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Stabilization and solidification a clay soil contaminated with MTBE

Abstract:

This paper presents an investigation into stabilization and solidification of a clay soil contaminated with MTBE (Methyl Butyl Ether) using two different agents (cement and mixture of bentonite and cement) through a program of laboratory experiments. The samples were prepared in two stages. In the first stage they were prepared with 20 and 30% cement but in the second stage they were prepared with 20 and 30% mixtures of bentonite and cement (with ratios of bentonite to cement equal to 1:1 and 3:1). Unconfined compression tests (UCT) and leaching tests using GC (Gas Chromatography) apparatus were conducted on the samples that were prepared in the above two stages at different curing times. The results show that by using cement, the strength of the soil is increased. The results of the leaching tests on contaminated soil show a major reduction in the concentration of MTBE. Adding cement to contaminated soil causes reduction in concentration of MTBE but by increasing the curing time the concentration of MTBE is increased. It is also indicted that using combination of bentonite and cement leads to reduction in MTBE concentration and the amount of reduction is decreased by increasing the curing time. The bentonite-cement ratio of 3:1 is more effective than 1:1 in reducing the concentration of MTBE.

Keywords: Contaminated soil, MTBE, Cement, Bentonite, Leaching test. Unconfined compression test, Curing time

Introduction

Stabilization/solidification (S/S) methods, sometimes called immobilization methods, change the physical state of a contaminated material, for example by solidifying a contaminated sludge, sediment or clay. In addition, chemical stabilization can reduce the availability of contaminant within a solid product of low permeability.

Currently, the stabilization/solidification systems can be classified according to the main stabilizing agent added. They can be based on cement/lime, pozzolona, silicate, thermoplastic or polymer systems. Stabilization and solidification is regard as an established technology for treating inorganic contaminants (Bishop, 1990 and USEPA, 1991). Sometimes the main stabilizing agent (lime, cement, etc.) may not be effective for immobilization of different organic contaminants. In order to increase the effect of S/S in such conditions a combination of main agent (lime, cement) with another binder can be considered. Pollard et al. (1991), Vipulanandan (1995) and Sora et al. (2002) indicated that organic compounds tend to have a detrimental effect on the properties of cementitious materials. Sora et al. (2002) showed inadequacy of cement to immobilize 2-mono chloro aniline (2-MCA) in contaminated soil. They showed a maximum of about 75% of 2-MCA was released in the leachate solution which indicates that the treatment is not suitable for the compound without using any adsorbent. Studies on the use of S/S methods with organic contaminants are comparatively less extensive than inorganic contamination (Sora et al., 2002 and Yilmaz et al., 2003). A possible technique for increasing the effectiveness of S/S for organic contaminants is to use another binder with

the main binder. In this way, the sorption of organic compound is increased and immobilization is improved, preventing their detrimental effects on binder hydration (Leonard and Stegemann, 2010).

Bentonite is one of the most efficient adsorbing agents for sorption of organic compounds (Cavalcante et al., 2005 and Belarbi and Al-Malack, 2010). Although cement-based S/S is a widely applied and well-established technique for the immobilization of organic hazardous constituents (Karamalidis and Voudrias, 2007) but S/S technology has run into difficulties when trying to solidify organic waste (Vipulanandan, 1995 and Ouki and Hills, 2002). Some researchers such as Botta et al. (2004) used organic clays for S/S of 2-chloroaniline. Most of the current research efforts in this area focus on organophilic clays which are formed by exchanging the naturally occurring cations, such as Na^+ , K^+ , Ca^{2+} and Mg^{2+} . Zhu et al. (2000) indicated that organophilic clays seem to be the most promising option as an adsorbent for organic hazardous waste. Organically-modified clays (organoclays), obtained by exchanging naturally occurring cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} and etc.) with organic cations, usually from quaternary ammonium salts bearing long ethyl chains, are able to adsorb organic chemicals like phenols, benzene, toluene and xylene. The sorption properties of organoclays have suggested their use in hazardous waste remediation as geosorbants. Al-Tabba and Perera (2005) used cement containing organophilic clay additives for remediation of a soil contaminated with high level of hydrocarbons. Vipulanandan and Krishean (1990) compared the results of two S/S treatments by cement and thermosetting polyester polymer. They found that polyester polymer is more effective than cement.

MTBE (Methyl Butyl Ether) with chemical formula $C_4H_9OCH_3$ is widely used as a gasoline oxygenate in many countries in the world. MTBE is manufactured via the chemical reaction of methanol and isobutylene. Both methanol and butane are obtained from natural gas and isobutylene is derived from butane. MTBE was developed in the 1970s as an octane that was enhanced to replace toxic additives such as lead in gasoline (Deeb et al., 2003). Although there is a widespread usage of MTBE, but it has become a pollutant due to its chemical and physical properties such as high water solubility. MTBE is often introduced into water supply aquifers by leaking. MTBE can be introduced to the environment from point sources (petroleum fuels leaking from storage tanks and pipelines, and fuel spills) and non-point sources. Most MTBE in soil and water is probably a result of fuel leaks or spills (An et al. 2002). Groundwater contamination by MTBE has been associated with gasoline, diesel fuel, jet fuel, heating oil, aviation fuel, and waste oil (Kostecki and Leonard, 1998). Non-point sources of MTBE in the environment include atmospheric distribution of MTBE in the vapor phase, and MTBE in precipitation. Due to its high solubility in water and low sorption tendency in soils it can rapidly penetrate to the layer of soil and enter the groundwater shortly after spill. The higher water solubility and persistence of MTBE can cause it to move faster than many other component of gasoline when released into aquifer. The toxicity of MTBE to animals and humans is well documented and it has been established that the MTBE is carcinogenic to animals (Belpoggi et al., 1995, Kamalan et al., 2009; Liang et al., 2010). Franklin (2000) reported that MTBE has become one of the most problematic pollutants in urban soils and groundwater worldwide. The use of MTBE in gasoline is widely

questioned in the USA and Europe because of its carcinogenic behavior and its use has been forbidden in the USA since 2003 (Atienza et al., 2005).

To the authors' knowledge, the cited literature does not include any published work on the S/S methods for preventing from leakage of MTBE in contaminated soil to the underground water. Only it has been stated that the adsorption of MTBE by soil is low. It is important to examine the different methods for preventing leakage of MTBE from contaminated lands to the aquifers and then choose the best method for remediation of contaminated soil by MTBE. The aim of this work is to investigate the S/S method for remediation of a clay soil contaminated by MTBE through experimental tests.

Material

Soil, Portland cement (C), MTBE and bentonite (B) are the main materials that were used in this work. The mechanical, physical and chemical properties of these materials are described in this section.

