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Chapter 26

REMEDIATION OF A CLAY CONTAMINATED WITH PETROLEUM HYDROCARBONS USING SOIL REAGENT MIXING

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Abstract: Soil reagent mixing (SRM) is a remediation technique whereby powder or slurried reagents are delivered and mixed in-situ or ex-situ with contaminated soils or sediments by augers or other types of soil mixers. This paper summarises the work carried out for a laboratory treatability study of SRM on clayey soil samples contaminated with petroleum hydrocarbon compounds from a petrol filling station site in Kent, UK. The study examined the effects of mixing binder reagents on the total soil and leachate concentrations of hydrocarbons. Quicklime, hydrated lime and ordinary Portland cement, in a number of different formulations, were used in the study. Furthermore, the addition of gypsum to some reagent formulations was evaluated in an attempt to improve the strength of the binder/soil mix. Temperature and evolution of volatiles were monitored during the mixing of soils with the reagents. The mixing of soil with binder reagents resulted in changes in physical and physico-chemical properties of the clay, and in significant decreases in total soils and leachate concentrations of petroleum hydrocarbon compounds. The mechanisms responsible for the decreases in concentrations were examined. Significant increases in the remoulded strength of the clay were observed upon addition of certain binder formulations.

Key words: Remediation; Soil Reagent Mixing; Solidification; Stabilisation; Clay; Petroleum; Hydrocarbons; Lime; Cement; Gypsum.

1. INTRODUCTION

Soil Reagent Mixing (SRM) is a remediation technique whereby powder or slurried reagents are mixed in-situ or ex-situ with contaminated soils or sediments by augers or other types of soil mixers. SRM is one of the few available remedial technologies to effectively treat low permeability soils. SRM with binders is an established treatment technology to reduce leachability and physically immobilize heavy metals in soils (Bone et al., 2004). This type of SRM application is commonly referred to as stabilization / solidification. A more limited experience exists for the application of SRM with binders to soils contaminated with organics, in particular hydrocarbons, due to a limited understanding of the mechanisms that take place. Volatilization, encapsulation within the clay particles macroaggregates produced by the clay / binder / porewater reactions (solidification) and chemical degradation seem to be the mechanisms responsible for the hydrocarbons treatment in SRM with binders rather than stabilization.

A limited number of studies exist on quicklime remediation of soils contaminated with organics, in particular petroleum hydrocarbons (Schifano et al, 2005; Schifano et al, 2006). Schifano et al, 2006 carried out laboratory treatability studies to treat a number of cohesive soils contaminated with petroleum hydrocarbons using quicklime mixing. The results of the study showed reduction of total soil and leachate hydrocarbon concentrations upon quicklime mixing. Increases in temperature, due to the exothermic hydration reaction of quicklime when in contact with porewater, appeared to promote the volatilization of the light petrol fractions (C5-C12) but were considered not entirely responsible for their concentration decreases. The decrease in concentrations of less volatile hydrocarbon fractions was attributed, at least in part, to a time-dependent mechanism of encapsulation of the large hydrocarbon molecules within clay macro-aggregates, produced by the clay / quicklime / porewater reactions. An initial high moisture content or addition of water during mixing hindered the volatilization of light hydrocarbons and resulted in higher post-treatment concentrations of volatiles in some silt and sand/kaolinite mixture samples. However, higher moisture contents in silt samples resulted in improved mixability, a more homogeneous distribution of quicklime and therefore enhanced encapsulation and better concentration reduction of heavy aromatics.

The clay / quicklime / porewater reactions, which include flocculation, ion exchange, carbonation, dissolution of clay minerals and pozzolanic reactions (Goldberg and Klein, 1952; Eades and Grim, 1960; Glenn and Handy, 1963; Diamond et al., 1964; Diamond and Kinter, 1965; Brinkman, 1979; Bell, 1996) are considered to be responsible for the encapsulation of hydrocarbons and for the increase in the drained and undrained shear strength of cohesive soils reported in the literature for binder treated soils (Wissa et al., 1965; Balasubramaniam et al., 1989; Mesri et al., 1999; Lindh, 2004; Holm, 2005). In addition, mechanisms, which may contribute to the formation of the clay macro-aggregates and improve the clay strength, may be cation linking, in which Ca ions link clay particles through their negative edges and binding of the clay particles by the silicate hydrates gels produced by the pozzolanic reactions (Clare and Cruchley, 1957; Diamond and Kinter, 1965; Croft, 1967).

Gypsum is often used as an additive to accelerate reactions and improve the strength of stabilised / solidified contaminated wastes (Conner, 1990). It has also been reported to reduce plasticity and swelling of expansive clays (Lopez-Lara et al., 1999; Graber et al., 2006), and increase strength of lime treated clays (Pimraksa and Thongchai, 2006). In particular, Pimraksa and Thongchai (2006) observed increases in strength upon adding up to 4% concentrations of dihydrate gypsum ($CaSO_4$ $2H_2O$) to a lime and flyash treated silty clay. The authors attributed the increase in strength to formation of large agglomerates, mostly calcium alumino silicate hydrates, which acted as bonding agents between clay particles and pozzolanic products. No formation of ettringite was detected in the samples despite the addition of gypsum.

This paper summarizes the work carried out for the treatability study of SRM, associated with the remediation of contaminated soils in a disused petrol filling station in Kent, UK. The results of several phases of intrusive investigations and a detailed quantitative risk assessment, carried out for the site, indicated that petroleum hydrocarbon compounds in the soils presented a significant risk to human health receptors, via inhalation of vapours and direct exposure and to groundwater receptors. A remediation strategy was designed to result in reducing the total soil and leachate concentrations of the hydrocarbon compounds, to minimize the risks to both human health and groundwater receptors. In addition, an improvement of the strength was required in order to increase bearing capacity of the foundation soils for future development of the site. In-situ SRM was selected as the optimum technology to achieve both the environmental and geotechnical goals associated with a residential redevelopment of the site. As a part of the evaluation of feasibility of SRM, a number of binder reagents, including quicklime, hydrated lime and ordinary Portland cement, were tested. Furthermore, the addition of Gypsum to some reagent formulations was evaluated in an attempt to improve the strength of the binder/soil mixes.

