Remediation of a clay soil contaminated with phenanthrene by using MgO and forced carbonation

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Abstract

BACKGROUND: The Stabilization and Solidification (S/S) technique is one of the most cost-effective, low-risk, and efficient remedial technologies for contaminated soils. In this research, the effect of MgO (Magnesium Oxide) on the remediation of a clay soil contaminated with phenanthrene with and without forced carbonation was studied by the S/S method. The effects of various parameters in reducing the mobility and leaching of phenanthrene were considered, including the percentage of MgO and curing time with and without forced carbonation, as well as the duration of carbonation.

RESULTS: The results of the leaching tests showed that by using 5% MgO, the initial concentration of phenanthrene ($32.7 \ mg \ kg^{-1}$) is changed to 9.16, 5.77, and $5.1 \ mg \ kg^{-1}$ for curing times of 7, 14, and 28 days. In addition, for the mixture of contaminated soil with 0.25% MgO and by using forced carbonation, the initial concentration is changed to 7.9, 4.3, and 3.73 $mg \ kg^{-1}$ after 4, 8, and 24 h of injection of CO_2. The S/S mechanisms for the removal of phenanthrene from soil include immobilization, adsorption, and encapsulation mechanisms. These stages are dependent on the hydration products of MgO.

CONCLUSION: A comparison of the results of the leaching tests without and with forced carbonation showed that forced carbonation can reduce the concentration of phenanthrene in a few hours with a small percent of MgO compared to the case without forced carbonation. Therefore, forced carbonation provides a cost-effective method for the remediation of contaminated soil.

Keywords: contaminated soil; Phenanthrene; magnesia; strength; forced carbonation

INTRODUCTION

Pollution of the environment by organic or inorganic matters has been a worldwide problem because of their harmful effects on human health. Polycyclic aromatic hydrocarbons (PAHs) are one of the major organic contaminants that pollute the environment. The origin of PAHs is due to industrial activities such as engine exhaust emissions, manufactured gas plants byproducts, domestic heating systems, and incomplete combustion of hydrocarbons contained in fuels. They are usually insoluble in water, and persistent in soil and are recognized as a harmful matter to the environment due to their carcinogenic behavior.[1,2] Recently, with the expansion of industrial sectors, more PAHs enter the soil which increases their concentration in soil. The flow of water in soil can transfer them from the top layers of soil to the bottom layers under gravity, allowing them to reach and pollute underground aquifers. The pollution of aquifers makes them unsuitable for drinking and causes serious problems for human health. There are many methods for remediation of contaminated soils such as bioremediation and stabilization and solidification methods. The method of Stabilization and Solidification (S/S) is a more common technique in comparison with the bioremediation method because bioremediation is limited to those compounds that are biodegradable. Not all compounds are susceptible to rapid and complete degradation. There are also some concerns that the products of biodegradation may be more persistent or toxic than the parent compound. Biological processes are often highly specific. Important site factors required for success include the presence of metabolically capable microbial populations, suitable environmental growth conditions, and appropriate levels of nutrients and contaminants. But the S/S method has many advantages in comparison with the bioremediation method such as low cost (because the reagents are widely available and inexpensive), and it can be used on a large variety of contaminants and in different types of soils.

This technique reduces the rate of motion of the contaminants in the environment and their toxicity. In this method, the migration of contaminants is reduced by isolating the contaminated soil in an impervious capsule. This method consists of mixing cementitious binders with contaminated soil to immobilize contaminating matters in the soil and improve the physical and mechanical properties of soil.[3] The conventional binders used in this method are Portland cement, lime, and pulverized fuel ash. Young[4] indicated that S/S is most suitable for immobilization of metals in soil and to a lesser extent organic matters because of the detrimental effects on the hydration and structural formation of materials. Conner[5] stated that soils contaminated with organic matters are not essentially stabilized with binders such as cement because only limited reactions occur between organic matter and cement at ambient temperature and pressure. This is due to hydrolysis, oxidation, and formation of organic salts. There are other binders for the S/S of soils. These binders include natural bentonite clays, organophilic clays, bitumen, and silica fume among others. The choice of binder is dependent on many factors such as the behavior of contaminating matters, soil condition, and the properties of the binder. The binders act as a key component in the S/S technique. Recently some researchers such as Hou et al.,[6] Shen et al.,[7] and Du et al.[8] used MgO as a binder for remediation of metal-contaminated soils and found satisfactory results. This is because MgO provides a suitable range of pH for precipitating most heavy metals, exchanging them with other metal cations and providing the hydrogen bonding between contaminants and MgO.[9] Wang et al.[10] performed several tests on a soil contaminated with heavy metals by using different binders. They reported that MgO is better in immobilizing heavy metals compared to Portland cement. Jin et al.[9] used a binder that involved replacing the 90% of MgO with GGBS. They reported that this combination not only maintained the metal and immobilized organic matters efficiency but also increased the strength of stabilized soil. Wang et al.[3] studied the effect of time on the physical and leaching behaviors of a contaminated soil by using MgO, GGBS, cement, and a combination of them as a binder. They found that MgOGGBS blends are able to provide higher strength and lower leachability of contaminants compared to Portland cement (PC) and

MgO only. Liska and Al-Tabbaa[11] showed that the reaction of MgO due to carbonation is very limited at ambient curing time and proposed the technique of forced carbonation to increase the carbonation process of the sample. Yi et al.[12] and Estabragh et al.[13] used the method of forced carbonation by increasing the CO_2 concentration in the sample stabilization of soil by MgO can result in a high strength due to carbonation in a few hours when the sample is under the pressure of CO2. Li and Yi[14] studied the stabilization and solidification of a contaminated soil with lead and zinc by using MgO as a binder through forcing CO_2 into the sample. They compared their results with those for samples of the same contaminated soil stabilized with cement. They reported that MgO is effective in the stabilization and solidification of soils.

Review of the previously published research works shows that there have been a lot of studies on the stabilization of natural clay soils and stabilization and solidification of soils contaminated with heavy metals by using MgO alone or a combination of MgO with other binders such as cement, lime, and GGBS. Estabragh et al.[13] studied the stabilization of a natural clay soil by using different percentages of cement and MgO as binders at different curing times by conducting a number of tests using the conventional stabilization methods. They also studied the effect of forced carbonation on the stabilization of samples that were made by mixing the soil with different percentages of MgO. Different tests were performed at the same pressure but at different times of forced carbonation. They concluded that cement is more effective than MgO in the stabilization of natural clay soil and that the forced carbonation technique is more effective than conventional stabilization methods for a natural clay soil. In the present study, the effect of different percentages of MgO on S/S of a clay soil contaminated with Phenanthrene is investigated through a program of conventional experiments as well as with forced carbonation under constant pressure and at various times. However, to date, no attention has been given to the stabilization and solidification of soils contaminated with organic matters by using MgO. In this work, for the first time, the remediation of a clay soil contaminated with phenanthrene is investigated by using conventional and forced carbonation S/S methods. The results obtained from the different stabilization methods are compared and discussed.

EXPERIMENTAL

Materials and methods

The main materials used in this research work were soil, phenanthrene, and MgO and their behaviors are as follows:

Soil
The soil used in this study represents an in-situ soil in the province of Alborz in Iran. This soil was a clay that was obtained from the area where pesticide and plastic production units are located. The required soil was collected from the district in the upstream of these units and it was without any contaminants.

