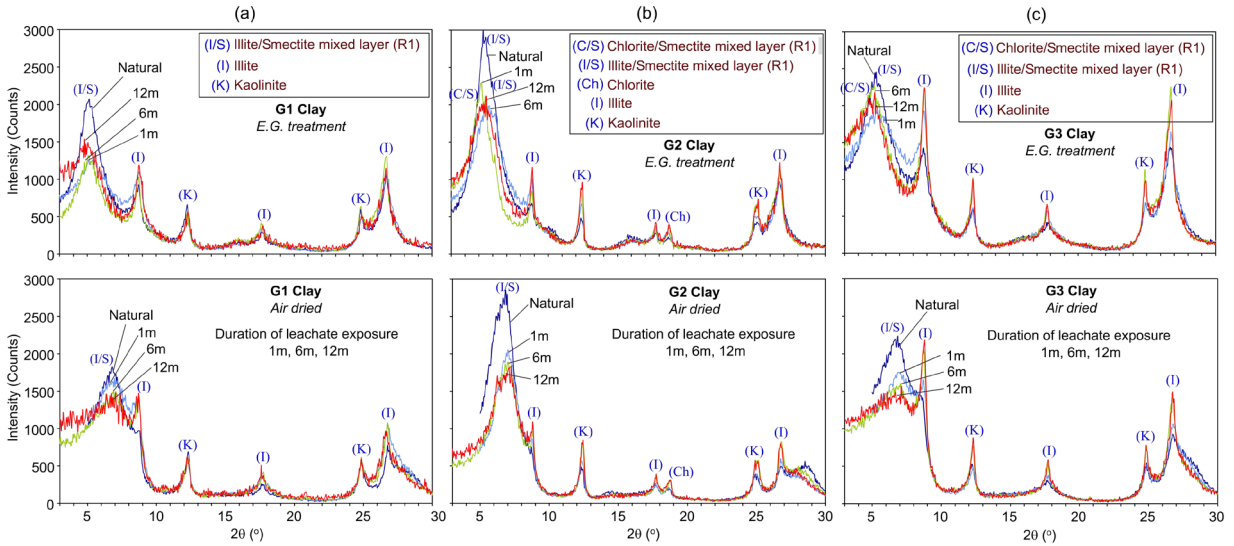


Figure 3. Comparison of XRD patterns obtained from oriented pastes of natural conditions and exposed: a) clay G1, b) clay G2, c) clay G3 (all clays were exposed to leachate for 1 month in odometer device under 5 kPa loading; m = months).

