

# Stabilisation/solidification of synthetic petroleum drill cuttings

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Available online 2 June 2006

## Abstract

This paper presents the results of an experimental investigation into the use of stabilisation/solidification (S/S) to treat synthetic drill cuttings as a pre-treatment to landfilling or for potential re-use as construction products. Two synthetic mixes were used based on average concentrations of specific contaminants present in typical drill cuttings from the North Sea and the Red Sea areas. The two synthetic drill cuttings contained similar chloride content of 2.03% and 2.13% by weight but different hydrocarbon content of 4.20% and 10.95% by weight, respectively; hence the mixes were denoted as low and high oil content mixes, respectively. A number of conventional S/S binders were tested including Portland cement (PC), lime and blast-furnace slag (BFS), in addition to novel binders such as microsilica and magnesium oxide cement. Physical, chemical and microstructural analyses were used to compare the relative performance of the different binder mixes. The unconfined compressive strength (UCS) values were observed to cover a wide range depending on the binder used. Despite the significant difference in the hydrocarbon content in the two synthetic cuttings, the measured UCS values of the mixes with the same binder type and content were similar. The leachability results showed the reduction of the synthetic drill cuttings to a stable non-reactive hazardous waste, compliant with the UK acceptance criteria for non-hazardous landfills: (a) by most of the binders for chloride concentrations, and (b) by the 20% BFS–PC and 30% PC binders for the low oil content mix. The 30% BFS–PC binder successfully reduced the leached oil concentration of the low oil content mix to inert levels. Finally, the microstructural analysis offered valuable information on the morphology and general behaviour of the mixes that were not depicted by the other tests. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Oil drill cuttings; Stabilisation/solidification; Petroleum wastes; Binders; Waste re-use

## 1. Introduction

One of the most complex types of industrial wastes is drill cuttings, which are generated in vast quantities from the drilling process of oil exploration and production activities (Fig. 1). Drill cuttings are heterogeneous, hazardous, soil-like wastes [1] containing significant percentages of hydrocarbons, heavy metals and water-soluble salts. The physical characteristics and the chemical composition of drill cuttings vary significantly according to the type of drilling fluid used, local geology, oil well location, rig operator, drilling techniques, recovery method and disposal scenarios of the cuttings [2].

Until recently, untreated drill cuttings were being discharged to seabed, which has resulted in significant negative ecological impacts adjacent to many oil platforms [3,4]. Therefore, stringent environmental regulations have been issued in developed countries, including the UK, to control the discharge of drill cuttings from offshore platforms. This has been reflected

in the Oslo and Paris Commission Decisions 92/2 and 2000/3 [5,6], which prohibit any discharge of drill cuttings containing more than 1% of oil by weight at sea. Likewise, the environmental laws in developing countries, such as Egypt, have prohibited any discharge of substances resulting from drilling and exploration in the territorial sea or the exclusive economic zone without prior treatment; while indicating maximum limits for discharge into other marine environments [7].

Therefore, onshore disposal of drill cuttings to landfill has become the most prominent approach practised by many petroleum companies. However, due to the scarcity of hazardous landfill sites and escalating landfill taxes, the current practice is to treat the cuttings prior to re-use or disposal, in order to remove oil from the cuttings and to reduce the leachability of other contaminants. Despite the existence of many treatment methods, viz. in-situ bioremediation, re-injection, thermal desorption, stabilisation and combustion, the presence of high percentages of contaminants has hindered the re-use of treated cuttings. Furthermore, the potential high cost associated with some treatment techniques e.g. re-injection and thermal desorption, the extensive energy dependency of thermal desorption and combustion

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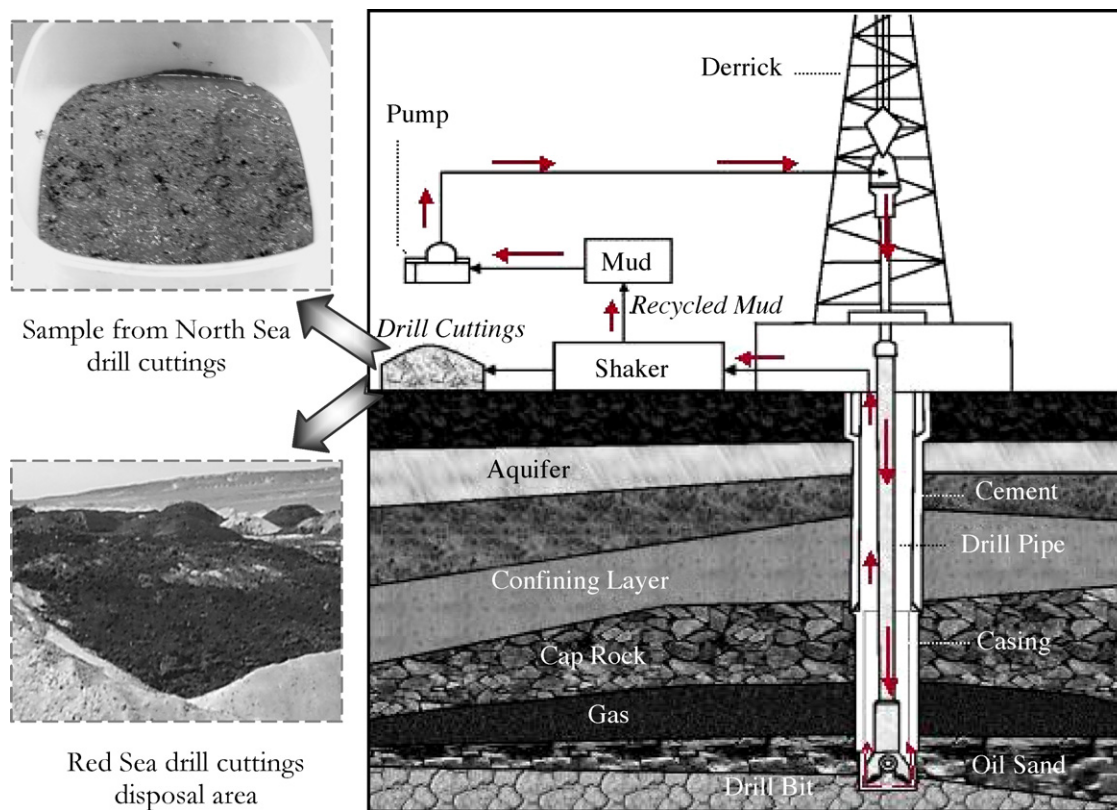


Fig. 1. Generation of drill cuttings from petroleum drilling operations.

methods and the slow process of bioremediation render these techniques unsustainable.