A number of contaminated clay samples were taken from the site and blended together. The homogeneised sample was mixed in the laboratory with different formulations of binder reagents and left to cure under laboratory environmental conditions. Concentrations of petroleum hydrocarbon compounds were determined on soil and leachate samples after a 28-day curing period. The effects of temperature on the mechanisms responsible for concentration reduction of petroleum hydrocarbons were evaluated by comparing the use of quicklime with that of hydrated lime and OPC slurries, which have less pronounced exothermic reactions. Changes in the physical and physico-chemical properties of the soil were quantified by examining pH, moisture content, liquid limit and plastic limit changes over the 28 day testing program. The unconfined compressive strength of the treated clay was measured on samples which had been compacted immediately after reagent mixing and left to cure in submerged condition in distilled water baths for 28 days.

2. MATERIALS AND METHODS

2.1 Materials

Natural samples of a clayey soil were taken from five trial pits, excavated in previously identified contaminated areas of a disused petrol filling station in Kent, UK. Soil samples taken from the trial pits were placed in double polyethylene bags and brought immediately to the Arcadis laboratory, where concentrations of Benzene, Toluene, Ethylbenzene and Xylenes (BTEX) were immediately measured to confirm that the samples taken were contaminated. The samples were then stored overnight in double polyethylene bags placed in sealed plastic containers. A number of contaminated soil samples were then selected, the gravel size constituents removed and the samples mixed together, using first a stainless steel spatula on a glass plate, and then a 2-inch pugmill mechanical mixer to produce a homogeneous sample. Moisture content, Atterberg limits, pH, total sulphate, Total Organic Carbon (TOC) and Loss on Ignition (LOI) of the homogenized sample were determined and are presented in Table 1. The untreated homogenized clay sample had a moisture content ranging between 33% and 34%, liquid limit ranging between 49% and 52% and plastic limit between 25% and 26%.

The homogenized clay was mixed with a number of binder reagents including quicklime, hydrated lime and ordinary Portland cement. The quicklime powder (Lhoist UK) used in the experiments contained at least 97% calcium oxide and small quantities of calcium carbonate, magnesia and trace elements. The hydrated lime powder (Lhoist UK) contained at least 92% calcium hydroxide and small quantities of calcium carbonate, magnesia and trace elements. Agricultural grade Gypsum (British Gypsum) was added to some reagent formulations in an attempt to improve the strength of the binder/soil mix. The gypsum contained 98% calcium sulfate dihydrated ($CaSO_4 \cdot 2H_2O$) and a minor amount of calcium carbonate and clay impurities. All the reagents were stored in sealed plastic containers at room temperature prior to be mixed with the soils.

Table 1. Soil Properties in Untreated and Treated Samples

	Time Days	**Untreated**	**QL_{20}**	**$QL_{10}G_{10}$**	**HL_{20}**	**$HL_{10}C_{10}$**	**$HL_{10}C_5G_5$**	**C_{20}**	**$C_{10}G_{10}$**
w (%)	t=0	33-34	18.3	25.6	35.7	34.6	36.8	35.3	38.0
	t=28	32.0	17.8	25.6	35.9	33.9	36.0	31.9	36.1
w_l (%)	t=0	49-52	48	53	60	66	65	61	66
	t=28	na	43	53	58	57	64	59	65
w_p (%)	t=0	25-26	34	35	31	35	42	44	42
	t=28	na	35	37	36	44	45	46	45
PI	t=0	24-26	14	18	29	31	23	17	24
	t=28	na	8	16	22	13	19	13	20
pH	t=0	7.9							
	t=28	9.3	12.7	12.6	12.6	12.6	12.6	12.6	12.1
Total Sulphate (mg/kg)	t=0	0.78	na	na	na	Na	na	na	na
	t=28	1.16	2.44	47.18	1.12	4.37	22.15	6.30	55.32
TOC (%)	t=0	0.91	na	na	na	Na	na	na	na
	t=28	0.97	0.68	0.53	0.58	0.74	0.83	0.84	0.76
LOI (%)	t=0	2.9	na	na	na	Na	na	na	na
	t=28	3.0	2.4	1.8	2.9	1.6	2.0	3.3	3.0
UCS (kPa)	t=28	46	141	484	90	395	524	1186	687
γ (Mg/m^3)	t=28	1.89	1.67	1.84	1.80	1.81	1.80	1.77	1.79

Notes: Untreat. = Untreated; t=0 = immediately after mixing; w = moisture content; w_l = liquid limit, w_p = plastic limit, PI = Plasticity Index; ppm = parts per million; UCS = Unconfined Compressive Strength; γ = bulk density; na = test not undertaken.

2.2 Methods

The experimental work was carried out in the laboratories of Arcadis Geragthy and Miller International (Arcadis GMI), Newmarket, UK. Chemical analyses were carried out by ALcontrol Geochem (Chester, UK) and undrained shear strength tests by Soil Property Testing (Huntington, UK), both UKAS accredited commercial laboratories. Preliminary chemical analyses on BTEX compounds were carried out in the Arcadis mobile analytical laboratory.

Moisture content, liquid and plastic limit of soils were determined using the BS1377:1990 Part 2(3), 2(4.4) and 2(5) methods (BSI, 1990). The liquid limit was determined using the one-point cone penetrometer test. Moisture contents were determined on duplicate samples. Temperatures were measured by inserting a digital thermometer (Electronic Temperature Instruments Ltd) into the soil samples. Evolution of Volatiles Organic Compounds (VOCs) during laboratory mixing of soil and reagents was detected using a hand-held Photo-Ionisation Detector (PID) (RAE Systems, miniRAE 2000).