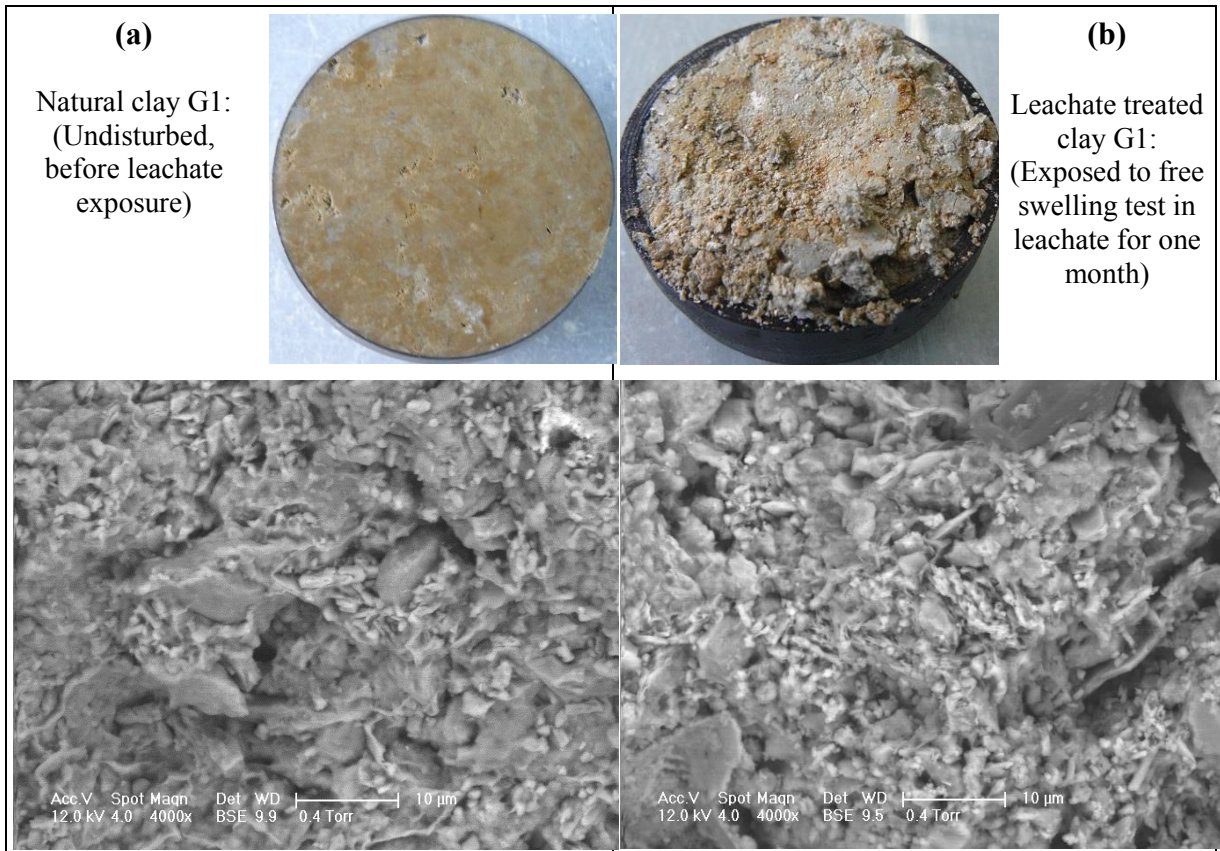


Figure 4. Snapshot and ESEM image of clay G1: a) before leachate, b) following the leachate exposure for 1 month (magnification is 4000x).



Figure 5. Snapshot and ESEM image of clay G2: a) before leachate, b) following the leachate exposure for 1 month (magnification is 4000 \times).

ESEM images, smectites were broken down with the effect of the leachate and transformed into a faulted structure.

3.2. Index properties

Interesting results were achieved from granulometry and Atterberg limit tests. As seen in Figure 7a, silt and clay content increased for all samples. The increase is dominant at approximately 0.005–0.002 mm particle size. Therefore, this change can be attributed to the increase in colloidal content. Despite the increase in the liquid limits of clays, plasticity indices are generally stable. A slight increase in G3 clay can be mentioned. The positions of G1 and G2 clays on the plasticity card reflect that they include I/S mixed layers. Without leachate exposure, they are located between the smectite and illite regions, and after leachate exposure they gradually move to the illite region with time and finally they turn into silt after 12 months. Similarly, the G3 clay, which always includes smectite-rich minerals before and after leachate exposure, expresses silt behavior. Before leachate the clays were classified as CH clays, but after exposure to leachate during 1 year they became high-plasticity silts, MH.

On the plasticity card, moving of clays into the illite region above the A line and towards the A line (clay/silt

border) is consistent with the XRD results indicating illitization. The increase in liquid limits complies with the increase in the colloidal content and smaller clay grains as seen in the ESEM images and the increase in their CECs.

The mineralogical and ESEM image analyses give important insights into the effects of leachate on clay microstructure. There are two important mechanisms that should be emphasized. The first one is that the smectites are transformed into illites, and I/S minerals are disintegrated into very small clay crystals as seen from the microscope images. The results of the hydrometer tests also show that colloidal content of the soils increased. This increase in the colloidal content naturally increases the content of ECs. It can be followed in Table 3 that both the amounts of illite and ECs are increased.