Soil

The soil that was chosen for this experimental work was a clay soil because the majority of petrol stations in the study area (Karaj city near Tehran) were founded on clay soil where the petroleum waste and leakage from storage tanks to ground was considerable. The physical, mechanical and chemical properties of this soil are shown in Tables 1 and 2. The soil can be classified as clay with low plasticity (i.e. CL according to the Unified Soil Classification System (USCS)). The optimum water content and maximum dry unit weight according to the standard compaction tests were 17.50 % and 17.75 KN/m³ respectively. XRD (X-ray diffraction) tests were conducted on samples of this soil. Based on the XRD tests the minerals of used soil were quartz, calcite, feldspar (Na, Ca),

feldspar (K) and clay minerals. The clay minerals of this soil consist of illite, chlorite and montmorillonite.

Cement

The cement used in this work was Portland type 1 with specific gravity of 3.15. The Blaine fineness of it was about 4100 cm²/g. The physical and mechanical properties of the cement are shown in Table 3.

MTBE

MTBE that was used in this work was a clear and colorless liquid with an ether like odor. It was a production of Merck Company in Hohenbrunn, Germany. Its molecular weight and density were 88.15 g/mol and 0.7407 g/mL respectively. It had melting and boiling points of -109⁰C and 55.2⁰C. The dielectric constant and sorption coefficient of it were 2.6 and 1.15. The value of its water solubility at 25⁰C was 51.26 g/L and diffusion coefficients in air and water were 0.0792 (cm²/s) and 9.41e-05 (cm²/s) respectively.

Bentonite

Bentonite of type Na-Montmorillonite was acquired commercially. The specific gravity (G_s) of the soil was 2.75. It had liquid limit (LL), Plastic limit (PL) and Plasticity index (PI) equal to 349.70%, 55.10% and 294.60% respectively. The optimum water content and maximum dry unit weight were 37.70% and 11.60 kN/m³ respectively. According to the Unified Soil Classification System (USCS), this soil can be classified as CH (clay with high plasticity). The results of chemical tests showed that the percent content of organic matter (O.C.) and CEC (Cation Exchange Capacity) of the soil were 0.072 % and 74.1 meq/100 g respectively with Na⁺ as the main cation. XRD (X-ray diffraction) tests were carried out on the samples of this soil. The results indicate that the minerals of

bentonite are quartz, calcite, cristobalite, zeolite, dolomite, halite and clay minerals. The results also show that the clay minerals of bentonite are composed of illite and montmorillonite.

Sample preparation

MTBE is a soluble matter in water and the amount of its adsorption by a silty soil was reported as 1.15 gr per kg of the soil after 12 hours (Estabragh et al., 2016). In order to better highlight the effect of MTBE on the behavior of soil and soil-cement, the amount of 3.0 g MTBE per kg of soil was selected. The soil used in this work was a clay, hence the adsorption of MTBE by this soil is different from the value that was reported by Estabragh et al. (2016). At this selected amount of MTBE (3 g/kg) a part of it is adsorbed by the particles of the soil and the rest remains between the void spaces between particles. The preparation of the samples was performed in two stages as:

- a- The desired weight of soil was mixed manually with MTBE at concentration of 3.0 gr per kg soil and then kept in a sealed plastic bag for about 48 hours in order to achieve equilibrium between MTBE and soil. Based on the previous work by other researchers such as Vipulanandan (1995) and Karamalidis et al. (2007) the ratios of 20 and 30% (by weight) of cement to the natural soil were chosen for preparing the mixture of soil-cement. The soil-cement mixture was prepared by adding 20 or 30% weight of cement to the natural soil or contaminated soil.
- b- The contaminated soil was prepared as explained in the above section. Bentonite was mixed with cement with the ratios of 1:1 (one part bentonite with one part cement) and 3:1 (three parts bentonite with one part cement). The mixture of

contaminated soil-cement and bentonite was made by adding 20 or 30% weight of cement-bentonite mixture to the contaminated soil.

Standard compaction tests were conducted on the natural soil and the prepared materials as explained above (soil-cement, contaminated soil-cement and mixture of contaminated soil with cement and bentonite at two selected ratios). The maximum dry unit weight and optimum water content were determined for each of these materials. In order to prepare different samples from the above materials for unconfined compression tests, each material was weighted with an accuracy of 0.1 g. They were mixed in a container and water was added up to the optimum water content. All mixing was performed manually and proper care was used to prepare homogenous mixture at each stage of mixing. Static compaction was applied for preparing cylindrical samples. The mixtures were compacted under predefined target load in three layers at the rate of 1.5 mm/min until the maximum dry unit weight corresponding to its standard compaction test was achieved. The length and diameter of the prepared samples were 100 and 50 mm respectively. After preparing the contaminated soil-cement, soil-cement-bentonite and uncontaminated materials, they were kept in a curing cabinet according to the ASTM D1632-7 for curing times of 3, 7, 14 and 28 days.

Experimental procedure

The influence of the treatments was studied based on the unconfined compressive strength and leachability of contaminated samples.

Unconfined Compression Strength (UCS) was used as a measure of the ability of a monolithic stabilized material to resist against the mechanical stress. Stabilization results from the hydration reactions in the product and durability of the stabilized material is a

key variable (Kogbara, 2014). UCS tests were performed on the prepared samples according to the ASTM D1633-07 standard. The rate of loading was selected as 1mm/min (as used by many researchers such as Kumar et al. 2007 and Estabragh et al. 2012 for mixtures of fly ash with clay and soil-cement respectively). The applied load was recorded continuously and the test was continued until failure of the sample was attained and the compressive strength determined.

Leaching tests were conducted on the grounded contaminated soil, contaminated soil-cement and contaminated mixture of soil cement with bentonite according to the USEPA (1992-1310b) method. Cylindrical samples of contaminated soil, contaminated soil-cement or contaminated mixture of soil-cement with bentonite for the desired curing time were grounded to the fine particles and then passed through a sieve with opening size of 9.5 mm. Deionized water was added to the grounded samples with ratio of 1:16 (soil:water). pH of the mixture was measured and it was tried to keep it around 5 by adding the solution of acetic acid with normality of 0.5 according to USEPA-1310b. The mixture was placed in an extractor and agitation was carried out for 24 hours. During this time, at various intervals, the pH of the solution was controlled to be nearly 5. After that the mixture was put on a flat table and a pre-specified volume of water was added to it. It was kept on the table until the settlement of particles was completed and the solid phase was separated from the liquid phase. The liquid phase was filtered through a 0.45 μ m membrane to remove suspended particles. The filtered liquid was then used for determination the amount of MTBE. A Gas Chromatography apparatus (model PU-4410 made by Philips) was used for analysis of the liquid phase. The temperatures of the injector, detector and its column were 200⁰C, 220⁰C and 100⁰C respectively. The GC

apparatus was calibrated using external standard compounds prior to performing the chemical analyses. A standard pure compound was injected to the apparatus and the peak in the chromatogram was assigned based on the retention time of the standard. The peak areas or heights are used to determine the concentration of released contamination from the sample. Comparing the response of the unknown concentration to that of the known (standard) concentration is used to find the amount of concentration in the released leaching liquid.