The work presented here is an experimental study in which synthetic drill cuttings were treated using the technique of stabilisation/solidification (S/S), in an attempt to reduce the hazardous nature of the drill cuttings prior to landfilling or to enable their re-use as value-added construction products. S/S involves the addition of binders which can effectively achieve: (a) chemical treatment (stabilisation) of the hazardous wastes by converting the contaminants into less soluble, mobile, or toxic forms, and (b) mechanical conversion (solidification) of the waste into a durable, dense and monolithic entity with structural integrity that is more suitable for storage, landfilling or re-use [8].

S/S of drill cuttings has many advantages since it requires minimal input of energy, results in lower atmospheric emissions [9] and can have potential applications in concrete works [10]. However, in the limited published work on this subject, the main disadvantage of utilising S/S to treat drill cuttings was reported to be the volume increase of the waste [9]. Despite the absence of any experimental work in those references [9,10], the potential leachability and interference of the high concentrations of chlorides with reinforced concrete have been cited as issues of concern.

In terms of experimental work, very little has been published in the UK and elsewhere on the use of S/S in the treatment of drill cuttings [11,12]. In one publication [11], 85–95% by weight of binders were utilised to convert drill cuttings to sub-base material for use in road construction. The incorporation of such extensive amounts of binders can place an economic barrier

to the practical implementation of the process. In another published work [12], the utilisation of 35% of conventional binders, viz. PC, pulverised fuel ash and lime, resulted in the successful treatment of drill cuttings for re-use as sub-base material in road construction. However, oil leachate concentrations were found to be around 1%, which are above the limit of the UK landfill acceptance criteria value for hazardous waste. Furthermore, the chloride leachate concentrations were not measured.

The purpose of the work reported here is to investigate the applicability of the use of much lower binder dosages and the use of a wide range of conventional and novel binders, which are industrial by-products or waste-based, to treat synthetic drill cuttings. The synthetic drill cuttings contained varied water contents as well as different concentrations of hydrocarbons and chlorides.

## 2. Drill cuttings data

Data collected from two different locations were employed to synthesize model drill cuttings with different properties. The first location is the North Sea area wherein a large number of offshore oil platforms exist. It has been estimated that the annual production of drill cuttings from the UK Continental Shelf lie between 50,000 and 80,000 tonnes [10]. Moreover, existing drill cutting piles, which have been built up in different locations [4] in the bottom of northern and central North Sea, are approximately equal to 12 million m<sup>3</sup> [13]. Data gathered from 14 different oil fields were processed to provide a range of values from which the statistical average composition of the North Sea drill cut-

Table 1  
Range of properties of the North Sea drill cuttings [2–4,9,10,15–17]

Property	Value	Property	Value
Particle size	4 $\mu\text{m}$ –20 mm	Liquid limit	33–70%
Gravel	1–7%	Plastic limit	16–35%
Sand	8–33%	Plasticity index	14–32%
Silt	37–62%	Density	1300–2700 kg/m <sup>3</sup>
Clay	16–25%	Shear strength	1.2–40 kN/m <sup>2</sup>
Water content	14–35%	pH	8–10.1

Table 2  
Average and maximum contaminant concentrations in North Sea [2–4,9,10,15–17] and Red Sea [14] drill cuttings

Contaminant	North Sea (% w/w)		Red Sea (% w/w)	
	Average	Maximum	Average	Maximum
Hydrocarbon	4.20	22.40	10.95	11.80
Chromium	0.005	0.02	0.10	0.40
Zinc	0.03	0.10	0.15	0.60
Barium	4.90	29.80	0.20	1.20
Lead	0.02	0.10	0.10	0.25
Chlorides	2.03	2.26	2.13	9.20

tings was calculated and used. These values are presented in Tables 1 and 2. The drill cuttings from the North Sea (Fig. 1) have been described as ‘biologically impoverished, poorly sorted, weakly cohesive oil-rich silts with a variable admixture of clay particles’ [13].

The second location is the Red Sea area where data from the Ras Shukier offshore oil production area, located in the Gulf of Suez, Red Sea—Egypt, were utilised. Ras Shukier consists of nine complex platforms where approximately 2740 tonnes of drill cuttings are generated annually [14]. The physical appearance of Ras Shukier drill cuttings (Fig. 1) is that of a pitch-black sticky clayey textured soil with a distinctive crude oil odour. The density of the drill cuttings pile ranges between 1200 and 1900 kg/m<sup>3</sup> with a water content of 20%. The average and maximum contaminant concentrations present in the Red Sea drill cuttings are also presented in Table 2.

### 3. Experimental work

Two synthetic mixes were used based on typical concentrations of specific contaminants present in drill cuttings from the North Sea and the Red Sea areas. These synthetic drill cuttings contained similar chloride contents of 2.03% and 2.13% by weight but different hydrocarbon contents of 4.20% and 10.95% by weight, respectively, and are hence denoted as low and high oil content mixes, respectively. The aforementioned contaminants were selected because conventional binders have been reported to be generally ineffective in their S/S treatment [8].

#### 3.1. Synthetic drill cuttings

Various attempts were made to obtain information on the typical composition of North Sea and Red Sea drilling cuttings.

Table 3  
Properties of the synthetic drill cuttings used

Property	Value
Base soil	
Sand	10%
Silt (silica flour)	50%
Clay 1 (polywhite kaolin E-grade)	20%
Clay 2 (calcium bentonite)	20%
Water content	
In the low oil content mix	20%
In the high oil content mix	27%
Liquid limit	51%
Plastic limit	25%
Plasticity index	26%
pH	9.0
Sodium hydroxide	0.05% or 500 mg/kg
Hydrocarbon content	
In the low oil content mix	4.20% or 42,000 mg/kg
In the high oil content mix	10.95% or 109,500 mg/kg
Chloride content	
In the low oil content mix	2.03% (3.32% or 33,200 mg/kg of NaCl)
In the high oil content mix	2.13% (3.48% or 34,816 mg/kg of NaCl)

It was found that the physical characteristics and contaminant levels varied significantly from one location to another in the North Sea area. For the Red Sea drill cuttings, very little information was available on their physical characteristics except for the water content, which was lower than that of the North Sea cuttings. Hence, the physical characteristics data available for the North Sea sediments was used to model the composition of the synthetic drill cuttings from both regions. A range of sediment compositions was tested to achieve typical Atterberg limit values of the North Sea drill cuttings.

