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Use of natural zeolites as an impervious liner in sanitary landfills

Utillsation des zéolites normaux comme recouvrement imperméable en remblais sanitaires

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ABSTRACT : The purpose of this study is to investigate certain features of a novel material proposed to serve as an impervious liner in sanitary landfills. Various ratios of bentonites and zeolites (B/Z) compacted at optimum water content were tested to determine the strength parameters, permeability, pH, heavy metals and other properties. A B/Z ratio of 0.10 was found to be an ideal landfill liner material regarding its low hydraulic conductivity and high CEC. The use of B/Z mixtures as an alternative to clay liners would significantly reduce the thickness of base liner for sanitary landfills.

RÉSUMÉ : Le but de ce travail est chercher les neauvaux imperméable materiaux pour remblais sanitaires. La résistance, la permeabilité, pH, lourd metal et les autres paramètres des zéolites at bentonites (B/Z) qui ont été pressés pour différente optimum eau contenu, ont été deteminés. Idèal material proportion a été trouvé comme 0.10 pour bas hydrolique conductivité et haute CECC (change capacité de cation). A la fin de ce travil on a trouvé que l'utilisation de B/Z melange au lieue de couche argileuse va diminuer serieusement intérieure couche dans les remblais sanitaires.

1 INTRODUCTION

Municipal waste disposal sites are the potential source of soil and groundwater contamination in most industrialized countries. Leachate generated from water percolating through waste is the principal carrier of soluble and suspended contaminants in the impermeable liner. Proper management of leachate is important to minimize the risk of contamination. Properly designed durable lining and capping systems are essential for the protection of the surrounding environment. Design and construction of proper lining system is important. Reliable landfill design may significantly reduce the risk to the environment. Natural clays and sand-bentonite mixtures or senthetic materials are preferred for municipal landfill design due to its low permeability and low expense.

Compacted natural clays are often used in constructing hydraulic barriers underneath waste containment systems. Typically, the hydraulic conductivity must be less than or equal to 1×10^{-7} cm/sec for soil liners and covers used to contain hazardous waste, industrial waste and municipal waste (Danial and Benson, 1990). In the absence of impervious natural soils, compacted mixtures of bentonite and sand have been used to form barriers for liquids (Kenney et al., 1992). The mixture of sand and bentonite are one of the lowest cost technologies available for constructing an impervious liner for waste water ponds and sanitary landfills. The imperviousness of these liners can be influenced by many factors such as matrix material (bentonite, kaolinite, sand, etc.) and the amount of fines content (Marcotte et al., 1994). One important aspect of the hydraulic barriers is the cation exchange capacity (CEC) of the liner material. The most abundant clay minerals such as illite, kaolinite and chlorite have CEC values between 5 and 40 meq/100g (Grim, 1968), whereas the natural zeolites have CEC values between 200 and 400 meq/100g (Bish and Guthrie, 1994).

The objective of this paper is to present landfill liner material composed of natural zeolite and bentonite. Bentonite serves as a pore sealant yielding low hydraulic conductivity, whereas the high CEC ability of zeolite content is utilized in purifying the

Table 1. Some physico-chemical properties of natural zeolite used in the experiments.

pH	8.20
Electrical Conductivity (milliSimens/cm)	0.53
Cation Exchange Capacity (meq/100g)	165
Specific Surface Area (m^2/g)	29.9
Specific Gravity	2.63

contaminants in the leachate. Various ratios of bentonite to zeolite (B/Z) are tested to obtain the most desirable mixture ratio of this ideal liner material for waste containment structures.

2 MATERIALS

2.1 Zeolite

Zeolites are a group of basic, hydrous alumino-silicate minerals. They have an open aluminosilicate framework structure containing channels filled with water molecules and cations which are usually exchangable at temperatures below 100°C. Natural zeolites are common in saline-alkaline lake deposits, hydrothermally altered volcanic or sedimentary rocks and deep-sea sediments (Bish and Guthrie, 1994). Clinoptinolite is one of the most predominant species of sedimentary zeolite and generally occurs in association with montmorillonite (Minato, 1980). The chemical composition of clinoptinolite is given by $(NaK)_6 (Al_6Si_{30}) O_{72} 20H_2O$. Natural zeolites have CECs usually between 100 and 400 meq/100g (Grim, 1968; Bish and Guthrie, 1994). X-ray diffraction analyses of zeolite give the following components: 71.39% Si, 13.30% Al, 3.69% K, 2.74% Mg, 0.94% Fe, 0.47 Na, 0.03% P and 0.01% S. Zeolite is much like a sandy soil with a high internal friction angle and low cohesion. Some physico-chemical properties of zeolite are given in Table 1.