Scanning electron microscopy (SEM) tests were conducted on the samples in order to observe the microstructure of the samples in different conditions. The necessary samples were made according to the maximum dry unit weight and optimum water content from standard compaction tests. A curing time of 7 days was considered for the soil-cement and contaminated soil-cement samples. Samples with dimensions of 1cm*1cm*1cm were prepared from natural soil, soil-cement, stabilized soil, and stabilized soil-cement as used by Trembley et al. (2002) and Estabragh et al. (2016) and scanned under SEM. The characteristics of performed tests (except the SEM tests) with the number of repetitions are shown in Table 4.

Results

Fig.1 shows the stress-strain curves for the natural soil, contaminated soil, uncontaminated soil-cement and contaminated soil-cement at curing time of 7 days. The results show that the final strength of natural soil is 392.7 kPa at 2.16% strain and for the contaminated soil they change to 164.4 kPa at 2.9 % stain. It is shown that the MTBE causes reduction in the final strength and increases the ductility of the soil sample. The results of uncontaminated soil-cement with 20% and 30% cement (see Fig.1) show that

the final strength of the samples with 20% and 30% cement are 3510.1 and 3954.1 kPa respectively. It is shown that the strength of the mixture of soil cement is increased in comparison with the natural soil and this increase of strength is dependent on the percent of cement; the higher the percent of cement the greater is the strength achieved. These results also indicate that by adding cement to the soil the ductility of the soil is reduced and the brittle behavior is increased as also indicated by Tang et al. (2007) and Bahar et al. (2004). Fig.1 shows the stress-strain curves of the contaminated soil-cement at 7 days of curing time. As shown in this figure the final strengths of the contaminated samples with 20% and 30% cement are 2711 and 3651 kPa at strains of 1.3 and 1.15 % respectively. Therefore adding cement to the contaminated soil increases the strength and reduces the ductility of the samples in comparison with contaminated soil. Fig.2. shows the final strength of the uncontaminated and contaminated soil-cement samples at different curing times (3, 7, 14 and 28 days). As shown in this figure, the strength of the contaminated soil-cement with 20% cement is 2681 kPa at 3 days curing time and it changes to 3981 kPa after 28 days of curing time. This trend is also observed for the contaminated soil-cement with 30% cement and uncontaminated soil-cement samples. It can be concluded that for a constant cement content the strength is increased with increasing the curing time. It is resulted from Figs.1 and 2 that the final strengths of contaminated soil-cement and uncontaminated soil-cement are increased with percent of cement and curing time. Comparison of the results shows that for a constant percent of cement and curing time strength of contaminated soil-cement is less than uncontaminated soil-cement. The stress-strain curves for contaminated soil mixed with 20 and 30% of combined bentonite and cement with ratios 1:1 (B:C) and 3:1 (3B:C) for 7 days curing

time are shown in Fig.3. As shown in this figure, the strength of contaminated soil is increased by adding 20 or 30% bentonite and cement. The increase in strength for 20 or 30% mixture of (3B:C) is considerably less than the mixture of (B:C). With 20% mixture of bentonite and cement with ratio (3B:1C) the final strength is 618 kPa but at the same percent with mixture ratio of (B:C) the strength is 1310 kPa. Fig.4 shows the variations of final strength for the contaminated soil samples that were mixed with 20 or 30% mixture of bentonite and cement at different curing times. As shown in this figure, the strength of the samples with 20 or 30% of (1:1) bentonite and cement is more than the samples at the same percent but with (3:1) ratio of bentonite and cement at the same curing time. At curing time of 3 days the strength of the sample composed of 20% (1:1) bentonite and cement is 1019 kPa but for the samples composed of 20% (3:1) bentonite and cement, it is changed to 341.7 kPa. However, in general mixing contaminated soil with mixture of bentonite and cement increases the strength of the sample.

Fig.5 shows the results of leaching tests that were obtained from the GC apparatus for samples of contaminated soil mixed with 20 and 30% cement. The results also show that the concentration of MTBE is 796 mg/L for the contaminated soil but it is decreased by adding cement to the contaminated soil. The concentrations of MTBE for 20 and 30% cement are 32.1 and 31.3 mg/L at curing time of 3 days (see Fig.5) but by increasing the curing time the concentration is increased. For curing time of 28 days the concentrations of MTBE for 20 and 30% cement are 76.66 and 61.35 mg/L that show an increase of nearly 100%. Comparing the results of the leaching test at 28 curing time (Fig.5) with the results of contaminated soil (796 mg/L) shows a reduction nearly 90% in the concentration of MTBE. It is resulted from Fig.5 that for the contaminated samples that

were mixed with 20 and 30% cement, the concentration of MTBE is increased by increasing the curing time. On the other hand comparing the results of concentration of MTBE in this figure (Fig.5) shows that, at a constant curing time the effect of 30 % cement is more than 20% in reducing the concentration of MTBE. The results of leaching tests for samples of contaminated soil with 20 and 30% mixtures of bentonite and cement (1:1) are shown in Fig.6. As shown in this figure by adding 20 and 30% of this mixture to contaminated soil the concentration of MTBE is changed to 25.14 and 18.96 mg/L at curing time of 3 days. By increasing the curing time the concentration of MTBE is reduced; at curing time of 28 days the concentration of MTBE value of them reaches to the 3.25 and 1.76 mg/L. Fig.7 shows the results of leaching tests for the contaminated soil with 20 and 30% mixtures of bentonite and cement (3:1) for different curing times. As shown in this figure, at curing time of 3 days the concentration of MTBE is 23.02 and 6.87 mg/L for 20 and 30% mixture of bentonite and cement. At curing time of 28 days these values change to the 0.4 and 0.04 mg/L respectively.

Figs.8a and b show the micrographs for the natural soil and the soil contaminated with MTBE. As shown in Fig.8a the flocculating structure is very obvious for the natural soil but in Fig.8b the micrograph shows that the penetration of the MTBE between the layers of clay changes the particles to a lamellar form with large pores between them. By adding 20% cement to the contaminated soil the lamellar structure of the soil particles is reduced and large pores change to small ones as shown in Fig.8c. In this figure the cementing products are not very obvious and only small amounts of them can be seen. Fig.8d shows the micrograph of the contaminated soil mixed with 20% cement at 7 days curing time. In this figure the cementing products are seen where they are with a lamellar form and

create a trellis like structure on and among the particles of soil. They are mainly calcium silicate hydrates as reported by Chequette et al. (1987).