It was composed of 2% sand, 45% silt, and 53% clay. The liquid limit (LL), plastic limit (PL), and plasticity index (PI) of the soil were determined as 47%, 26%, and 21%, respectively. Based on the results of grain size distribution and Atterberg limits, it was classified as a clay with low plasticity (CL) in USCS (Unified Soil Classification System). The maximum dry unit weight (γdmax) and optimum water content (wopt) of the soil were 16.8 kNm^{-3} and 18.5% respectively, according to the standard compaction test. Based on the results of XRD tests, the minerals of the soil were quartz, calcite, clay minerals (illite, chlorite, and montmorillonite), feldspar (Na, Ca), and feldspar (K). Chemical tests were also conducted on the samples of soil and the results of the chemical composition of the soil are presented in Table 1.

Table 1. Chemical composition of soil

Chemical component	Amount	Chemical component	Amount
pH	8.0	Cl^- (meq L^{-1})	60.0
EC^a (dS m^{-1})	10.74	HCO_3^- (meq L^{-1})	4.0
Na^+ (meq L^{-1})	42.0	SO_4^{2-} (meq L^{-1})	83.0
Ca^{2+} (meq L^{-1})	24.0	$CaCO_3$ (%)	10.2
Mg^{2+} (meq L^{-1})	10.0	O.C.^{b} (%)	0.05

^{a} Electrical conductivity.
^{b} Organic content.

Phenanthrene

Phenanthrene is from the polycyclic aromatic hydrocarbons (PAHs) group which is a large group of organic compounds that exist in different combinations in the environment. Phenanthrene is found at high concentrations in PAH-contaminated surface soils, sediments, and waste sites.[15] It has been indicated as a major pollutant for the environment.[16] The phenanthrene used in this work was a product from Merck Company. It is composed of three fused benzene rings with the chemical formula C14H10. It is colorless and crystal-like, but it can also look yellow in color. Its molecular weight and density are 178.23 g mol^{-1} and 1.18 g cm^{-3} respectively. The dielectric constant and water solubility of it are 2.72 and 1.15 mg L^{-1}. It has a melting point between 97-100 °C and a boiling point of 336 °C. Phenanthrene is usually used to make dyes, plastics, pesticides, explosives, and drugs.

MgO

A commercial reactive MgO was used in this work that was in powder form with white color. It consisted of MgO, CaO, SiO_2, Fe_2O_3, and Al_2O_3 with percentages of 94.2, 1.7, 0.85, 0.62, and 0.16% respectively. Its specific gravity and molecular weight were 3.55 and 40.304 $gmol^{-1}$. It had a specific surface of 250–300m^2 g^{-1} and the mean size of its particles was 60 μm.

Sample preparation

Contaminated soil with phenanthrene was prepared artificially with concentration of 1200 mg kg^{-1} (mass of phenanthrene/mass of dry soil). Saichek and Reddy[17] used contaminated soil with phenanthrene at concentration of 500 mg kg^{-1}. USEPA[18] also recommended the concentration of 500 mg kg^{-1}. In this work, to enhance the observed effect of phenanthrene on the behavior of contaminated soil and the mixture of contaminated soil and MgO, concentration of 1200 mg kg^{-1} was chosen. The solubility of phenanthrene in water is very low but it can be dissolved in acetone. Therefore, a mixture of acetone-phenanthrene was made and it was added to (sprayed on) a specific mass of soil and mixed by hand until a homogenous mixture was obtained. The prepared mixture was spread in a flat tray and was kept in the tray for about 1 week so that the acetone was evaporated from the contaminated soil and the soil became dry. Standard compaction and Atterberg limits tests were conducted on the prepared contaminated soil and its mixture with different percentages of MgO. For the unconfined compressive strength tests, the samples were made from natural soil, contaminated soil, the mixture of uncontaminated soil with MgO, and the mixture of contaminated soil with MgO at different percentages. The water contents of these mixtures were brought to their w_{opt} that were obtained from the corresponding compaction tests.

The prepared samples should be homogenous and repeatable in order to reduce the associated errors and achieve valid results. To achieve this, the samples were prepared by static compaction in three layers, as used by researchers such as Sharma.[19]

Characterization and experimental tests
The soil characterization tests carried out in this work are Atterberg limits and compaction.

The Atterberg limits of used material were determined by conducting LL and PL tests on the materials according to the ASTM standard. Compaction tests were also conducted for the determination of the γ_{dmax} and w_{opt}.

Figure 1 shows a schematic diagram of tests that were conducted for S/S of the contaminated soil. UCS and SEMwere the experimental tests as used by researchers such as Jebeli and Heidarzadeh,[20] Heidarzadeh et al.,[21] González-Santamaría et al.,[22] and Botta et al.[23] The main aim of conducting the UCS tests was to use the results as an indicator, to determine the resistance of solidified and stabilized materials against loading. Also, scanning electron microscopy (SEM) tests were conducted to study the microstructure of the clay under different conditions (different percentages of MgO, curing times, and durations of CO_2 injection) and to determine the produced carbonate materials. The samples were prepared with maximum dry unit weight and optimum water content as obtained from the corresponding compaction curves. Leaching tests were used to determine the leachability of the contaminating substance for various percentages of MgO at various curing times. In this research, the percentage of MgO and curing time were considered as the variables in the conventional and force carbonation of S/S methods. A brief description of these experimental tests follows.
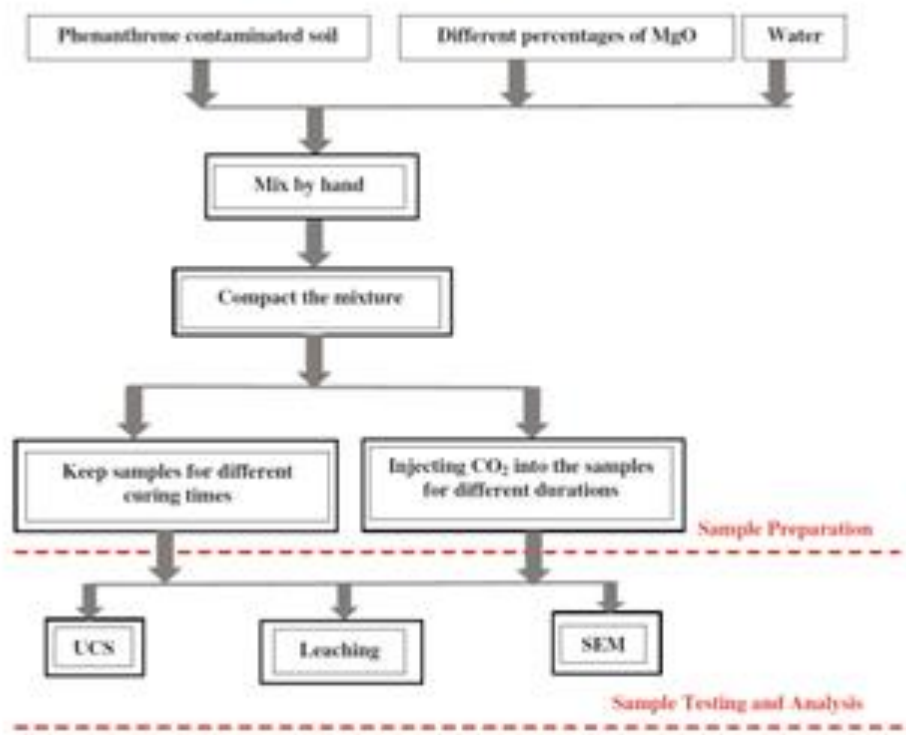

Figure 1. Schematic diagram of Stabilization and Solidification of phenanthrene contaminated soil.