The physical characteristic and chemical composition of the synthetic drill cuttings used in this experimental work are illustrated in Table 3. The contaminants were modelled using paraffin oil and sodium chloride. The selection of paraffin oil to model the organic component present in the drill cuttings was based on three main reasons. Firstly, paraffin liquid is a mineral oil with a carbon range of C10–C30 that covers the range of organic compounds found in the North Sea and Red Sea drill cuttings [13,14]. Secondly, paraffin oil has a lower toxicity making it suitable for laboratory experiments and thirdly, paraffin liquid is much easier to analyse than crude oil. Sodium hydroxide was added to the soil mix in order to provide the high pH medium of the cuttings. The water contents of 20% and 27% of the North Sea and Red Sea drill cuttings, respectively, were used in the corresponding synthetic mixes.

#### 3.2. Binder system

A number of different binders, including a range of conventional as well as less-conventional or waste binders, were tested to assess their ability to treat the synthetic drill cuttings. Detailed information on the full range of binders was given elsewhere

Table 4  
Summary of the five binders used

Binder system	Dry binder composition	Ratio by weight of dry binder
Portland cement (PC)	PC	1
Blast-furnace slag–PC (BFS–PC)	BFS:PC	1:1
Microsilica–PC	Microsilica:PC	1:1
MgO cement (PFA–MgO–PC)	PFA:MgO:PC	4:1:5
Hydrated lime–PC (lime–PC)	Lime:PC	1:1

[18,19]. This paper concentrates on the behaviour of five of those binders whose details are given in Table 4. Those binders were selected in order to cover the full range of properties attained and consisted of:

- Portland cement (PC).
- Blast-furnace slag (BFS), which is a by-product of the iron manufacturing process.
- Microsilica or silica fume, which is a by-product from electric arc furnaces that are employed in the manufacture of ferrosilicon or silicon metal.
- Pulverised fuel ash (PFA) or fly ash (Class F), which is a by-product from the combustion of pulverised coal in coal-fired power stations. The utilised PFA is a stable, fine powder that is air-dried and passing through 600  $\mu\text{m}$  sieve.
- Magnesium oxide (MgO) cement, which is a mixture of PC, PFA and reactive magnesia (MgO) from the calcining of magnesium carbonate at  $\sim 850^\circ\text{C}$  and is expected to be a more sustainable type of cement than PC [20].
- Hydrated lime.

As seen from Table 4, the utilised binders were either PC only or a combination of 50% PC with one of the other binders (lime, MgO and PFA, BFS and microsilica) in an attempt to facilitate direct comparison between them. Since the water content in the two synthetic drill cutting mixes is different and in order to produce the same consistency for the S/S mixes, water to dry binder ratios of 0.4:1 and 0.6:1 for low and high oil content mixes, respectively, were adopted. The chemical compositions of the aforementioned binders are given in Table 5.

Table 5  
Chemical composition of binders used

Component	PC (% by weight)	BFS (% by weight)	Microsilica (% by weight)	PFA (% by weight)	MgO (% by weight)	Hydrated lime (% by weight)
SiO <sub>2</sub>	20.10	37.10	93.0	48	1.10	2–6
Al <sub>2</sub> O <sub>3</sub>	4.85	8.80	1.0	27	0.20	0.2–0.6
Fe <sub>2</sub> O <sub>3</sub>	3.40	1.93	1.0	9	0.18	0.1–0.3
CaO	63.75	40.00	1.2	3.3	1.15	–
MgO	1.05	11.50	0.5	2	97.35	–
SO <sub>3</sub>	3.05	–	–	0.6	–	–
Na <sub>2</sub> O	0.70	–	0.5	1.2	–	–
K <sub>2</sub> O	–	–	1.0	3.8	–	–
C	–	–	2.0	4–7	–	–
Ca(OH) <sub>2</sub>	–	–	–	–	–	80–90
Mg(OH) <sub>2</sub>	–	–	–	–	–	0–6

### 3.3. Sample preparation and testing

The base soil constituents of the drill cuttings were first mixed together with tap water, to which the sodium chloride and sodium hydroxide were added; followed by the addition of paraffin oil. The wet binder was then prepared by manually mixing the constituents and was then added to the drill cuttings. The dry binder content was 10%, 20% and 30% by weight. After thorough mixing, the mixes were placed in cylindrical moulds (50 mm  $\times$  100 mm) and left to cure for 28 days at a temperature of  $21 \pm 2^\circ\text{C}$  and a relative humidity of  $95\% \pm 3\%$  prior to testing.

## 4. Testing procedure

A set of physical and chemical tests together with microstructural analyses was conducted on the different mixes. The testing procedures employed are summarised in the section below.

### 4.1. Unconfined compressive strength (UCS) test

UCS values were measured according to ASTM test method D1633 [21] by applying a vertical load axially at a constant strain rate of 0.045 in./min until failure of the cylindrical specimen. Although there is no direct correlation between the UCS and the leaching behaviour of materials, this test was used as an indirect method to determine whether the waste has been chemically transformed into a monolith [11]. In order to understand the effect of the contaminants in the synthetic drill cuttings on the UCS, an additional control mix was prepared following the same procedure but without the addition of any contaminants. For this control mix, only the 30% dry binder content was used with a water to dry binder ratio of 0.4:1 similar to that used with the low oil content mix.

### 4.2. Leachability and chemical analysis

The NRA leaching test [22] has been the UK-approved leaching test since 1994 until recently superseded by the new EU leaching tests (BS EN 12457) [23] for granular waste. The EU leaching test (BS EN 12457) is quite similar in its procedure to

the NRA test, where the latter was adopted for all the experimental investigations. In this test, a representative sample, 100 g, was taken from the centre of the 28 days UCS samples after testing and reduced to a particle size of less than 5 mm (but not finely ground). The sample was then mixed with 1 L of the extraction fluid in fluorinated polyethylene (FPE) containers and agitated using a rotating agitator at  $30 \pm 2$  rpm for 24 h. The extraction fluid used was de-ionised water, with a conductivity of  $1 \mu\text{s}/\text{cm}$ , which was carbonated to a pH of 5.6, as specified in the NRA test procedure, to simulate acid rain conditions. After the agitation, the sample was filtered using a vacuum-filter of size  $0.45 \mu\text{m}$  to separate any solid particles from the leachate. The pH of the filtered leachate was measured by ATC Piccolo2 (HANNA) pH-meter with an accuracy of  $\pm 0.01$  units.

#### 4.2.1. Analysis of chloride concentrations

The chloride content was measured by the ion chromatography (IC) technique. The ion chromatography uses ion-exchange eluant to separate atomic or molecular ions based on their interaction with the eluant. The leachate was diluted up to three times in order to be analysed by the IC.