Soil samples were placed in standard sealed glass jars and sent, inside coolboxes, with ice packs to ALcontrol Geochem Laboratory for the chemical analyses immediately after reagent mixing. The samples received by the laboratory were stored at 4 °C and tested within 24 hours of receipt. Total Petroleum Hydrocarbon Working Group compounds (TPH) and 16 speciated Polynuclear Aromatic Hydrocarbon (PAH) analyses were carried out. TPH as measured, according to the Total Petroleum Hydrocarbon Working Group, is split between aliphatic and aromatic hydrocarbon species and banded by carbon number. The aliphatic hydrocarbons generally have lower volatility than the aromatic hydrocarbons and require the use of an extraction method to prepare for analysis. The aromatic range compounds, typically found in gasoline and are extracted by using a volatilization method. The Gasoline Range Hydrocarbons (GRO) (C4-C10), including benzene, toluene, ethylbenzene, xylenes (BTEX) and MTBE, concentrations were determined by Gas Chromatography - Flame Ionization Detection using a method based on US EPA Methods 8021b (USEPA, 1996a) and 602 (USEPA, 1984); the Extractable Petroleum Hydrocarbon (EPH) (C10-C40) concentrations by Gas Chromatography - Flame Ionization Detection Massachusetts Department of Environmental Protection, 1998 Method (Massachusetts Department of Environmental Protection, 2003); the PAH by Gas Chromatography – Mass Spectrometry US EPA Method 8100 (USEPA, 1996b). EPHs and PAHs were extracted using Accelerated Solvent Extraction system (ASE) followed by solvent reduction using a Zymark Turbovap. The soluble organics were extracted from the soil sample using Hexane as the solvent.

Leachates were extracted from soil samples using the National Rivers Authority (NRA) leaching test (Lewin et al., 1994).The soil samples were left to stand in a slurry state (water to solid ratio 10:1) for 24 hours inside new sterilized glass vessels with polytetrafluoroethylene (PTFE) lids. Distilled/deionised water with a pH of 5.6 was used to prepare the slurry samples. The slurry samples were filtered and centrifuged and the extract water submitted for further analyses. Glass fiber filters (Whatman 1.6μm) and centrifuge glass vials, with PTFE lids, were used to minimize adsorption of hydrocarbons. All vials and vessels were discarded after use.

The QA/QC procedures for the analytical methods used in this study consisted of the standard ALcontrol laboratories QA/QC procedures, that is one reagent-blank leachate sample was analyzed for every 20 leachate samples, one certificate reference material tests and one reagent-blank test were analyzed for every 20 soil samples.

Unconfined compression tests were carried out on compacted untreated and treated samples. The samples were compacted inside 75mm diameter, 6.35mm thick wall PVC cells using a Standard Proctor Hammer. The soils were compacted in three layers to produce 150 mm long samples. The compaction procedure was modified with respect to BS1377-4:1990 (BSI, 1990) to account for the different compaction mould area with respect to standard Proctor tests. The number of blows for each layer was computed in such a way as to deliver the same compaction energy as in the standard Proctor test. The samples were then left to cure under tap water for 28 days before being submitted to Soil Property Testing laboratory for Unconfined Compressive Strength (UCS) Testing. UCS tests were carried out using the BS1377:1990 Part 7(7) method (BSI, 1990).

2.3 Preparation of Samples

The homogenized clay sample was mixed in the laboratory with the selected reagent formulations. Initially, the mixing was carried out by hand using a stainless steel spatula on a glass plate. During this stage, temperature and evolution of VOCs were monitored. After approximately 30 minutes of hand mixing, the soils were passed through a 2-inch pugmill mechanical mixer. Seven different reagent formulations were used in this study, including single and multiple reagent formulations. The amount of reagents in terms of soil dry weight basis (w/w) were: 20% quicklime (sample QL_{20}), 10% quicklime and 10% gypsum (sample QL_{10}/G_{10}), 20% hydrated lime (sample HL_{20}), 10% hydrated lime and 10% cement (sample $HL_{10}C_{10}$), 10% hydrated lime, 5% cement and 5% gypsum (sample $HL_{10}C_5G_5$), 20% cement (C_{20}) and 10% cement and 10% gypsum (sample $C_{10}G_{10}$). The binder reagents formulations used in the experiments and the resulting treated samples are summarized in Table 2.

Table 2. Treated Samples: Reagent Formulations

Reagent (%)	**QL_{20}**	**$QL_{10}G_{10}$**	**HL_{20}**	**$HL_{10}C_{10}$**	**$HL_{10}C_5G_5$**	**C_{20}**	**$C_{10}G_{10}$**
Quicklime	20	10	-	-	-	-	-
Hydrated Lime	-	-	20	10	10	-	-
OPC	-	-	-	10	5	20	10
Gypsum	-	10	-	-	5	-	10
Water	-	-	10	10	10	10	10

Dry quicklime and gypsum were added to the soil as powders in the preparation of samples QL_{20} and $QL_{10}G_{10}$; all other reagent formulations were added as slurries, using an amount of distilled water corresponding to an increase of soil moisture of 10%, in terms of soil dry weight basis (w/w). After mixing, a portion of the soil-binders mixtures were stored in sealed polyethylene containers in the laboratory, at natural moisture and temperature conditions for 28 days. The untreated clay sample was stored for control purposes. The untreated and treated samples were placed in sealed glass jars with coolboxes, provided with ice packs and sent to ALcontrol Geochem Laboratory for the chemical analyses. The samples received by the laboratory were stored at 4 °C and tested within 24 hours from receipt.

