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Geotechnical, Chemical and Structural Characterization of Waste Clay from Boron Production

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Abstract

Turkey has 72% of the world's boron reserves and takes the first place with a reserve of 1.8 million tons. Each year 600,000 tons of waste clay results from boron production. For that reason, there is a growing interest to develop novel products based on this kind of waste. In this study, geotechnical, chemical and structural characterization of waste clays from boron enterprises was performed to investigate the potential use in landfills. For this purpose, waste clay was obtained from Eskişehir Kırka Boron Works and it was characterized by using geotechnical analyses (water content, specific weight, liquid limit, plastic limit, standard proctor compaction test, unconfined compressive strength tests, sieve analysis, hydrometer test, hydraulic conductivity), chemical and structural analyses (cation exchange capacity (CEC), XRF, ICP-MS, XRD, SEM, FT-IR). According to the results, the waste clay has a water content of 39.2% and a specific weight of 2.77 g/cm^3. According to liquid limit (58%) and plastic limit (30%) values, plasticity index was calculated as 28%. Standard proctor compaction test showed that the most effective compression ratio was obtained at the optimum water content of 33%. The unconfined compressive strength was 2.16 kg/cm^2, the swelling potential was 10.4% and the permeability constant was obtained as 3.5×10^{-11} m/s at 33% water content. Soil classification was performed according to the results of sieve analysis, hydrometer test, liquid and plastic limit tests and it was determined as to be high-plasticity clay (CH). Cation exchange capacity of the clay was 55 meq /100 g waste clay. BET analysis showed that the specific surface area of the clay is 5.12±0.1 m^2/g. The results of XRD, XRF, ICP-MS and FT-IR analyses prove that the waste clay is mostly composed of dolomite, magnesium oxide, tincal and quartz. These characterization data will form a background for further studies regarding to potential uses of the waste clay in solid waste landfill sites.

Keywords: Boron, impermeable layer, solid waste landfill, waste clay

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Introduction

Boron minerals have a strategic importance due to they are used in the manufacture of a variety of industrial products including glass, ceramic, textile, detergent, metallurgical and fire-retardant materials. Turkey has 72% of the world's boron reserves and takes the first place with a reserve of 1.8 million tons. Eskisehir Kırka Boron Works has the biggest boron reserve in Turkey. Eti Mine Works has 41% of the world's boron production. On the other hand, 900,000 tons boron derivative wastes are generated during the 1 million tons borax pentahydrate ($Na_2B_4O_7.5\ H_2O$) production (Boron Sector Report, 2010). There have been so many studies related with the utilization of these wastes in ceramic, cement and brick production. In this study, different from other studies, it was aimed to perform the geotechnical, chemical and structural characterization of waste clay from boron production in order to investigate the potential use in solid waste landfills.

Annually, 27 million tons of municipal solid wastes are generated in Turkey and there are only 69 numbers of landfills in 2014. The impermeable liner that is used for new landfills must have sufficient quality in terms of physical, chemical, mechanical and hydraulic to protect soil and ground water. Synthetic clays are also used in the case of natural clay is not available but this situation increases the costs. Consequently, in case of the wastes generated in Kırka Boron Mines will be used as an impermeable liner in landfills it would be beneficial from the economical aspect by recovery of a waste material.

In this study, geotechnical analyses (water content, specific weight, liquid limit, plastic limit, standard proctor compaction test, unconfined compressive strength tests, sieve analysis, hydrometer test, hydraulic conductivity), chemical and structural analyses (cation exchange capacity (CEC), XRF, ICP-MS, XRD, SEM, FT-IR) were carried out to determine the characteristic of the waste clay supplied from Eskisehir Kırka Boron Mines.

Materials and Methods

The waste clay samples used in this study were taken from Kırka Boron Mine Works. These as-received samples were dried in a drying oven at 105°C and were grounded to obtain homogeneous test samples. Characterization of the test samples were grouped into two sections as geotechnical and chemical and structural analyses.