#### 4.2.2. Analysis of oil concentrations

The oil concentration was measured using the ‘oil mat’ method. This technique utilises an oil mat, which is an absorbent medium, used by industry for absorbing oil spills. The oil absorbent mat repels water and water-based products, but absorbs petroleum-derived fluids such as oil and diesel fuel. The oil mat is made of 100% polypropylene and is lighter than water, so when placed on the surface of a body of water, it remains afloat and absorbs any oil present. The oil mat used (Pig Corp., product number 460) is a medium weight mat with an absorption capacity of  $0.347 \text{ mL}/\text{cm}^2$  [24].

The recovery level of the oil mat technique was measured and compared with that of the partition-gravimetric method, which is the standard method for the examination of wastewater recommended by the American Water Works Association of the Water Environment Federation [25]. The oil mat technique was tested using different known oil concentrations ranging between 0.01% and 20% by weight. It was found that the recovery level of this technique was as high as 98.5% at the higher concentration end (oil concentrations greater than 1%) and around 82% at lower concentrations [19]. The partition-gravimetric method, involves the extraction of dissolved or emulsified oil from water by direct contact with an extracting solvent [25], in this case toluene. This method was tested using different known oil concentrations ranging between 0.1% and 20% by weight and resulted in a recovery level of up to 85%. The observed precision of this method was low, as also reported by others [26], partly caused by the intermediate handling stages. Therefore, the oil mat technique was preferred for determining the leached oil concentrations.

#### 4.3. Sorption tests

A set of sorption experiments was carried out to assess the chloride sorptive capacity of all the binders and the base soil.

The sorption experiments involved placing 100 g of binder in different concentrations of sodium chloride solutions with a solid to liquid ratio of 1:10 in FPE bottles. The water used for the solution was the same as that used in the leaching tests. The FPE bottles were agitated for 24 h and then analysed using IC as detailed above. The sorptive capacity, which is the amount of chloride (mg) sorbed by 1 g of the binder, was then calculated. Moreover, the individual binder constituents, the synthetic base soil and the individual components of base soil were tested for their chloride leachability using the procedure described above.

#### 4.4. Microstructure analysis

The microstructure examination was carried out using scanning electron microscopy (SEM) [JEOL model JSM-820]. A small sample was taken from the centre of the UCS specimen, vacuum-dried and mounted on an aluminium stub using a strong carbon-cement adhesive. The specimen was further gold-coated to enhance its conductivity.

### 5. Experimental results and discussion

#### 5.1. Unconfined compressive strength (UCS)

A summary of the UCS values of the control, the low and the high oil content mixes at 28 days is presented in Fig. 2. The results were observed to have an average margin of error of  $\pm 11\%$  and all the samples tested had a density of  $1950 \text{ kg}/\text{m}^3 \pm 2\%$ . The trend observed was that the UCS generally increased with increasing binder content. The UCS values ranged from 1720 to 4570, 780 to 4490 and 540 to 4130 kPa for the control, the low oil content and the high oil content synthetic drill cutting mixes, respectively. The UCS results revealed that the PC, BFS-PC and microsilica-PC mixes had a similar performance and produced higher UCS values than the mixes containing PFA-MgO-PC and lime-PC binders.

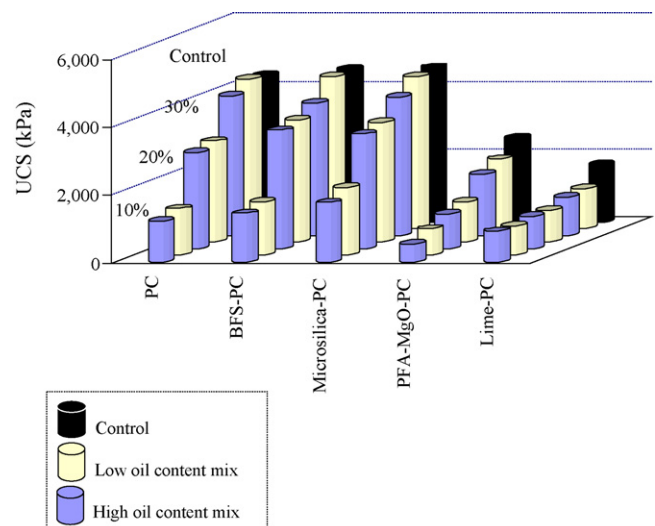


Fig. 2. UCS of the control, the low and high oil content mixes at 28 days.

Table 6  
Chloride leaching behaviour of the binders, synthetic base soil and base soil constituents

Binder	Leached chloride concentration (mg/L)	Leachate pH
Portland cement	1.8	12.6
Blast-furnace slag	5.8	11.6
Microsilica	0	8.0
Pulverised fuel ash	6.2	9.6
MgO	0.03	11.4
Hydrated lime	1.4	12.5
Synthetic base soil	50.5	9.8
Sharp builders sand	9.6	–
Polywhite kaolin E-grade	10.0	–
Calcium bentonite	197.2	–
Silt (silica flour)	11.0	–

Despite the significant difference in the hydrocarbon content in the two synthetic cuttings, the measured UCS values of the mixes with the same binder type and content were similar. The comparison between the 30% dry binder content of the low oil content mixes with their corresponding control mixes, showed that there is no reduction in the UCS for PC, BFS–PC and microsilica–PC binders mixes. On the other hand, the analogous mixes with PFA–MgO–PC and lime–PC binders displayed a reduction in their UCS of up to 30% than those of the corresponding control mixes.

Some organic contaminants are known to interfere with the cement hydration process impairing the strength development due to the reduction in the formation of a crystalline structure resulting in a more amorphous material [27]. However, the similar UCS results from the two synthetic mixes and the control mixes indicated that the effect of oil content of up to 10.95% on the UCS values was insignificant. This could be attributed to the fact that some mineral oils have been reported to have no detrimental effect on the physical properties of the S/S treated materials [28] although that study looked at much lower oil concentrations than used here.

The wide range of the observed UCS results indicated various possible end-use scenarios for the treated material. For burial purposes the UCS values could be as low as 140 kPa [29], while for the production of construction materials, blocks and bricks much higher UCS values of 580 kPa [29], 2.8 and 7 MPa, respectively, are required [30]. Furthermore, the lower UCS values could find applications in areas where low-grade materials are acceptable or could be employed for ground improvement works.

## 5.2. NRA leachability

### 5.2.1. Leachability and sorption isotherms of the binders

The results of the chloride leachability of the individual binder constituents, the synthetic base soil and the individual components of base soil are summarised in Table 6. It was observed that the background level of chloride leached from the binders is relatively small whilst that from the base soil is comparatively large; mainly attributed to the presence of calcium bentonite in it.