Approximately 24 hours after mixing the binder reagents, the samples of the soil-binders mixtures were compacted inside 75mm diameter PVC cells. Prior to placing the soils, a layer of silicone grease was spread on the wall of the cells in order to minimize friction during the subsequent extrusion of the samples. After compaction, the samples were left in the cells and placed into polyethylene containers, where they were loaded using steel discs placed on the soil samples. Discs of geotextile material were placed between the soil and the steel disc. The load applied corresponded approximately to the computed average effective overburden stress in the zone of expected in-situ treatment. The containers were then filled with tap water to allow the loaded samples to cure in wet conditions. After 28 days curing the samples were unloaded and submitted inside the cells to the laboratory for extrusion and determination of unconfined compressive strength (UCS).

3. RESULTS

3.1 Temperature and PID measurements during mixing

Temperature and PID readings were intermittently monitored during hand mixing the binder reagents and the clay. Noticeable temperature increases were observed in the samples mixed with powdered quicklime. Temperature increases for all other samples were minimal. The differences in maximum temperatures in the different samples can be explained in terms of the exothermic hydration reaction taking place during mixing of dry quicklime, as opposed to limited hydration reactions during the mixing of cement, gypsum and hydrated lime slurries to soil. Maximum temperatures measured during mixing are presented in Table 3.

Table 3. Temperature measurements and PID readings during mixing

	QL_{20}	$QL_{10}G_{10}$	HL_{20}	$HL_{10}C_{10}$	$HL_{10}C_5G_5$	C_{20}	$C_{10}G_{10}$
T_o T_{max} (°C)	9.6 70	10 26	10 13	na 15	10 15	12 14	na 16
PID_{max} (ppm)	84 163	249 246	213 631	na 167	9.5 24.6	1.5 63	na 36.1

The maximum temperatures recorded were: 70°C (QL_{20}), 26°C ($QL_{10}G_{10}$), 13°C (HL_{20}), 15°C ($HL_{10}C_{10}$), 15°C ($HL_{10}C_5G_5$), 14°C (C_{20}) and 16°C ($C_{10}G_{10}$).

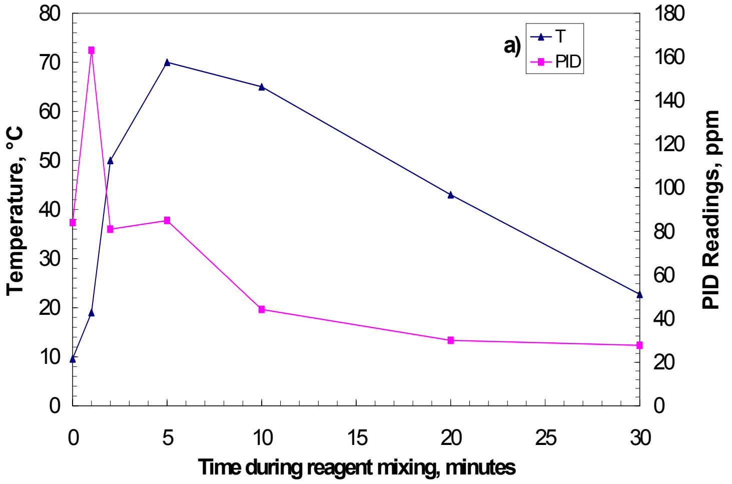

Figure 1.

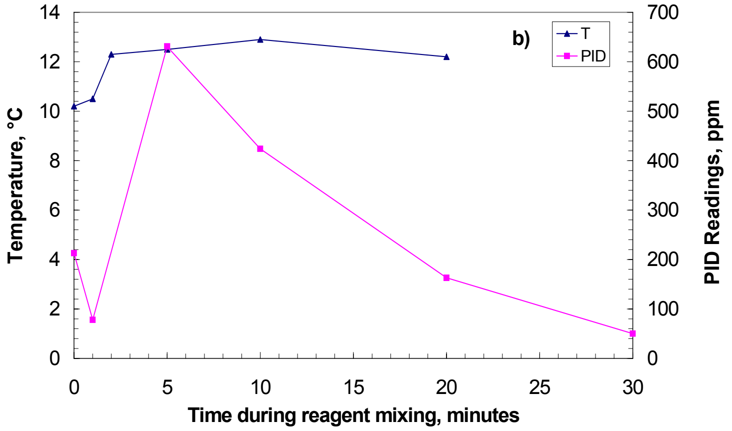

Figure 1. Temperatures and PID readings during mixing of samples a) QL_{20} and b) HL_{20}

As shown in Figure 1, in sample QL_{20} the temperature was observed to increase rapidly during the first few minutes of mixing, then reached a maximum value and eventually gradually decreased. High values of PID readings were obtained during the soil mixing before and after adding the binder reagents (Figure 1a). As shown in Figure 1, a progressive decrease in the values of PID readings was observed as the reagent mixing progressed.

3.2 Physical, Physico-Chemical and Mechanical Properties

Changes in the physical and physico-chemical properties of the soil upon reagent mixing were quantified by examining pH, moisture content, liquid limit and plastic limit changes over the 28 day testing program.

The pH of treated samples was measured after 28 days curing. Results of pH measurements are presented in Table 1. A significant increase in pH upon binder reagent mixing was observed in all samples. Moisture content, liquid limit and plastic limit were determined on the clay immediately after adding the reagents and after 28 days of curing. The results are presented in Table 1. These show that immediately after mixing, the liquid limit slightly decreased in sample QL_{20}, slightly increased in $QL_{10}G_{10}$ and significantly increased in all other samples. The liquid limit determined after a 28-day curing period are smaller than the values immediately after mixing, indicating a decreasing trend of liquid limit with time.

Plastic limit immediately increased in all samples and continued to increase during the 28 days curing period. Considering that the addition of the binder reagent slurries increased the moisture content of the samples by 10%, with respect to the untreated clay moisture content, it can be concluded that the addition of binders resulted in a decrease in moisture content in all the samples. The moisture content continued to decrease with time, as indicated by the 28 day curing measurements.