2.2 Na-Bentonite

Commercially powdered bentonite clay was used to improve the physical and chemical characteristics of B/Z mixtures. It was selected as the cohesive soil medium since it absorbs metals and organics . It is highly colloidal, plastic and inexpensive material.

Table 2. Some physico-chemical and index properties of Na-bentonite used in the experiments.

pH	9.5
Electrical Conductivity (millisimens/cm)	2.69
Cation Exchange Capacity (meq/100g)	90
Specific Gravity	2.60
Silt (%)	12
Clay (%)	88
Liquid Limit (%)	447
Plastic Limit (%)	60
Shrinkage Limit (%)	32

Table 3. Grain size distribution for the crushed zeolite used in the experiments.

Sieve Numbers	Percentage
#10-#20	20
#20-#40	20
#40-#60	20
#60-#100	10
#100-#200	10
<#200	20

X-ray diffraction analyses of bentonite give the following components: 59.49% Si, 18.06% Al, 0.91% K, 2.42% Mg, 4.14% Fe, 3.72% Ca, 2.50 Na and 0.10% S. Bentonite is a highly cohesive material with a small angle of internal friction of 5°. Some physico-chemical properties of bentonite are given in Table 1.

3 TESTING

Bulk zeolites were first crushed and then sieved. The grain size distribution for the crushed zeolite is given in Table 3 and it corresponds to silty sand. The mixtures of bentonite and zeolite were prepared on the basis of dry weights. The chosen bentonite/zeolite (B/Z) ratio was 0.1. First dry zeolite was mixed with distilled water and then dry bentonite was added. The conventional Standart Proctor test was employed to prepare the specimens for the strength, permeability, consolidation and leachate experiments. Optimum moisture content and maximum dry density of B/Z=0.1 mixture were 39% and 16.00 kN/m³. It could also be determined pH, electrical conductivity and heavy metal amounts of B/Z=0.1 mixture before and after leachate test.

4 EXPERIMENTAL RESULTS

4.1 Strength properties of Bentonite-Zeolite Mixtures

The unconfined compressive strength test (UCS) following the 7, 14 and 28 days curing periods was used to evaluate potential increases in strength for stabilized mixtures compared to unstabilized specimens.

The bearing capacity of the landfill is an important parameter that requires the liner material is firmed enough to sustain a static load exerted by the overlying body of waste. Mixtures with small bentonite contents may have a strong load which is supporting the micro-structure, where zeolite grains make up the micro-structure and the pores are filled by the swelling bentonite, which may provide additional strength due to excess pressure exceeding the free-swell capacity of bentonite (Kenney et al., 1992). The swelling mechanism of compacted bentonite was given by Tuncan et al. (1998). It in mixture, the bentonite content makes up the matrix and it fills up the pores between the zeolite grains as it swells.

In order to determine the strength properties of B/Z mixtures, a series of tri-axial tests were carried out. The triaxial test type is the unconsolidated-undrained test (UU). First, the mixtures were compacted at optimum water content. Small samplers were then driven into the compaction mold. Using an extruder, the sample was taken out for testing. For each sample at least three experiments were conducted. Cell pressures of 70, 175, 280 kN/m² were used. The internal friction angle and cohesion of mixtures are given in Table 4. The variation of unconfined compressive

Table 4. Shear Strength Parameters of B/Z Mixtures.

Curing Period (day)	Cohesion (kN/m²)	Internal Friction Angle (°)
Fresh	20	20
7	25	24
28	28	26
56	30	35

Table 5. Unconfined Compressive Strength values of B/Z Mixtures.

Curing Period (day)	Unit Weight (kN/m²)	UCS (kN/m²)
Fresh	17.0	87
7	17.1	128
28	17.4	133
56	17.0	160

Table 6. Permeability of B/Z Mixtures.