3.3. Mineral transformation and kinetics of clays

It was clearly seen that not only were the positions of I/S, C/S, or S peaks affected, but also the widths of the peak profiles were increased, and they became asymmetric due to leachate exposure. In addition to this, disintegrations were apparent in the smectite structures. Similar supporting mineralogical findings also exist in the works of Batchelder et al. (1998) and Joseph et al. (2003). Oztoprak

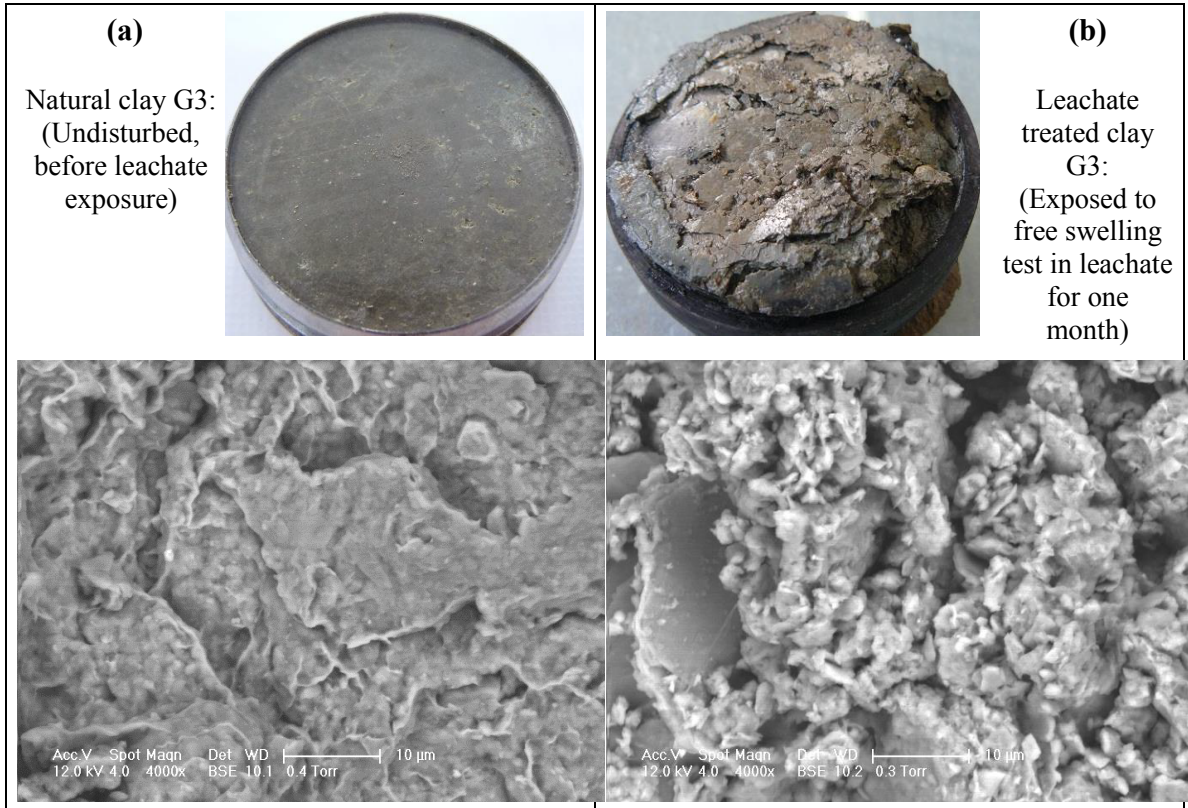


Figure 6. Snapshot and ESEM image of clay G3: a) before leachate, b) following the leachate exposure for 1 month (magnification is 4000 \times).