The UCS of the untreated clay in a remolded condition, and of the treated samples, was determined after 28 days of wet curing inside the PVC compaction cells. The results are presented in Table 1 and Figure 2. An "Estimated Undisturbed" strength value is also presented in Figure 2. This was computed on the basis of the empirical relationship between liquidity index and sensitivity of the clay (Terzaghi et al., 1996). It can be observed that increases in UCS with respect to the clay remolded UCS were achieved in all treated samples. Particularly significant increases in UCS were observed in samples C_{20}, $C_{10}G_{10}$, $HL_{10}C_5G_5$, $QL_{10}G_{10}$ and $HL_{10}C_{10}$.

As for practical reasons a total amount of reagents and gypsum of 20% was selected for all samples. A full assessment on the effect of adding gypsum on the strength of the binder treated soils is not possible. However, comparisons of samples QL_{20} and $QL_{10}G_{10}$, $HL_{10}C_{10}$ and $HL_{10}C_5G_5$ and C_{20} and $C_{10}G_{10}$ suggest that adding gypsum appears to have favorable effects on the strength of soils treated with a predominantly lime based reagent formulation, and less favorable effects on that of cement based formulations.

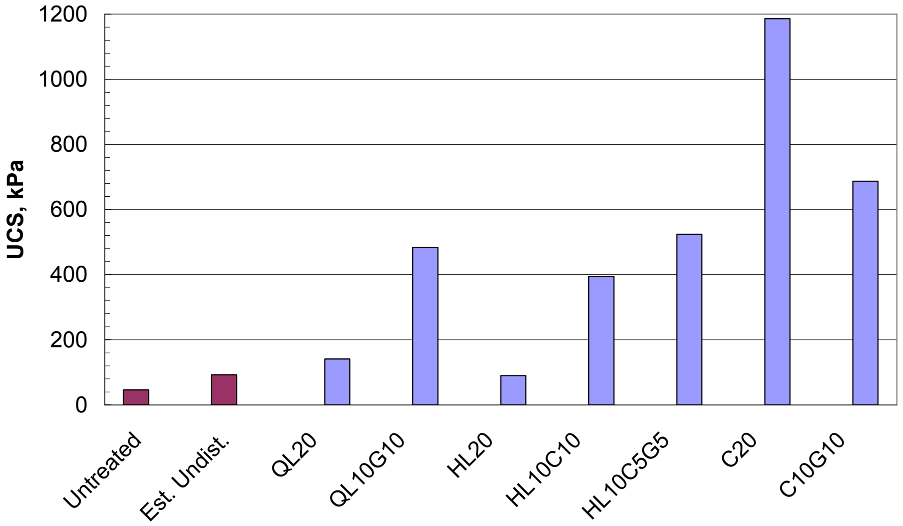

Figure 2. Unconfined Compressive Strength of Treated and Untreated Samples

3.3 Concentrations of Petroleum Hydrocarbons

3.3.1 Total Soil Concentrations

Concentrations of BTEX, MTBE, TPH and PAH measured in the untreated clay and in the clay samples after 28 day curing time are presented in Table 4 and Table 5. The concentrations of BTEX, MTBE and TPH measured in sample $HL_{10}C_5G_5$ are also presented in Figure 3. All treated samples present significantly smaller concentrations of BTEX, MTBE and all ranges of Total Petroleum Hydrocarbons TPH working groups than the untreated sample. Particularly significant decreases in concentrations of BTEX and light aliphatic (>C5-C12) and aromatic (>EC8-EC16) compounds were observed in all treated samples.

The percent decrease of GRO (C4-C12) concentrations in the treated samples ranged between 97% and 99.8%, that of TPH between 80% and 91%. Some increases in concentrations of heavy aliphatics were observed in samples $QL_{10}G_{10}$ (>C16-C35), C_{20} and $C_{10}G_{10}$ (>C21-C35). A slight increase in the concentration of aromatics range >EC21-EC35 was also observed in sample $HL_{10}C_{10}$.

Concentrations of PAH compounds also generally decreased upon treatment with binder reagents. Significant concentration reductions were observed for the rather volatile naphthalene, whereas negligible changes or even small increases, with respect to the untreated clay, were observed for a number of PAH compounds in sample $C_{10}G_{10}$ and for heavier compounds, such as benzo(a)pyrene and benzo(b)fluoranthene in a number of samples.

Table 4. Concentrations in mg/kg of Speciated Total Petroleum Hydrocarbon (TPH), BTEX/MTBE compounds in untreated and treated samples

Sample Identity	**Untreated**	**QL_{20}**	**$QL_{10}G_{10}$**	**HL_{20}**	**$HL_{10}C_{10}$**	**$HL_{10}C_5G_5$**	**C_{20}**	**$C_{10}G_{10}$**
GRO (C4-C12)	495.65	2.17	1.27	14.87	2.10	0.96	0.96	2.03
MTBE	38.72	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Benzene	6.78	0.02	0.03	0.04	0.03	0.03	0.02	0.02
Toluene	47.68	0.06	0.06	0.28	0.08	0.06	0.06	0.05
Ethyl benzene	20.80	0.02	<0.01	0.08	0.03	<0.01	<0.01	<0.01
m & p Xylene	75.13	0.12	0.09	0.29	0.13	0.12	0.10	0.09
o Xylene	32.55	0.07	0.04	0.22	0.06	0.06	0.05	0.04
Aliphatics C5-C6	3.26	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Aliphatics >C6-C8	110.83	<0.01	<0.01	2.48	<0.01	<0.01	<0.01	<0.01
Aliphatics >C8-C10	41.78	0.21	0.08	1.51	0.15	0.07	0.06	0.15
Aliphatics >C10-C12	22.18	0.54	0.34	3.08	0.56	0.21	0.23	0.58
Aliphatics >C12-C16	37.30	9.13	13.69	15.59	14.90	10.73	25.74	16.53

