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Graduate School of Natural and Applied Sciences
Department of Geological Engineering
Master Thesis

UŞAK VE UKRAYNA KİLLERİNİN SERAMİK HAMMADDESİ OLARAK DEĞERLENDİRİLMESİ VE KARŞILAŞTIRILMASI

EVALUATION AND COMPARISON OF UŞAK AND UKRAINIAN CLAYS AS CERAMIC RAW MATERIALS

Ocak 2018

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REPUBLIC OF TURKEY

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Tural AGHAYEV

11/01/2018

ABSTRACT

EVALUATION AND COMPARISON OF UŞAK AND UKRAINIAN CLAYS AS CERAMIC RAW MATERIALS

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For thousands of years, clay has been an indispensable natural material for ceramics. Its industry in the last century rapidly grows in all over the world which reveals the need to seek new ceramic raw materials. As such, the well-known kaolinite deposits in Uşak had been widely explored and used, so the investigation of the new resources from the same area is needed. The present study aims to characterize one of these new raw materials, called Uşak clay (Usc) mineralogically, physico-chemically and technologically by comparing with a well-known reference ceramic raw material, Ukrainian clay (Ukc). For this study, various analyses were carried out, they were X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Flourescence (XRF), Differential Thermal and Thermogravimetric Analysis (DTA -TG), atterberg limits, particle size distribution and specific technological tests like bending and compressive strength, total linear shrinkage, color, water absorption and unit volume mass at temperatures between 800°C -1430°C.

Usc is illitic material including dominantly quartz in association with few dolomite and kaolinite while Ukc is composed of mostly kaolinite with relatively low amount of quartz, illite and dolomite. Usc contains total alkali oxides (K_2O and Na_2O) more than these of Ukc. Al_2O_3 was measured in higher amount in Ukc while SiO_2 was determined in higher amount in Usc. The amount of Fe_2O_3 was determined more in Usc than that of Ukc. CaO was found more in Ukc however MgO was found relatively in higher amount in Usc. The abundance of TiO_2 was found to be less than 0.5% for each sample.

The bending strength of Usc was 1 MPa at 800 °C; by increasing temperature it reached its maximum value of 19.4 MPa at 1300 °C. However, Usc melted totally at 1430 °C where the highest bending strength value of Ukc (3.4 MPa) was observed. Although, total linear shrinkage of both clay samples showed an equal value of 3.73 % at 1000 °C, Usc shrinkaged more (11.89% at 1300 °C) at higher temperatures. On the contrary, Ukc shrinkaged less and reached 6.56% at the same temperature. The value of water absorption was followed with high percentages of 17.7% for Usc and 25.73% for Ukc at 1100 °C. Usc and Ukc had very close unit volume mass values of 1.65 g/cm^3 and 1.5 g/cm^3, respectively. As another important ceramic characteristic, maximum whiteness was observed at 1000 °C for Usc (83.59%) and at 1100 °C for Ukc (94.21%).

Because of low plasticity and high amount of SiO_2, Usc can be used as a filler to reduce plasticity as well as viscosity in the slip casting applied ceramics. On the other hand, Usc contains higher K_2O, Fe_2O_3, and MgO than Ukc as flux agents and also it was melted at less firing temperature. Due to these characteristics, Usc can be more favorable than Ukc to be used together with the high temperature resistant materials in order to reduce temperature rate and to possibly obtain more improved mechanical strength at less firing temperature. This property of Usc creates an energy saving feature, which makes it substantial for the economy of ceramic industry. Comparison between the two materials presently studied and the selected commercial raw materials for ceramics reveal that Ukc and Usc are both suitable for white ceramics. Furthermore, Usc is not suggested as raw material of refractory.

Keywords: Ceramic, Technological Properties, Industrial Application, Physico-chemical Properties, Firing Characteristics

ÖZET

UŞAK VE UKRAYNA KİLLERİNİN SERAMİK HAMMADDESİ OLARAK DEĞERLENDİRİLMESİ VE KARŞILAŞTIRILMASI

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Killer, binlerce yıldan bu yana, seramik için vazgeçilmez doğal hammadelerden biri olmuştur. Son yüzyılda, dünya genelinde seramik endüstrisindeki hızlı gelişmeler, yeni hammadde ihtiyacının varlığını ortaya çıkarmıştır. Buna örnek olarak, Uşak'ta bulunan ve bilinen kaolin yatakları uzun zamandır kullanılmaktadır, bu nedenle, aynı bölgede yeni hammadde arayışına ihtiyaç duyulmuştur. Bu çalışma, sözü edilen yeni hammaddelerden biri olan Uşak kilini (Usc) mineralojik, fiziko-kimyasal ve teknolojik açıdan değerlendirmeyi, aynı zamanda dünyaca seramik malzemesi olarak referans kabul edilen Ukrayna kili (Ukc) ile karşılaştırmayı amaçlamıştır. Bu çalışma için, çeşitli analitik yöntemler uygulanmıştır; bunlar x-ışını difraktometresi (XRD), taramalı elektron mikroskopisi (TEM), Fourier Dönüşüm İnfrared Spektroskopi (FTIR), x-ışını floresansı (XRF), diferensiyal termal ve termogravimetri analizi (DTA-TG), atterberg limitleri, tane boyu dağılımı ve 800°C -1430°C sıcaklıkları arasında uygulanan özel teknolojik testleri-eğilme ve basınç dayanımı, toplam doğrusal küçülme, renk, su emme ve birim hacim kütlesi-olarak verilebilir.

İllitik bir malzeme olan Usc, illit dışında baskın olarak kuvarz ve eşlik eden dolomit ve kaolinit içerirken; Ukc ise baskın olarak kaolinit ve göreceli olarak daha az miktarda kuvars, illit ve dolomit minerallerinden oluşmaktadır. Alkali oksitlerin (Na_2O ve K_2O) toplam miktarı Usc örneğinde daha çok belirlenmiştir. Al_2O_3 miktarı Ukc örneğinde daha çok olduğu bulunurken, SiO_2 miktarı ise Usc örneğinde daha yüksek sayıda bulunmuştur. Ukc örneği ile karşılaştırıldığında, Usc Fe_2O_3 miktarını daha çok içermektedir. Ayrıca, CaO, Ukc örneğinde nispeten daha yüksek bulunurken, MgO ise Usc örneğinde nisbeten yüksek miktarda bulunmuştur. TiO_2 bolluğu, her iki örnek için, %0.5'den az değerlerde bulunmuştur.

Uşak kilinin eğilme dayanımı 800 °C ısıda 1MPa ölçülmüştür ama bu değer artan ısı ile yükselerek, 1300 °C'da 19.4 MPa'a ulaşmıştır. Ancak, 1430 °C'da Uşak kili tamamen erimiştir. Ukrayna kilinin bu sıcaklık değerinde maksimum eğilme dayanımına (3.4 MPa) ulaştığı gözlenmiştir. Toplam doğrusal küçülmenin 1000°C sıcaklıkta her iki örnekte %3.73 oranında eşit değer göstermesine rağmen, daha yüksek sıcaklıkta bu değer Usc için artmıştır (1300 °C sıcaktlıkta %11.89). Bunun aksine, Ukc aynı sıcaklıkta daha az küçülme göstererek, %6.56 oranında küçülmüştür. Uşak kilinin su emme kapasitesi 1100 °C sıcaklıkta %17.7 olarak hesaplanırken, Ukrayna kilinde bu değer aynı ısıda %25.73 olarak belirlenmiştir. Her iki örneğin birim hacim kütleleri birbirine yaklaşık değerler göstermiştir (Usc 1.65 g/cm^3 ve Ukc 1.5 g/cm^3). Diğer

önemli seramik özelliklerinden biri olan pişme renklerine göre ise Usc en yüksek beyazlık değeri (%83.59) 1000 °C sıcaklık, Ukc maksimum beyazlık değeri ise (%94.21) 1100 °C'de gözlenmiştir.

Usc plastik olmadığından ve aynı zamanda yüksek miktarda SiO_2 içerdiğinden plastikliği yüksek hammaddeler ile karıştırılarak düşük plastiklik elde etmek amacı ile kullanılabilir. Ayrıca döküm tekniği uygulanarak üretilen seramik ürünlerinde döküm viskozitesini azaltmak için de kullanılabilir. Bunun yanı sıra, Ukc ile Usc karşılaştırıldığında, Usc'nin yüksek sıcaklıkta akışkan olan K_2O, Fe_2O_3 ve MgO oksitlerini daha yüksek miktarda içerdiği ve düşük sıcaklıkta eridiği gözlenmiştir. Tüm bu özelliklerinden dolayı, Usc Ukc'ye göre, yüksek sıcaklığa dayanımlı malzemelerle karıştırılarak sıcaklığı düşürmek ve mekanik dayanımı daha düşük sıcaklıkta elde etmek konularında tercih edilebilir. Usc'nin bu özelliği enerji tasarrufu ile seramik endüstrisi için oldukça önemli bir faktörün varlığını ortaya çıkarmıştır.

Bu çalışmada konu edilen iki malzemenin birbiri ve de seramik yapımında kullanılan ticari hammadeler ile karşılaştırılması sonucunda, her iki malzemenin de, beyaz seramiklere uygun olduğu ortaya konmuştur. Ayrıca, Usc'nin refrakter hammadesine uygun olmadığı belirlenmiştir.

Anahtar Kelimeler: Seramik, Teknolojik Özellikler, Endüstriyel Uygulamalar, Fiziksel ve Kimyasal Özellikler, Yanma Karakterleri

To my family

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SYMBOLS AND ABBREVIATIONS

XRD	X-ray Diffraction
XRF	X-Ray Flouresence
SEM-EDS	Scanning Electron Microscope-Energy Dispersive X-Ray Spectrometry
DTA-TG	The Differential Thermal Analysis- Thermogravimetry
FTIR	Fourier Transform Infrared
θ	Theta
CEC	Cation exchange capacity
LL	Liquid limit
PL	Plastic limit
PI	Plasticity Index
TS	Turkish Standart
Å	Angstrom
LOI	Loss on ignition

1. INTRODUCTION

Clays have been part of our life in various ways since ancient time. Because of physico-chemical properties, clays are used in diverse fields such as ceramics, cosmetics, drilling muds, absorbing agents, papers, cements, filtering agents, landfills, medicine, cat litter, rubber etc. (Konta, 1995; Murray, 2007; Chang, 2002; Çelik, 2010, Zanelli et al., 2015). Within these sectors, ceramic has a special role whose products we use as a dinnerware, sanitaryware, floor tile, wall tile, electrical insulators and more than mentioned ones. Ceramic is one of dynamic industries with growing technological innovation and market trends day by day.

1.1. Clays as Ceramic Raw Material

The clay minerals differ from each other in terms of structure and composition because of their particular physical and chemical properties. These properties bring advantages to use them for different purposes. In ceramic industry, kaolinite is most preferred clay mineral. The reasons that make kaolinite indispensable are mentioned by Grim, (1962) as follow:

- Kaolinite is white or near-white color even after firing at high temperature.
- It has fine particle size.
- The pure kaolins are molten or fused at 1850°C which allow kaolinite to be used as refractory.
- It has very low cation exchange capacity and relatively low surface area.
- It has low absorption capacity that brings advantage to the product having very low water absorption properties.
- It has low shrinkage capacity after firing to compare with other clay minerals.
- It is easily shaped and maintained the shape after firing.

Illite is used mostly in manufacturing of brick and red tiles, because it contains Fe_2O_3 in relatively higher amount than other clay minerals. Smectite minerals are used in ceramic industry if plasticity is required to increase and also developing firing resistant. However, because of uncontrollable shrinkage properties of smectite, it is preferred to use in small amount. Beside clay minerals, other non-clay materials are also used in ceramic industry. The examples of these materials are sodium feldspar, potassium feldspar, quartz, nepheline syenite, talc, whiting agregats, zircon and etc. (Carty, 1998). The potassium feldspar and sodium feldspar are mostly used for increasing fluxes in ceramic body (Grim, 1962; Carty 1998) at high temperature which develops technological properties. Quartz is commonly used as a filler to decrease plasticity and viscosity that provides resistance to cracking during drying. The other materials mentioned above are used for the purpose of increasing whiteness as well as mechanical resistant of ceramic products (Grim, 1962; Carty 1998).

1.2. Turkey's Position in The Ceramic Industry

Amoung various industries, ceramic industry has a special position in Turkey. Many cities in Turkey host ceramic factories. The majority of these ceramic factories made Turkey Europe's third and the world's sixth largest ceramic tile exporter according to Turkish Ceramics Federation (TCF) report (TCF, 2009). Beside tile, other kind of ceramic products were produced in Turkey as well. Another aspect that also tells that ceramic is one of the oldest industry in Turkey, is ancient pottery findings. Nowadays, many places in Turkey host at least one ceramic factory dealing with manufacturing of ceramic products or raw materials of ceramics. Uşak is one of the famous cities of Turkey with its ceramic industry. This may be because of economical mineral deposits in Uşak. One of these deposits is Karaçayır kaolinite deposit which had approximately one million tonnes of reserves according to 8th Five-Year Development Plan – State Planning Organisation of Turkey (2001). Geology, mineralogy, geochemistry of Karaçayır kaolinite deposit has been studied by Seyhan (1972), Karaağaç (1975), Fujii et al. (1995) and Kadir and Erkoyun, (2013). The other one called Hallaçlar kaolinite deposit is also important in ceramic industry and investigated by Erkoyun and Kadir, (2011). Both kaolinite deposits have been used by ceramic factories in Uşak province for a long time (Kadir and Erkoyun, 2013). It was stated by Kadir and Erkoyun (2013) that, Karaçayır area dominantly consists of kaolinization, illitization, smectitization coexistent with high degrees of silicification and Fe (oxyhydr) oxidation.