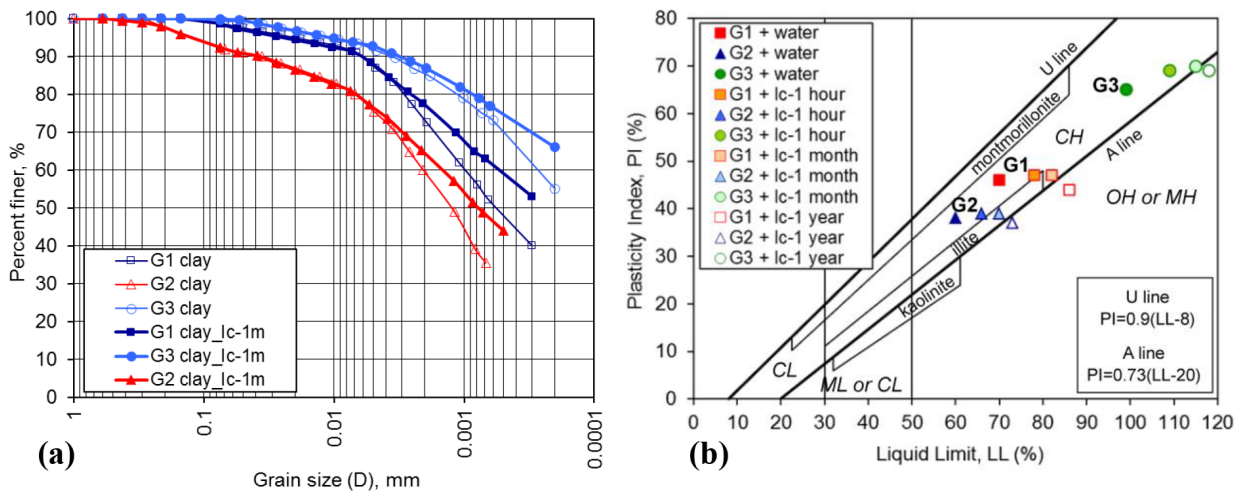


Figure 7. Effect of leachate: a) on the particle size distribution of the clays, b) on the locations of the clays on the plasticity card, before and after exposure to leachate (plasticity card was produced from Mitchell and Soga, 2005).

and Pisirici (2011) also expressed these findings in their work and they used the same mixed-layer minerals as in this paper. However, this paper includes the time effect by treating the clay samples for 6 and 12 months more. In this way, mineral transformation is understood better and

transformation rates of illite and I/S minerals motivated the investigation of the kinetics of clays.

All clays, which were exposed to leachate for 12 months, were transformed into smectite-rich minerals. Increasing interlayer spacing in the XRD imprints of EG-

treated samples can be attributed to the breaking of the illites from I/S mixed layers. The increasing amount of illites, chlorites, and kaolinites is a clear indication of this mechanism (Figure 3; Table 3). However, illitization (or chlorite increase) can be attributed to three mechanisms, which are also depicted in Figure 8:

- 1) Neoformation of illites/chlorites by coordination of Si, Al, K, and hydroxyls
- 2) Breaking apart of illite/chlorite minerals from I/S and C/S mixed layers
- 3) Coalescence of illite/chlorite particles and collapsed layers

By means of interlayer spacing, it can readily be interpreted that illites were broken apart from mixed layers. In this context, if mineral transformation had occurred and some smectites were yielded to illites, interlayer spacing of I/S minerals would have decreased. However, the illites were probably broken apart due to cation demixing or exchange, as depicted in Figure 8. In addition to this, the decrease in interlayer spacing can also be explained by

the replacement of an exchange cation (Laird, 2006). The probability of exchanging NH_4^+ , Na^+ , and K^+ instead of Ca^{+2} and Mg^{+2} seems quite high when the amounts of ECs presented in Table 3 are taken into account. This result is compatible with the sequence of ion exchange selectivity by smectites described by Stumm (1992) and McBride (1994) as follows: $\text{Al}^{3+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{NH}_4^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$. The highest increase in amounts was observed in NH_4^+ and Na^+ ions. K^+ ions followed them. However, a decrease was observed in the amount of Ca^{+2} ions for the clays exposed to the leachate. The cation exchange and demixing mechanisms are swelling mechanisms, which were comprehensively defined by Laird (2006) and were caused by NH_4^+ , Na^+ , and K^+ cations. Gaucher et al. (2006) and Gautier et al. (2010) indicated that NH_4^+ is the most favorable monovalent cation for smectites and has an important effect on the loss of integrity and the increase of permeability of clay barriers. However, in this work, Na^+ and K^+ cations also had a considerable role for exchange and corresponding I/S mixed-layer mineral dissolution.