Discussion

The surface charges on clay particles are negative (anions). These negative surface charges attract cations and the positively charged side of water molecules from surrounding water. Consequently, a thin film or layer of water (called adsorbed water) is bonded to the mineral surfaces. The thin layer of water is known as the diffuse double layer (DDL). The thickness of this layer is dependent on a number of factors such as dielectric constant, absolute temperature, etc. The structure of soil is dependent on the variations in the thickness of DDL, so, shrinking of this layer causes a flocculated structure in the soil.

Adsorption of contaminants to the soil particles is a surficial attachment. Adsorption can be divided into physical and chemical adsorption. Physical adsorption of contaminants in the pore water by soil occurs as a result of the attraction of contaminants to the surface of the clay minerals. Physical adsorption mainly involves Van der Waals forces and is characterized by low energy of adsorption. Chemical adsorption or chemisorption involves the formation of stronger and more permanent bonds of chemical nature (i.e. covalent bonding) with energies more than physical adsorption. The nature of organic compounds is different from the soil. The properties of organic compounds such as shape, size, polarizability and water solubility are important factors in the adsorption of the organic chemicals by the soil. Yong (2010) indicated that the mechanisms for binding organic compounds can be through London-Van der Waals, hydrophobic reaction, hydrogen bonding, charge transfer, ligand and ion exchange.

Bentonite is a very highly plastic clay which contains large quantities of montmorillonite (or smectites) and expands when it is in contact with water in liquid form or in vapor form. This is related to the mineralogical composition of the elementary layer or structural unit of the montmorillonite. According to Mitchell and Soga (2005), the structure of montmorillonite is a unit made of an alumina octahedral sheet sandwiched between two silica tetrahedral sheets. The alumina octahedral structure is composed of an aluminum atom and six hydroxyls in an octahedral coordination whereas the silica tetrahedral is composed of a silicon atom and four oxygen atoms in a tetrahedral coordination. In the 2:1 layer type silicates substitution of Si^{+4} by Al^{+3} in tetrahedral sheet or Mg^{+2} by Li^{+1} in an octahedral sheet results in a positive charge deficiency (Rindley and Brown, 1980). To balance the layer charge cations are introduced between layers. Interlayer cations in the smectite group are hydrated exchangeable cations. The cation exchange capacity intercalation makes smectite clays unique and is an important factor in their activity for various reactions of organic molecules (Soma and Soma, 1989).

Fig.1 shows that the final strength of the soil contaminated with MTBE is less than the natural soil whereas, according to the theory of DDL its strength should be higher because its dielectric constant is lower. The reduction in dielectric constant causes reduction in the thickness of DDL and leads to flocculated structure of the soil and hence increase in strength. The results obtained are in agreement with those that were reported by Ratnaweera and Meegoda (2005) but are in contradiction to the assumptions of DDL theory. The role of viscosity of MTBE is important in explaining these results. The viscosity of MTBE is 0.36 mPa-s that is more than water. Increasing viscosity facilitates displacement of the particles which leads to reduction of strength (Estabragh et al.; 2016

and Ratnaveera and Meegoda; 2005). Figs 8a and b show the micrographs of the natural soil and the soil contaminated with MTBE. As shown in Fig.8a the structure of the natural soil is in a flocculated form but by adding MTBE to the soil, the degree of flocculation is decreased and particles are changed to a lamellar form with large pores between them (Fig.8b). The change in structure of the soil can be due to chemical reaction of MTBE with pore water. The hydrolysis of MTBE in water produces an alcohol. By oxidation action alcohol can produce an acidic aqueous condition which can break the bond between the particles of soil and change them to smaller particles. As shown in Fig.8b the friction between the particles is less than the natural soil. The structure of the contaminated soil includes larger pores than the natural soil (Fig.8a). Therefore, the contaminated soil is more compressible condition and its strength is less than natural soil.

The results in Fig.1 show that adding cement to the natural soil increases the final strength and the amount of increase is a function of percent of cement and curing time. When cement is mixed with a clay soil and water is added to it, hydration of the cement occurs rapidly. One of the major hydration products is hydrated lime. The reaction of the carbon dioxide in soil, air and pore water produces carbonic acid. The reaction results in the dissociation of lime into Ca^{+2} and OH^{-1} . The change in the structure of the soil is a consequence of cation exchange of monovalent alkali ions dissociated divalent calcium ions in the pore water. This would lead to a flocculated structure in the soil and reduction in its plasticity. The increase in the strength of soil-cement with time is mainly due to pozzolanic reactions. Calcium hydroxide in the soil water reacts with silicates and aluminates (pozzolans) from clay particles form cementing materials. Calcium ions react

with the dissolved SiO_2 and Al_2O_3 and form hydrated gels of calcium silicate hydrate (CSH) and calcium aluminate hydrate (CAH). These gels bind the soil particles and develop strong linkage between the minerals and the aggregates to form a structure whereby the particles of soil can no longer slide over each other. Therefore, not only does cement destroy the soil plasticity, but it also increases the strength of it. By comparing the results in Figs.1 and 2 it can be concluded that the strength of contaminated soil-cement is less than uncontaminated soil-cement at the same curing time and percent of cement. By adding MTBE to the soil a part of is adsorbed by the soil particles. This adsorbed MTBE covers the surface of the soil particles and prevents from chemical reaction of cement with soil particles. Another major part of MTBE is solved in pore water and the chemical composition of pore water retards the cement setting process by forming a protective layer around the cement grains, thus hindering the formation of calcium hydroxide (Sora et al., 2002).

Stabilization refers to the fixation of a contaminant to the chemical structure of a soil material. Stabilization is generally done by adding a chemical agent such as lime or cement to the contaminated soil. Stabilization of organic contaminants can occur through a number of processes such as sorption and physical encapsulation in the mass of soil-cement. In this work, cement and a mixtures of cement and bentonite with different percentages were used for stabilization of a clay soil contaminated with MTBE. MTBE is a polar organic compound (Squillace et al., 1997) which be adsorbed by clay minerals. The adsorption of MTBE by soil is dependent on the type of soil and for a specific soil other factors such as temperature, pH are important. This may be due to hydrolysis of MTBE in aqueous solution that produces a kind of alcohol. The oxidation of alcohol may

produce an acidic solution and hence decrease the pH of the solution and change it to an acidic aqueous. The acidic characteristics of the pore fluid gradually break down the bonds between the particles which leads to increase in the MTBE concentration in the leaching tests. Fig.5 shows that the cement is effective in stabilization of MTBE but with increasing the curing time its effect is reduced and concentration of MTBE in the leaching tests is increased.