1.3. Ukrainian Clay in Ceramic

The Ukrainian clay, very famous in international ceramic markets has been widely used to due its well compatible properties (Dondi et al., 2003; Zanelli et al., 2015; Allegretta et al., 2016), therefore, it is taken as a reference material in this study to compare the viability of Uşak clay for ceramics. Ukrainian clay from the Andreevskoe deposit are best materials reported by Romanenko, (2002). It was classified as basic (content of Al_2O_3 + TiO_2 after calcination 30 – 40%) and semi-acid (content of Al_2O_3 + TiO_2 after calcination 15 – 30%), refractory (heat resistance above 1580°C), and high-melting (heat resistance 1350 – 1580°C) (Avgustinik 1975). Using the Attenberg method at the Chair of Ceramics, Refractories, Glass, and Enamels of the Kharkov State Polytechnical University classify the Ukrainian clay from Andreevskoe deposit I class ceramic raw material since the plasticity number of all grades of clay exceeds 15 (Romanenko, 2002). Allegretta et al, (2016) used Ukrainian clay in their study to investigate the effects of the nature, percentage and grain size of the temper and firing temperature, on the thermo-mechanical properties of pre-industrial ceramics, by using both an experimental and a numerical approach. They determined spinel-type phase (e.g. γ-Al_2O_3) structure and composition. Dondi et al., (2003) studied different clay materials as well as Ukrainian clay from Donbas basin by outlining the influence of clay mineralogy and particle size on the technological properties of both unfired and fired porcelainized stoneware tiles. They reported that Ukrainian clays exhibit a high content of clay minerals and a low percent of quartz, with rather high amounts of interstratified illite/smectite. Also, it was found that Ukrainian clay is the finest and most plastic materials within different samples from various regions.

1.4. Purpose of Study

The growing ceramic industry and the lack of sufficient raw material in Uşak create the necessity of evaluating the new raw material. Taking this problem into consideration, Uşak clay which has been used in ceramic industry is selected for the present study. This thesis study aims to investigate the suitability of Uşak clay as a ceramic raw material by comparing the properties of Ukrainian clay which is very famous in the world ceramic markets. The Ukrainian clay shows high plasticity, convenient behavior under compaction and drying, easy sintering etc., all of which make it suitable suitable raw material in ceramic industry (Dondi et al., 2003; Galos, 2011a,b; Zanelli et al., 2015).

1.5. Scope

To reveal the suitability of Uşak and Ukrainian clay as ceramic raw materials, both samples were investigated in terms of their mineralogical, chemical and physical properties. In addition to the standard analysis, technological characteristics such as water absorption, linear shrinkage, bulk density, bending strength and color change, were also studied. The mineralogical contents were determined by X-ray Diffraction (XRD) and Fourier Transform Infrared (FTIR). The micromorphology of minerals was defined by using Scanning Electron Microscope (SEM). The composition of major oxides was measured by X-Ray Flourescence (XRF) as well as energy dispersive X-ray spectrometry (EDS). The differential thermal analysis- thermogravimetry was used in this study to find out thermal behaviors of the studied samples. Cation exchange capacity (CEC) was determined by methlyene blue test. Particle size distribution was determined by using wet sieve and hydrometer analysis. Liquid limit and plastic limit were determined by casagrande apparatus.

2. MATERIALS AND METHODS

To realize this study, lots of heavy bags (10-14 kg each) from Ukrainian and Uşak clay samples were taken from the stackpile of a ceramic factory in Uşak, Turkey by using a hand shovel. In order to have a better homogeneity in a representative samples, sampling procedure was done carefully from each part of the pile and mixed thoroughly to have a composite sample. Approximately 90 kg sample for technological tests and 5 kg for mineralogical, geochemical and physical characterization tests were prepared. Samples from Ukranian clay and Uşak clay piles are abbreviated as Ukc and Usc in this manuscript, respectively.

2.1. Mineralogical and Chemical Analysis

Mineralogical composition of the studied samples were determined by X-ray diffraction analysis, operating a Panalytical Expert Pro diffractometer equipped with a Cu tube at 40kV voltage and 30mA current in Mineralogy-Petrography Laboratory at General Directorate of Mineral Research and Exploration. The diffractograms were plotted between 4°-70° 2θ with a scanning rate of 2°/min. Mineral identification was based on the combined methods of Moore and Reynolds (1989), Thorez (1976) and Chen (1977). Semi-quantitative analysis on the average mineralogical composition of both samples were done comparetively using the methods of Cook et al., (1975) based on the heigth of the peaks on diffractograms and the method based on the chemical analysis by XRF.

In order to identify clay minerals, the clay size (<2μm) fraction was seperated from the bulk composition in Clay Mineralogy Laboratory at Engineering Faculty, Muğla Sıtkı Koçman University. 3 gr sodium hexametaphosphate ($NaPO_3$) was added to each samples to prevent particles sticking together and settling down faster. The clay-size fractions were analyzed by X-ray diffractometer (GNR APD 2000 PRO) equipped with Cu tube at 40 kV voltage and 30 mA current with a scanning between 2°-30° 2θ and scanning rate of 2°/min applying air-dried, ethylene glycol bath and heated to 500°C treatments in X-ray Diffraction laboratory of Geological Engineering Department at Pamukkale University. The purpose of applying ethylene glycol bath was to evaluate the swelling clays whereas heat-treatment to 500°C was to distinguish the kaolinite phase with its meta-stable characteristics.

Whole rock chemical analysis of the major elements was performed by Thermo ARL X-ray flourescence on powder pellets in Analytical Chemistry Laboratory at General Directorate of Mineral Research and Exploration.

Ukc and Usc clay samples were also examined by scanning electron microscopy (SEM, JEOL JSM-7600F) at an accelerating voltage of 15 kV to identify the micromorphology of the minerals constituted in Research and Application Centre for Research Laboratories at Muğla Sıtkı Koçman University. Elemental characterization of the samples were analysed using the SEM equipped with and energy dispersive X-ray spectrometry (EDS) (Oxford Instruments).

Characterization studies continued with operating Fourier-transform infrared (FTIR) analysis in Mineralogy-Petrography Laboratory at General Directorate of Mineral Research and Exploration. FTIR was performed on a Perkin Elmer Spectrum Version 10.03.07 spectrophotometer. Spectra were recorded in transmission mode, the scanning rate was 450-4000 cm^{-1}, with a resolution pf 4 cm^{-1}, 10 scans signal-averages for each sample.

Cation exchange capacity (CEC) of each sample were measured in Clay Mineralogy Laboratory at Engineering Faculty, Muğla Sıtkı Koçman University by methlyene blue test. For each, 50 g clay sample passed from no:200 sieve were blended with 50 ml distilled water. Methylene blue solution was prepared according to the method of Jones (1964). CEC was calculated by following formula (2.1)

$$CEC = \frac{100}{f} \times V_{cc} \times N_{MB} \tag{2.1}$$

f-weight of clay sample

V_{cc}-amount of methylene blue diluted added to the clay sample

N_{MB}-Normality was calculated by formula (2.2)

$$N_{MB} = \frac{W_{MB}}{320} \times \frac{100 - x}{100} \tag{2.2}$$

W_{MB}-weight of methylene blue

x-moisture content of methylene blue

2.2. Thermal Analysis

Thermal behaviours of Ukc and Usc samples were studied by Rigaku Thermoflex TG 8110 from 25 °C to 1050 °C at a rate of 10 °C/min in Industrial Raw Materials and Ceramic Materials Research Laboratory at General Directorate of Mineral Research and Exploration.

2.3. Physical Properties

2.3.1. Determination of atterberg limits

Liquid limit (LL), plastic limit (PL), particle size distribution and specific gravity of each sample were measured in Clay Mineralogy Laboratory at Engineering Faculty, Muğla Sıtkı Koçman University. Liquid limit (LL) and plastic limit (PL) analyses were carried out by Casagrande apparatus according to Bowles (1992). Totally 250 g of each sample passed from no:40 sieve were used in this analysis. The samples were mixed with a small amount of water in separate porcelain dishes (about 250 ml capacity). After samples reached enough consistency, some from each sample were placed on casagrande apparatus. Surface of the pat was smooth and than carefully cut a groove by grooving tool. Crank of casagrande was rotated at approximately 120 rpm. For Uşak clay sample firsly, 11 mm groove was recorded after 28 blows, for Ukrainian clay sample 12 mm grove was recorded after 40 blows. Small pieces of samples were taken from middle of groove and put in weight-known cans and then cans were weighted together with samples. All the samples were removed from casagrande aparatus and little water was added and mixed by using straight edge steel and again placed on the casagrande aparatus. For Uşak clay samples, second groove 12 mm was seen after 20 blows, for Ukrainian clay 12 mm was seen after 21. Third groove 12 mm of Uşak sample was determined after 9 for Uşak clay sample and 13 blows for Ukrainian clay. For the PL test, 25 gr soil which 12 mm groove was seen after 48 blows was taken and put on the smooth glass. The samples were rolled between the fingers on a glass plate. When soil thread diameter down to 3 mm and it was crumbled, soil was put in the can. The can was left in oven about 24 hour at 110°C. Plasticity index (PI) was calculated by the difference between LL and PL. Table 2.1; 2.2; 2.3 and 2.4 and Figure 2.1 show the calculation process of LL, PL and PI.

Table 2.1. Liquid Limit Determination By Casagrande

Liquid Limit Determination By Casagrande	1	2	3	1	2	3
Can No	Ukc17	Ukc18	Ukc19	Usc14	Usc15	Usc16
Weight of Can (Wcan) (gr)	30.02	31.50	32.25	30.46	32.00	31.79
Weight of Wet Soil and Can(Wws+ Wcan)(gr)	37.02	38.51	39.17	36.67	37.13	38.61
Weight of Dry Soil and Can (Wds+ Wcan) (gr)	34.95	36.55	37.43	35.37	36.09	37.00
Weight of Dry Soil (Wds) (g)	4.93	5.05	5.18	4.91	4.09	5.21
Weight of Moisture (W_m) (g)	2.07	1.96	1.74	1.30	1.04	1.61
Water Content (Wc) (%)	42.0	38.8	33.6	26.5	25.4	30.9
Number of Blows	13	21	40	20	28	9

Table 2.2. Plastic Limit Determination

Plastic Limit Determination	1	2	1	2
Can No	Ukc20	Ukc14	Usc9	Usc10
Weight of Can (W_{can}) (gr)	31.85	30.81	29.37	29.37
Weight of Wet Soil and Can (W_{ws}+ W_{can}) (gr)	35.26	32.77	31.60	31.60
Weight of Dry Soil and Can (W_{ds}+ W_{can}) (gr)	34.56	32.42	31.31	31.31
Weight of Dry Soil (W_{ds})(gr)	2.71	1.61	1.94	1.94
Weight of Moisture (W_m) (gr)	0.70	0.35	0.29	0.29
Water Content (W_{cl}) (%)	25.8	21.7	14.9	14.9

Weight of moisture was calculated by formula (2.3):

$$W_m = (W_{ws} + W_{can}) - (W_{ds} - W_{can}) \tag{2.3}$$

Weight of content was calculated using formula (2.4):

$$W_c = \frac{W_m}{W_{ds}} * 100 \tag{2.4}$$

Table 2.3. Calculation of LL, PL and PI.

Casagrande	Ukc	Usc
Liquid Limit (LL) (%)	38.0	25.7
Plastic Limit (PL) (%)	23.8	14.9
Plasticity Index (PI) (%)	14.2	10.8

Table 2.4. Equation of Casagrande Line

	x's Coefficient	Constant
Ukc	-3.26	148.87
Usc	-3.18	106.78

LL, PL and PI were calculated by following formula (2.5), (2.6), (2.7) respectively:

$$LL = \frac{25 - 148.87}{-3.26} \tag{2.5}$$

$$PL = \frac{W_{cl1} - W_{cl2}}{2} \tag{2.6}$$

$$PI = LL - PL \tag{2.7}$$

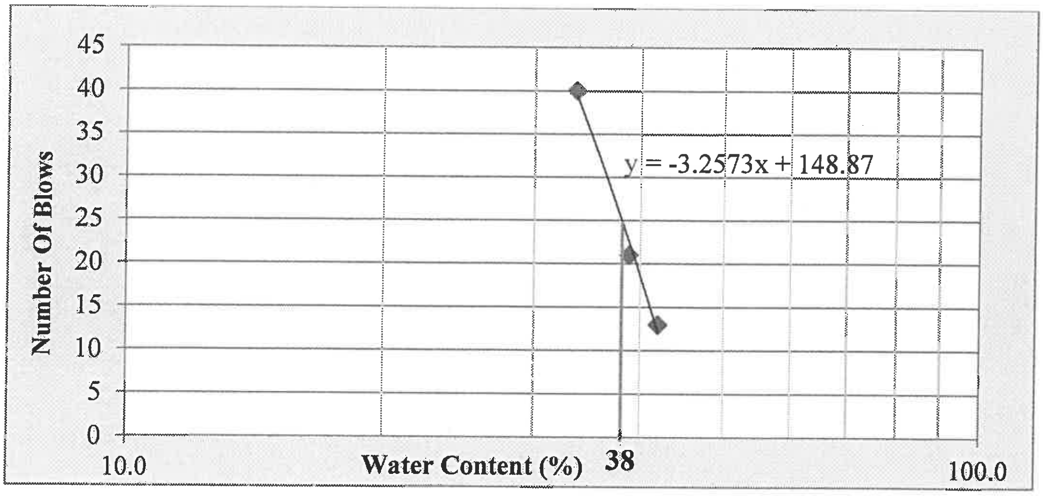


Figure 2.1. Liquid Limit results from casagrande cup method

2.3.2. Determination of particle size distribution

For particle size distribution, coarse-fraction from each sample was separated by wet seiving method based on TS 4790 standards. Silt (< 63 μm) and clay (< 4 μm) size fractions were measured by hydrometer analysis using 152 H hydrometer according to Bowles (1992). To avoid flocculation, 5g sodium hexametaphosphate ($NaPO_3$) was added to each.