Geotechnical Analyses

The geotechnical analyses were carried out according to the methods given in Table 1.

Table 1. *Analysis Methods applied on Waste Clay*

Analysis	Method
Water content	ASTM D 4643-08
Specific weight	ASTM D 854-10
Liquid limit	ASTM D 4318-10
Plastic limit	ASTM D 4318-10
Standard proctor compaction test	ASTM D 698-12
Unconfined compressive strength	ASTM D 2166-13
Sieve analysis	ASTM D 422-63
Hydrometer test	ASTM D 422-63
Hydraulic conductivity	ASTM D 5856-95
Swelling potential	ASTM D 4546-08

Chemical and Structural Analyses

CEC capacity of the waste clay was determined according to the EPA method 9081. ICP-MS analysis was performed to determine the elements in the waste clay according to EPA Method 200.8 via Agilent 8800 ICP-MS/MS. As a preparation step for the analysis, the sample was digested by Mileston Start D Microwave Digestion System microwave according to EPA Method 3051B. XRD analysis was performed in order to examine the mineralogical character of the waste clay. Rigaku Rint 2200 XRD Analyzer was used with 5°-80° and at a rate of 0.2˚/min for this aim. XRF analysis was performed in order to determine the chemical analysis of the waste clay via Rigaku ZSX Primus equipment. SEM analysis provides examination of the sample surface to nanometric scales. Zeiss SUPRA 50VP Scanning Electron Microscope was used for the analysis. As a preparation step, the sample was covered with gold for 40 seconds with presence of argon gas in order to prevent electrical load.

FT-IR analysis of the waste clay was performed via Perkin Elmer Spectrum 100 FT-IR, at the wavelength of 4000-400 cm^{-1}. The analysis sample was prepared as KBr-clay pellets with a clay content of 0.01%. Spectrum is sketched against a KBr pellet. BET analysis was performed via Quantochrome Autosorb 1-C BET instrument. The sample was prepared for the analysis by degassing at 300˚C for 17 hours.

Results and Disussion

Geotechnical Properties of the Waste Clay

According to the applied tests results, the waste clay has a water content of 39.2 % and a specific weight of 2.77 g/cm^3. Plasticity properties of the waste clay was shown in Table 2. Plasticity index (PI) was calculated as to be 28% according to the liquid and plastic limit values. PI provides the requirement of materials that are planned to be used in municipal solid waste landfills must have a PI value smaller than 50 (Daniel and Wu, 1993).

Table 2. *Plasticity Properties of the Waste Clay*

Analysis	Value (%)
Liquid limit	58
Plastic limit	30
Plasticity index	28

The optimum water content of the waste clay was determined as to be 33% by performing the standard proctor compaction test. After then, unconfined compressive strength test was applied to the sample with optimum water content (33%). As a result, unconfined compressive strength of compacted sample was determined as to be 2.16 kg/cm^2. Suggested unconfined compressive strength for clay liners in municipal solid waste landfills is minimum 2 kg/cm^2 (Daniel and Wu, 1993). For that reason, waste clay is appropriate for using in landfills in terms of unconfined compressive strength.

Sieve analysis and hydrometer test results are used to sketch the grain size curve and percentages of gravel, sand, silt and clay which are 0%, 1.74%, 20.76% and 77.5%, respectively. According to the results, 98.26% of the sample was found that has a diameter of smaller than 0.074 mm. Thus, the waste sample can be classified as fine-grained. Sieve analysis, hydrometer test, liquid and plastic limit test results were examined together in order to determine the soil classification of the waste clay which is determined as CH (high plasticity clay).

Hydraulic conductivity was carried out falling-head permeability test. Permeability constant of the compacted sample with optimum water content (33%) was calculated as to be 3.5×10^{-11} m/s. According to the Regulation of Sanitary Landfills, the minimum allowable permeability constant (k) for municipal and hazardous waste landfills is 1×10^{-9} m/s in Turkey (Regulation of Sanitary Landfills, 2010). The permeability test results showed that waste clay sample is appropriate for using in landfills.