Figs.6 and 7 show that the combination of cement and bentonite is more effective in reducing the MTBE concentration than cement alone, particularly when the bentonite to cement ratio is 3:1. The concentration of MTBE decreases with increasing the curing time. It can be said that, due to its polar behavior, the majority of MTBE is adsorbed by bentonite and its encapsulation by cement is not important. The combination 3:1 is more effective in reducing the concentration of MTBE compared to the 1:1 combination. Therefore, increasing the percent of bentonite causes increase in the adsorption of MTBE and reduces the concentration of MTBE.

Conclusion

The solidification and stabilization technique was investigated through a program of laboratory experiments involving remediation of a clay soil contaminated with MTBE. The results showed that cement is a good agent for reducing the concentration of MTBE and it can not be considered as a stabilizing agent for increasing the curing time. The results highlighted that adding a combination of bentonite and cement as an agent is effective in decreasing the concentration and mobility of MTBE in leaching. It was also shown that the strength of the sample was increased by using two agents (bentonite and

cement) and leaching of MTBE to the environment was decreased. The obtained conclusions are:

- The strength of contaminated soil is increased by adding cement or mixture of cement and bentonite. The amount of increase in strength is a function of the amount of cement or mixture of cement-bentonite and curing time. The amount of increase in strength is less for contaminated soil-cement than the uncontaminated soil-cement.
- Concentration of leaching liquid is decreased by adding cement to contaminated soil but it is increased by increasing the curing time.
- Mixture of bentonite-cement causes decrease in the concentration of leaching liquid and the rate of decrease is reduced by increasing the curing time. The 3:1 mixture of bentonite-cement is more effective in reducing the concentration of MTBE in comparison with the 1:1 mixture.
- Using a mixture of bentonite-cement as an agent is more effective in solidification and stabilization of soil contaminated with MTBE than using cement only.

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Table 1. Physical and mechanical properties of soil

Soil properties	Values
Specific gravity	2.71
<i>Consistency limit</i>	
Liquid limit	44.5 %
Plastic limit	15.4 %
Plastic index	29.1 %
USCS Classification	CL
<i>Compaction study</i>	
Optimum water content	17.90 %
Maximum dry density	17.75 KN/m ³
<i>Grain size analysis</i>	
Sand	0.0%
Silt	25 %
Clay	75 %

Table 2. Chemical composition of soil

Chemical component	Amount	Chemical component	Amount
pH	7.8	Mg ²⁺ (meq/L)	11.25
EC ^a (dS/m)	13.2	Cl ⁻ (meq/L)	62.5
Na ⁺ (meq/L)	108.69	CO ₃ ²⁻ (meq/L)	0.6
K ⁺ (meq/L)	0.20	HCO ₃ ⁻ (meq/L)	5.0
Ca ²⁺ (meq/L)	35.0	SO ₄ ²⁻ (meq/L)	72.91
Ca CO ₃ (%)	10.2	O.C. ^b (%)	0.11

a-Electrical Conductivity

b- Organic Content

Table 3. Physical and mechanical properties of cement

Properties	Standard Designation	Value
Normal consistency (%)	ASTM C 187-10	29.2
Primary setting time (min)	ASTM C 191-08	108
Final setting time (min)	ASTM C 191-08	180
Compressive strength (MPa) 7days 28 days	ASTM C 109-08	23 34
Tensile strength (MPa) 7 days 28 days	ASTM C 190-85	1.6 2.4
Flexure strength (MPa) 7 days 28 days		3.1 4.2

Table 4. Characteristics of different tests

Test No.	Materials	Curing time (day)				Test		Repetition
		3	7	14	28	Strength	Leaching	
1	Soil					+		3
2	Soil+MTBE					+	+	3
3	Soil+20% cement	+	+	+	+	+		3
4	Soil+30% cement	+	+	+	+	+		3
5	Soil+MTBE+20% cement	+	+	+	+	+	+	3
6	Soil+MTBE+30% cement	+	+	+	+	+	+	3
7	Soil+MTBE+20% (B-C)	+	+	+	+	+	+	3
8	Soil+MTBE+30% (B-C)	+	+	+	+	+	+	3
9	Soil+MTBE+20% (3B-C)	+	+	+	+	+	+	3
10	Soil+MTBE+30% (3B-C)	+	+	+	+	+	+	3

+ = test done, B = Bentonite, C = Cement

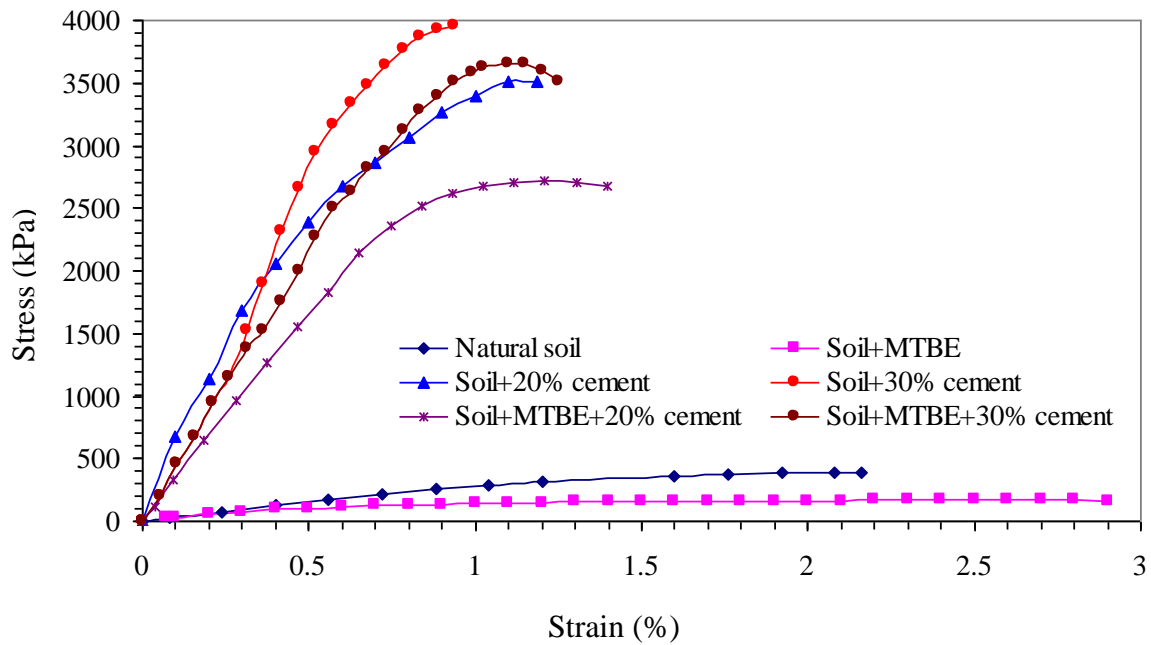


Fig.1. Stress-strain curves for natural soil, contaminated soil, soil-cement and contaminated soil-cement