Specific gravity analyses was realized using 200 gr samples taken from Ukrainian and Uşak clay and 500 ml volumetric flask based on Bowles (1992). By using vacuum machine, air was pumped out from volumetric flask until bubble disappear in order to create vacuum environment. The calculation results of specific gravity and particle size distribution were given in Table 2.5 and 2.6 respectively.

Table 2.5. Determination of specific gravity

Specific Gravity calculation	Ukc1	Ukc2	Usc1	Usc2
Volume (mL)	500	500	500	500
Temperature (°C)	21	21	21	21
Mass of flask + water = M_{bw} (gr)	753.75	775.96	752.6	770.7
Mass of flask + water + soil = M_{bws}(gr)	805.06	834.63	814.32	844.33
Dish W_d (gr)	707	831.36	707.37	817
Dish+Dry soil (W_d+W_{ds}) (gr)	797.73	920.11	807.74	925.37
Dry soil (M_s) (gr)	90.73	88.75	100.37	108.37
M_w	39.42	30.08	38.64	34.75
a (21°C)	0.9998	0.9998	0.9998	0.9998
G_s	2.301	2.949	2.597	3.118

Mass of dry soil was determined by formula (2.8)

$$M_s = (W_d + W_{ds}) - W_d \tag{2.8}$$

Mass of water was calculated by formula (2.9)

$$M_w = M_s + M_{bw} - M_{bws} \tag{2.9}$$

Table 2.6. Calculated Values of 152H Hydrometer test

Elapsed time (min)	Temperature (°C)	Actual Hyd. Reading (Ra)	Corr. Hyd. Reading (Rc)	Finer (%)	Hyd. Corr. Only for meniscus, R	L	L/t	K	D (mm)
0.5	19	47	40.7	81.807	48	8.4	16.8	0.0138	0.05656
1	19	46	39.7	79.797	47	8.6	8.6	0.0138	0.04047
2	19	44	37.7	75.777	45	8.9	4.45	0.0138	0.02911
4	19	43	36.7	73.767	44	9.1	2.275	0.0138	0.02081
8	19	42	35.7	71.757	43	9.2	1.15	0.0138	0.0148
15	19	39	32.7	65.727	40	9.7	0.646667	0.0138	0.0111
30	19	37	30.7	61.707	38	10.1	0.336667	0.0138	0.00801
60	19	35	28.7	57.687	36	10.4	0.173333	0.0138	0.00575
120	19	33	26.7	53.667	34	10.7	0.089167	0.0138	0.00412
240	19	30	23.7	47.637	31	11.2	0.046667	0.0138	0.00298
480	17	22	15.3	30.753	23	12.5	0.026042	0.0142	0.00229
1200	19	12	5.7	11.457	13	14.2	0.011833	0.0138	0.0015
1470	19	10	3.7	7.437	11	14.5	0.009864	0.0138	0.00137

Specific gravity of soil was calculated by formula (2.10)

$$Gs = a \times \frac{M_s}{M_w} \tag{2.10}$$

Correction factor "a" in specific gravity test was obtained by following formula (2.11):

$$\alpha = \frac{\rho_T}{\rho_{20°C}} \tag{2.11}$$

Values of L (effective depth) was obtained from accepted numbers that are suitable to original hydrometer Reading (corrected for meniscus only) based on ASTM soil hydrometer 152H. The value of L for 152H hydrometer was calculated as following (2.12) formula:

$$L = 16.3 - 0.1641R \tag{2.12}$$

Temperature correction factors (C_T) for 19°C is -0.3 and for 17°C is -0.7. The corrected hydrometer reading (Rc) for grams of soil in suspension is computed by formula (2.13):

$$R_c = R_a - zero\ correction + C_T \tag{2.13}$$

Zero correction was found 6.

The percentage of finer was compute by formula (2.14):

$$Percent\ finer = \frac{a \times R_c}{M_s} \times 100\% \tag{2.14}$$

Correction factor "a" was calculated in hydrometer test by usining formula (2.15):

$$a = \frac{1.65G_s}{2.65\ (G_s - 1)} \tag{2.15}$$

Since the temperature of the soil-water suspension are independent of the test, K is computed using formula (2.16):

$$K = f(T, G_s, \eta) \quad (2.16)$$

The diameter of particle was calculated following formula (2.17):

$$D = K\sqrt{\frac{L}{t}}\ mm \quad (2.17)$$

2.4. Technological Tests

All the technological tests on Ukc and Usc samples were performed in Industrial Raw Materials and Ceramic Materials Research Laboratory at General Directorate of Mineral Research and Exploration. Less than 2.8 mm size fractions from each sample were prepared to have a rectangular prism bodies with 25 mm x 25 mm x 115 mm dimensions for technological tests. The bodies prepared from each sample were dried overnight at room temperature and were again dried in kiln for 4 hours at 55 °C first and then for 24 hours at 110 °C to determine the characteristics of linear drying shrinkage and dry bending strength. To measure the total linear shrinkage, bending strength and compressive strength at various temperatures, each body from Ukc and Usc samples were fired in kiln at 800 °C, 900 °C, 1000 °C, 1100 °C, 1150 °C, 1300 °C and 1430 °C with a heating rate of 150 °C/hours. Linear drying and total linear shrinkage values were calculated with the formula (2.18)

$$\%S_d = \frac{L_p - L_d}{L_p} X100 \quad (2.18)$$

where Sd= linear drying shrinkage or total linear shrinkage as percentage (%), Lp= length before drying or firing temperatures and Ld= length after drying or firing temperatures.

Bending strength test operated 4.5 N/min load on the dried and fired bodies using TS 4790 standards. The bending strength values were calculated with the formula (2.19):

$$M = \frac{3.P.L}{2.a.h^2} \quad (2.19)$$

where M stands for the dry or fired bending strength (N/mm^2), P shows the breaking (bending) force (N), L means the distance between supports (mm), a is the width of breaking point of the body (mm) and h refers to the thickness of breaking point of the body (mm).

For the compressive strength tests, 2 new bodies from each sample with 10-15 cm^2 surface area and 1.5 cm height were formed by cutting from the previously fired bodies. Compressive strength test was carried out by applying the stress at the same time to both sides of each body with increasing pressure rate of 5-6 kgf/cm^2 in every second until the body was broken. Compressive strength values were calculated with the formula (2.20):

$$F_b = \frac{P_k}{A_0} \times k \quad (2.20)$$

where Fb is compressive strength of body (kgf/cm^2), Pk refers to the load applied to break the body (kgf), A_0 stands for the surface area of the body (cm^2) and k is the shape factor of the body (standard as 0.5).

Color changes were identified by Minolta Chroma Meter CR-300 model reflected light colorimeter and firing status of the bodies were determined at 800 °C, 900 °C, 1000 °C, 1100 °C, 1150 °C, 1300 °C and 1430 °C temperatures by nacked eye.

Water adsorption properties were tested by keeping them in water for 24 hours and boiling them in water for 5 hours after firing the bodies at 800 °C, 900 °C, 1000 °C and 1100 °C separately. The water adsorption test was performed using TS EN 772-21 and TS EN 772-7 standards.

Unit volume mass property of each body was calculated at 800 °C, 900 °C, 1000 °C and 1100 °C temperatures using TS EN 771-1 standards. Additionally, firing status was recorded by naked eye and hardness of the bodies fired at the same temperatures mentinoned in the unit volume mass test were recorded according to the Mohs hardness scale.

3. RESULTS

3.1. Mineralogical and Chemical Characterization

3.1.1. X-ray diffraction analysis (XRD)

X-ray diffractograms of bulk Ukc and Usc samples were given in Figure 3.1. Kaolinite, quartz, illite and dolomite minerals were identified in both samples.

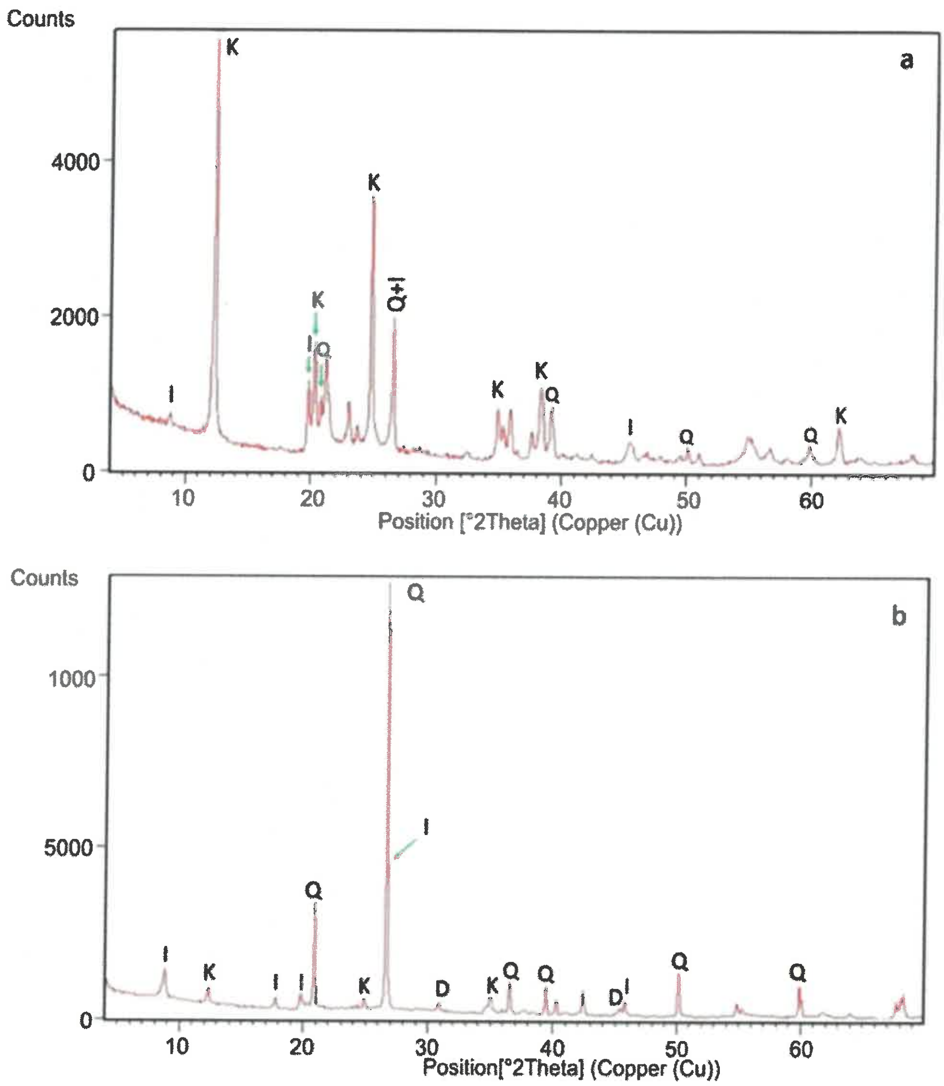


Figure 3.1. XRD patterns of unoriented powders of (a) Ukc and (b) Usc: I-illite, Q-quartz, K-kaolinite, D-dolomite.

The weak 7.16Å peak at 12.3° 2θ (Figure 3.1b) and more intense peak of 7.18Å at 12° 2θ (Figure 3.1a) represent the present of kaolinite. Basic reflection of quartz was identified with 3.35 Å at 26.5° 2θ in both samples where it has very intense peak in Usc and relatively weak in Ukc sample. The illite reflections were recognized with its major 10Å peak at the range of 8.75°-8.87° 2θ in both samples but the higher one was observed in Usc and very veak one in Ukc. The peak at 2.89 – 2.90 Å at 31 ° 2θ confirm presence of dolomite in Usc sample. Figure 3.2 shows X-ray diffractograms of clay fraction where (a) belongs to Ukc and (b) belongs to Usc.