Swelling potential test was applied to the waste sample with optimum water content (33%). The sample was compacted for the analyses and swelling potential was determined as to be 10.4%. Gromko (1974) classified the soils which have swelling potential is smaller than 10% as low swelling degree. In this case, waste clay sample provides the requirement of materials that are planned to be used in landfills.

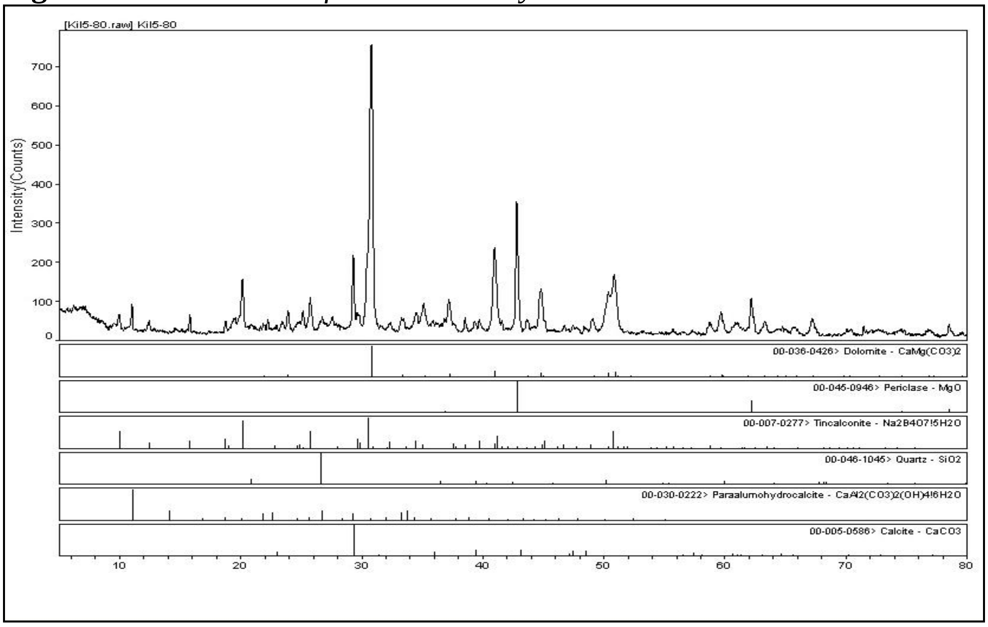
Geotechnical analyses results showed that the waste clay is appropriate for using it as a clay liner in solid waste landfill sites due to especially its unconfined compressive strength, swelling potential, PI values and permeability.

Chemical and Structural Properties of the Waste Clay

High CEC values denote the clay is able to hold more contaminants. Clay minerals have different CEC values such as 3-15 meq/100 g clay for kaolinite and 80-150 meq/100 g clay for montmorillonite (Young, 1976). CEC value of the waste clay was determined as to be 55 meq/100 g clay. This result shows that the waste clay would be more preferable than the kaolinite clay in terms of clay-organic matter interaction.

XRD spectrum of waste clay is shown in Figure 1. According to the figure, the most dominant phases observed in the XRD pattern are dolomite, magnesium oxide, tincal, quartz, para aluma hydrocalcite and calcite. The highest peak is due to presence of dolomite. Similar XRD patterns were observed for the waste clay from Kırka Boron Mine Works by other researchers (Kavas, 2005; Kurama etal., 2004; Kozulu, 2003). Additionally, Eti Mine Works Department of Research and Development has reported that dolomite amount in the waste clay may be up to 45% (Mergen et.al., 2001).

Figure 1. *XRD Pattern of the Waste Clay*



According to XRF analysis results (Table 3), the most dominant compounds in the waste clay sample are magnesium oxide, quartz and calcium oxide. Alike these results, other studies indicated that magnesium oxide, calcium oxide, quartz and aluminum oxide are the most dominant compounds in waste clay from Kırka Boron Works (Kavas, 2005; Çırak, 2010).