Table 7  
Chloride sorption coefficients for individual binders constituents and sorptive capacity for the specific chloride concentration present in the drill cuttings

Binder	Freundlich			At the drill cuttings concentration	
	$k_f$	$1/n$	$R^2$	Sorptive capacity (mg/g)	pH
PC (powder)	5.0E–04	1.08	0.95	0.92	12.5
Blast-furnace slag	3.1E–08	2.1	0.70	0.38	11.0
Microsilica	1.2E–07	1.9	0.01	0	7.5
Pulverised fuel ash	2.9E–07	2.00	0.90	0.38	9.6
MgO	1.7E–02	0.62	0.92	1.43	11.6
Hydrated lime	5.8E–07	1.9	0.95	0.31	12.3

Correlation between the quantity of chloride sorbed and the equilibrium concentration (final concentration of the leachate) showed that the sorption behaviour followed the Freundlich empirical isotherm as summarised in Table 7. This is in agreement with the findings of [31], which emphasised that the relationship between the bound chloride and the free chloride could be described by Freundlich isotherms, at high free chloride concentrations (i.e. higher than 0.35 mg/L). The Freundlich relationship equation is:

$$Q = k_f C_e^{1/n}$$

where  $Q$  is the quantity of chloride sorbed (mg/g),  $C_e$  the equilibrium concentration of chloride (mg/L),  $k_f$  the Freundlich capacity parameter, and  $1/n$  is the Freundlich isotherm parameter.

From Table 7, it is evident that MgO and PC have the highest sorptive capacity for chloride of 0.92 and 0.95, respectively, which is also reflected in their high Freundlich capacity parameter ( $k_f$ ) as well as their isotherm parameter ( $1/n$ ). Furthermore, the values of the correlation factor ( $R^2$ ) showed that the blast-furnace slag and microsilica do not correspond well to the Freundlich isotherms.

### 5.2.2. NRA leachate pH

The leachate pH is usually used as an indicator of how the heavy metals and chlorides will behave since it has been reported that significant binding of high levels of heavy metal and chloride is usually achieved with the high pH [8,32]. The NRA leachate pH values for all the low and high oil content mixes are presented in Table 8. The values have an average margin of error of  $\pm 0.7\%$ . The results exhibited a range of values of between 10.3 and 12.7, with most over 11. The PFA–MgO–PC mix showed

Table 8  
Average NRA leachate pH for the low and high oil content mixes at 28 days

Binder system	Low oil content mix binder content			High oil content mix binder content		
	10%	20%	30%	10%	20%	30%
PC	12.1	12.4	12.4	12.0	12.4	12.6
BFS–PC	11.9	12.1	12.3	12.0	12.2	12.4
Microsilica–PC	10.3	10.5	10.6	10.5	10.4	10.6
PFA–MgO–PC	11.8	12.2	12.3	10.9	12.0	12.0
Lime–PC	12.5	12.6	12.7	12.1	12.5	12.4

a slightly lower pH while the microsilica–PC mix displayed a notable decrease in the leachate pH of around 2 units than the average pH value. The correlation between the NRA leachate pH and the chloride leachability is discussed in the subsequent section.

### 5.2.3. Chloride leachability

Chloride can be chemically bound during binder hydration to form: (a) chloro-aluminate/Friedel's salt ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$ ) or (b) chloro-aluminoferrite ( $3\text{CaO}\cdot\text{Fe}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$ ); the latter being less important because of its greater solubility and slower rate of formation [33]. The 28-day leachate concentrations of chloride in the low and high oil content drill cuttings–binder mixes are presented in Fig. 3. The results have an average margin of error of  $\pm 8.0\%$ . The untreated drill cuttings were also leached and showed leaching of almost all the chloride content highlighting the poor binding capacity of their soil constituents. For the low oil content mix, the untreated synthetic drill cuttings leached 1830, 1580 and 1410 mg/L of chlorides from the 10%, 20% and 30% dry binder mixes, respectively. On the other hand, for the high oil content mix, the untreated synthetic drill cuttings leached 1940, 1690 and 1500 mg/L of chlorides from the 10%, 20% and 30% dry binder mixes, respectively.

The NRA leachate concentrations of chloride for both oil content mixes were similar and ranged between 1040–1640 and 1050–1850 mg/L for low and high oil content mixes, respectively. This corresponds to a percentage reduction of bound

chlorides of between 2% and 30%, which is equivalent to an immobilisation capacity of between 2 and 60 mg/g of the dry binders (excluding the drill cutting constituents). The results showed a decrease in the leached concentration as the dry binder content increased. Moreover, it was observed that the initial and leached chloride contents were similar, for both the low and high oil content mixes, which could suggest that the increase in the oil content from 4.2% to 10.95%, did not have a significant impact on the leaching of the chloride.

Although the chloride leachability results from the different binders were within the same range, it was observed that the PC only binder outperformed all the other binders. The PFA–MgO–PC, BFS–PC and lime–PC binders exhibited a relatively better performance than the microsilica–PC binder. This could be attributed to the fact that materials like PFA and BFS form additional hydrates in their hydration reactions, which help in chloride stabilisation [34]. On the other hand, a decrease in the chloride binding capacity due to the presence of microsilica was observed. That could be attributed to the lower pH of microsilica, which tends to increase the solubility of Friedel's salt [32,34].

According to the UK landfill acceptance criteria, limit values for chloride concentrations, in compliance leaching tests using BS EN 12457, are 80, 1500 and 2500 mg/L for inert waste, stable non-reactive hazardous waste (disposed in a non-hazardous landfill) and hazardous waste, respectively [35]. For all the binder mixes, the chloride leachate concentrations exceeded the limit value for inert waste. However, for the 30% and 20% of all binders–mixes, all the lime–PC mixes, and those of low oil content mixes of PFA–MgO–PC, the chloride leachate concentrations were within the limit for the stable non-reactive hazardous waste; hence comply with the UK acceptance criteria for non-hazardous landfills. This also indicates that greater binder contents might be required to immobilise the chlorides to inert levels.

### 5.2.4. Paraffin oil leachability

The oil concentrations in the NRA leachates are presented in Fig. 4 on a log scale because of the wide range measured. The concentrations ranged between 10–2260 and 100–2730 mg/L for the low and high oil content synthetic drill cutting mixes, respectively. Those results had an average margin of error of up to  $\pm 15\%$ . The results displayed a wide range of values, which correspond to percentage reduction of stabilised oil of between 0–99% and 33–97% for the low and high oil content mixes, respectively, as shown in Table 9. These percentage reductions are equivalent to immobilisation capacities ranging from 0 to 240 and 90 to 440 mg/g for the low and high oil content mixes, respectively.