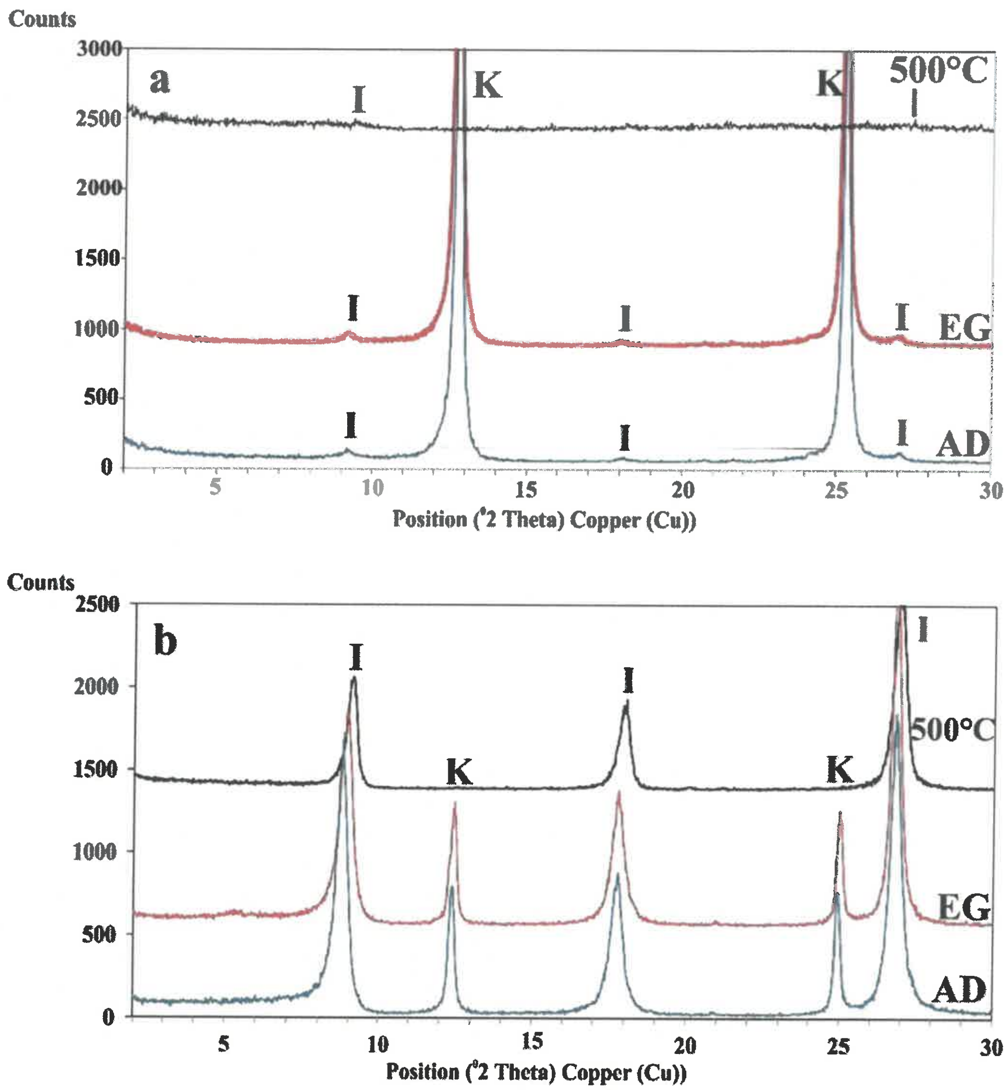


Figure 3.2. XRD patterns of (a) oriented Ukc sample; (b) oriented Usc sample: I-illite, K-kaolinite, air-dried (AD), ethylene glycol solvated (EG) and heated at 500°C (500°C).

Without showing any difference from bulk X-ray diffractograms, clay fraction also demonstrate that Ukc is consist of kaolinite more than Usc by identifying very intense reflections of kaolinite and relatively little reflection at 7 Å and 3.58 Å in air-dried (AD) x-ray diffractogram for Ukc and Usc respectively (Figure 3.2a and 3.2b). Kaolinite wasn't affected by ethylene glycol (EG) treatment therefore no changes were recognized. However, after heat treatment, the reflection of kaolinite collapsed and disappeared at 500 °C (Figure 3.2a and b). Illite sharp peak in Usc and very minor peak in Ukc was detected with 10 Å at 8.2° 2θ in AD condition (Figure 3.2b and 3.2a). The reflections of illite were observed with no change in EG solvation and heating up 500 °C which don't affect the structure of illite (Figure 3.2a and 3.2b). The result of mineralogical analyses showed that both samples consist of the same mineral assemblages but at different values. Using heigth of the peaks on diffractograms and major oxides values from XRF, bulk mineralogical composition of the Ukc and Usc sample were calculated (Table 3.1). It was found that kaolinite is most dominant in Ukc with 52%. On the other hand, Ukc contains relatively high amount of quartz (35%) and very small amount of illite (8%) (Table 3.1). On the contrary of Ukc, quartz was found most dominant as being 56% and illite was calculated relatively high (26%) in association with small amount of kaolinite (12%), dolomite (6%) for Usc sample (Table 3.1).

3.1.2. X-ray flourescence analysis (XRF)

The results of bulk geochemical analysis by XRF are given in (Table 3.1). The results of mineralogical analysis are well correlated with geochemical results. Both samples dominantly consist of SiO_2 and Al_2O_3. The high amount of Al_2O_3 in both samples are related to kaolinite and illite. Additionally, the amount of alkaline oxides (K_2O and Na_2O) is very low (1%) in Ukc sample represented by the low amount of illite, while it is relatively higher (3%) in Usc sample confirming relatively higher amount of illite in the compositions. Similarly, for both samples, very low amounts of CaO and MgO (2% for Ukc and 2.2% for Usc samples) indicate the very low amounts of dolomite in their compositions. Total value of Fe_2O_3 is low in Ukc (0.3%) sample and in Usc (1.2%). Another remarkable issue is amount of loss on ignition (LOI) that Ukc has 8.4% LOI, but Usc has 4.3%. The relatively high value of loss on ignition (LOI) in Ukc sample (8.37%) with respect to that in Usc sample (4.27 %) is associated with the relatively higher amount of kaolinite content. LOI also is increasing with presence of clay minerals. On the other hand, it was found that coarse grains in both of samples are $CaCO_3$. The amounts of $CaCO_3$ were determined with 2% and 2,92% in Usc and Ukc samples respectively.

Table 3.1. Bulk chemical and mineralogical compositions of Ukc and Usc samples.

Component %	Ukrainian clay	Uşak clay
SiO_2	63,4	73,2
TiO_2	0,5	0,1
Al_2O_3	24	15
Fe_2O_3 total	0,3	1,2
MgO	0,2	0,8
CaO	1,8	1,4
Na_2O	0,1	0,1
K_2O	0,9	3,1
L.o.I.	8,37	4,27
Quartz	35	56
Dolomite	5	6
Kaolinite	52	12
Illite	8	26
Total	100	100

3.1.3 Scanning electron microscopy-energy dispersive x-ray spectrometry analysis (SEM-EDS)

Micromorphology of the minerals were characterized by FEG-SEM studies. Two habits of kaolinites were found in Ukc sample as booklet stacks of platelets (Figure 3.3a) and mosaic of kaolinite plates (Figure 3.3b). Thin coating of kaolinite crystals around quartz grain (Figure 3.3c) and curling form of kaolinite (Figure 3.3d) are also recognized in scanning electron images of Ukc sample. SEM images of Usc sample reveal the quartz crystals with conchoidal fractures and partly coated with kaolinite plates (Figure 3.3e) and booklet form of kaolinte crystals (Figure 3.3f). Additionally, mosaic form of kaolinite together with filamentous illite were observed in Usc sample (Figure 3.3g and h). EDS reflections of Al, Si also confirmed that morphological form in Figure 3.3b belongs to kaolinite (Figure 3.3b). On the other hand, the booklet form of kaolinite crystals in Figure 3.3e were supported by the EDS reflections of Si – Al (Figure 3.3f). Intense Si peak was seen in EDS diagram (Figure 3.3d) which was applied quartz crystal (Figure 3.3c). Additionally, Si-Al-K peaks in EDS (Figure 3.3h) illustrated crystal forms in Figure 3.3g represents kaolinite and illite.

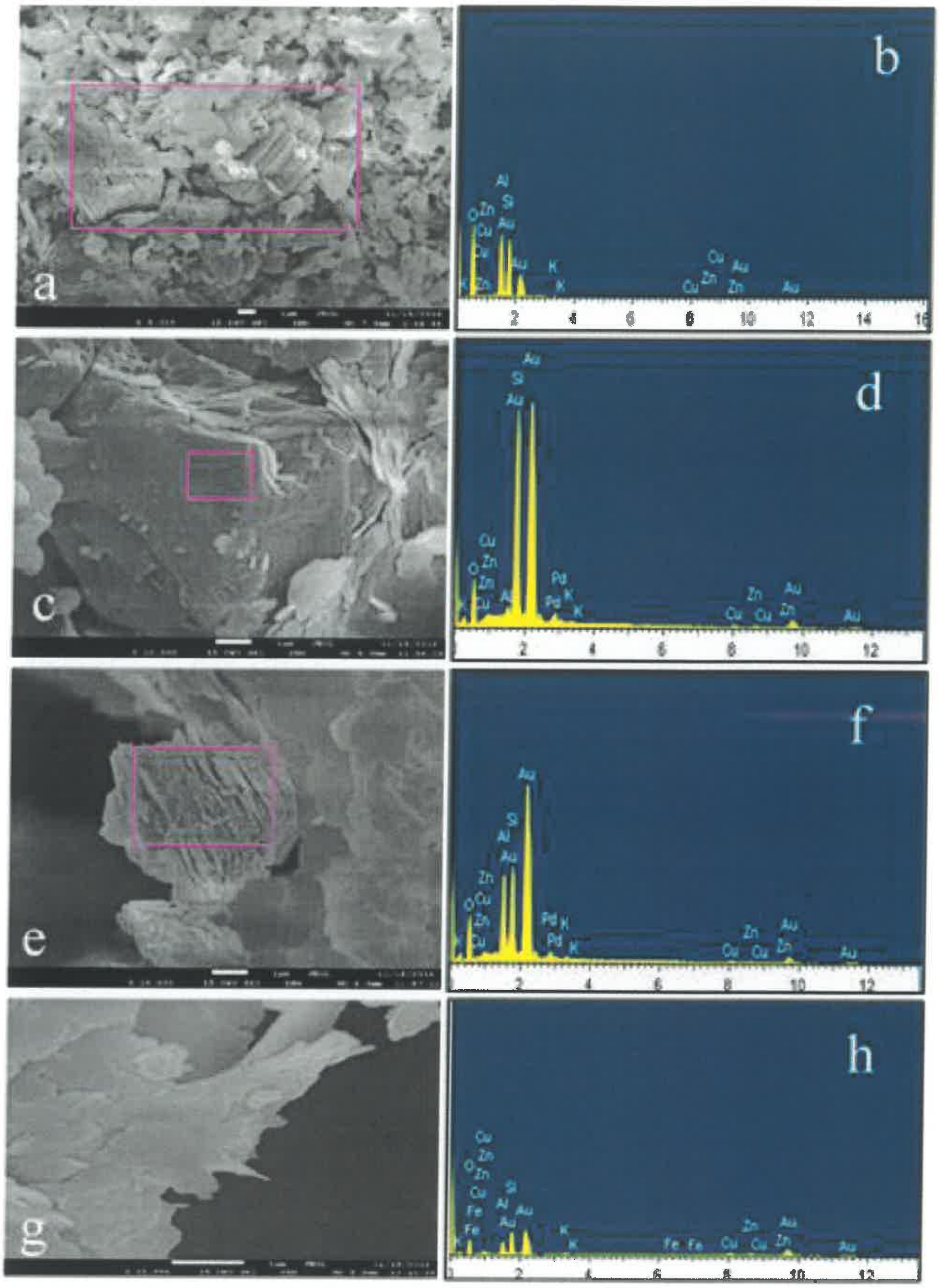


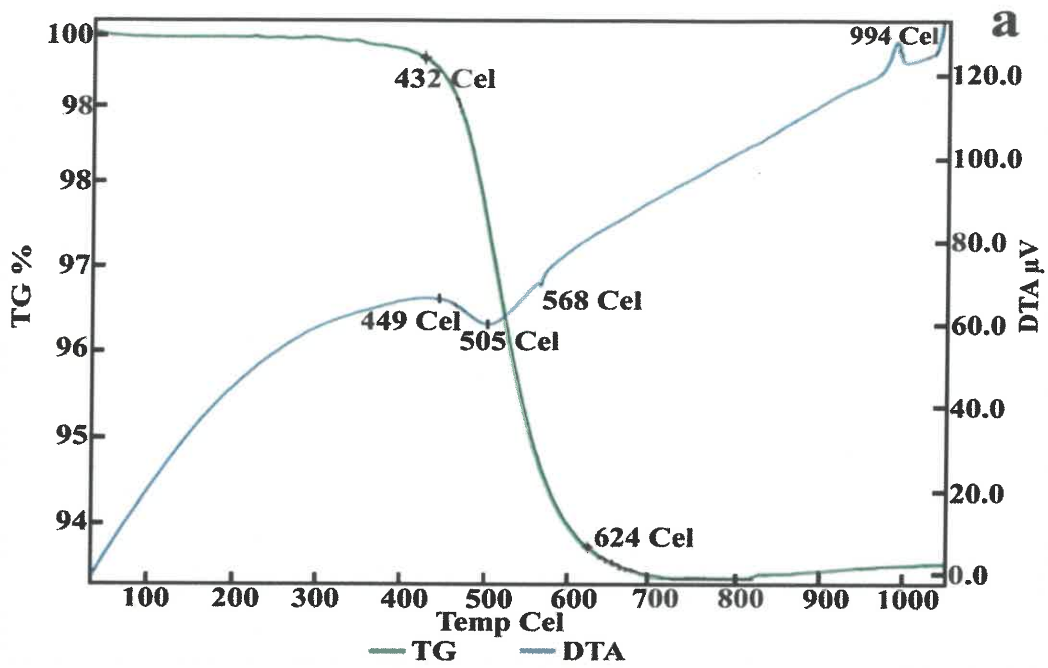
Figure 3.3. SEM micrographs and EDS of Ukc and Usc samples: (a) kaolinite booklet stacks of platelets Ukc sample; (b) EDS spectrum of a; (c) quartz crystals with conchoidal fractures and partly coated with kaolinite plates, (d) EDS spectrum of b; (e) booklet form of kaolinte crystals; (f) EDS spectrum of e; (g) mosaic form of kaolinite together with filamentous illite in Usc sample; (h) EDS spectrum of g.