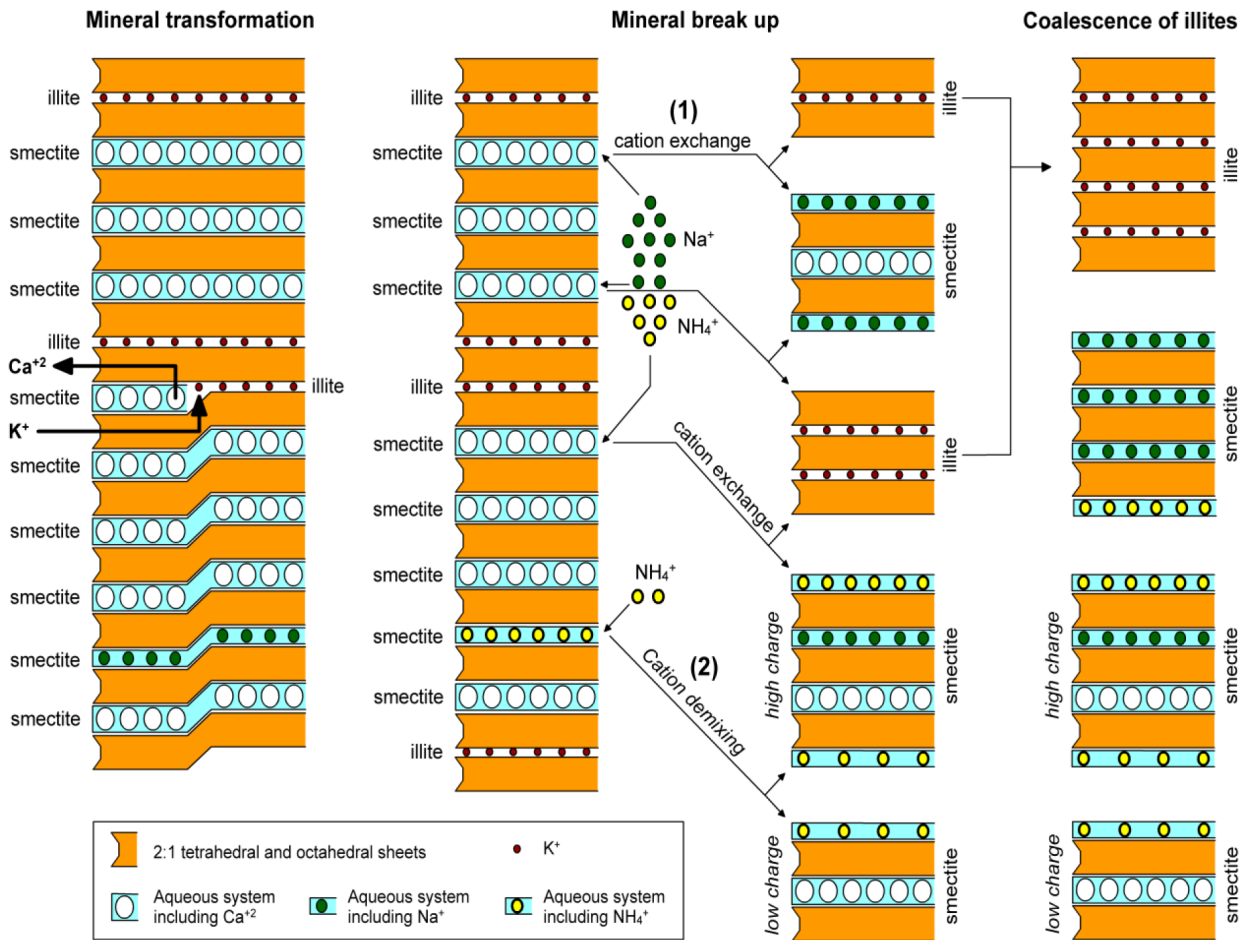
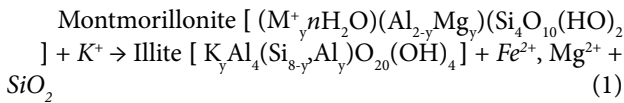


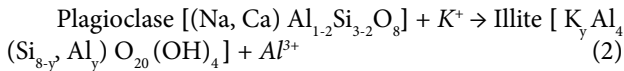
Figure 8. Schematic diagram for mechanisms depicting possible transformation and/or breaking apart of I/S mixed-layer minerals exposed to leachate and coalescence of illites (modified from Oztoprak and Pisirici, 2011).