Fig. 4 indicates that the PC, BFS–PC and lime–PC binders are the best mixes for all dry binder contents and for the drill cuttings from both synthetic mixes. Furthermore, the 30% PFA–MgO–PC binder with the low oil content mix performed well in oil immobilisation with percentage reduction of 88%, while microsilica–PC was the worst binder in the treatment of oil with a total oil reduction of up to only 60%. Since the relatively good performance of lime–PC in both synthetic mixes in

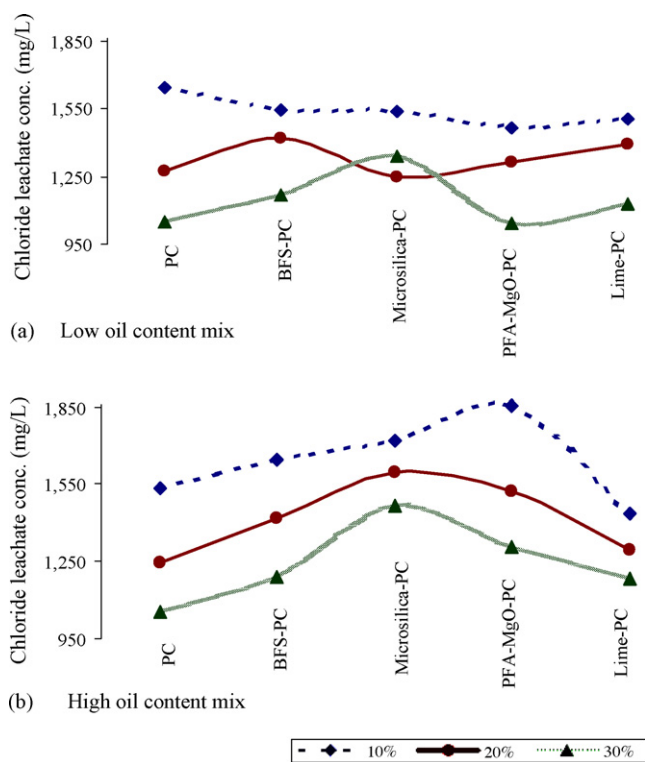


Fig. 3. Leachability of the chloride from all binder mixes at 28 days for the (a) low oil content synthetic drill cuttings, and (b) high oil content synthetic drill cuttings.

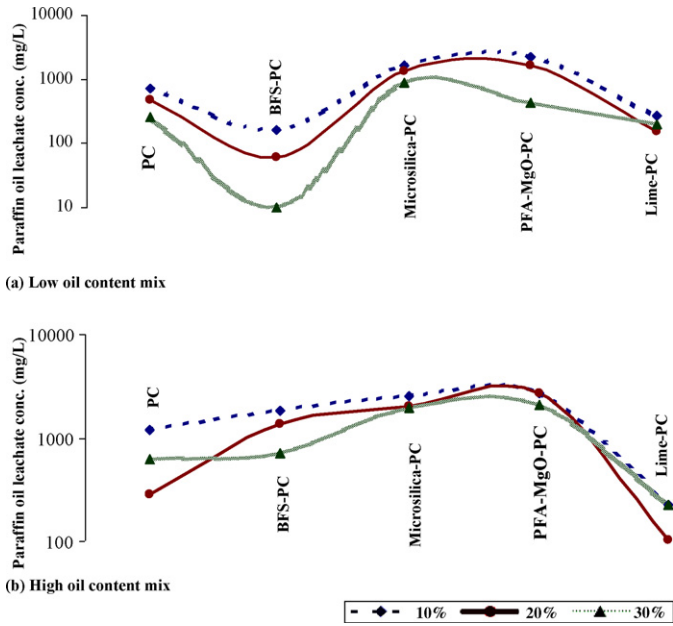


Fig. 4. Leachability of the paraffin oil from all binder mixes at 28 days for the (a) low oil content synthetic drill cuttings, and (b) high oil content synthetic drill cuttings.

Table 9

Percentage of oil reduction in the low and high oil content mixes at 28 days in relation to oil leachate concentrations of untreated synthetic drill cuttings

Binder system	Low oil content mix binder content			High oil content mix binder content		
	10%	20%	30%	10%	20%	30%
PC	67	75	85	70	93	87
BFS-PC	93	97	99	55	66	85
Microsilica-PC	28	29	48	38	50	60
PFA-MgO-PC	0	12	88	33	34	56
Lime-PC	88	92	94	94	97	95

terms of oil stabilisation was evident, further investigations are currently being carried out on this binder.

The UK landfill acceptance criteria limit value for total organic carbon content of 600 mg/L for hazardous waste [35] was used in the absence of more relevant values. This means that the untreated drill cuttings would be classed as hazardous waste. The corresponding limit values for compliance leaching tests using BS EN 12457, are 50, 80 and 100 mg/L for inert waste, stable non-reactive hazardous waste (to be disposed in non-hazardous landfill) and hazardous waste, respectively. From the results of the low oil content synthetic mix displayed in Fig. 4, it is obvious that the performance of the 30% BFS-PC binder has successfully immobilised the oil content to inert waste level by a total oil reduction of 99% as shown in Table 9. Furthermore, the 20% BFS-PC and 30% lime-PC binders of the low oil content mix managed to convert the drill cuttings to a stable