3.1.4. Differential thermal and thermogravimetric analysis (DTA -TG)

The results of the thermal analysis on Ukc and Usc samples are demonstrated in Figure 3.4a and Figure 3.4b, respectively. The DTA-TG was measured in a temperature range of 25 °C -1050 °C. The broad endothermic peak at 505°C for Ukc sample, indicates dehydroxylation of kaolinite and illite that were also detected in X-ray diffractograms. The small endothermic peak at 565°C for Usc and 568°C for Ukc, were due to transformation of α-quartz to β-quartz (Grim and Rowland, 2009). A weak exothermic peak at 1004 °C for Usc (Fig. 4b) and slightly more intense one at 994 °C for Ukc sample (Fig. 4a) were observed due to the formation of mullite (Insley and Ewell, 1935; Brindley and Nakahira, 1959; Grim and Rowland, 2009; Çelik, 2010). For both samples, second exothermic peaks were also recorded at over 1050 °C for Ukc sample (Fig. 4a) and at 1040 °C for Usc sample (Fig. 4b). The mass loss was approximately 6.7% for Ukc (Fig. 4a) and 4.5% mg for Usc (Fig. 4b) samples.

3.1.5. Fourier transform infrared analysis (FTIR)

The infrared spectra for the bulk samples are shown in Figure 3.5a and 3.5b. The presence of clay minerals in both samples of Ukc and Usc were confirmed by the absorption bands near 3700-3620 cm^{-1} region (Azzi et al., 2016). The sharp OH-streching band at 3695-3670-3652 and 3620 cm^{-1} coupled with OH-deformation bands of 938 cm^{-1} and 913 cm^{-1} are characteristics for the kaolinite in Ukc sample (Udvardi et al., 2014; Bennour et al., 2015a; Zaied et al., 2015) (Figure 3.5a). Relatively broad absorption band at 697 cm^{-1} of quartz in Ukc sample was observed in Si-O bending region (Figure 3.5a). Weak band near 1030 cm^{-1} in Si-O streching region together with 3620 cm^{-1} band in OH-streching region confirm the presence of illite as well (Udvardi et al., 2014; Bennour et al., 2015b; Zaied et al., 2015) (Figure 3.5a). Strong absorption bands of quartz at 692 cm^{-1} and 796 cm^{-1} were recognized in Si-O bending and Si-O stretching regions of the infrared spectra of Usc sample, respectively (Udvardi et al., 2014; Bennour et al., 2015b) (Figure 3.5b). Intense bands at 3620-3651-3695 cm^{-1} OH-deformation band demonstrate the presence of kaolinite and at 913 cm^{-1} Si-O beninding, quartz was determined in Usc sample (Udvardi et al., 2014; Azzi et al., 2016) (Figure 3.5b). The diagnostic band of dolomite in Usc sample was revealed at 1431 cm^{-1} in C-O streching region (Udvardi et al., 2014; Bennour et al., 2015b) (Figure 3.5b).



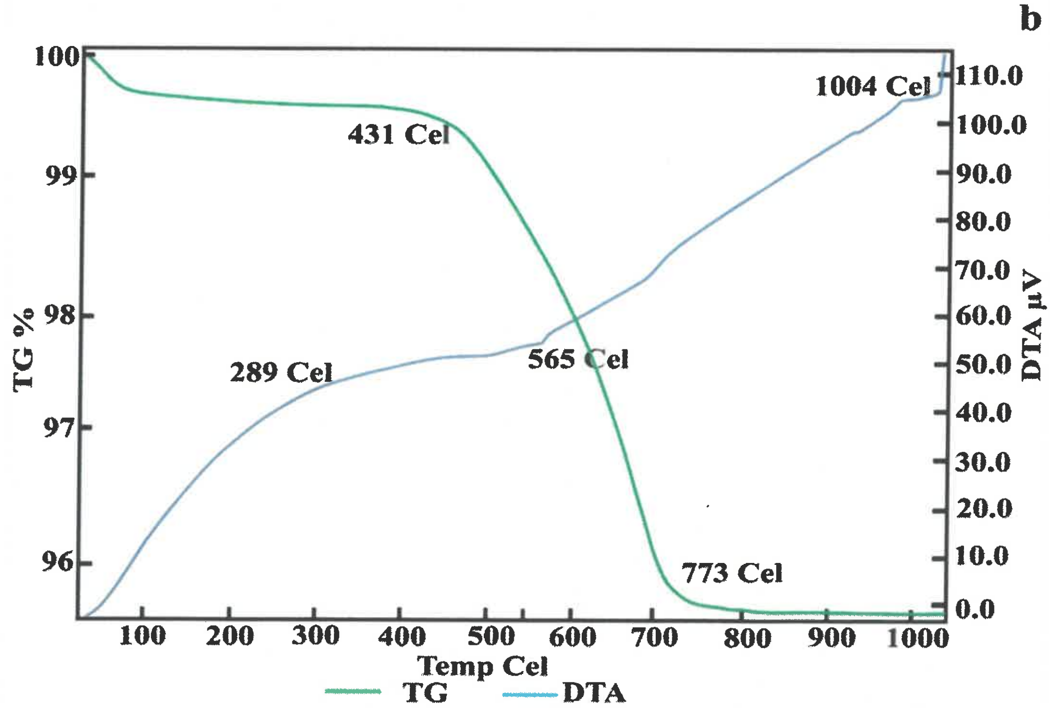


Figure 3.4. DTA/TG curves of (a) Ukc and (b) Usc.

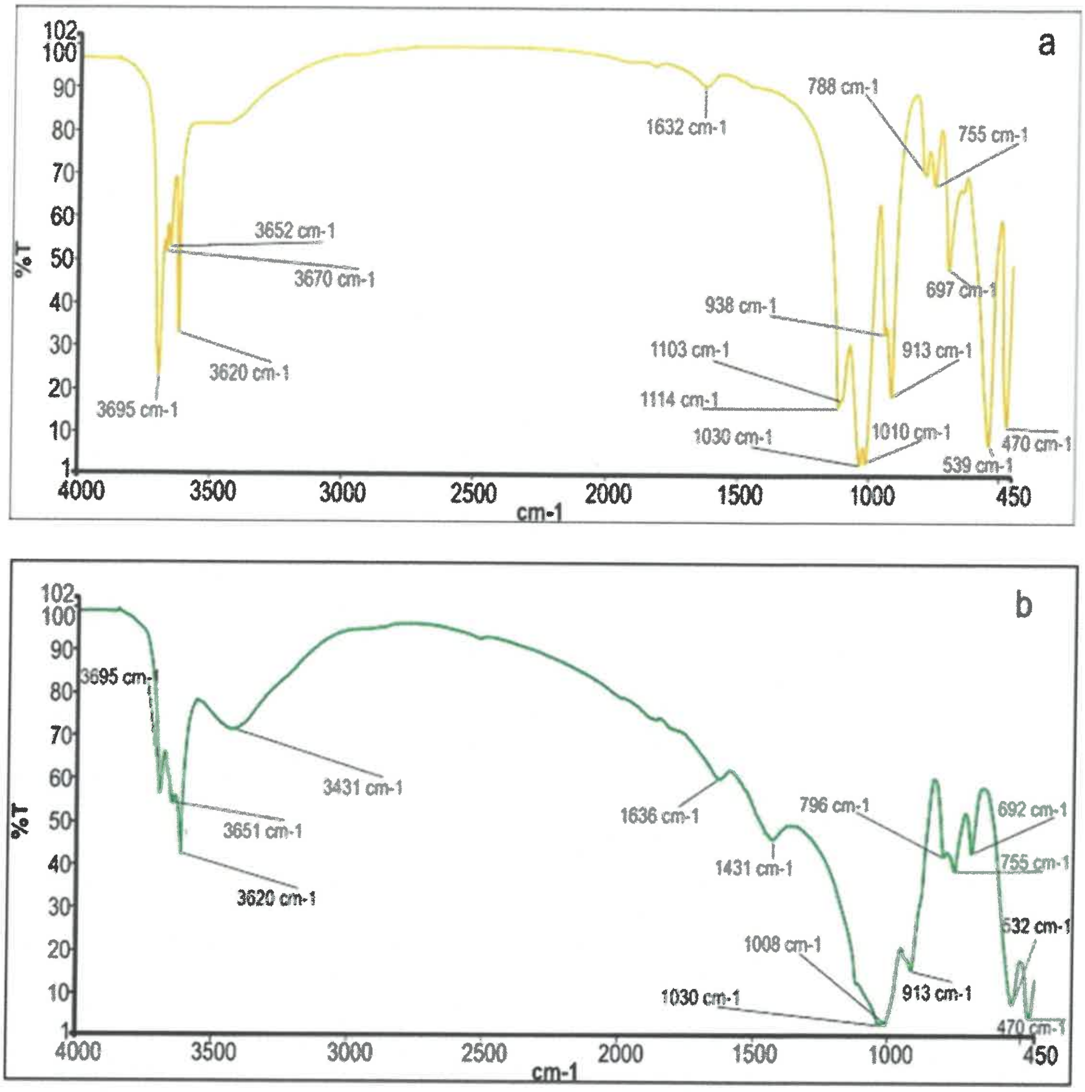


Figure 3.5. FTIR spectrum of (a) Ukc and (b) Usc samples.

3.1.6. Cation exchange capacity analysis (CEC)

Cation exchange capacity for both clay materials were determined by methylene blue test (Jackson, 1979) as 3.73 meq/100 g for Ukc sample and 5.97 meq/100 g for Usc sample. For both, the values are well-matched with the clays of low specific surface areas (Bain et al., 1994) (Table 3.2. and Figure 3.6a and b). Since the percentages for finer fraction of Ukc samples is much greater than Usc sample and the specific surface area of kaolinite is relatively smaller than illite, the findings are in strong aggrement with the mineralogical findings.

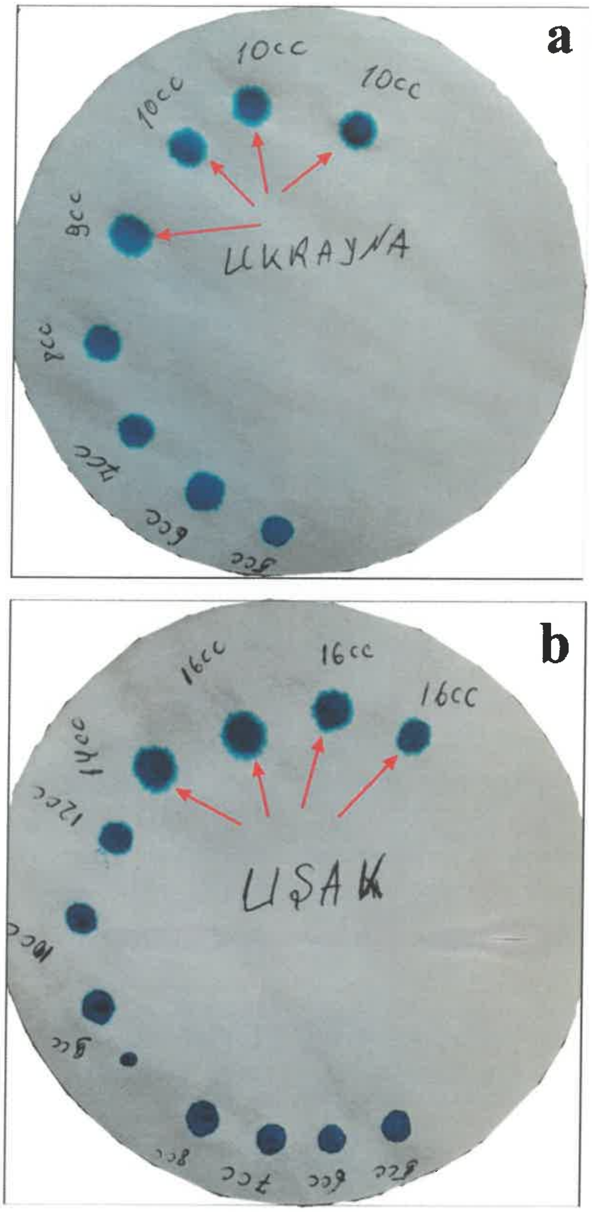


Figure 3.6. The result of Methlyene blue test: (a) Ukc, (b) Usc.

3.2. Physical Properties

The plasticity is a property of materials that lets it to be deformed under stress without breaking and also to keep shape produced after stress is finished (Grim, 1962). PL, LL and PI values of Ukc and Usc samples were given in Table 3.2. LL and PI values of Ukc and Usc were marked on the Holtz and Kovacs (1981) diagram in Figure 3.7. Although, PI amounts of both clays are almost same, as seen from the diagram, Ukc fall in medium plastic area while Usc matches low plastic zone.

Table 3.2. Dry bending strength and linear shrinkage, Atterberg limits, Cation exchange capacity and particle size distribution of Ukc and Usc samples.

Parameter	Unit	Ukc	Usc
Technological properties			
Dry bending strength	MPa	0,29	0,68
Linear drying shrinkage	% mass	3,36	4,11
Consistency limits			
Liquid Limit	% mass	38	25,7
Plastic Limit	% mass	23,8	14,9
Plasticity Index	% mass	14,2	10,8
Cation exchange capacity	meq/100g	3,73	5,97
Particle size distribution			
Sand (> 63 μm)	% mass	14	18
Silt (4–63 μm)	% mass	32	58
Clay (<4 μm)	% mass	54	25

The high plastic materials bring some disadvantages also as being more difficult to dry and reducing the wearing down of the equipment for grinding and conformation (Monteiro and Vieira 2004). Particle size distribution was demonstrated in Table 3.2. regarding to percentages of sand, silt and clay size materials. Particle size distribution of the raw materials are quite important for many studies and even finer fraction size distribution is diagnostic for ceramic products (Mahmoudi et al., 2008; Çelik, 2010). The content of fine fraction (<4 μm) was about 54% for Ukc sample, whereas 25% for Usc clay sample (Table 3.2). Relatively coarser fraction (4-63 μm) was about 32% for Ukc sample and 58% for Usc sample. Much coarser fraction (>63 μm) was about 14% for Ukc sample and 18% for Usc sample (Table 3.2).