Sample Identity	**Untreated**	**QL_{20}**	**$QL_{10}G_{10}$**	**HL_{20}**	**$HL_{10}C_{10}$**	**$HL_{10}C_5G_5$**	**C_{20}**	**$C_{10}G_{10}$**
Aliphatics >C16-C21	17.38	10.76	21.06	13.66	15.46	13.12	38.36	19.17
Aliphatics >C21-C35	9.56	5.70	12.04	7.43	9.58	5.43	9.00	6.92
Total Aliphatics C5-C35	242.29	26.34	47.21	43.75	40.65	29.55	73.38	43.35
Aromatics >EC8-EC10	191.15	0.53	0.25	2.86	0.45	0.28	0.25	0.36
Aromatics >EC10-EC12	33.27	0.81	0.51	4.62	0.84	0.31	0.34	0.86
Aromatics >EC12-EC16	4.17	1.54	<0.01	1.82	<0.01	0.21	1.41	0.77
Aromatics >EC16-EC21	8.95	6.47	3.28	7.42	4.73	3.43	5.63	7.07
Aromatics >EC21-EC35	33.03	26.34	22.17	22.09	35.96	16.72	31.10	28.78
Total Aromatics C6-C35	325.03	35.77	26.30	39.13	42.09	21.04	38.81	37.92
TPH	567.32	62.11	73.51	82.88	82.74	50.58	112.18	81.26

3.3.2 Hydrocarbons Concentrations in Leachates

No standardized leaching tests for organic compounds are available at present (Hansen et al., 2004; Wiles and Barth, 1992). Batch leaching tests, such as NRA test, were originally developed to assess leachability of metals from a solid matrix. A quantitative interpretation of batch leach tests for organic compounds is complicated by a number of relatively unknown factors, such as effects of suspended matter, dissolved organic matter and other colloidal particles. Therefore, results of leaching tests were used to qualitatively assess the mass transfer to porewater of petroleum hydrocarbons in the soil samples treated with binder reagents.

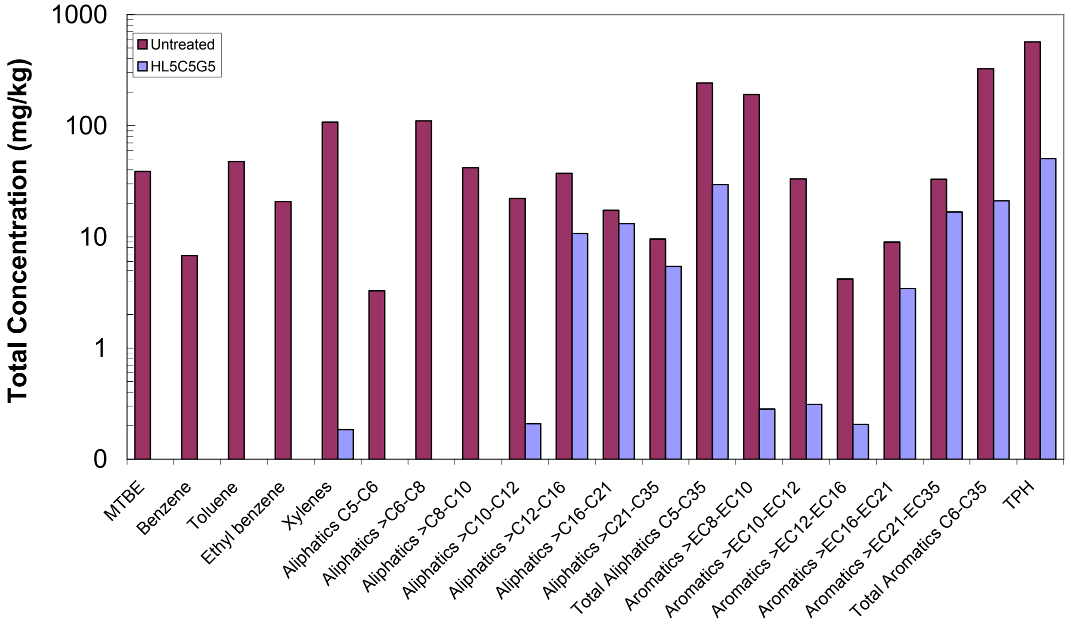

Figure 3. Concentrations of Speciated Total Petroleum Hydrocarbon (TPH), BTEX/ MTBE compounds in untreated clay and in sample $HL_{10}C_5G_5$.

Petroleum hydrocarbon concentrations were measured in the leachates extracted from the untreated sample and from the treated samples after 28 day curing time.

The concentrations of BTEX, MTBE, TPH and PAH compounds measured in the leachates are presented in Tables 6 and 7. The concentrations of hydrocarbons measured in the leachates from the treated samples are generally substantially smaller than those from the untreated sample. The percent decrease of GRO (C4-C12) concentrations in the treated samples ranged between 96% and 100%, that of TPH between 95% and 100%. Slight increases of fluorene and phenanthrene concentrations in leachates from treated samples were observed in a number of samples.

4. DISCUSSION

The mixing of the petroleum hydrocarbons contaminated clay with single or multi-component formulations of binder reagents resulted in a decrease in total soil concentration of petroleum hydrocarbons. A comparison of leaching test results between the untreated and treated clay, together with the results of total soil concentration, demonstrates that the binder reagent mixing resulted also in a decrease of mass transfer of petroleum hydrocarbons.