Table 3. *XRF Analysis Results*

Compound	Mass, %	Compound	Mass, %	Compound	Mass, %
MgO	23.29	SiO_2	16.89	CaO	16.82
Na_2O	7.76	Al_2O_3	1.99	SrO	1.00
K_2O	0.88	Fe_2O_3	0.68	SO_3	0.44
Cr_2O_3	0.11	MnO	0.03	Cl	0.03
CuO	0.02	P_2O_5	0.01	L.O.I.*	30.06

*L.O.I: Loss on Ignition

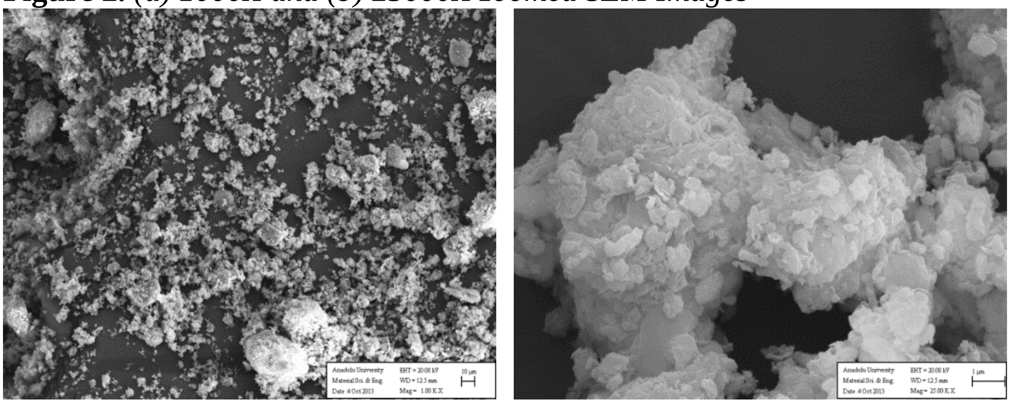
Results of the ICP-MS analysis are given in Table 4. The most dominant elements in the waste clay are magnesium, calcium, boron and sodium. ICP-MS analysis results are consistent with XRD and XRF results.

Table 4. *ICP-MS Analysis Results*

Element	Amount (g/kg)	Element	Amount (g/kg)
Mg	68.41	Li	0.93
Ca	51.98	Zn	0.52
B	35.49	Ni	0.18
Na	18.43	Ba	0.08
K	9.37	Mn	0.07
Al	6.63	Cu	0.02
Sr	5.72	As	0.02
Fe	2.11	Cr	0,01

1000X and 25000X zoomed SEM images of the waste clay are given in Figure 2. Figure 2 shows that the waste clay is formed of sheets and smaller particles. The average particle size or structure could not be determined because of the many different shaped and sized particles exist in the waste clay.