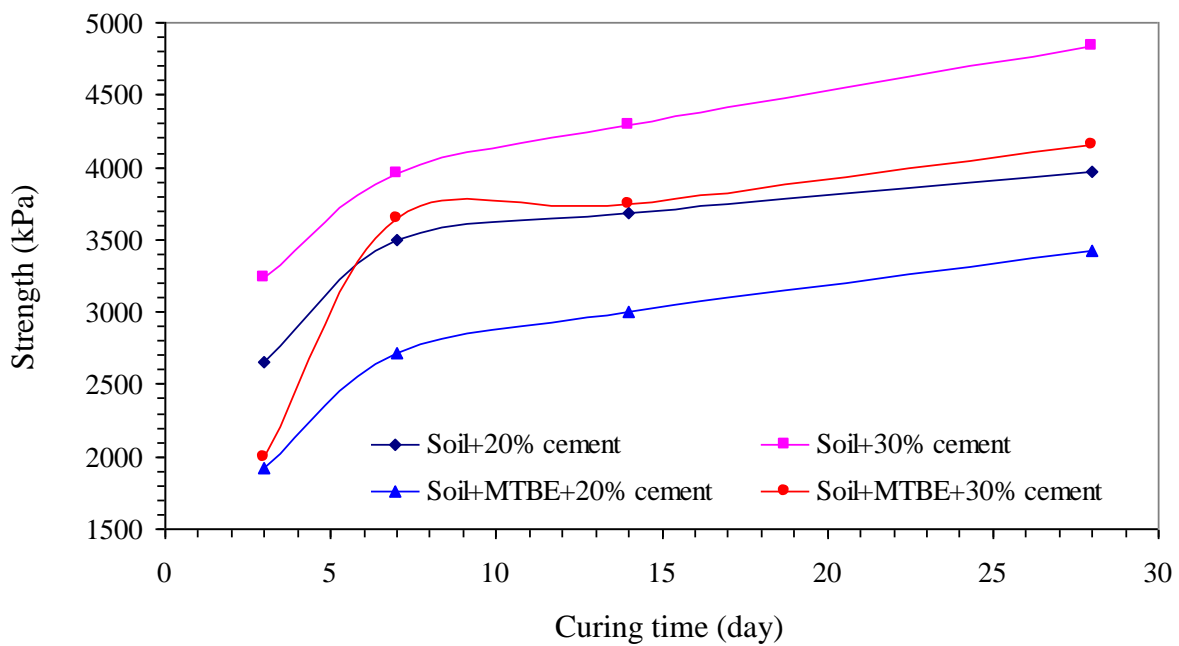
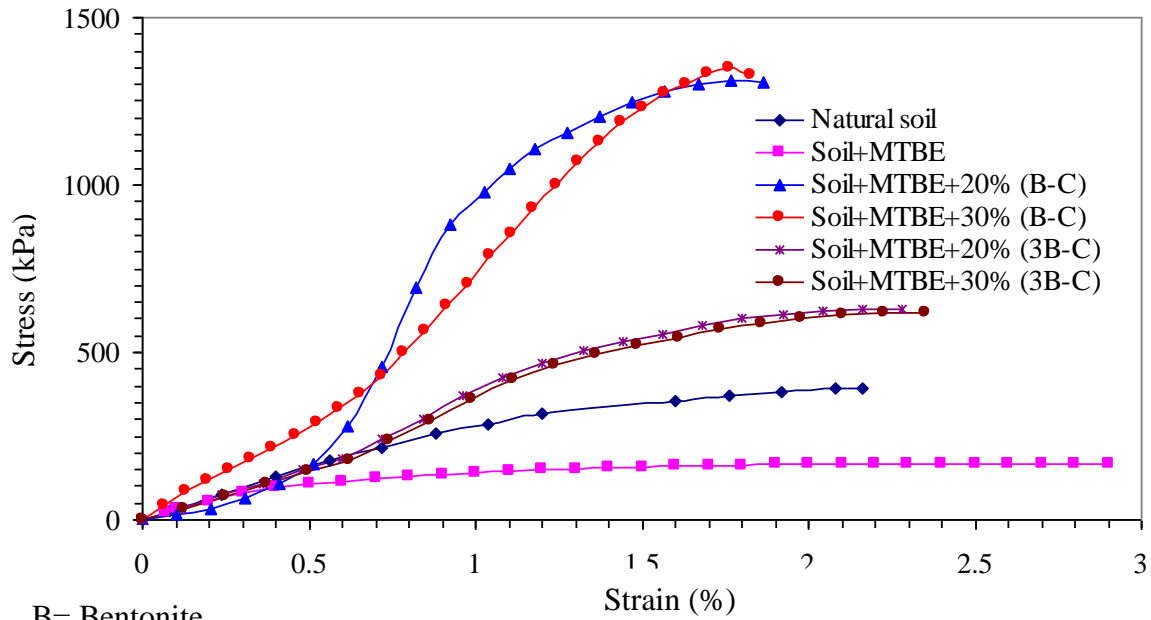
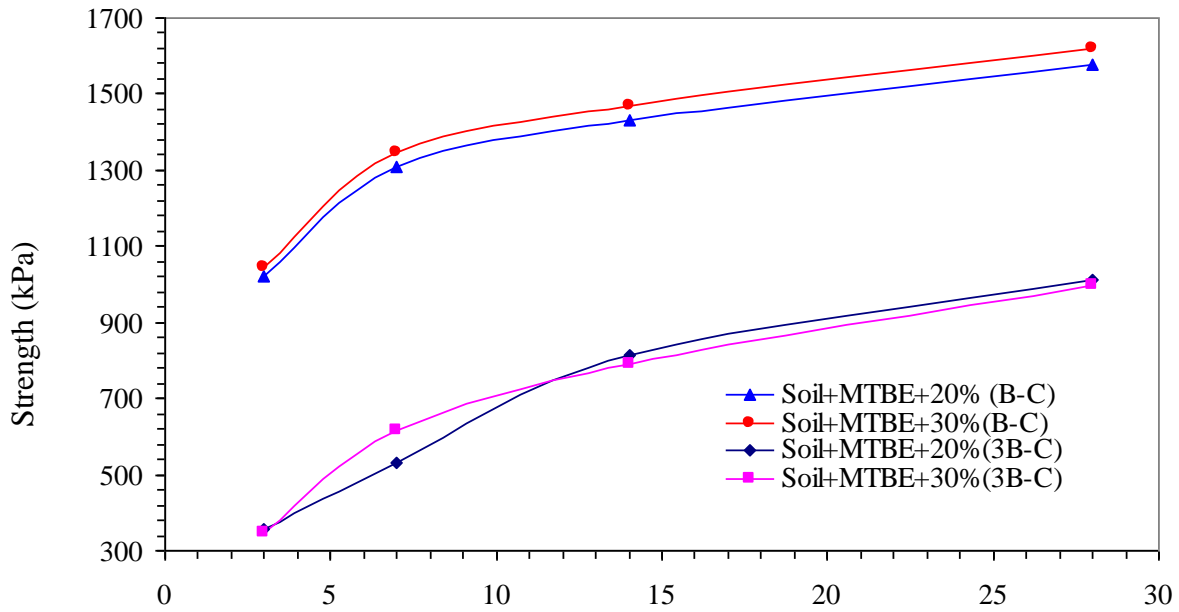