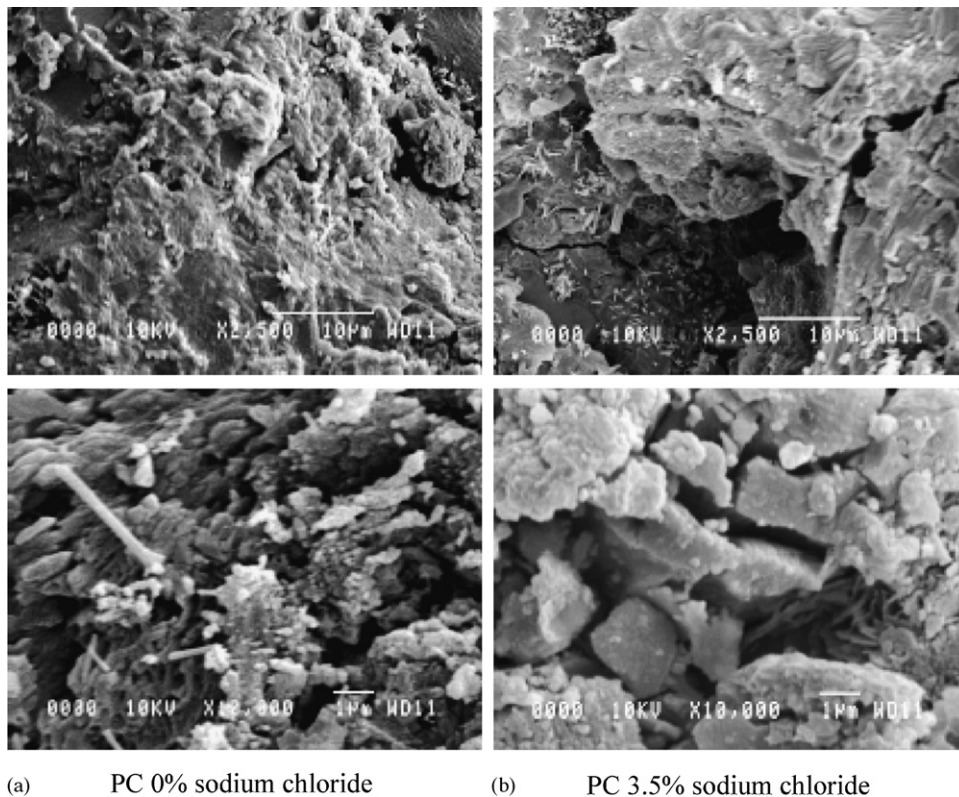


Fig. 5. SEM micrographs at 28 days for the PC binder grout with sodium chloride concentration of (a) 0% and (b) 3.5%.



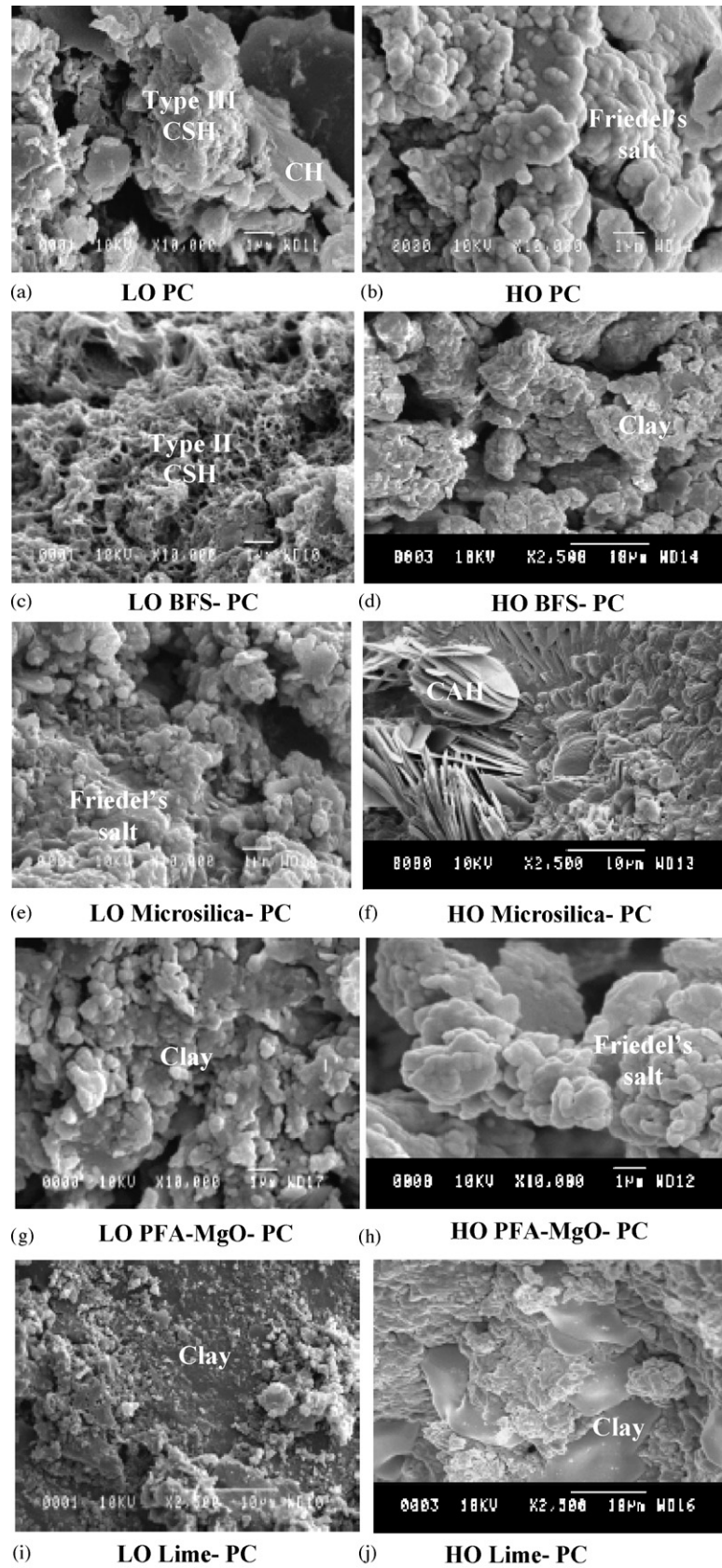


Fig. 6. SEM micrographs of the fractured surfaces of the 30% binder mixes of the low oil content synthetic drill cuttings (LO), and the high oil content synthetic drill cuttings (HO) at 28 days.

non-reactive hazardous waste, and reduced their oil concentrations to values compliant with the UK acceptance criteria for non-hazardous landfills.

### 5.3. Scanning electron microscopy (SEM)

#### 5.3.1. Effect of chlorides on microstructure

The effect of the addition of 3.5% sodium chloride on the microstructure of the PC binder grout was investigated. Fig. 5(a) and (b) shows micrographs of the normal hydration products of PC binder grout after 28 days and the corresponding hydration products from 3.5% sodium chloride–PC under two different magnifications. The two SEM micrographs of the 0% sodium chloride–PC mix (Fig. 5(a)) show a more compact structure than that of the 3.5% sodium chloride–PC mix (Fig. 5(b)) which contains more voids. The effect of the presence of chloride in PC has been reported to cause a permeable microstructure that could be attributed to the ability of chlorides to deflocculate colloidal calcium silicate hydrate particles [33].

#### 5.3.2. Drill cuttings–binders microstructure

Fig. 6(a)–(j) shows typical SEM micrographs of the fracture surfaces of 30% binder mixes for the two synthetic cuttings at 28 days. The micrographs show the general features associated with the cement hydration in the mixes.