The change in the texture and the increase in the voids are clear in the ESEM images of the clays. This can be attributed to only the breakage of the tips of clay crystals. Although big cracks were formed in the sample during free swelling in leachate, spillage and disintegration were observed to be very limited during eye examination of samples. Faulted structure and colloidal content, however, cause the increase of charge in the clay and therefore an increase in swelling. Furthermore, Laird (2006) mentioned that collapses occur in the crystal structure of smectites during cation exchange, which causes a swelling by increasing the electrical load. This view is supported also in this study by electron microscope images given in the previous section.

In means of changes in the chemical structures, successive intercalation of illites in smectite stacks were occurred. Although this transformation led to limited formation of new illites, it seems possible. As shown by Meunier (2005), transformation of smectite minerals to illite (hydrous mica) and chlorite will release silica and aluminum. The reaction of smectite to illite transformation produces quartz and ferromagnesian phyllosilicate:



The decreases of SiO₂ in the chemical compositions of the clay samples are clear in Table 3. On the other hand, another possible transformation reaction in the clays due to leachate may be illite formation from albite:



This would be accomplished by aluminum Al³⁺ release, which may define the decrease of Al₂O₃ in all three samples in Table 3. All these chemical analysis results can be interpreted such that some amount of tetrahedral and octahedral structures was partly destroyed, and this finding may show that smectite to illite transformation took place with the effect of the leachate.

It is well known that smectite transforms into illite at high pressure, high alkalinity, and/or at high temperatures. On the other hand, Eberl et al. (1986) and Bauer and Velde (1999) showed that even at low temperatures (20–150 °C), high-alkalinity solutions (K⁺-saturated solutions) with high pH values transformed smectite into illite. In accordance with this finding, the leachate examined in this study is found to have a high amount of K⁺ ions (i.e. high alkalinity) and a high pH value. Thus, it is possible to state that chemical reaction of the clays with leachate is the main reason for the significant increase of illite obtained in the XRD analyses of the 3 clays that were

exposed to leachate at 23–25 °C. Nonetheless, it would not be erroneous to consider two factors together: the transformation of smectite into illite and the breakup of illites from I/S mixed-layer minerals.

The progressive increase of the illite (or chlorite) and the decrease of the smectite content in illite/smectite and chlorite/smectite mixed layers in diagenetic or hydrothermal formations are classically thought to be due to a single mineral reaction of the smectite to illite type. The transformation requires activation energy that can be referred to as the distribution of energy inside the crystal lattice and its inner and outer surfaces. In this context, the required activation energy for this type of mineral transformation was obtained in most of the work (Meunier, 2005). Activation energy is an important indicator to reflect the illitization of natural smectites of clay barriers. In the literature, many attenuation models for smectites exist. The general kinetic equation may be written as follows (Pytte, 1982; Pytte and Reynolds, 1989; Huang et al., 1993; Meunier, 2005):

$$-\frac{dS}{dt} = k[K^+]^m S^n \quad (3)$$

Here, *k* is a rate constant, [K⁺] is moles of potassium cations, and *m* and *n* are constants.

The order of the attenuation relation would change; however, Meunier (2005) indicated that a second-order relation (*n* = 2) does successfully define the smectite decrease. Huang et al. (1993) showed the success of this agreement by using *n* = 2 for their mixed-layer smectites. In addition to this, the authors also showed that using 1 for *m* was appropriate. However, both Pytte and Reynolds (1989) and Cuadros and Linares (1996) preferred using *n* = 5 and *m* = 1 for their model.