Strength tests

Unconfined compressive strength (UCS) tests were conducted on samples of natural soil, mixtures of natural soil with MgO, contaminated soil, and mixtures of contaminated soil with different percentages of MgO according to the ASTM standard. UCS tests were also conducted on the samples of mixtures of natural soil and contaminated soil with various percentages of MgO under constant CO_2 pressure of 50 kPa at different times. A triaxial apparatus was used for applying CO2 to the sample under pressure. Details of the apparatus and the test procedure can be found in Estabragh et al.[13]

SEM tests

In order to find the effects of microstructure on the soil properties, SEM (scanning electron microscopy) tests were performed on samples of natural soil, contaminated soil, and mixtures of them with various percentages of MgO. Before testing, the samples were broken into small pieces and then dried by vacuum for a few days. They were then placed on metal stubs, sputter coated by gold and moved to the apparatus.

Leaching test and analytical method

The purpose of S/S is to immobilize the leaching of contaminants and to reduce the toxicity level and solubility of the contaminants through reactions with additives and binders. The efficiency of the S/S method in terms of reducing contaminant mobility is evaluated through hydraulic conductivity and leaching tests (Albino et al.[24-25]). This method has lower cost and energy consumption in comparison with other remediation methods (Ma et al.[26]). Therefore, in this research the S/S method was considered to remediate a soil contaminated with phenanthrene. In this study, the Extraction Procedure (EP) toxicity test of the EPA (United State Environmental Protection Agency),[27] Method 1310b was used for conducting leaching tests. It is the most common test that can show the efficiency of the S/S process. For conducting this method, the prepared samples were grounded into particles less than 9.5 mm. Then they mixed with distilled water at a ratio of 1:16. Then the pH of the mixture was measured after 15-, 30-, and 60-min intervals and adjusting the pH around 5 by adding 0.5 N acetic acid gradually (the maximum amount of used acid was 4mL per g of soil according to this method of testing). Then the mixture was placed on a shaker for 24 h. After that, distilled water was added again to it to dilute the mixture until the ratio of solid to liquid of it became 1:20. Then it was placed on a flat surface so that the solid particles were separated from the liquid phase by deposition of the solid particles. In order to remove the suspended particles from the fluid phase, it was passed through a 0.45 μm filter and then analyzed by a spectrophotometer.

An Alpha 1900S Double spectrophotometer was used for analyzing the prepared liquid phase. Before performing the main test, the apparatus was calibrated and the wavelength for adsorption of phenanthrene was determined. For calibration, the prepared solution of phenanthrene with different concentrations were injected into the apparatus and the wavelength for phenanthrene was found as 250 nm. Then the calibration curve was obtained based on the determined wavelength of phenanthrene (i.e., 250 nm). A spectrophotometer was used in this work because the organic content of the natural soil was not considerable (see Table 1). Wloka and Placek[28] used an HPLC and a spectrophotometer to the determination of the concentration of PAHs in a contaminated soil. They reported that at a low percentage of organic content in natural soil, the obtained concentrations of PAHs in leaching tests with the two apparatus were nearly the same.

Each test was repeated three times and if the results were nearly the same the average of them was considered as final results. In a few cases where the results of one of the repeated tests had a significant difference from others, it was disregarded and the average of the rest of them was considered.

RESULTS

The results obtained from the tests are discussed below.

Atterberg limits and compaction parameters
The results of the Atterberg limits (LL, PL, PI) and compaction parameters (γ_{dmax} and w_{opt}) of the materials used in this work are shown in Table 2. It is seen in this table that the values of LL, PL, and PI for the natural soil are 47, 26, and 21%, respectively. The results show that adding MgO to natural soil results in increase in the values of LL and PL in comparison with natural soil. The values of LL, PL, and PI for contaminated soil are 42, 22, and 20%, respectively (Table 2). There is a small reduction in their values in comparison with the natural soil. For mixtures of contaminated soil and MgO, LL and PL are increased by increasing the percentage of used MgO. For example, for the mixture of contaminated soil with 10% MgO, the values of LL and Pl are 51.5 and 32% but for the mixture with 30% MgO they are changed to 54 and 38%, respectively. It is seen from the comparison of the results that with the same percent of MgO, the variations of LL and PL for a mixture of contaminated soil are less than the mixture of natural soil.

Table 2 also shows that γ_{dmax} and w_{opt} of the natural soil are 16.8 kNm^{-3} and 18.5%. When 5% MgO is mixed with the soil they are changed to 15.2 kNm^{-3} and 21.0%, respectively (i.e., the γ_{dmax} decreases and the wopt increases). The γ_{dmax} and w_{opt} for contaminated soil are 16.8 kNm^{-3} and 16.0, respectively. For the mixture of contaminated soil with MgO, the γ_{dmax} is decreased and w_{opt} is increased by adding 5, 10, 20, and 30% of MgO.

Table 2. Atterberg limits and compaction parameters for natural soil and contaminated soil with different percentages of MgO

Material	LL (%)	PL (%)	PI (%)	γ_{dmax} (kN m^{-3})	W_{opt} (%)
Soil (N[a])	47.0	26.0	21.0	16.8	18.5
Soil (N) + 5% MgO	50.0	32.0	18.0	15.2	21.0
Soil (N) + 10% MgO	51.0	33.0	18.0	15.0	21.0
Soil (N) + 20% MgO	52.0	35.0	17.0	14.9	22.8
Soil (N) + 30% MgO	55.0	38.0	17.0	14.8	23.7
Soil + P[b]	42.0	22.0	20.0	16.8	16.0
Soil + P + 5% MgO	50.0	30.0	20.0	15.3	21.8
Soil + P + 10% MgO	51.5	32.0	19.5	15.1	22.0
Soil + P + 20% MgO	53.0	35.0	18.0	15.0	23.5
Soil + P + 30% MgO	54.0	38.0	16.0	14.8	24.0

[a] Natural.
[b] Phenanthrene.

Strength
The stresses and strains were calculated from the recorded data for the samples tested in the UCS tests with and without forced carbonation. The final strength of the samples and the corresponding strains were determined from these stress–strain curves and the results are shown in Figs. 2 and 3. Figure 2 shows the variations of final strength of the natural soil and the contaminated soil with different percentages of MgO at specific curing time. As shown in this figure, for a given curing time, by increasing in the percent of MgO the final strength is increased for both natural and contaminated soils. On the other hand, at a constant percent of MgO, the final strength is increased by increasing the curing time. Figure 3 presents the final strengths of mixtures of contaminated soil with 0.25, 0.5, and 1.5% MgO, carbonated with CO_2 under the pressure of 50 kPa at different injection times (i.e., 4, 8, and 24 h). As shown in this figure, for a

constant injection time, a higher percent of MgO results in a higher strength. Also, at a given percentage of MgO, increasing the time of injection results in the increase in the final strength.
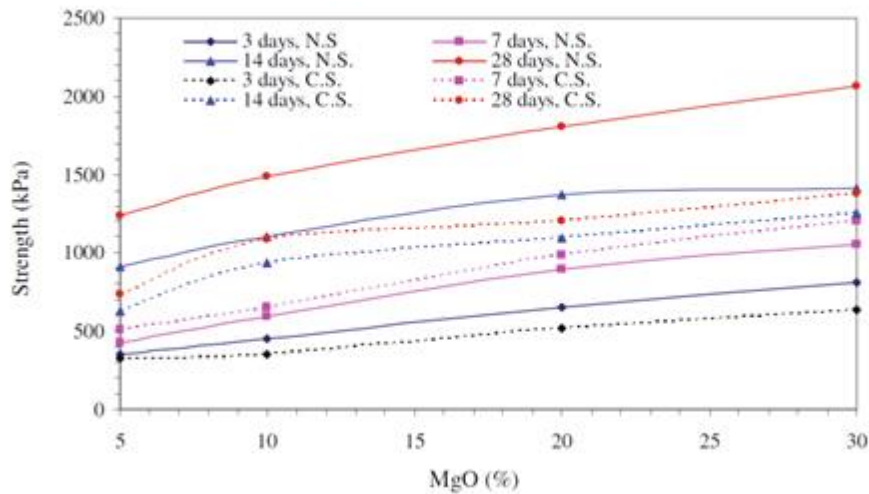