Curing Period (day)	kx10⁻⁸ (cm/sec)
Fresh	1.37
7	2.60
28	3.59
56	3.11

strength (UCS) values is given in Table 5. Unconfined compressive strength values of mixtures increase with curing time as expected.

4.2 Coefficient of Permeability (Hydraulic Conductivity) of Bentonite-Zeolite Mixtures

The triaxial permeability test was used to evaluate the hydraulic conductivity of the specimens. 98 Pa of cell pressure, 7 Pa of backpressure and 14 Pa of hydraulic head were applied for permeation of rain water through the specimens. The stabilized mixture's permeability may be used as a measure of its capability to physical isolation of contaminants as well as an indicator of internal movement of water.

The hydraulic conductivity (k) of mixture depends on such parameters as bentonite content, the grain size distribution of zeolite and the compaction effort of the mixture. Hydraulic conductivity tests were performed on compacted specimens in the laboratory at optimum moisture content. The triaxial permeability test was used to evaluate the hydraulic conductivity of the specimens. A 98 kPa of cell pressure, 7 kPa of back pressure and 14 kPa of hydraulic head were applied for permeation of water through the specimens. Municipal leachate and different laboratory prepared solutions were used as a permeant. The permeability test results are given in Table 6.

It can be observed that the average hydraulic conductivity of mixtures ranges from 1x10⁻⁸ to 3x10⁻⁸ cm/sec. The leachates collected from permeability apparatus test of different samples has different pHs after leachate test. These leachates were collected after 24 hours steady water permeation through the saturated matrix of each sample. In literature, coefficient of permeabilities for sanitary landfills in France, in Germany and the United states are 10⁻⁶ cm/sec (Street,1994), 10⁻¹⁰ cm/sec (Street, 1994) and 10⁻⁸-10⁻¹⁰ (Carol et al., 1992), respectively.

4.3 Leachate Test

Sanitary leachate was used as a permeant in order to simulate the natural environment. The leachate test was conducted to estimate the contamination of soil under the sub-base. Specimens were a height of 11.5 cm and a diameter of 10 cm. First, 7 Pa of back pressure and 14 Pa of hydraulic head were applied to the specimen in the triaxial permeability test apparatus until the saturation was completed. Then, all drainage to and from the specimen was closed so that drainage from the specimen did not occur. After that, leachates were collected (30 ml) after 24 hours to analyze for total metals, pH and electrical conductivity. Next, all drainage to and from the specimen was again closed so that drainage from the specimen did not occur. Finally, leachates were col-

Table 7. Allowable total metal concentrations in sanitary leachate water and soil.

	Pb	Ni	Zn	Cu	Cr
Leachate (mg/l)	5.0	<1.0	---	<5.0	5.0
Soil (mg/kg)	100	100	300	100	100

Table 8. Total metal concentration, pH and electrical conductivity of sanitary leachate and B/Z mixture.

	Ni	Zn	Cu	pH	EC (mS/cm)
Leachate (mg/l)	0.18	0.42	0.03	6.71	2.33
Fresh	0.14	0.01	0.03	8.24	3.11
7 Day	0.47	0.05	0.04	8.42	3.20

Table 9. pH, electirical conductivity and cation exchange capacity of B/Z mixture after leachate test.

B/Z Mixture	EC (mS/cm)	pH	CEC (meq/100g)
Fresh	0.88	8.68	103
7 Day	0.72	8.85	101

Table 10. Total metal concentrations B/Z mixtures after leachate test.

B/Z Mixture	Pb	Ni	Zn	Cu	Cr	Mo	Co
Fresh	43.3	9.0	26.3	4.1	0.1	2.0	2.3
7-Day	40.5	5.7	26.0	2.9	0.1	2.0	2.3

lected after 48 and 72 hours and the same procedure was applied to them.

One of the best indicators of the stabilization efficiency is the result of a leaching test on the stabilized mixture. Leachate is the major long-term concern in the stabilization of wastes. Leaching can be defined as the process by which a component of waste is transported mechanically or chemically into solution from the S/S matrix by the passage of a solvent such as water (Poon 1989). The leachability of metals was reduced at a high pH between 9 and 10 due to the formation of insoluble hydroxides or the adsorption phenomena (van der Sloot et al. 1989). Allowable total metal concentrations in leachate and waste water disposed in soil are given in Table 7. Total metal concentration, pH and electrical conductivity of sanitary leachate and B/Z mixture are given in Table 8.