To calculate the required activation energy (*E_a*) to change the mineral content and type by leachate, the Arrhenius equation, which establishes the relation with temperature (*T*) and rate constant (*k*), was utilized.

$$k = Ae^{-E_a/RT} \quad (4)$$

In this equation, *R* is the perfect gas constant (8.314 J mol⁻¹ K⁻¹ or 1.987 cal mol⁻¹ K⁻¹). This equation can be defined as

$$\ln k = \ln A - \frac{E_a}{R} \frac{1}{T} \quad (5)$$

When Eqs. (3) and (5) are merged and proper adjustments are made, Eq. (6) will be exploited. Further arrangements would cause the calculation of *E_a* through Eq. (7).

$$\frac{dS}{dt} = -Ae^{-\frac{E_a}{RT}} [K^+]^m S^n \quad (6)$$

$$E_a = -RT \ln \left(\frac{S_0^{n-1} - S^{n-1}}{S_0^{n-1} S^{n-1} [K^+]^m A (t_0 - t)} \right) \quad (7)$$

In this equation, S_0 is initial smectite percent in I/S mixed layers for time t_0 ; S is smectite fraction after leachate exposure for time t .

Although leachate exposure to smectites does not correspond to thermodynamic rules, if the rate constant (k) of leachate-treated clay and heated clay in KCl solution can be coupled, then the obtained activation energy from thermodynamic rules may correspond to the activation energy required for mineral dissolution/transformation of clay exposed to leachate. In this context, to estimate the activation energy for mineral breakup and/or mineral transformation, the methodology of Huang et al. (1996) was adopted. According to this, the $k - T$ relation in Eq. (3) was used and clay samples that were not reacted in contact with the leachate previously were placed in an oven in KCl solution with molarity $[K^+] = 0.037$ for 2 and 7 days at $T = 100, 200,$ and 300 °C. This molarity corresponds to the $[K^+]$ of the used leachate. Temperatures over 300 °C and waiting period longer than 7 days were not selected, since the rate of I/S decrease became close to the leachate case. After taking the samples from the oven, they were EG-treated and XRD prints and mineral amounts were obtained, as seen in Table 4. An example is given in Figure 9 regarding how the $\ln k - 1/T$ relation was constructed, and Arrhenius parameters were calculated. In means of thermodynamic relations designated A and E_a values are given in Table 5 and E_a values are between 3.6 and 4.8 kcal for the three clays. The same relation was used for calculating the activation energy of mineral changes due to leachate exposure. In this context, calculated A values and I/S or S amounts from leachate exposure tests at $T = 24$ °C were considered and E_a values for each exposure duration were obtained (Table 5). It should be noted that if the K^+ concentrations are similar, the effects of 1 year of leachate exposure on smectite decrease correspond to temperature exposure at $T = 100-300$ °C for 2 to 7 days.

A very low activation energy within the first 30 days could be attributed to the breaking up of illites from the

I/S mixed layers. However, afterwards, the required energy progressively increased and reached 4.0–5.5 kcal. This increasing energy could be interpreted as the new formation of illites in smectite stacks. A similar activation energy (5 kcal) was only calculated by Howard and Roy (1985) in the literature. However, other values for the required activation energy of natural smectites and clay barriers are approximately 20–30 kcal (Pytte and Reynolds, 1989; Huang et al., 1993; Pusch and Madsen, 1995). Therefore, it is difficult to evaluate the transformation of smectites to illites. Maybe preliminary mineral transformation is valid for this duration. With these findings, using I/S and C/S mixed-layered İstanbul clays as a clay barrier cannot be advised. They are subject to changes in the mineral content and structure, which may lead to permeability increases and attenuation capacity decreases.

4. Conclusions

Three different Oligo-Miocene aged İstanbul clays, which included smectite-illite mixed-layer minerals, were subjected to landfill leachate under low pressure for 30 days, 180 days, and 360 days. The mineralogy and chemical structures were observed to be significantly affected. Ion exchange reactions caused dissolution in the crystal structure of smectite-illite mixed-layer minerals. Snapshots and ESEM images of samples also demonstrated the changes in the texture and structure, which were the result of mineral transformations, mineral content changes, and chemical reactions.

The high ionic domain and alkalinity of landfill leachate, especially $NH_4^+, Na^+,$ and K^+ cations, caused faulted structures and mineral disintegrations, which also caused an increase in colloidal content. The thickness of the double diffused layer was increased, clays moved to the illite region on the plasticity card, and, at the end of 1 year, they all started to behave as silts.