The absence of ettringite, needle-like crystals of calcium sulfoaluminate hydrates, in all the micrographs is obvious. However, the micrographs show an abundance of the amorphous, gel-like hydration products typical of calcium silicate hydrate (CSH) with its three different morphologies [36], viz. Type (I) which grows in the paste capillary voids with a fibrous-acicular form; Type (II) which forms a reticulated or honey comb structure and Type (III) which is a denser-almost spherical form. Moreover, the presence of the large prismatic, hexagonal crystals that could be typical of portlandite (calcium hydroxide (CH)), monosulphate and calcium aluminate hydrate (CAH) is also evident. This indicates an expected accelerated hydration stage due to the presence of chloride in the mixing water [37] which further accelerates the formation of ettringite (AFt) from the hydrating aluminate phase until all the sulphates are consumed and consequently promotes the preferential formation of the hexagonal crystals of Friedel's salt [33].

In general, the difference in the SEM micrographs of both synthetic mixes supports the fact that the pore structure of the two types of mixes is different. This could suggest that the oil content affects the morphology of the crystals formed during hydration, which is accompanied by a general decrease in the proportion of the hydration products and their existence as discontinuous crystals [38]. These changes in the microstructure produced a slight difference in the UCS behaviour as presented in Fig. 2. Furthermore, samples that yielded the highest UCS values, e.g. the synthetic mixes containing 30% of PC, BFS–PC and microsilica–PC binders, were characterised by a very dense structure.

Both the PC only binder micrographs of the low and high oil content mixes (Fig. 6(a) and (b)) show a discontinuous, porous

and open structure, which could have been originally filled with water. Type (III) CSH with its distinguished feature of dense-almost spherical configuration was abundant which gave the mix its high UCS values.

In Fig. 6(c) and (d), the BFS–PC binder micrographs display higher level of hydration associated with the large specific surface area of BFS (400–500 m<sup>2</sup>/kg), which is in agreement with the findings of other work [39]. This is clear from the reticulated or honeycomb structure of Type (II) CSH, which appeared prolifically in the low oil content mix micrographs, whilst Type (I) had less presence. This mix shows abundance of hydration products, which correlates well with its high UCS values.

In the microsilica–PC binder SEM micrographs of the low oil content mix (Fig. 6(e)), the proportions of the crystals increased within a slightly interconnected network of hydration products. The presence of Type (III) CSH gel was apparent with its amorphous configuration. In the microsilica–PC binder SEM micrograph of the high oil content mix (Fig. 6(f)), monosulphate and calcium aluminate hydrates (CAH) (C<sub>2</sub>AH<sub>8</sub> and C<sub>4</sub>AH<sub>19</sub>), which are the main products of C<sub>3</sub>A (tricalcium aluminate), were evident. This was further confirmed by the appearance of the well-formed plates of C<sub>2</sub>AH<sub>8</sub> mineral in the micrographs. This development of CAH supports the findings of other work [33] that emphasised the marked presence of CAH in the microstructure of the cement mixed with seawater. The increased types of hydration products in the microsilica–PC, compared to the PC only binder mixes, could be attributed to the finer particle sizes, larger surface area and higher silicon dioxide content in the microsilica, which contributed to the high UCS values of the mixes. In similar experiments, without the presence of the oil, it was observed that the amount of the Friedel's salts decreased with the addition of microsilica where more of the stable CASH (calcium aluminium silicate hydrates) were formed than CSH [34].

The PFA–MgO–PC binder mixes (Fig. 6(g) and (h)) lacked almost any crystalline phase, which indicated the presence of fewer hydration reactions and correlated with its low UCS values. The lime–PC binder micrographs (Fig. 6(i) and (j)) appear as featureless structures, which indicated poor crystalline hydration phases that corresponded well to its low UCS values.

## 6. Conclusions

Drill cuttings are a complex type of hazardous waste, which are generated as a result of the oil drilling operations. This paper presents an experimental investigation of the use of stabilisation/solidification to treat synthetic drill cuttings with conventional and novel binders using three different dry binder contents, viz. 10%, 20% and 30%. Two synthetic mixes were considered with concentrations of oil and chloride similar to the typical values of drill cuttings from the North Sea and the Red Sea areas. The mixes contained 4.20% and 10.95% oil and 2.03% and 2.13% chlorides by weight, respectively.

The unconfined compressive strength (UCS) results at 28 days indicated that the UCS values were generally improved with increasing binder content. The observed UCS values cov-

ered a broad range and hence encompassed a wide possibility of feasible applications. The results also showed that the oil content in the synthetic drill cuttings of up to 10.95% had no significant effect on the corresponding UCS.

The leachate pH results showed a range of values for both synthetic mixes of between 10.3 and 12.7, with most over 11. The NRA leaching results confirmed that more chlorides were immobilised at higher pH values. Furthermore, the trend of the chloride leaching results showed a decrease in the leached concentration as the dry binder content increased for the two synthetic drill cuttings. Thus, it can be concluded that the oil content did not have a significant impact on the leaching behaviour of the chloride from the aforementioned mixes. From the 28 days NRA chloride leachate results, it was evident that the S/S treatment could effectively convert the synthetic drill cuttings to a stable non-reactive hazardous waste, and could reduce their chloride concentrations to values compliant with the UK acceptance criteria for non-hazardous landfills. This reduction was successfully achieved by all the 20% and 30% binder content mixes used but only by some of the 10% binder content mixes.

The general trend in the oil concentration in the 28 days NRA leachates showed that oil stabilisation increased with the increase in the percentage of binder added. The PC, BFS–PC and lime–PC binders outperformed the other binders for both synthetic drill cuttings. According to the UK landfill acceptance criteria limit, the 30% BFS–PC binder successfully immobilised the oil concentrations in the low oil content mix to inert waste. Moreover, the 20% BFS–PC and 30% lime–PC binders of the low oil content mix managed to convert the drill cuttings to a stable non-reactive hazardous waste, and reduced their oil concentrations to values compliant with the UK acceptance criteria for non-hazardous landfills.

The SEM micrographs displayed an advanced level of hydration due to the presence of chlorides and it was also observed that the hydration products were discontinuous and limited due to the presence of the oil in the mixes. The fact that the SEM micrographs of both mixes were different advocates the conclusion that the oil content affects the morphology of the crystals formed during hydration.

Since the potential for the lime–PC binder in both chloride and oil stabilisation was evident, further investigations are being carried out to optimise its relative performance. Despite the superior UCS performance of microsilica–PC mixes, their poor chloride and oil leachability rendered this binder less suitable in the S/S treatment of both chlorides and oil.

This work presented a useful assessment of the effectiveness of a range of binders in the stabilisation/solidification of the chloride and oil in two different oil content synthetic drill cuttings. It highlighted strong and weak aspects of the treatment and suggested areas that require further investigations.

### Acknowledgements

The authors are grateful to Cambridge Overseas Trust, Overseas Research Student Awards Scheme and BP Egypt for their provision of financial support to the first author.

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