4.4 Electrical Conductivity, pH and Cation Exchange Capacity

The pH of specimens was measured by a pH meter (Cole Parmer 39000-50). Twenty grams of air dried (20±3°C) specimens were sieved at No. 40, homogeneously mixed with 50 ml distilled water and then left for 1 hour to determine the pH of mixtures according to EPA Method 9045 (Test 1986). Accumulation and migration of salt were measured by a conductivity meter (Omega CDB-70). Approximately two hundred and fifty grams of air dried (20±3°C) specimens were sieved at No. 16, homogeneously mixed with distilled water to make a pasty mixture and then left for 24 hours to determine the electrical conductivity (EC) of mixtures (Wilcox 1946; Karakouzian et al. 1996). The extent of the accumulation and migration of salt measured by electrical conductivity is strongly influenced by climate. Sites located in arid areas have the highest EC values in the surface soil ranging from 3 to 10 milisimens/cm, whereas sites locates in humid areas typically had EC values less than 1 milisimens/cm (Ryan et al. 1983).

CEC is an important parameter the attenuation of leachate through a clay liner. If the CEC of a clay liner is high, more contaminants is removed from the leachate. Removal of the contaminants in leachate usually requires thick clay liner buit under the landfill. Sodium saturation method was used to determine the CEC of mixtures (Chapman, 1965).

Cation exchange capacity (CEC) was determined by sodium saturation method (Chapman 1965). First, four grams of specimens sieved at No.100 were saturated with 100 ml sodium acetate (NaOAc) to replace the exchangeable cations. Second, specimens were washed with 100 ml isoprophyl alcohol (CH₃CH(OH)CH₃) to remove the excess saturating salt. Third, specimens were washed with 100 ml ammonium acetate (NH₄OAc) which released the absorbed sodium back into the solution. The amount of sodium was determined by an atomic absorption spectrophotometer (AAS) (Perkin Elmer AAS 3110). All CEC measurements were made at pH 7 solution of the specimens. The pH was controlled by pH meter (Cole Parmer 39000-50) using either sodium hydroxide (NaOH) or acetic acid (C₂H₄O₂). The CEC refers to the total amount of cations which are held exchangeably by a unit mass or a weight of soil

(meq/100gr soil). The CEC of a soil depends on its clay, humus and organic matter content. The CEC is an indication of the relative capacity of a soil to retain metal ions (API 1983). Electrical conductivity, pH and cation exchange capacity of B/Z mixture after leachate test are given in Table 9.

4.5 Total Metal Content

Stabilized and unstabilized specimens were dried at 105°C for 24 hours and ground to pass through a No. 100 sieve. Ten grams of the specimens were then digested in 3:1 concentrated nitric acid and hydrochloric acid mixture for 2 hours at 80°C. The diluted digests were then filtered through a 0.2 mm cellulose nitrate filter (Harding and Goyette 1989). Copper, zinc, chromium, cadmium, nickel and lead were determined by AAS. Barium was determined by an inductively coupled plasma (ICP) spectroscopy (Schmadzu 1000-II, Sequential type). All metal analyses were performed in the laboratory.

The control of pH is necessary for metal stabilization in most S/S systems. Heavy metals can precipitate as hydroxides at pH values, generally between 9 to 11 (Lanouette 1977). High pH is desirable because metal hydroxides have minimum solubility in the pH range between 7.5 and 11 (Connor 1990). The solubility of chromium, zinc, nickel and lead is minimal in the pH range between 7.5 and 9. Solubility increases rapidly above pH 9 (Connor 1990). The soil pH should be maintained between 6 and 8 to minimize the immobilization and degradation processes (API 1983). Metals such as arsenic, barium, cadmium, chromium, cobalt, copper, lead, mercury, molybdenum, nickel, zinc and vanadium are toxic metals according to federal or state agencies in the USA (API 1983).