Figure 2. Variations of strength with MgO content (%) for natural and contaminated soils at different curing times without forced carbonation. N.S. = Natural soil, C.S. = Contaminated soil.
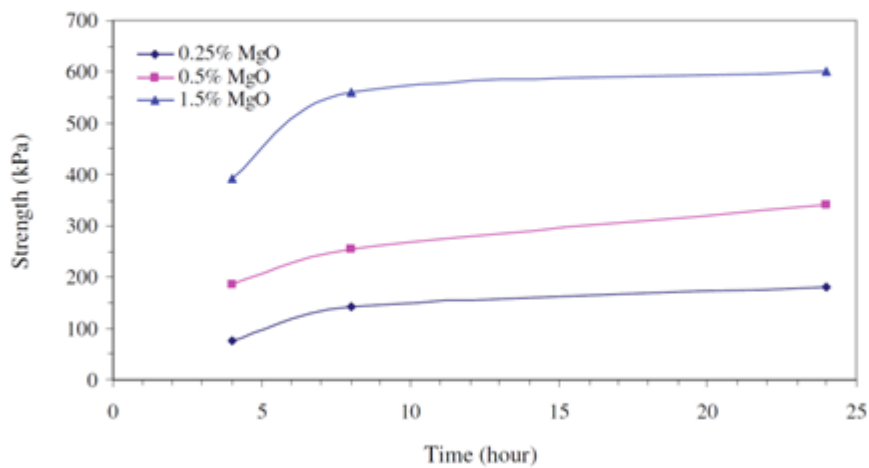

Figure 3. Variations of strength with time for different percentages of MgO for contaminated soil in forced carbonation tests.

Leaching tests

Figure 4 shows the results of leaching tests on contaminated soil samples that were stabilized with 5, 10, 20, and 30% MgO at various curing times. As it is seen in this figure, the initial concentration of phenanthrene in contaminated soil is 32.7 mg kg^{-1} but it is reduced by adding MgO. For 5% MgO the initial concentration of phenanthrene (32.7 mg kg^{-1}) is changed to 9.16, 5.71, and 5.1 mg kg^{-1} for curing times of 7, 14, and 28 days, respectively. It is resulted that at constant percentage of MgO, there is a reduction in the concentration of phenanthrene by increasing the curing time. A similar trend of variations in the concentration of phenanthrene is seen in Fig. 4 for the other percentages of used MgO. When the contaminated soil is mixed with 20% MgO, the concentration of phenanthrene reached 3.74, 2.1, and 1.5 mg kg^{-1} after 7, 14, and 28 days of curing, respectively. Comparing the results, for example for 5 and 20% MgO at the curing time of 7 days, shows that the concentration of phenanthrene is 9.16 and 3.74 mg kg^{-1}. It is seen that both the percentage of MgO and the curing time are effective in reducing the

concentration of phenanthrene. In other words, a higher percentage of MgO and a longer curing time would result in more reduction in the concentration of phenanthrene. Figure 5 shows the results of leaching tests for stabilized soil with different percentages of MgO by forced carbonation with different injection times of CO_2. The results show that by adding 0.25% MgO to the contaminated soil, the concentration of phenanthrene is changed from its initial value (32.7 mg kg^{-1}) to 7.19, 4.36, and 3.73 mg kg^{-1} for 4, 8, and 24 h injection of CO_2, respectively. The corresponding concentrations are 3.41, 3.1, and 2.3 for the soil stabilized with 0.5% MgO at the same times. A similar trend is observed for soil stabilized with 1.5% MgO. It is seen that increasing the time of forced carbonation and percentage of MgO reduce the concentration of phenanthrene in contaminated soil. The comparison of the results for the tests with and without forced carbonation (Figures 4 and 5) shows that with 5% MgO without forced carbonation, the concentration of phenanthrene was reduced by 9.16, 5.71, and 5.1 mg kg^{-1} for curing times of 7, 14, and 28 days. With forced carbonation and with 0.25% MgO, these values were 7.19, 4.36, and 3.73 mg kg^{-1} after 4, 8, and 24 h, respectively. It is observed from the comparison of the results that with forced carbonation, the concentration of phenanthrene is reduced more than in the case without forced carbonation, even with a lower percent of MgO.
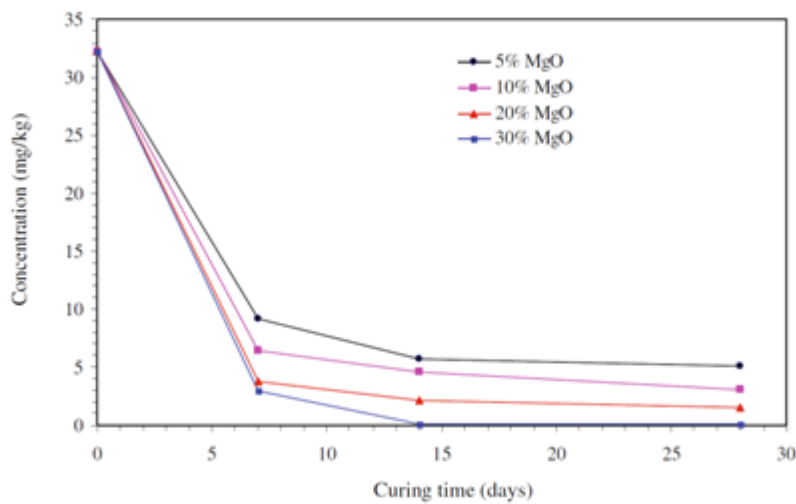

Figure 4. Variations of concentration of phenanthrene at different percentages of MgO versus curing time.
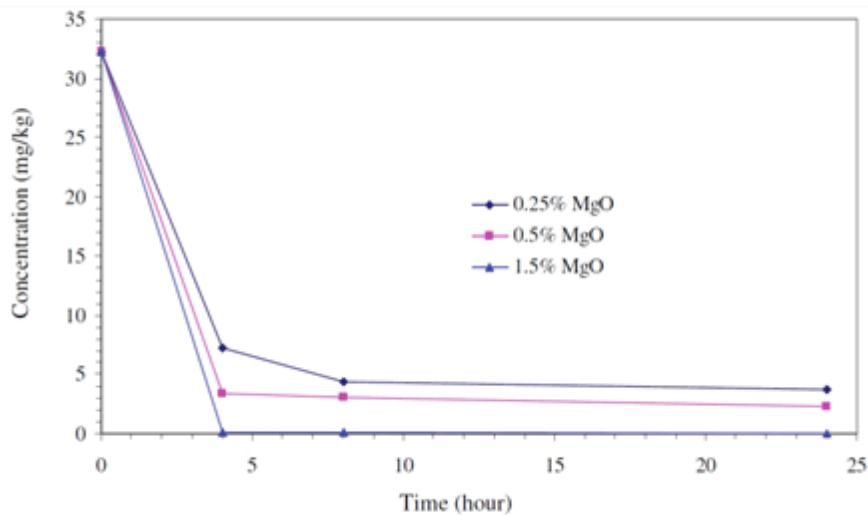

Figure 5. Variations of concentration of phenanthrene at different percentages of MgO versus time of forced carbonation.