3.3. Technological Properties

The results of firing status, color chances, compressive strength and hardness were given in Table 3.3. As seen from Table 3.3, Usc was sintered at 1150°C and melting sign was observed on its appearance at 1300°C and finally Usc melted totally at 1430°C.

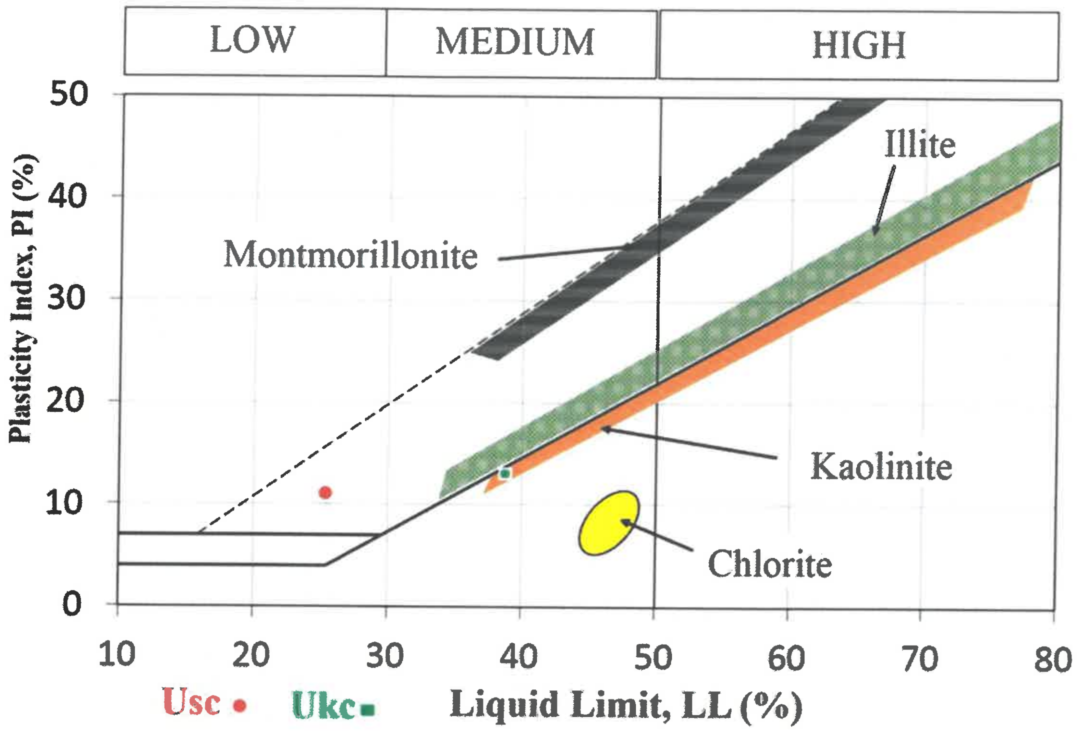


Figure 3.7. Location of Ukc and Usc samples on Holtz and Kovacs (1981) diagram.

The compressive strength of Ukc was 0.2 MPa more than that of Usc at 800°C, however at other temperatures, Usc showed better compressive strength characteristics than those of Ukc. Although, white was determined as dominant color for both samples, firing color of Ukc were determined whiter than Usc at all the firing temperatures. By increasing firing temperature, decreases were followed in values of Usc red color. The amount of yellow color for Usc was determined high when compared with green, blue, red color values. Ukc reached the whitest values at 1100°C and 1150°C while Usc reached maximum whiteness value at 1000°C. Hardness of both samples was found in same values.

3.3.1. Unit volume mass test

Variations of unit volume mass for Usc and Ukc were illustrated in Figure 3.8. Generally, there was no sharp change in both of them. Very slightly increase was observed in unite volume mass of Ukc at 900°C, whereas unite volume mass of Usc illustrate increase above 1000°C. Ukrainian clay remained unchanged after 900°C. Another remarkable issue is Usc had higher values of unit volume mass at all the temperature than those of Ukc.

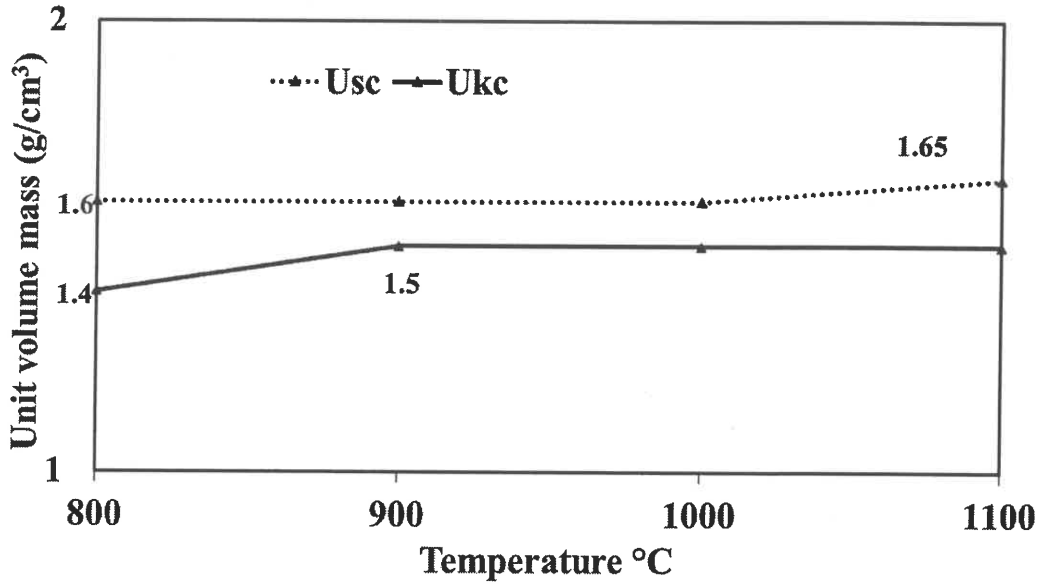


Figure 3.8. Unit volume mass Ukc and Usc at various temperatures

3.3.2. Water absorption test

Water absorption test was the other technological test to define the category to which ceramic products belong (Dondi et al., 2014; Çelik, 2010). Ukc(24h) and Usc(24h) demonstrate both samples keeping in the water for 24 hours. Ukc(5h) and Usc(5h) illustrate both of them boiled 5 hours in the water. Ukc is generally followed being higher water absorption values than Usc at all the tested temperature (Figure 3.9.). Although, water absorption of bodies is influenced more by boiling process than keeping body in the water, Usc(5h) showed low water absorption (15,24%) when compared with water absorption value of Usc(24h) (17%) at 800°C. The temperature between 800°C and 1000°C, percentage of Usc(5h) water absorption rised from 15,24% to 18,5%. At the same temperatures, same appearance but with small expansion, was seen also in Ukc (24), changing from 24,46% to 25,2%. However, values of Usc(24h), Usc(5h) and Ukc(24h), Ukc(5h) were followed by a decrease above 1000°C.

Table 3.3. Technological properties of Ukc and Usc.

	Temperature	°C	800	900	1000	1100	1150	1300	1430
Usc	Firing color/status		Beige/sintered	Beige/sintered	Beige/sintered	Beige/sintered	Sintered	melting start	bodies melted totally
	Color values	L	81,35	82,59	83,59	82,34	80,18	73,39	
		a	+5,13	+4,87	+4,47	+2,97	+3,53	-0,54	
		b	+13,02	+12,58	+12,76	+15,68	+5,37	+9,16	
	Compressive strength	MPa	4	5,3	5,4	7,1	8,2	13	
	Hardness	mohs	2	2	2	3	-	-	-
Ukc	Firing color/status		Beige/sintered	Beige/sintered	Beige/sintered	Beige/sintered	Beige/sintered	Beige/sintered	Beige/sintered
	Color values	L	92,32	93,26	93,76	94,21	94,16	89,19	89,14
		a	+0,29	-0,24	-0,04	-0,12	+0,36	+0,45	-0,81
		b	+4,17	+3,5	+2,43	+2,02	-3,8	+7,75	+5,83
	Compressive strength	MPa	4,2	4,7	5,1	5,6	6	9,5	8
	Hardness	mohs	2	2	2	3	-	-	-

Note: L - value of white coloura

a – from 0 to (+100) red color; from 0 to (-100) value of green color;

b – from 0 to (+100) yellow color; from 0 to (-100) value of blue color.

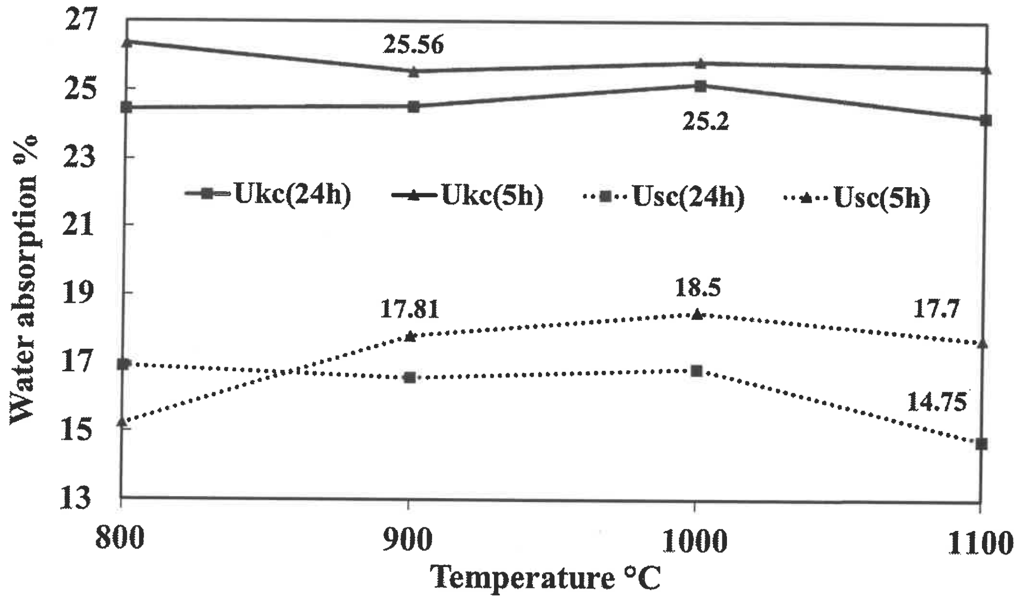


Figure 3.9. Water absorption values of fired Ukc and Usc at various temperatures.

3.3.3. Total linear firing shrinkage test

Figure 3.10. illustrates how the linear firing shrinkage of Usc and Ukc changed depending on various firing temperatures. Although, Ukc was found more plastic than Usc which has affected the development of liner shrinkage (Ngun et al., 2011), but as seen clearly from the curves, values of Usc linear shrinkage at all temperatures except 1000°C, are very high when compared with Ukc. The moderately sharp rise in Usc between 1000°C-1100°C is also considerable. The biggest growth has been followed in total linear shrinkage of Usc at temperatures ranging from 1150°C to 1300°C. The most remarkable increase in total linear shrinkage of Ukc was seen at 1300°C however after this temperature Ukc remain stable.

3.3.4. Bending strength test

Bending strengths of Ukc and Usc were displaced in Figure 3.11. Effects of high temperature on bending strength of both samples is clearly seen especially after 1150 °C. Usc illustrated excellent bending strength characters at all temperatures as compared with Ukc. The notable development was recorded in bending strength of

Usc starting from 1000°C and finally Usc reached the highest value of diagram at 1300°C. No remarkable changes were seen in value of Ukc bending strength until 1150°C. However, bending strength of Ukc started to increase after 1150°C. However, it is not the case for Usc; it only showed very slight increase after 1150°C.

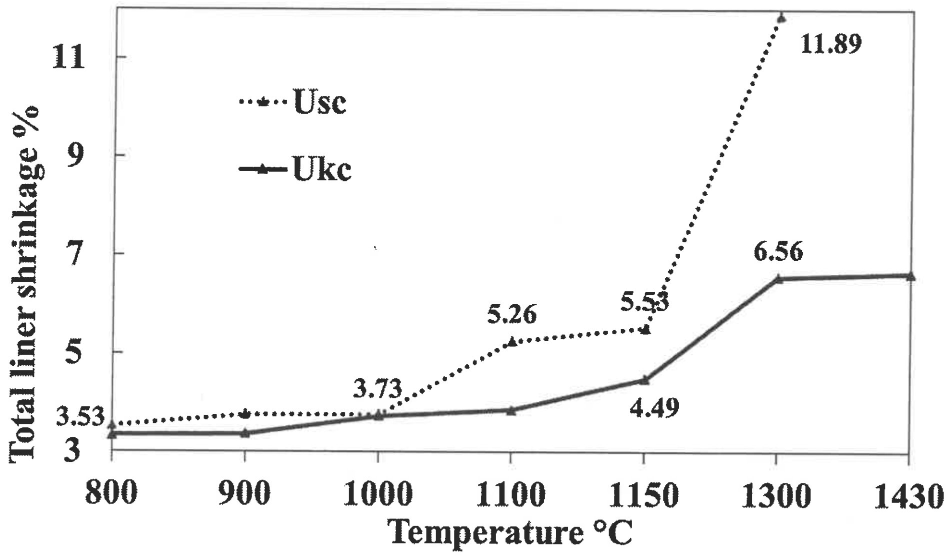


Figure 3.10. Total linear shrinkage values of fired Ukc an Usc at various temperatures.