Fig.2. Variations of final strength with curing time for natural soil, contaminated soil, soil-cement and contaminated soil-cement



B= Bentonite
C= Cement

Fig.3. Stress-strain curves for natural soil, contaminated soil, contaminated soil with different combination of bentonite and cement



B= Bentonite
C= Cement

Fig.4. Variations of final strength with curing time for natural soil, contaminated soil, contaminated soil with different combinations of bentonite, cement and soil-cement

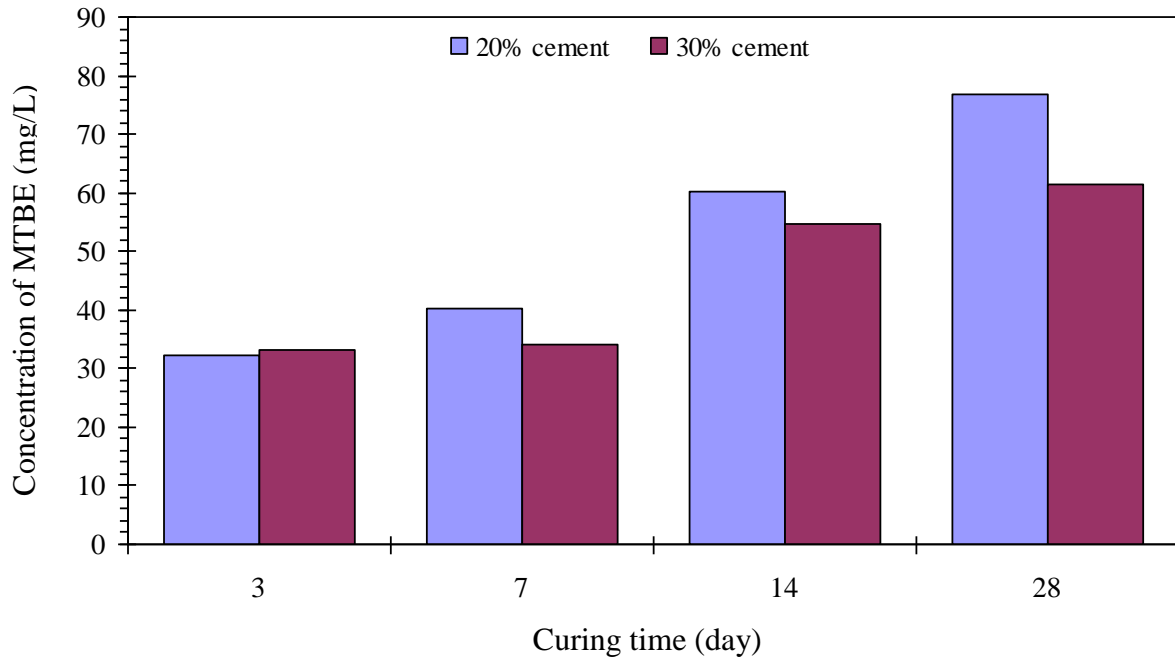


Fig.5. Variations of MTBE during leaching tests due to 20 and 30 % cement at different curing times

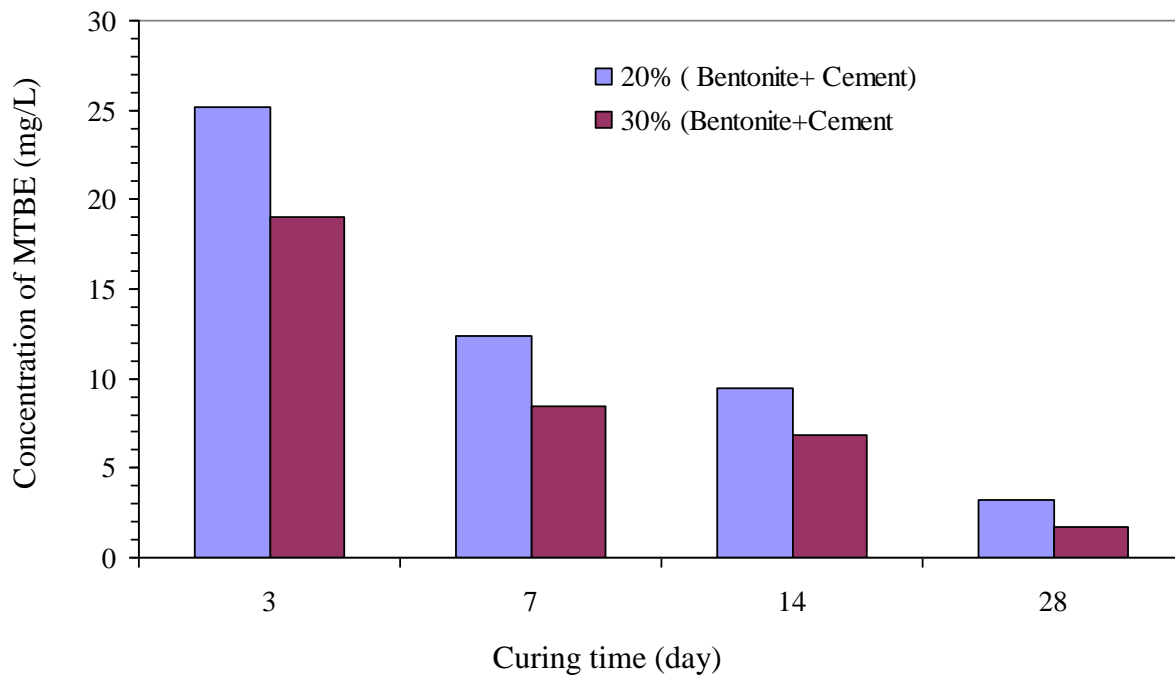


Fig.6 Variations of MTBE during leaching tests due to 20 and 30 % combination of bentonite and cement with ratio (1:1) at different curing times