SEM tests

Figure 6 shows the micrographs for the natural soil and mixtures of the natural soil with various percentages of MgO at the curing time of 28 days. The SEM micrograph of the natural soil is presented in Fig. 6(a). It is seen from this figure that the natural soil is composed of particles with different sizes without any bonding between them. The images for mixtures of soil with 5, 10, 20, and 30% MgO are depicted in Fig 6(b)–(e) respectively. The carbonation products of MgO are observed in Fig. 6(b)–(e). In Fig. 6(c), (d) brucite and nesquehonite products are seen between the pores of the soil. Figure 7 depicts the SEM images of contaminated soil and mixtures of contaminated soil with various percentages of MgO at the curing time of 28 days. It is seen in Fig. 7(a) that the soil particles in the contaminated soil are in the form of nearly parallel sheets and the sizes of spaces between particles are less than the natural soil (Fig. 7(a)). The products of carbonation (brucite and nesquehonite) are also seen in Fig. 7(b)–(e). The SEM images for the contaminated samples treated with 0.25, 1, and 1.5% MgO under 8 and 24 h of forced carbonation are shown in Fig. 8. The carbonation products such as brucite and nesquehonite are observed in this figure. The results show that in this method the carbonation products are produced in a shorter period of time.
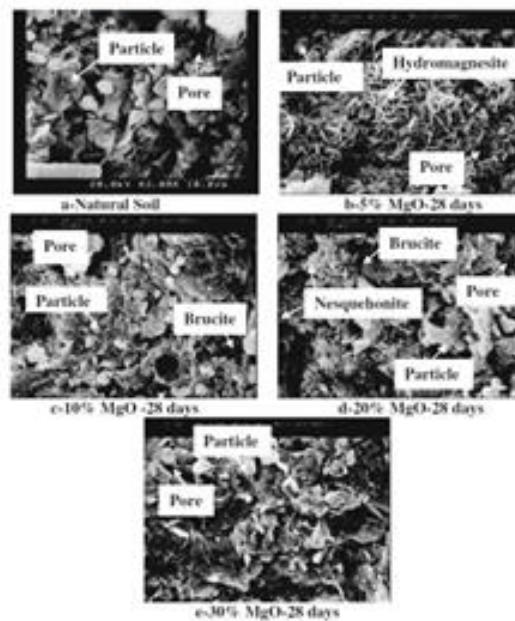

Figure 6. Micrographs for the natural soil and mixtures of natural soil with different percentages of MgO at curing time of 28 days.
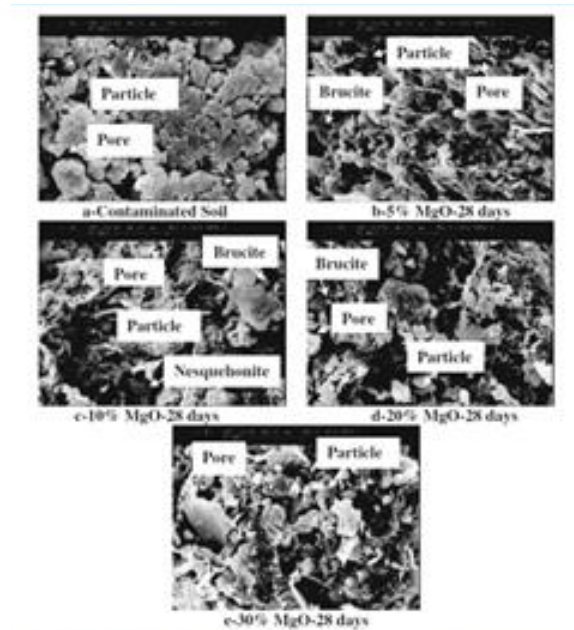
Figure 7. Micrographs for the contaminated soil and mixtures of contaminated soil with different percentages of MgO at curing time of 28 days.
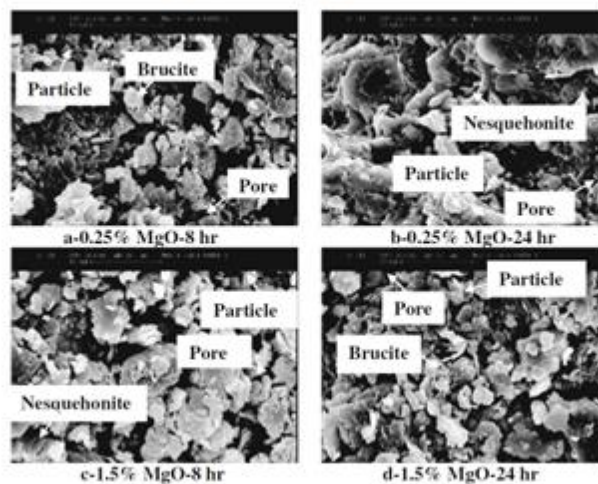

Figure 8. Micrographs for the mixtures of contaminated soil with different percentages of MgO at different times of forced carbonation.

DISCUSSION

Clay particles carry negative charges on their surface (anions). They can attract cations and also the surrounding molecules of water from their positively charged side. As a result, a thin layer of water is attached by a strong bond to the surface of clay minerals that is termed diffuse double layer. The change in the thickness of this layer can result in the formation of different structures in the soil, namely flocculated and dispersed structures, which is important in the behavior of soils.[29] In addition to the type of soil structure, the cation exchange capacity (CEC) of clay has a significant effect on the soil behavior and properties. The exchange cations are cations that are pasted to the surface of clay particles and are able to replace with other cations.[29]

Atterberg limits and compaction parameters

Table 2 shows the values of Atterberg limits for the natural and contaminated soils and mixtures of them with different percentages of MgO. It is seen from this table that the values of LL and PL for the natural soil are 47 and 26% respectively. By adding MgO the values of LL and PL are increased. The specific surface of MgO (250–300m2 g−1) is more than the soil. When MgO is added to soil, it replaces a certain amount of soil particles. In other words, a material with higher specific surface is substituted with part of the soil and this results in increase in the values of Atterberg limits. The Atterberg limits increase with increasing the MgO content (Table 2). Liska et al.[30] and Estabragh et al.[13] reported similar results on the variations of Atterberg limits of their used soils that were mixed with MgO. Liquid Limit and PL for contaminated soil are 42 and 22% respectively that are less than those for the natural soil. This could be because some of the particles are covered by phenanthrene which prevents from adsorbing water, hence leading to reduction in LL and PL. Liquid Limit and PL are higher for mixtures of contaminated soil and MgO. This is due to the high specific surface of MgO that replaces soil particles.