Total metal concentrations of B/Z mixtures after leachate test period are given in Table 10. Total heavy metal values after leachate test of B/Z mixtures are lower than allowable limits.
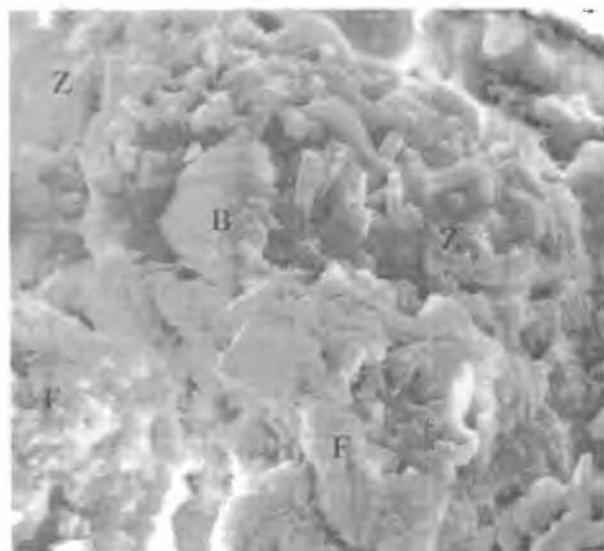
4.6 Scanning Electron Microscopy

Undisturbed specimens were prepared for scanning electron microscopy (SEM) analysis. Specimens were examined for microstructure (fabric) by SEM and for chemical composition by the energy dispersive x-ray (EDX) technique using a LEO 440 model scanning electron microscope. The SEM specimens were prepared by critical point drying technique as outlined by Bennett et al. (1977). They were initially treated with acetone and a critical point drying apparatus was utilized to replace the acetone with CO₂. Specimens were held on an aluminum sample holder with adhesive type. Later, they were coated with gold to minimize charge build up and examined under the SEM. Specimens were then scanned for chemical composition using EDX.

The scanning electron microscope is an ideal tool to observe the features of the fabric of soil. Soil microstructure is a function of the fabric and the physico-chemistry of the soil-waste-additive system. Microstructural units are not only composed of single particles but also compounds particles held together by physicochemical forces. Compounds particles are domains, aggregates, agglomerates, flocculates and organic compounds. Physicochemical forces are responsible for aggregating clay particles and holding them together.
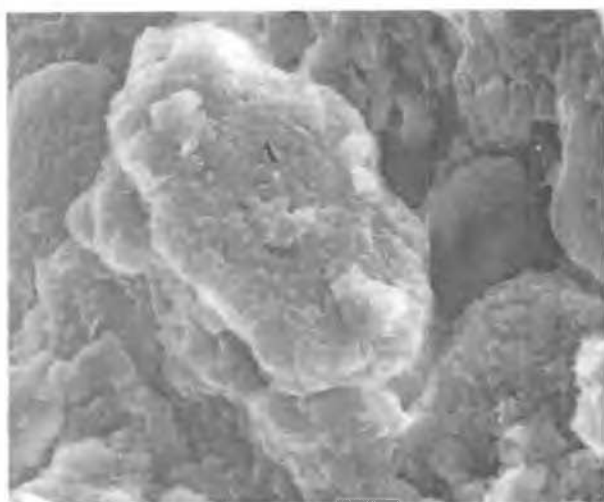
(a)

(b)

Figure 2. The SEM micrograph of bentonite/zeolite mixture. (a) Magnification x 2000, (b) Magnification x 1500 (B:bentonite, Z:zeolite, A:agglomerated structures, F:flocculated structures)

The scanning electron micrographs of B/Z mixtures are given in Figures 1 (a) and 1 (b). Flocculated and agglomerated structures can be seen from these Figures. When the zeolite is mixed with water, agglomerated structure can be formed. After adding bentonite to the zeolite, the agglomerated structures are cemented and bounded. After 7-day curing period, unconfmed compressive strength values of B/Z mixtures were doubled compared to fresh specimen. This is due to the flocculated, agglomerated and cemented structure.

5 CONCLUSIONS

Laboratory test results show that zeolite can be used as an impervious liner for the sanitary landfill. The bentonite-zeolite mixture proposed in this study should serve not only as a hydraulic barrier, but also as chemical filter. Cation exchange capacity of zeolite is very high compared to the bentonite. Therefore, heavy metals can be hold by the zeolite. B/Z mixture can also be used as a foundation of sanitary landfill.

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