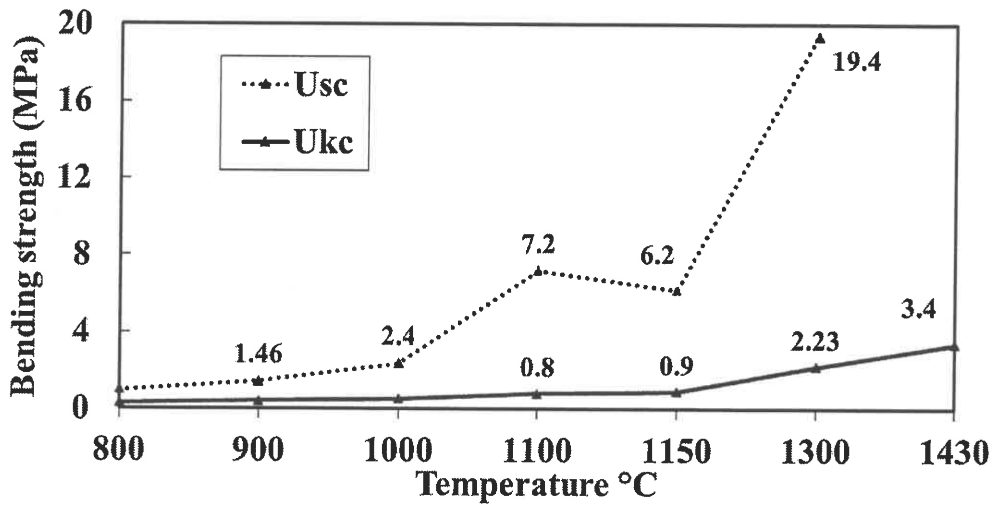


Figure 3.11. Bending strength values of fired Ukc an Usc at various temperatures.

4. EVALUATION OF THE FINDINGS WITH THE CONVENTIONAL RAW MATERIALS

Based on values of SiO_2, Al_2O_3 and other oxides Ukc and Usc were pointed on triangular diagram of Fabbri and Fiori (1985) in Figure 4.1 in order to categorize the raw materials in terms of ceramic industry usage. As seen from the following triangular diagram, Ukc falls in b and b1 areas which indicates white stoneware for German and English whereas Usc falls in the area is very close to white stoneware for German (b). It can be connected with relatively high amount of Fe_2O_3 in Usc that have an improtance role in development of coloration.

Using mineral composition, the locations of Ukc and Usc were determined in triangle diagram of Dondi et al. (2014) (Figure 4.2.) that classifies light-firing clays. As seen from the diagram, Ukc is located in area where low grade kaolin (LK) type of clays are mostly dominant, however Usc is located in an area dominated by raw kaolin (RK) and kaolinitic loam (KL) type of clays.

Both samples were placed on Wrinkler's diagram (developed by Nyakairu et al., 2002) (Figure 4.3.) based on their particle size distribution results in order to classify the suitability of Ukc and Ucs to be used in common bricks (I), vertically perforated bricks (II), roofing tiles and Masonny bricks (III) and hallow products (IV). As seen from the triangular diagram (Figure 4.3.), Ukc clay can be utilized in hallow products, while Usc clay is convenient for the common bricks.

Besides the comparison between Ukc and Usc samples, some conventional raw materials selected from recent literature were also used to check suitability of the studied samples for the ceramic industry. The major oxide compositions of the samples from this study were listed together with the commercial raw materials for earthenware and tableware (Dondi et al., 2001; DPT, 2001), for brick and tile (Arkun, 1980) and for floor tile (DPT, 2001) in Table 4.1. Additionally, some technological properties of the samples from the present study were compared with the commercial raw materials for earthenware and tableware (Dondi et al., 2001), for typical kaolin products and fine-, rough-ceramics and roof tile (DPT, 2001) in Table 4.2.

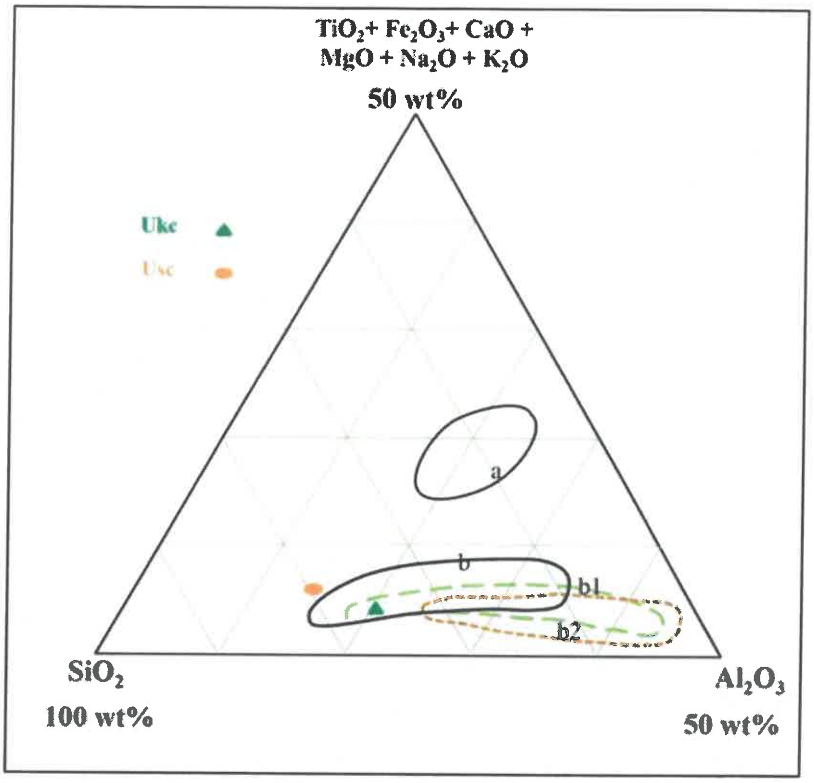


Figure 4.1. Triangular diagram of Ukc and Usc: SiO2/Al2O3/other oxides. a = red stoneware (Italy); b, b1, b2 = white stoneware for German, English, and French industries, respectively (data from Fabbri and Fiori, 1985).

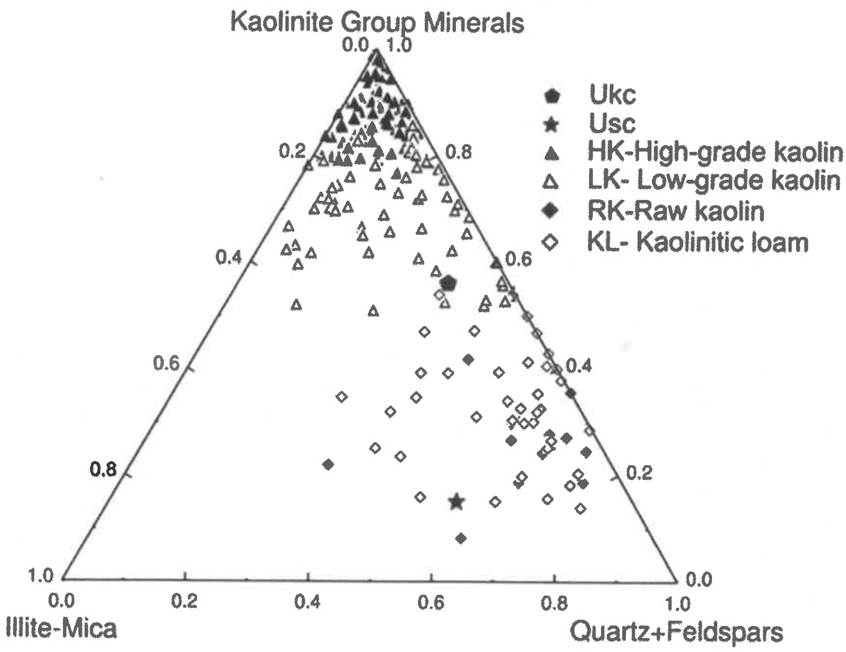


Figure 4.2. Ukc and Usc locations in mineralogical composition of light-firing clays for ceramic tiles (Dondi et al., 2014).

Chemical compositions of Ukc sample are compatible with the other commercial raw materials suitable for earthenware, tableware, brick and tile and floor tile (Clay**) except the raw material from Bilecik-Söğüt (Clay***) highly used in tile production (DPT, 2001) (Table 4.1.). On the other hand, the major oxide compositions of Usc sample is very consistent with raw material from Bilecik-Söğüt (Clay***) (Table 4.1.). Additionally, Fe_2O_3 values of both Ukc and Usc samples were lower than those of the other commercial raw materials of ball clay for tableware, commercial clays for floor tile (DPT, 2001) and raw materials for brick and tile (Arkun, 1980). The low amount of Fe_2O_3 allows the ceramics products to remain in white color (Dondi et al., 2014). Compatible with the other raw materials, relatively high amount of Al_2O_3 is related with the presence of kaolinite and illite in the mineralogical compositions of both samples (Murray, 2007). The bulk density value of Ukc (1.47 g/cm^3) at 1100 °C is lower than Usc (1.66 g/cm^3). Mechanical strength of the ceramic raw materials increases with bulk density (Ngun et al., 2011; Lee and Yeh, 2008), additionally bulk density remarkably increases over 1100 °C (Ngun et al., 2011; Lee and Yeh, 2008). The bulk density values of Ukc and Usc at 1100 °C are almost compatible the commercial raw materials at relatively high temperatures (1170 °C) for earthenware and tableware (Table 4.2.).

The water absorption of Ukc (24.27 %) is higher than Usc (14.75 %) at 1100 °C. In the study of Cengiz and Kuşcu (2010), limited values of water absorption are reported as between 8%-18%, dry and firing shrinkage values $\leq$ 10 at max 1100 °C and plasticity water of 25-35%, hardness 3 at 1000°C for bricks and tiles. Regarding these values, Usc is said to be mostly suitable for brick and tiles (Table 4.2.). On Winkler's diagram (Figure 4.3.), it was also classified as suitable for brick production. The measured Moh's hardnesses of both Ukc and Usc were also 2 between 800 – 1000 °C and becomes 3 at 1100 °C. With respect to the firing shrinkage values of the studied samples, that of Ukc (6.56 % at 1300 °C) matches well with the commercial raw materials for fine and rough ceramics (DPT, 2001) (Table 4.2). In this context, the firing shrinkage values of Usc at 1150 °C and 1300 °C are highly compatible with the typical kaolins (DPT, 2001) (Table 4.2).

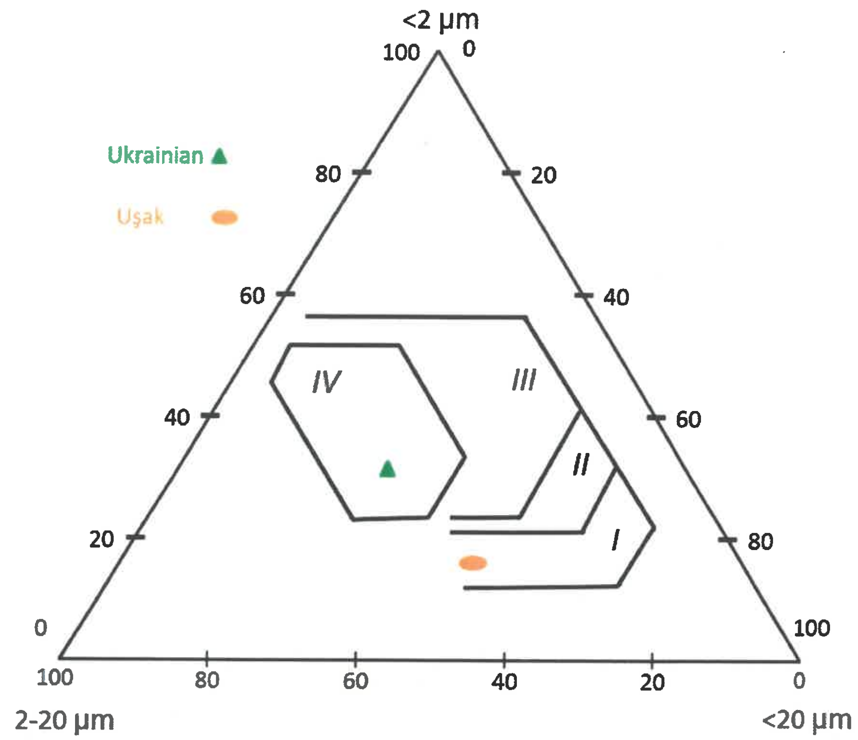


Figure 4.3. Grain size classification of Ukc and Usc on Winkler's diagram (developed by Nyakairu et al., 2002). Fields indicate: (I) common bricks, (II) vertically perforated bricks, (III) roofing tiles and masonry bricks, and (IV) hollow products.

Table 4.1. Comparison of Ukc and Usc with other standard values of raw materials (DPT, 2001; Arkun, 1980; Dondi et al., 2001) used in ceramic industry.

Component	Unit	Research samples		M. Dondi et al. 2001 Earthenware tableware		DPT, 2001 Tableware	Arkun, 1980 Brick and Tile	DPT, 2001 Floor tile	
		Ukrainian clay	Uşak clay	TF0	TF2	Ball clay*	Limit values	Clay**	Clay***
SiO_2	% mass	63,4	73,2	66,2	64,8	66	42 - 64	62	74,5
TiO_2	% mass	0,5	0,1	0,3	0,3	1,6	-	1	0,6
Al_2O_3	% mass	24	15	18,7	19	28	15 - 20	23	15
Fe_2O_3 total	% mass	0,3	1,2	0,5	0,6	1,2	2,8 - 7	2	2,5
MgO	% mass	0,2	0,8	0,2	0,2	0,5	0,8-6,2	0,9	0,5
CaO	% mass	1,8	1,4	3	3	0,2	0,7 - 9,5	0,5	0,3
Na_2O	% mass	0,1	0,1	0,1	0,1	0,2	0-6	0,3	0,3
K_2O	% mass	0,9	3,1	0,8	0,8	2,2	0,6 - 1,7	2,5	1
L.o.I.	% mass	8,37	4,27	10	10,5	-	6,3-11,5	7,5	5,5

Note: (* Ball clay in Gemany), (** Clay from Şile, Istanbul), (*** Clay from Bilecik-Söğüt).