Table 5. Concentrations in mg/kg of Speciated Polynuclear Aromatic Hydrocarbons (PAH) in untreated and treated samples

Sample Identity	**Untreated**	**QL_{20}**	**$QL_{10}G_{10}$**	**HL_{20}**	**$HL_{10}C_{10}$**	**$HL_{10}C_5G_5$**	**C_{20}**	**$C_{10}G_{10}$**
Naphthalene	4.55	0.19	0.16	0.19	0.23	0.21	0.17	0.32
Acenaphthylene	0.06	0.05	0.05	0.05	0.05	0.04	0.04	0.05
Acenaphthene	0.31	0.10	0.10	0.09	0.09	0.05	0.06	0.18
Fluorene	0.56	0.21	0.26	0.20	0.19	0.14	0.15	0.36
Phenanthrene	2.01	1.27	1.44	1.27	1.17	0.97	0.97	1.93
Anthracene	0.34	0.29	0.33	0.28	0.26	0.22	0.19	0.46
Fluoranthene	2.33	1.80	1.97	1.68	1.69	1.50	1.33	2.51
Pyrene	1.78	1.50	1.50	1.30	1.38	1.14	1.11	2.06
Benz(a)anthracene	0.79	0.69	0.76	0.62	0.70	0.66	0.56	0.95
Chrysene	0.83	0.68	0.74	0.61	0.69	0.66	0.56	0.93
Benzo(b)fluoranthene	1.00	1.07	1.27	1.06	0.91	1.32	1.00	1.33
Benzo(k)fluoranthene	0.35	0.31	0.43	0.30	0.31	0.30	0.22	0.45
Benzo(a)pyrene	0.61	0.57	0.64	0.54	0.62	0.61	0.52	0.84
Indeno(123cd)pyrene	0.37	0.32	0.32	0.27	0.37	0.31	0.27	0.42
Dibenzo(ah)anthracene	0.18	0.08	0.11	0.07	0.08	0.09	0.09	0.13
Benzo(ghi)perylene	0.41	0.32	0.36	0.31	0.38	0.35	0.31	0.45
PAH 16 Total	16.47	9.42	10.42	8.83	9.11	8.56	7.52	13.34

The decrease of total soil concentrations of light hydrocarbons can be partly explained in terms of volatilization during the mixing process, as suggested by the large PID readings in Table 1 and Figure 1. A comparison of Figure 1 a and b suggests that the rate and magnitude of volatiles release during the soil mixing process is mainly related to the mechanical mixing action and possibly, in the case of quicklime reagent, in part to temperature effects. Other mechanisms responsible for the decreases in concentrations of volatiles could be the mixing at a molecular level of a portion of the compounds with the clay / pozzolanic products matrix, as observed by Butler et al. (2000) and Nestle et al (2001) for Toluene in cement matrices.

Table 6. Concentrations in μg/l of Speciated Total Petroleum Hydrocarbon (TPH), BTEX/MTBE compounds in leachate samples

Sample Identity	**Untreated**	**QL_{20}**	**$QL_{10}G_{10}$**	**HL_{20}**	**$HL_{10}C_{10}$**	**$HL_{10}C_5G_5$**	**C_{20}**	**$C_{10}G_{10}$**
GRO (C4-C12)	28912	<10	<10	1270	<10	<10	<10	<10
MTBE	614	<10	<10	<10	<10	<10	<10	<10
Benzene	158	<10	<10	<10	<10	<10	<10	<10
Toluene	2158	<10	<10	<10	<10	<10	<10	<10
Ethyl benzene	1138	<10	<10	<10	<10	<10	<10	<10
m & p Xylene	3095	<10	<10	<10	<10	<10	<10	<10
o Xylene	1826	<10	<10	<10	<10	<10	<10	<10
Aliphatics C5-C6	<10	<10	<10	<10	<10	<10	<10	<10
Aliphatics >C6-C8	5974	<10	<10	15	<10	<10	<10	<10
Aliphatics >C8-C10	3403	<10	<10	136	<10	<10	<10	<10
Aliphatics >C10-C12	2176	<10	<10	366	<10	<10	<10	<10
Aliphatics >C12-C16	307	<10	<10	<10	<10	<10	<10	<10
Aliphatics >C16-C21	186	<10	<10	<10	<10	<10	<10	<10
Aliphatics >C21-C35	204	<10	<10	<10	<10	<10	<10	<10
Total Aliphatics C5-C35	12250	<10	<10	517	<10	<10	<10	<10
Aromatics >EC8-EC10	11164	<10	<10	204	<10	<10	<10	<10
Aromatics >EC10-EC12	3265	<10	<10	549	<10	<10	<10	<10
Aromatics >EC12-EC16	136	26	82	222	63	57	62	61

Sample Identity	Untreated	QL_{20}	$QL_{10}G_{10}$	HL_{20}	$HL_{10}C_{10}$	$HL_{10}C_5G_5$	C_{20}	$C_{10}G_{10}$
Aromatics >EC16-EC21	172	25	51	55	29	42	44	33
Aromatics >EC21-EC35	308	<10	<10	<10	<10	<10	<10	<10
Total Aromatics C6-C35	17361	51	133	1030	92	99	106	94
TPH	29611	51	133	1547	92	99	106	94

The magnitude of concentration decreases of the heavy aliphatic and aromatics were similar for quicklime treated samples, for which large temperature increases were measured during reagent mixing, and other samples where negligible increases in temperature were measured. Therefore, it can be concluded that temperature effects do not play a major role in the decreases in concentrations of heavy aliphatics and aromatics in the clay samples.

The decreases in concentration of the heavy aliphatic and aromatics can be explained in terms of a strong association between the petroleum hydrocarbon compounds and the solid constituents of the samples.

Table 7. Concentrations in mg/kg of Speciated Polyneuclear Aromatic Hydrocarbons (PAH) in leachate samples