Table 2 presents the results of compaction tests for mixtures of natural soil and contaminated soil with various percentages of MgO. As shown in this table, the γ_{dmax} and w_{opt} for the natural soil are 16.8 kNm^{-3} and 18.5%, respectively. By adding MgO, the γ_{dmax} is decreased and w_{opt} is increased. These changes in γ_{dmax} and w_{opt} are increased with increasing the percent of MgO. This could be because MgO produces larger pores in the soil mass. These results are consistent with the results that were obtained by Vandeperre et al.[31-32] A similar trend is observed in Table 2 for contaminated soil with various percentages of MgO. The γ_{dmax} and w_{opt} of the contaminated soil are 16.8 kNm^{-3} and 16.0%, respectively. It is seen that the wopt of the contaminated soil is less than the natural soil. This could be due to the structure of the contaminated soil which is different from the natural soil.

Strength

It is seen from the results in Fig. 2 that when MgO is added to the natural soil, the strength of soil (305 kPa) is increased and the amount of increase is related to the percentage of MgO and curing time; the higher the MgO content or the longer the curing time, the greater is the achieved strength. It can be said that when MgO is added to the soil, the hydration starts by adsorbing the free water in the space between the soil particles. The hydration of MgO is similar to the hydration of cement.[33] Exchange of ions also occurs between the minerals of soil and MgO in the early stages of mixing soil with MgO. Yi et al.[12] stated that during the hydration, MgO is changed to Mg(OH)$_2$ that is called brucite. Brucite reacts with CO_2 and produces nesquehonite (MgCO$_3$, 3H$_2$O), hydromagnesite (4MgCO$_3$, Mg(OH)$_2$, 4H$_2$O), and dypingite (4MgCO$_3$, Mg(OH)$_2$, 5H$_2$O). These produced materials are shown in the micrographs in Fig. 6(b)–(e). The production of these materials continues with time during the carbonation process by adsorbing water and CO_2. The production of these materials can enhance the strength of the soil. Unluer and Al-Tabbaa[34-35] reported that between the produced materials, nesquehonite has a higher strength than the other products (hydromagnesite and dypingite). These results are consistent with the findings that were reported by Estabragh et al.[13] The results show that the strength of contaminated soil (199 kPa) is about 35% less than natural soil (305 kPa). This could be attributed to the difference in their structure. Figure 6 indicates that the natural soil has a flocculated structure, but the structure of the contaminated soil (Fig. 7(a)) is nearly dispersed. In the flocculated structure, the friction between particles is more than the dispersed structure and this type of structure (dispersed) causes reduction in the strength of contaminated soil. Figure 2 also shows that by adding MgO to the contaminated soil, the strength of it is increased. It is seen that the percentage of MgO and curing time are effective in increasing the strength of soil. Comparison of the results in Fig. 2 indicates that for a given percentage of used MgO and curing time or at constant percent of MgO with changing the curing time, the final strength of stabilized contaminated soil is less than the stabilized natural soil. It can be said that the structure of

contaminated soil is less flocculated than natural soil (see Fig. 7(a)) and its particles are nearly parallel to each other in comparison with the natural soil (Fig. 6(a)). Therefore, the spaces between particles in the contaminated soil (and hence the penetration of the MgO between the particles) are less than the natural soil. On the other hand, some of the soil particles could be covered with phenanthrene. These conditions may reduce the production of the carbonation materials in comparison with the stabilized uncontaminated soil, hence resulting in reduction in strength. The increase in the strength is dependent on the production of materials that are produced during the carbonation process. It is possible to increase the rate of carbonation by forcing carbonation with pressurized gaseous CO_2 in soil which would result in reduction in time for treatment. Figure 3 shows the strength of contaminated soils subjected to forced carbonation for 4, 8, and 24 h. The results show that the rate of increase in the strength is higher between 4 and 8 h than between 8 and 24 h. It is concluded that the majority of carbonation products are produced between 4 and 8 h as shown in Fig. 8. The results also show that increasing the percentage of MgO increases the strength of the contaminated soil. Comparison of the results in Fig. 3 shows that the strength of the soil treated with 1.5% MgO after 24 h of forced carbonation is 561 kPa but the strength of the soil treated with 5% MgO after 7 days of curing is 506 kPa (see Fig. 2). During forced carbonation, both CO_2 and MgO, as binder, contribute to the treatment of soil. These results are consistent with those that were reported by Yi et al.[36] and Estabragh et al.[13]

Leaching
Figures 4 and 5 show the results of the leaching tests that were conducted on the samples without and with forced carbonation, respectively. As shown in these figures, after 7 days or 4 h of testing the majority of reduction in the concentration of phenanthrene occurred in the samples of the two methods. The clay particles may adsorb a major part of phenanthrene or phenanthrene can be deposited as a salt between the space of particles due to the chemical reactions. Adsorption of the contaminant to soil particles is called surficial attachment.[37] Adsorption can be divided into physical or chemical adsorption. Physical adsorption results from van der Waals forces where the contaminants in pore water are attracted to the surface of clay particles by physical adsorption. Chemical adsorption is mainly due to the formation of strong and relatively permanent bonds between soil particles and contaminated substances (i.e., covalent bonding). These formed bonds are stronger than the bonds due to physical adsorption. The properties of organic contaminants are different from the soil. Therefore, the behaviors of organic contaminants that are important in adsorption to soil are such as shape, size, polarity, and water solubility. Leonard and Stegemann[38] and Zampori et al.[39] stated that the binding mechanisms between binders and organic compounds are physical entrapment in the produced matrix and sorption on the surface of hydration products rather than the chemical reaction. Yong[37] indicated that the mechanisms for binding organic chemicals can be through van der Waals hydrophobic reaction, hydrogen bonding, charge transfer, and ion exchange. In the present work, MgO is used as a binder. During hydration, $Mg(OH)_2$ (brucite) is produced and an alkaline environment is formed with pH in the range of 9.0–10.5.[14] In this range of pH, better precipitation occurs in comparison with binders such as lime or cement.[3] The $Mg(OH)_2$ (brucite) also produces ions of Mg^{+2} and OH^{-1}. These produced ions are effective in the adsorption of organic matters to the surface of soil particles by hydrogen ions or through exchange ions. By increasing the amount of produced brucite, more adsorption of phenanthrene occurs. Figures 4 and 5 show that the majority of reduction in the concentration of phenanthrene occurs at the early stage of curing and the amount of reduction is increased by increasing the percentage of MgO. This is due to the production of brucite; with a higher percent of MgO more brucite is produced resulting in greater reduction in concentration. Comparison of the results in Figs 4 and 5 shows that with 5% MgO and without forced carbonation, after 7 days of curing the concentration of phenanthrene reaches 9.16 mg kg^{-1} but with forced carbonation, with 0.25% MgO it reaches 7.19 mg kg^{-1} only after 4 h. This indicates that forced carbonation increases the