Table 4.2. Comparison on the technological properties of Ukc and Usc with commercial clays in ceramic industry in ceramic industry.

Component	Unit	This work		Dondi et al. 2001		DPT, 2001			
		Ukrainian clay	Uşak clay	Earthenware tableware		Clay1**	Clay2**	Clay3**	Kaolin*
				TF0	TF2				
Drying shrinkage	% mass	3,36	4,11	-	-	5-8	6	-	-
Firing shrinkage	% mass	4,49 (1150°C)	5,43 (1150°C)	0,9 (1170°C)	1,4 (1170°C)	-	-	-	5,5-9 (1180°C)
		6,56 (1300°C)	11,89 (1300°C)	-	-	3-4 (1350°C)	5-6 (1350°C)	5-6 (1350°C)	8-14 (1280°C)
Water absorption	mass	24,27 (1100°C)	14,75 (1100°C)	-	-	-	-	-	15-19,6 (1180°C)
Firing color (1300°C)	% mass	dirty white	beginning of melting	-	-	White	Cream	White-Cream	-
Color values	% mass	94,16 (1150°C)	80,18 (1150°C)	-	-		-	-	88-92 (1180°C)
Bulk density	g/cm^3	1,47 (1100°C)	1,66 (1100°C)	1,74 (1170°C)	1,75 (1170°C)	-	-	-	-
Plastic limit	% mass	23,15	20,18			36	30-40	-	-

*Typical Kaolins used in manufacture of ceramic products over the world (DPT, 2001).

** Accepted standard clays used in fine ceramics (Clay1), rough ceramics (Clay2) and floor tile (Clay3)

5. DISCUSSION

High amount of SiO_2 and Al_2O_3 are related to presence of illite especially kaolinite (Murray, 2007) in Ukc and Usc. Al_2O_3 is one of the most important oxides for the ceramic industry which provide raw materials remain in white color after firing (Dondi et al., 2014; Çelik, 2010). But it dosen't mean that only Al_2O_3 is a factor to affect color change. Also, Fe_2O_3 are responsible in coloration (Dondi et al., 2014; Çelik, 2010) as well as CaO, MgO, MnO and TiO_2 (Kreimeyer, 1987) and temperature of firing all have significant effects in variation on the color of fired bodies. Less amount of Fe_2O_3 and high Al_2O_3 were the main reasons of Ukc to be determined whiter than Usc. The ternary diagram (Figure 4.1) also showed that Ukc belogs to white stoneware for German and English whereas Usc falls in area near white stoneware for German. On the other hand, due to amount of Fe_2O_3, Murray (2007) classified that if the clay contains Fe_2O_3 amount between 1-5%, it is accepted as tan-burning clays and if the amunt of Fe_2O_3 is less than 1 percentage, this clays are called white firing clays. Values of Fe_2O_3 are clearly seen in Table 3.1. This analysis allows Ukc to be considered as white firing clays, however Usc is considered as tan-burning clays. Furthermore, amount of Fe_2O_3 between 0-3% is considered as light-firing bodies that Ukc and Usc contain Fe_2O_3 oxides within this range. The amount of alkaline oxides (K_2O and Na_2O) are low (1%) in Ukc sample represented by the low amount of illite, while they are relatively higher (3%) in Usc sample confirming relatively higher amount of illite in the compositions (Table 3.1). K_2O, Na_2O and Fe_2O_3 act as flux materials during heating (Dondi et al., 1999; Çelik, 2010; Mefire et al., 2016). Considering the total amount of flux oxides in Usc (Table 3.1), it helps to understand why Usc was followed with melting as starting from 1300°C (Table 3.3). For both samples, very low amounts of CaO and MgO (2% for Ukc and 2.2% for Usc samples) indicate the very low amounts of dolomite in their compositions. $CaCO_3$ coarse grains were found under 3%. Because high amount of $CaCO_3$ coarse grains can cause cracking of bodies in high temperatures. On the other hand, $CaCO_3$ creates calcification process in kilns which developes volume of fired bodies.

Although, plasticity of Ukc was determined more than Usc, the total linear shrinkage of Usc was found in higher amounts than Ukc. This is may be related with proportion of illite in Usc which is more swelling mineral than kaolinite. Because, plastic limit of illite is considered between 35–60%, while plastic limit of kaolinite is in range of 25–40% (Mitchell, 1993). Moreover, water absorption and porosity are followed being high numbers in the products made by raw materials including high amount of limestone that decreases quality of raw materials (TS 4790, 1986). The water absorption of Ukc was observed with very high differences to compare with Usc. The water absorptions of both samples strated to develope after 1000°C. Athough, both samples had high water absorption values, Milheiro et al. (2005) limits the values of water absorption as <25% for brick and >20% for roof tile. Furthermore, Dondi et al. (2014) divides tiles into 5 groups as body type according ISO 13006 standards. With respect to these 5 groups, a raw material with water absorption >10% is suitable for porous tiles. This classification presents that both Ukc and Usc with high water absorption and low bending strength values can be used for porous tiles. In the study of Cengiz and Kuşcu (2010), limited values of water absorption 8%-18%, dry and firing shrinkage values ≤ 10 at max 1100 °C and plasticity water 25-35%, hardness 3 at 1000°C for tiles are reported. Regarding these standards values, Usc is said to be suitable for tiles. As another notable issue, Ukc was found more plastic (Figure 3.7), interestingly Usc showed higher total linear shrinkage. Remarkable rises were seen in total linaea rshrinkage of Usc above 1000°C while there was minor changing at 1150°C. At the same temperature, bending strength of Usc went down suddenly that may be connected with occurrence of high porosities within fired body (Dondi et al., 2001) In any case, Usc illustrated excellent bending strength properties in comparison with Ukc. As all the technological properties, bending strength of Usc also started to develope after 1000°C that aggrees with exothermic peak of new phase formations at 1004°C and 1040°C in DTA-TG graph (Figure 3.4b). Considering values of Ukc at 1100°C in Figure 3.8, Figure 3.9, Figure 3.11, it should not be hard to summarize that lowest mechanical strength is the reason of highest water absorption and lowest unit volume mass at same temperature. In Figure 4.2, Usc was classified as RK and KL type of clays (Dondi et al., 2014) which shows possiblity of Usc to be used as a sort of raw material for ceramics due to the presence of quartz, kaolinite and flux materials. However, it was suggested to use this type of clays as a raw material of tile, if it is too economical. In addition to the usage area, Usc can be also considered as versatile raw material which is able to address for vitrified bodies up to 20–25% (Dondi et al., 2014). Usc sample, due to its melting behaviour at 1430 °C, is not categorized as a refractory, however, the kaolinite-dominated Ukc sample with its melting point at about 1850°C clearly points its refractory property (Murray, 2007).

6. CONCLUSION

Mineralogical, physico-chemical and technological properties of Uşak and Ukrainian clays were investigated in this study to reveal their suitability as ceramic raw materials. The first basic differentiation between the materials evaluated in this study appears to be related with their mineralogical compositions as kaolinite-dominated Ukrainian clay sample (Ukc) and Uşak clay sample (Usc). Using all the data, it is concluded that:

- The presence of low Fe_2O_3 and abundance of Al_2O_3 in Usc and Ukc provides white color after firing.
- The amount of higher fluxing oxides and less fire-resistant minerals were suggested to be the reason of being melted for Usc at 1300 °C.
- The new phase formations at 1004°C and 1040°C on DTA-TG curves explain remarkable developments in technological properties of Usc after 1000 °C.
- The reason of Usc to show higher total linear shrinkage values is because of higher illite amount in Usc.
- The low mechanical strength values of Ukc have resulted from the high porosity of fired body which also cause higher water absorption in Ukc.
- In terms of atterberg limits and particle size distribution, Ukc sample is more plastic and finer than Usc sample.
- On the other hand, the water absorption and bending strength values of Usc are relatively more favourable for the ceramics than those of Ukc.
- Nevertheless, in terms of color and refractoriness, both of which increases the quality of the raw material for the ceramics, Ukc sample is more suitable than Usc sample.

- Chemically, Ukc sample looks more favourable than Usc sample to be used as a raw material in production of tile, white stoneware, earthenware and tableware.
- The low amount of clay size materials in Usc creates a need to gather an extra grinding for coarser fraction.
- Because of poor plasticity and high amount of SiO_2, Usc can be used to reduce plasticity as well as viscosity in the slip casting applied ceramics.
- On the other hand, firing color of Usc was determined as white that make possible to use it in light color required ceramics.
- Because the melting started at 1300°C, Usc is not categorized as a refractory.
- However, this property brings an important economical qualification for Usc to develop technological characters at less firing temperature.

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EDUCATION AND TRAINING

01/2015- **Master of Science in Geological Engineering**

Graduate School of Natural and Applied Sciences, Mugla Sitki Kocman University, Mugla, Turkey

09/2007-05/2011 **Bachelor of Science in Department of Applied Geochemistry, Petrology and Mineralogy**

Baku State University, Baku, Azerbaijan

PERSONAL SKILLS

Mother tongue: Azerbaijan

Other language(s)

	UNDERSTANDING		SPEAKING		WRITING
	Listening	Reading	Spoken interaction	Spoken production	
English	C2	C2	C2	C2	C2
	I studied my profession in English at Mugla Sitki Kocman University				
Russian	A2	A2	A1	A1	A2
Turkish	C2	C2	C2	C2	C2

Levels: A1/A2: Basic user - B1/B2: Independent user - C1/C2 Proficient user
Common European Framework of Reference for Languages

Computer and program skills

- **Windows XP/7, MS Office 2003 – 2016**
- **ArcGIS**
- **CorelDRAW X7**

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PERSONAL SKILLS

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	I studied my profession in English at Mugla Sitki Kocman University				
Russian	A2	A2	A1	A1	A2
Turkish	C2	C2	C2	C2	C2

Levels: A1/A2: Basic user - B1/B2: Independent user - C1/C2 Proficient user
Common European Framework of Reference for Languages

Computer and program skills

- **Windows XP/7, MS Office 2003 – 2016**
- **ArcGIS**
- **CorelDRAW X7**

- **TERMA Radar and AIS (Automatic Identification System): for maritime Surveillance**

Experience on instruments

- **X-ray diffraction (Panalytical Expert Pro diffractometer)**
- **Scanning Electron Microscopy (SEM, JEOL JSM-7600F) X-ray spectrometry (EDS) (Oxford Instruments)**
- **Thermo ARL X-ray Fluorescence**
- **Fourier-transform infrared spectroscopy (FTIR)**
- **Thermal gravimetric-Differential thermal analysis (TG -DTA Rigaku Thermoflex TG 8110)**
- **Determination of Cation Exchange Capacity of Clayey soil by Methylene Blue**
  click the link: https://www.youtube.com/watch?v=Ged3vVJZUgs
- **Specific gravity analysis**
- **Plastic Limit and Liquid Limit of soils**
- **Ceramic raw materials Technological tests (water absorption, total linear shrinkage, bulk density, compressive and bending strengths)**
- **Hydrometer analysis**
  click the link: https://www.youtube.com/watch?v=X-kLxiJVh64

Publications

- **Aghayev, T.** and Küçükuysal, C., (under review). Ceramic properties of Uşak Clay in comparison with Ukrainian Clay. *Clay Minerals.*

- **Aghayev, T.** and Küçükuysal, C., 2017 Mineralogical, fiziko-chemical and technological characterisation of Uşak clay. *17th National Clay Symposium, Abstract Book*

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Scientific Research Projects

Mineralogical, Micromorphological, Geochemical and Isotopic Characteristics of Neogen Lacustrine Sediments in Çameli Basin (Denizli, Gb Turkey).

Ceren Küçükuysal, Tural Aghayev, Merve Gülcan, 2015
Scientific Research Project Office(No:15/079) of Mugla Sitki Kocman University

Evaluation of Uşak clay as ceramic raw materials and comparison with Ukrainian clay.

Ceren Küçükuysal, Tural Aghayev, 2015
Scientific Research Project Office(No:15/195) of Mugla Sitki Kocman University

Red Mediterranean Soils (Terra Rossa) in Muğla Polje: Mineralogical, Micromorphological, Geochemical and Pedological Characteristics

Ceren Küçükuysal, Murat Gül, Tural Aghayev, Merve Gülcan, 2016

TUBITAK Project no: 116Y027

ADDITIONAL INFORMATION

Honours and awards

- Azerbaijan Republic Scholarship for Candidates that Got High Score in TQDK.
- XVI International Clay Conference Grant,
- The Scholarship student at Project no: 116Y027 of Scientific and Technological Research Council of Turkey.
- D category Grant of Azerbaijan Youth Foundation under The President of Republic of Azerbaijan.

Memberships

- Earth Sciences Society
- Azerbaijan Society of Petroleum Geologists

Certifications

- Ceramic Raw Materials Technological tests (*water absorption, total linear shrinkage, bulk density, compressive and bending strengths*) (General Directorate of Mineral Research and Exploration)
- Fourier-transform infrared spectroscopy (General Directorate of Mineral Research and Exploration)
  The 1st International Oil and Gas Summer School in Baku Azerbaijan

References

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