Sample Identity	Untreated	QL_{20}	$QL_{10}G_{10}$	HL_{20}	$HL_{10}C_{10}$	$HL_{10}C_5G_5$	C_{20}	$C_{10}G_{10}$
Naphthalene	233.79	19.29	19.47	78.21	24.78	15.59	17.93	17.20
Acenaphthylene	0.57	0.17	0.28	0.52	0.19	0.17	0.15	0.17
Acenaphthene	3.27	3.43	3.50	6.17	2.82	2.97	2.64	2.84
Fluorene	4.26	5.71	6.28	8.84	4.60	5.60	4.45	4.67
Phenanthrene	12.52	12.17	14.89	17.29	9.74	11.55	10.83	11.29
Anthracene	3.23	2.26	2.88	3.35	1.80	2.12	2.12	2.20
Fluoranthene	10.63	3.19	4.56	4.55	2.62	3.20	3.57	3.81
Pyrene	8.27	2.03	3.01	2.95	1.71	2.08	2.34	2.48
Benz(a)anthracene	3.18	0.13	0.23	0.20	0.11	0.14	0.15	0.17
Chrysene	2.43	0.13	0.22	0.21	0.12	0.15	0.18	0.19
Benzo(b)fluoranthene	1.31	<0.01	<0.01	0.03	<0.01	<0.01	<0.01	<0.01
Benzo(k)fluoranthene	1.65	<0.01	<0.01	0.04	<0.01	<0.01	<0.01	<0.01
Benzo(a)pyrene	1.88	<0.01	<0.01	0.04	<0.01	<0.01	<0.01	<0.01
Indeno(123cd)pyrene	0.64	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Dibenzo(ah)anthracene	0.26	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Benzo(ghi)perylene	0.94	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
PAH 16 Total	288.80	48.50	55.31	122.39	48.47	43.55	44.38	45.01

This would hinder their extraction and determination by the analytical procedure used. Permanent conversion of long chains hydrocarbons into volatile compounds, which evaporate into the atmosphere (Soundararajan, 1992), or degradation of the compounds, possibly due to chemical or electrochemical oxidation processes, would also account for the decrease in concentrations. The association mechanism may be explained in terms of encapsulation of hydrocarbons within the clay particles macroaggregates, produced by the clay / quicklime / porewater reactions. The progressive hardening of the pozzolanic products hinders the release of the compounds in the porewater. The hypothesized encapsulation mechanism appears to be substantiated by the changes in physico-chemical properties of the treated samples. The observed increase in plastic limit is typical of clays treated with binder reagents (Clare and Cruchley, 1957; Hilt and Davidson, 1960; Zolkov, 1962; Jan and Walker, 1963; Wang et al., 1963; Brandl, 1981; Rogers and Glendinning, 1996, Bell, 1996; Mesri et al., 1999). This has been attributed to formation of clay macro-aggregates, which entrap large volumes of water (Mesri et al., 1999). The changes in liquid limit are also consistent with literature results, which show either increase (Clare and Cruchley, 1957; Brandl, 1981; Bell, 1996) or decrease (Zolkov, 1962; Jan and Walker, 1963; Wang et al., 1963; Brandl, 1981; Bell, 1996) possibly as a result of changes in specific surface area of the clay upon binder treatment. In fact, while the addition of binders to clays results in destructuration of clay minerals, which gives rise to formation of high specific surface area calcium silicate and aluminate hydrates, it also results in the replacement of monovalent ions by Calcium and the formation of stable clay particle packets, or domains, through cation-linkage, and thus in a tendency to reduce specific surface area of clays (Diamond et al., 1964).

The small increases in concentrations of heavy aliphatics and aromatics observed in the soil and leachate samples, are probably the result of the release of these compounds, which are initially sorbed on the Soil Organic Matter (SOM), as the increase in pH associated with the binder mixing makes the SOM unstable (Bone et al., 2004).

A large increase in the UCS over the remolded value was achieved in all the treated samples but HL_{20} and, to a certain extent, QL_{20}. The large increase in clay strength upon binder mixing is considered to be a result of an increase in interparticle contact area (Terzaghi et al, 1996), caused by the formation of clay macro-aggregates and domains, and interparticle bonding by the silicate hydrates gels produced by the pozzolanic reactions. The lower UCS values obtained in samples HL_{20} and QL_{20} might have been the result of premature failures along a weak zone of the samples during UCS test. The UCS results suggest that reagent mixing resulted in an increase of UCS over the estimated undisturbed value. This conclusion could have a significant practical implication on the in-situ remediation process, as the binder mixing effects would compensate and overcome any loss in strength due to the remolding effect of mechanical mixing and, therefore, result in strength larger than the original undisturbed strength of the clay.

The apparent favorable effects of gypsum, on the strength of soil treated with a predominantly lime based reagent formulation, is in agreement with findings of Pimraksa and Thongchai (2006), and may be explained as a result of formation of large agglomerates which act as bonding agents between clay particles / pozzolanic products system. In the case of cement treated soil, it seems possible that the large sulphate content (Table1), resulting from addition of gypsum to sample $C_{10}G_{10}$, caused formation of ettringite, which is known to cause expansion and development of cracks (Pimraksa and Thongchai, 2006). The propagation of these cracks might have created weakness zones resulting in smaller compression strength than in sample C_{20} in which no gypsum was added.

5. CONCLUSIONS

The treatability study summarized in this paper confirmed that SRM with binders is a viable technique for remediation and improvement of geotechnical properties of the petroleum contaminated clayey soils, at a petrol filling station site in Kent, UK.

Mixing soils with lime and cement binder reagents resulted in significant decreases in total concentrations and leachability of petroleum hydrocarbon compounds and, therefore, reduced the risks of exposure for both human health and groundwater receptors, for a residential end-use redevelopment of the site. In addition, the treatment simultaneously improved the strength of the foundation soils for future development of the site. Addition of gypsum appears to improve the strength of the samples treated with a predominantly lime based reagent formulation, and to have less favorable effects on the strength of cement based formulations.

The decreases in petroleum hydrocarbons concentrations may be explained by a number of mechanisms, such as volatilization, encapsulation within the pozzolanic products matrix or the clay macro-aggregates voids, and possibly degradation of the hydrocarbon compounds promoted by the binder mixing. PID measurements indicated significant volatilization of light hydrocarbons during the mixing of the clay. The rate and magnitude of volatiles release during the soil mixing process is mainly related to the mechanical mixing action. Larger increases in temperature measured in the samples treated with quicklime, did not appear to result in higher reductions of hydrocarbons, than in samples treated with binder reagents with less pronounced exothermic reactions. Volatilization of light compounds during mixing is not of concern for the full scale SRM application since such emissions can be captured by appropriate vapor control devices (Brown et al., 1992).

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