Figure 2. *(a) 1000X and (b) 25000X zoomed SEM Images*

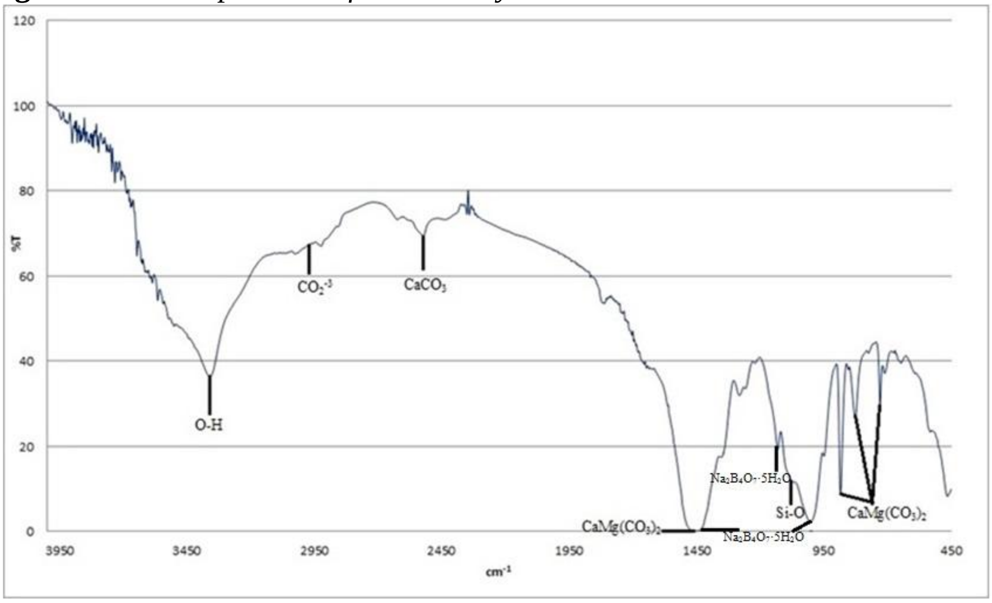


(b) (a)

Examination of the FT-IR analysis showed that the peak at 3362 cm^{-1} is related to O-H stretch which occurs because of absorbed water (Figure 3). The peak at 2526 cm^{-1} is related to O-H bonding (stretch) which shows presence of calcite (Davarcıoğlu et. al., 2005). Peaks at 3050 and 2850 cm^{-1} wavelength values are related to presence of carbonate (Ji et. al., 2009).

According to XRD, XRF and ICP-MS results dolomite was the most dominant compound in the waste clay and this is also proven by the peaks at 1450, 883, 827 and 728 cm^{-1} shown on the FT-IR spectrum (Çırak, 2010). The peaks in the intervals 1482-1426 cm^{-1} and 1130-1000 cm^{-1} are related to B-O bond which is a mark of tincal presence (Gümüs et. al., 2011, Park etal., 2004). The sharp peak at 1450 cm^{-1} is due to dolomite while the peaks at 883 and 728 cm^{-1} are also show dolomite presence by indicating the bonds between magnesium and calcium with carbon atoms (Ca-C and Mg-C) (Jarrahian et. al., 2012). Quartz presence in the clay is proven by the peak at 1058 cm^{-1} shown on the FT-IR spectrum (Yalçın et. al., 2001).

Figure 3. *FT-IR Spectrum of Waste Clay*



The results of XRD, XRF, ICP-MS and FT-IR analyses are reliable when compared to each other and all have proven that the waste clay is mostly composed of dolomite, magnesium oxide, tincal and quartz.

The specific surface area of the clay was determined to be 5.12±0.1 m^2/g. Specific surface area of clays which have dolomite as dominant compound was found as to be 2.2 m^2/g (Maček 2013). In the study of Hoşten and Çırak(2013) specific surface area of the waste white clay obtained from Kırka Boron Mine Works was indicated as to be 10.9 m^2/g in 2013.

BET analysis result of our study was different than the results of the studies mentioned above and also there were some differences about the other analyses results. This may be due to differences in the process between the date these studies were performed and present time process.

Conclusions

Both geotechnical, chemical and structural analyses have proven that the clay could be used as an impermeable liner in solid waste landfill sites. The potential of using generated boron derivative wastes (900,000 tons per 1,000,000 tons borax pentahydrate production) in sanitary landfills is promising an improvable alternative. Also the clay could be used as a geomembrane line after mixing with different materials. Further studies will be designed for using the waste clay to develop a geomembrane material.

Kırka Boron Mine Works may have applied optimization studies in the past 10 years and decreased the boron amount in the waste by recycling or by a recovery process which would definitely change analysis results. Also there are 6 different tailing ponds in the establishment, sampling may be done from different ponds. Under these circumstances, chemical and structural analyses results of the waste clay determined that the clay is appropriate to use in solid waste landfill sites due to its CEC and BET values.

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