Very low activation energy within the first 30 days could be attributed to the breaking up of illites from I/S mixed layers and coalescence of illite particles. These results may be the consequence of the weak connection between smectites and illites. However, afterwards, the required

Table 4. Kinetic model parameters and kinetic energy of treated clays.

	Percent of I/S or S in clay						
	T = 24 °C	T = 100 °C		T = 200 °C		T = 300 °C	
Clay	Air-dried	2 days	7 days	2 days	7 days	2 days	7 days
G1	80	77	73	71	61	64	47
G2	94.5	91	87	86	76	76	53
G3	82	79	73	71	58	64	49

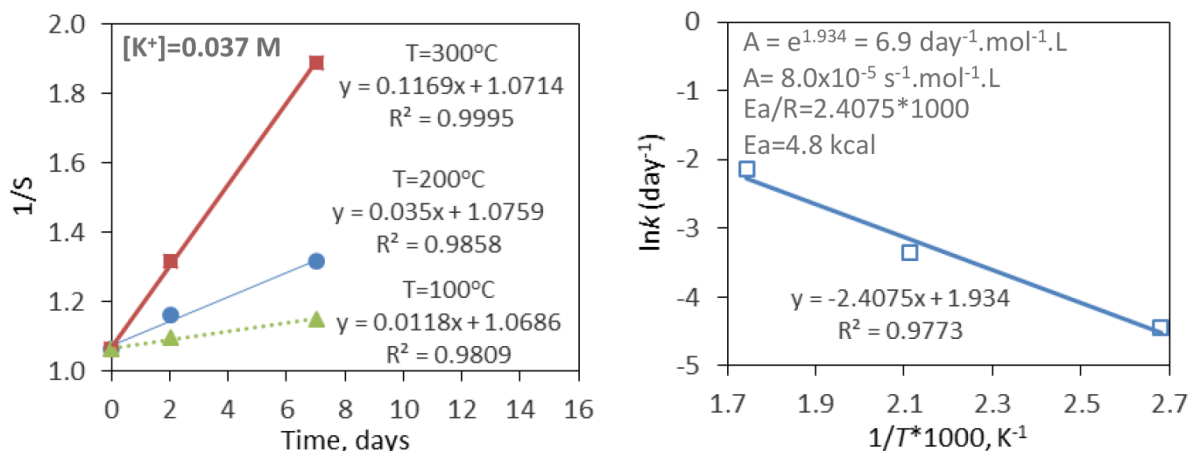


Figure 9. a) Experimental data to fit second-order kinetic model for G2 clay (untreated with leachate); b) experimental results for finding the Arrhenius parameters, E_a and A , of G2 clay for $[K^+] = 0.037 \text{ M}$ and $T = 100, 200, 300^\circ\text{C}$ ($R = 1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$).

Table 5. Kinetic model parameters (for $[K^+] = 0.037 \text{ M}$) and activation energy of clays according to their exposure duration with leachate.

Clay	Arrhenius parameters		E_a (kcal) for leachate exposure		
	A ($\text{s}^{-1} \text{ mol}^{-1} \text{ L}$)	E_a (kcal)	0–1 m	6–12 m	6–12 m
G1	5.3×10^{-5}	4.1	1.7	3.8	4.8
G2	8.0×10^{-5}	4.8	2.5	4.3	5.5
G3	3.2×10^{-5}	3.6	1.3	3.3	3.9

energy progressively increased and reached 4.0–5.5 kcal. Although it seems to be limited, the increasing trend of activation energy may be attributed to the formation of new illites in smectite stacks.

Mineral transformations/dissolutions, particle realignment of smectites, and coalescence of illite and/or chlorite particles led to structural changes in İstanbul clays. The loss of integrity in all clay samples was apparent and affected the increase of permeability, which would also cause the decrease of attenuation capacity. As a

consequence of these findings, the utilization of mixed-layer İstanbul clays is questionable for clay barriers of landfills or sealing material of hazardous wastes.

Acknowledgments

This work was supported by the Scientific Research Projects Coordination Unit of İstanbul University, Project No: UDP-16491. The authors would also like to extend their special thanks to Dr Gülsüm Yılmaz and Oğuz Firidin for their support during the tests and analyses.

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