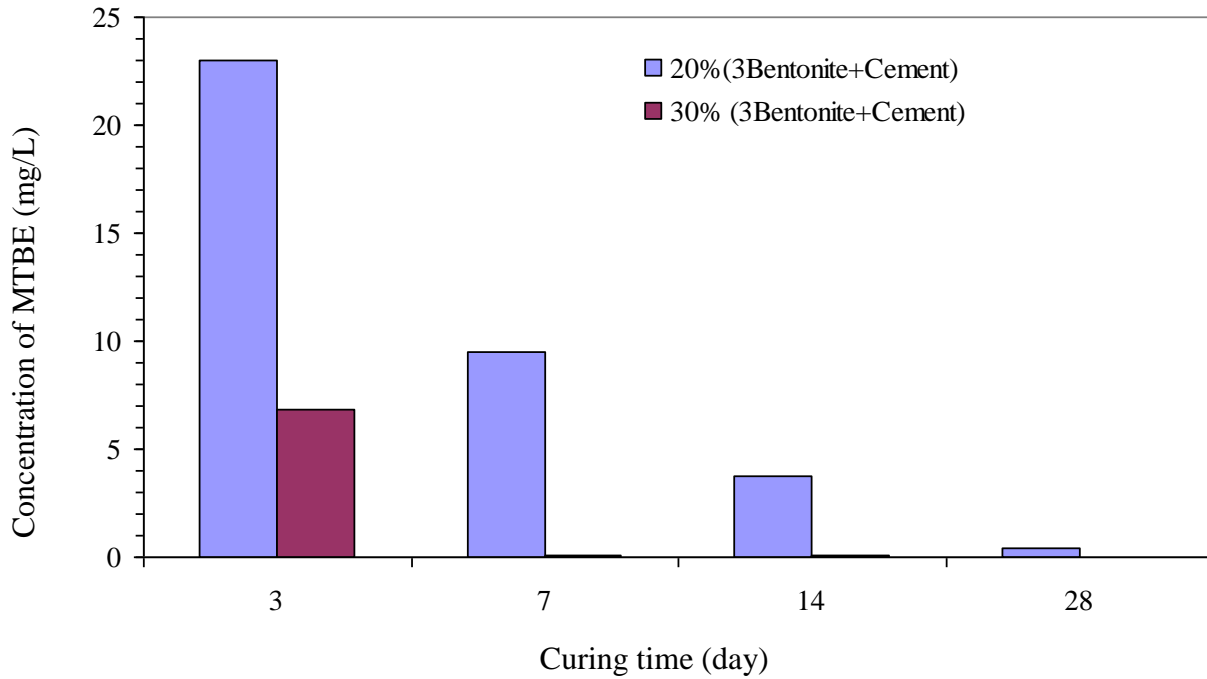


Fig.7 Variations of MTBE during leaching tests due to 20 and 30 % combination of bentonite and cement with ratio (3:1) at different curing times

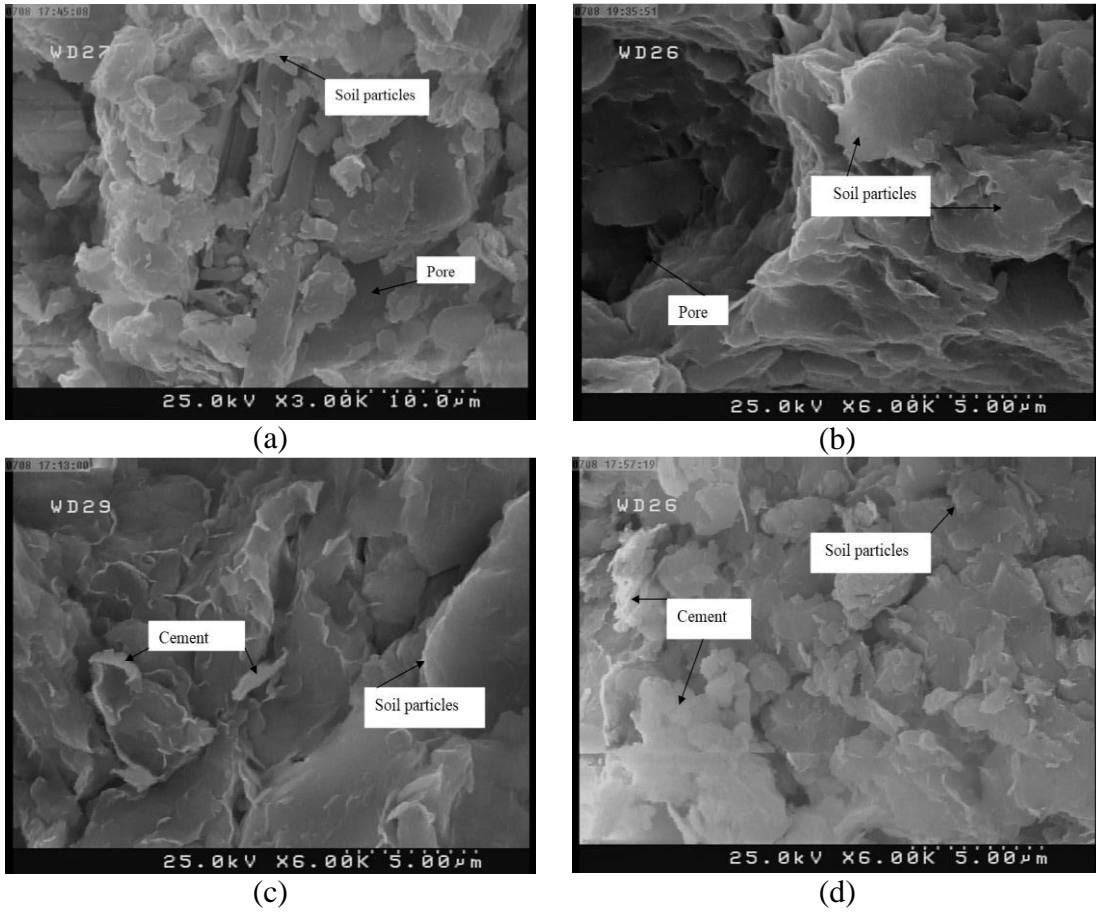


Fig.8. Micrographs of (a) natural soil, (b) soil+MTBE, (c) contaminated soil +20% cement, (d) contaminated soil 30% cement