rate of production of brucite. The results (Figs. 4 and 5) also show that after 7 days of curing (or 4 h for forced carbonation) the rate of reduction in concentration is not significant. After 7 days (or 4 h for forced carbonation) the produced hydration products such as brucite, nesquehonite, hydromagnesite, and dypingite result in encapsulation of the contaminant. The hydration products are able to accommodate a wide variety of extraneous cations as well as organic compounds by hydrogen bonding, hence providing an excellent host for contaminants.[3] Figure 9 shows a schematic diagram of different stages of the S/S technique and its mechanism. As shown in this diagram, S/S involves immobilization of the contaminants through reactions with additives and binders by adsorption and precipitation mechanisms instead of removing them. This occurs by hydration of the MgO and production of the carbonation products such as brucite. Therefore, this process reduces the mobility and leaching, as well as the toxicity level and solubility of the contaminants. The reduction in the concentration of the contaminant by increasing the curing time or duration of CO_2 injection may be due to the progressive encapsulation of contaminating material by production of other carbonation products such as nesquehonite, dypingite, and hydromagnesite that becomes more significant with increasing the curing time or duration of CO_2 injection and by increasing the percentage of MgO. Therefore, the higher degree of immobilization of the organic matter is due to the amount and structure of produced brucite. Leonard and Stegemann[38] stated that high organic contaminants in a soil can prevent from producing the binder materials. They can also produce considerable micro and macro structural changes to the hydration products and affect the mechanical behavior of remediated contaminated soil.
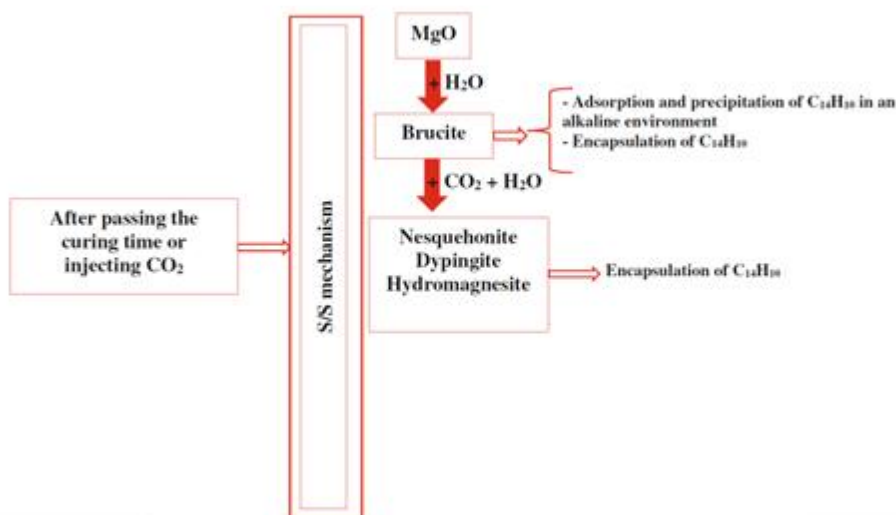

Figure 9. Schematic diagram for Stabilization and Solidification mechanism.

The World Health Organization/International Program on Chemical Safety (WHO/IPCS)[40] indicated that the acceptable level of PAHs (Poly Aromatic Hydrocarbons) components in soil is between 1–3 mgkg^{-1}. The results of the present work showed that in the conventional tests, by using 20 and 30% MgO, the remaining phenanthrene in the soil reached 1.5 and 0.1 mg kg^{-1} after 28 days of curing. The results of the forced carbonation tests indicated that by using 0.5 or 1.5% MgO the final remaining phenanthrene in the soil was 2.32 and 0.05 mg kg^{-1} respectively after 24 h of testing. These values are within the range of acceptable values recommended by WHO/IPCS and hence, the contaminated soil with these levels of phenanthrene would not be harmful to the environment. Furthermore, these values are far below the precautionary value of 3 mg kg^{-1} set in Germany for soils with organic matter content ≤8% (Desaules et al.[41]). The results also showed that the forced carbonation method is better than the conventional method

as it can remediate the soil to within the acceptable range by a small percent of MgO and in a limited time.

CONCLUSION

In this work, the remediation of a clay soil contaminated with phenanthrene by using MgO as a binder was investigated. A series of tests were conducted without and with forced carbonation. It was revealed from the results that this method is effective in remediation of soils contaminated with phenanthrene. It was also found that increasing curing time is effective in the reduction of the concentration of phenanthrene. The main conclusions are:

- MgO, as an additive material, can increase the strength of both natural and contaminated soils through the carbonate materials that are produced due to its hydration. The amount of these products is dependent on the percentage of MgO used and the curing time. For the contaminated soil, the strength at a given percentage of MgO is less than the natural soil as the existence of phenanthrene prevents from binding of the soil particle to each other. In addition, it is found that the strength of mixture of natural or contaminated soil with MgO is increased by forced carbonation in a shorter period of time due to the formation of carbonate products in the early stage of MgO hydration.

- The results of the leaching tests show that the concentration of phenanthrene is reduced for the mixture of MgO with contaminated soil in the conventional or forced carbonation methods. The reduction in the concentration of phenanthrene is caused by adsorption, conversion to inert materials, or encapsulation, depending on the amount of formed carbonate products that are in turn a function of the percentage of MgO and the curing.

- Comparison of the leaching results reveals that in the forced carbonation method with a lower percentage of MgO and a shorter time, a greater reduction in the concentration of phenanthrene is obtained than in the conventional method. Therefore, the forced carbonation method is more economical and more efficient than the conventional method.

CONFLICT OF INTEREST

There is no conflict of interest in this paper.

REFERENCES

1 Masih A and Taneja A, Polycyclic aromatic hydrocarbons (PAHs) concentrations and related carcinogenic potencies in soil at a semi-arid region of India. Chemosphere 65:449–456 (2006). https://doi.org/10.1016/j.chemosphere.2006.01.062.

2 Menzie CA, Potocki BB and Joseph S, Exposure to carcinogenic PAHs in the environment. Environ Sci Technol 26:1278–1284 (1992). https://doi.org/10.1021/es00031a002.

3 Wang F, Jin F, Shen Z and Al-Tabbaa A, Three-year performance of insitu mass stabilised contaminated site soils using MgO-bearing binders. J Hazard Mater 318:302–307 (2016). https://doi.org/10.1016/j.jhazmat.2016.07.018.

4 Young JF, A review of the mechanisms of set-retardation in Portland cement pastes containing organic admixtures. Cem Concr Res 2: 415–433 (1972). https://doi.org/10.1016/0008-8846(72)90057-9.

5 Conner JR, Chemical Fixation and Solidification of Hazardous Wastes. Van Nostrand Reinhold Publisher, New York, pp. 183–201 (1990).

6 Hou D, Gu Q, Ma F and O'Connell S, Life cycle assessment comparison of thermal desorption and stabilization/solidification of mercury contaminated soil on agricultural land. J Cleaner Prod 139:949–956 (2016). https://doi.org/10.1016/j.jclepro.2016.08.108.

7 Shen Z, Zhang J, Hou D, Tsang DCW, Ok YS and Alessi DS, Synthesis of MgO-coated corncob biochar and its application in lead stabilization in a soil washing residue. Environ Int 122:357–362 (2019). https://doi.org/10.1016/J.ENVINT.2018.11.045.

8 Du YJ, Wu J, Bo YL and Jiang NJ, Effects of acid rain on physical, mechanical and chemical properties of GGBS–MgO-solidified/stabilized Pb-contaminated clayey soil. Acta Geotech 15:923–932 (2020). https://doi.org/10.1007/s11440-019-00793-y.

9 Jin F, Wang F and Al-Tabbaa A, Three-year performance of in-situ solidified/stabilised soil using novelMgO-bearing binders. Chemosphere 144:681–688 (2016). https://doi.org/10.1016/j.chemosphere.2015.09.046.

10 Wang F, Shen Z and Al-Tabbaa A, An evaluation of stabilised/solidified contaminated model soil using PC-based and MgO-based binders under semi-dynamic leaching conditions. Environ Sci Pollut Res 25: 16050–16060 (2018). https://doi.org/10.1007/s11356-018-1591-4.

11 Liska M and Al-Tabbaa A, Ultra-green construction: reactive MgO masonry products. Proc Inst Civ Eng: Waste Resour Manage 162: 185–196 (2009). https://doi.org/10.1680/warm.2009.162.4.185.

12 Yi Y, Lu K, Liu S and Al-Tabbaa A, Property changes of reactive magnesia–stabilized soil subjected to forced carbonation. Can Geotech J 53:314–325 (2016). https://doi.org/10.1139/cgj-2015-0135.

13 Estabragh AR, Khajepour H, Javadi AA and Amini M, Effect of forced carbonation on the behaviour of a magnesia-stabilised clay soil. Int J Pavement Eng 23:1691–1705 (2020). https://doi.org/10.1080/10298436.2020.1821023.

14 Li W and Yi Y, Stabilization/solidification of lead- and zinccontaminated soils using MgO and CO2. J CO2 Util 33:215–221 (2019). https://doi.org/10.1016/j.jcou.2019.05.029.

15 Moody JD, Freeman JP, Doerge DR and Cerniglia CE, Degradation of Phenanthrene and anthracene by cell suspensions of mycobacterium sp. strain PYR-1. Appl Environ Microbiol, 67:1476–1483 (2001). https://doi.org/10.1128/AEM.67.4.1476-1483.2001.

16 Andersson JT and Achten C, A critical look at the 16 EPA PAHs. Polycyclic Aromat Compd 35:43–146 (2015). https://doi.org/10.1080/10406638.2015.1005241.

17 Saichek RE and Reddy KR, Effect of pH control at the anode for the electrokinetic removal of phenanthrene from kaolin soil. Chemosphere 51:273–287 (2003). https://doi.org/10.1016/S0045-6535(02)00849-4.

18 USEPA, A Resource for MGP Site Characterization and Remediation. EPA/542-R-00-005. United State Environmental Protection Agency,Washington, DC (2000).

19 Sharma RS, Mechanical Behaviour of Unsaturated Highly Expansive Clays. Ph.D. thesis. University of Oxford, Oxford, UK (1998).

20 Jebeli MT and Heidarzadeh N, Enhancement of the quick lime-based solidification/stabilization of oily wastes using modified clay. J Chem Technol Biotechnol 96:2265–2274 (2021). https://doi.org/10.1002/JCTB.6752.

21 Heidarzadeh N, Jebeli MT and Taslimi T, Cement-based solidification/stabilization of phenol-contaminated soil by bentonite and organophilic clay. Remediation 28:87–96 (2017). https://doi.org/10.1002/rem.21545.

22 González-Santamaría DE, López E, Ruiz A, Fernández R, Ortega A and Cuevas J, Adsorption of phenanthrene by stevensite and sepiolite. Clay Miner 52:341–350 (2017). https://doi.org/10.1180/CLAYMIN.2017.052.3.05.

23 Botta D, Dotelli G, Biancardi R, Pelosato R and Sora IN, Cement-clay pastes for stabilization/solidification of 2-chloroaniline. Waste Manage 24:207–2016 (2004). https://doi.org/10.1016/j.wasman.2003.10.005.

24 Albino V, Cioffi R, De Vito B and Santoro L, Evaluation of solid waste stabilization processes by means of leaching tests. Environ Technol 17: 309–315 (1996a). https://doi.org/10.1080/09593331708616389.

25 Albino V, Cioffi R, Santoro L and Valenti GL, Stabilization of residue containing heavy metals by means of matrices generating calcium Trisulphoaluminate and silicate hydrates. Waste Manage Res 14: 29–41 (1996b). https://doi.org/10.1177/0734242X9601400104.

26 Ma F, Wu B, Zhang Q, Cui D, Liu Q, Peng C et al., An innovative method for the solidification/stabilization of PAHs-contaminated soil using sulfonated oil. J Hazard Mater 344:742–748 (2018). https://doi.org/10.1016/J.JHAZMAT.2017.11.015.

27 USEPA. Method 1310B, Extraction procedure (EP) toxicity test method and structural integrity test, in 1310B, Publication SW-846: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. United State Environmental Protection Agency, Washington DC (1992).
2646

28 Włóka D and Placek A, Study of the effectiveness of the new method for the rapid PAHs analysis in soil. Acta Innov 17:5–11 (2015).

29 Mitchell JK and Soga K, Fundamentals of Soil Behavior, 3rd edn. John Wiley & Sons Publisher, New York, pp. 143–193 (2005).

30 Liska M, Vandeperre LJ and Al-Tabbaa A, Influence of carbonation on the properties of reactive magnesia cement-based pressed masonry units. Adv Cem Res 20:53–64 (2008). https://doi.org/10.1680/adcr.2008.20.2.53.

31 Vandeperre LJ, Liska M and Al-Tabbaa A, Hydration and mechanical properties of magnesia pulverized fuel ash and Portland cement blends. J Mater Civ Eng 20:375–383 (2008a). https://doi.org/10.1061/(ASCE)0899-1561(2008)20:5(375).

32 Vandeperre LJ, Liska M and Al-Tabbaa A, Microstructures of reactive magnesia cement blends. Cem Concr Compos 30:706–714 (2008b). https://doi.org/10.1016/j.cemconcomp.2008.05.002.

33 Vandeperre LJ, Liska M and Al-Tabbaa A, Mixtures of pulverized fuel ash, Portland cement and magnesium oxide: strength evolution and hydration products, inProceedings of the 6th International Conference Science Engineering Environment. Port Yugosl Eng Acad, Belgrade, pp. 539–550 (2006).

34 Unluer C and Al-Tabbaa A, Green construction with carbonating reactive magnesia blocks: effect of cement and water contents, inProceedings of the International Conference on Future Concrete. Dubai, UAE (2011).

35 Unluer C and Al-Tabbaa A, Effect of aggregate size distribution on the carbonation of reactive magnesia based porous blocks, in Proceedings of the 18th Annual International Sustainable Development Research Conference. Hull, UK (2012).

36 Yi Y, Al-Tabbaa A and Liska M, Properties and microstructure of GGBSmagnesia pastes. Adv Cem Res 26:114–122 (2014). https://doi.org/10.1680/adcr.13.00005.

37 Yong RN, Geoenvironmental Engineering: Contaminated Soils, Pollutant Fate, and Mitigation. CRC Press Publisher, Florida, USA, pp. 55–96 (2001).

38 Leonard SA and Stegemann JA, Stabilization/solidification of petroleum drill cuttings. J Hazard Mater 174:463–472 (2010). https://doi.org/10.1016/j.jhazmat.2009.09.075.

39 Zampori L, Stampino PG and Dotelli G, Long-term leaching test of organo-contaminated cement-clay pastes. J Hazard Mater 170: 1041–1049 (2009). https://doi.org/10.1016/j.jhazmat.2009.05.076.

40 WHO (World Health Organization), Selected Non-Heterocyclic Polycyclic Aromatic Hydrocarbons. Environmental health criteria No. 202. World Health Organization, Geneva (1998).

41 Desaules A, Ammann S, Blum F, Brändli RC, Bucheli TD and Keller A, PAH and PCB in soils of Switzerland—status and critical review. J Environ Monit 10:1265–1277 (2008). https://doi.org/10.1039/B807206J.