

Contents lists available at ScienceDirect

## Journal of Hazardous Materials



journal homepage: www.elsevier.com/locate/jhazmat

## Stabilization/solidification of petroleum drill cuttings

### Sunday A. Leonard\*, Julia A. Stegemann

Department of Civil Environmental and Geomatic Engineering, University College London, Chadwick Building, Gower Street, London WC1E 6BT, United Kingdom

#### ARTICLE INFO

Article history: Received 31 July 2009 Received in revised form 13 September 2009 Accepted 14 September 2009 Available online 20 September 2009

Keywords: Petroleum drill cuttings Stabilization/solidification (S/S) Cement Fly ash Factorial design Waste utilization

#### ABSTRACT

A systematic treatability study was conducted for the treatment of drill cuttings, a waste generated during petroleum exploration and production, by stabilization/solidification with Portland cement (CEM I), with the addition of high carbon power plant fly ash (HCFA), an industrial by-product, as a novel sorbent for organic contaminants. A factorial design experiment was adopted to investigate the effects of waste-to-binder ratio, binder formulation, and curing time on response variables including unconfined compressive strength (UCS), hydraulic conductivity, porosity, leachate pH, and acid neutralization capacity (ANC) of the s/s products. Results show that all factors had significant effects on the properties of the s/s products. Drill cuttings addition both reduced UCS, but HCFA improved hydraulic conductivity, relative to CEM I only s/s products. Drill cuttings addition had little effect on the ANC of products prepared with CEM I only, and improved that of products containing HCFA. Management options assessment based on performance criteria adapted from regulatory and other guidance suggests that the s/s products could find application as controlled low-strength materials, landfill liner, and landfill daily cover. This work demonstrates how a systematic treatability study can be used to develop a s/s operating window for the management of a particular waste type.

© 2009 Elsevier B.V. All rights reserved.

#### 1. Introduction

#### 1.1. Drilling fluids and cuttings

Drilling fluids (or drilling muds) are used as lubricants and coolants during the drilling of crude oil. They also help maintain hydrostatic pressure, stabilize the well bore, and lift out cuttings from drilled wells to the surface [1,2]. They are classified as waterbased, oil-based or synthetic, depending on the continuous phase liquid, which may be water, diesel/mineral oil, or non-aqueous fluids such as olefins, esters, and linear paraffin, respectively [1,3,4]. Drilling fluids are further composed of weighting materials such as barite and haematite, viscosifiers such as bentonite or attapulgite clay, and dispersants such as tannins. The mixture of drilling fluids with small pieces of formation rock generated during drilling are referred to as drill cuttings. The management of drilling cuttings poses a problem to the oil and gas industry because of the quantities generated and their content of both organic and inorganic contaminants. A survey by the American Petroleum Institute (API) revealed that  $6 \times 10^9$  Lpa of drill cuttings are generated in the US [5]. Between 50,000 and 80,000 tpa of drill cuttings have also been reported to arise in the UK [6].

The contaminants present in drill cuttings depend on the chemistry of the drilling mud used and the composition of the formation rock [7]. These contaminants include petroleum hydrocarbons, such as aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and heavy metals, including barium, lead, zinc, mercury, chromium, arsenic, and nickel [4,8,9]. Oil-based drilling muds are more harmful to the environment because of their diesel/mineral oil content but may still be the best option for some drilling conditions; synthetic drilling muds have lower toxicity, however their biodegradation properties are similar to those of oil-based mud [3]. Hence, drill cuttings management is governed by stringent regulations, even for water-based drill cuttings [2,10,11], and there is a need for effective management options for these wastes.

Reported management options for drill cuttings are expensive (e.g., slurry reinjection [12]); thermal desorption [13]; and incineration [14]), require intensive energy use (e.g., incineration and thermal or microwave desorption [15]), time consuming (e.g., biological methods such as bioremediation [16] and phytoremediation [17]), or environmentally unsustainable (e.g., disposal in landfills [18]; reuse in construction without prior treatment [19]). Recent studies [20,21] have also shown the possibility of using stabilization/solidification (S/S) with hydraulic binders as a possible treatment option, with the potential of using the stabilized/solidified (s/s) product for useful purposes. This work explores this management option.

<sup>\*</sup> Corresponding author. Tel.: +44 (0) 207 735 7667; fax: +44 (0) 207 380 0986. *E-mail address:* sunday.leonard@ucl.ac.uk (S.A. Leonard).

<sup>0304-3894/\$ -</sup> see front matter © 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2009.09.075

#### 1.2. Stabilization/solidification (S/S)

S/S aims to immobilize contaminants in wastes or contaminated soils by the addition of hydraulic binders. Stabilization involves converting contaminants into a less toxic and/or less soluble form, while solidification involves creation of a durable solid matrix to encapsulate contaminants. S/S is a widely accepted waste management technology, which the USEPA identified as the best demonstrated available technology for over 50 US Resource Conservation and Recovery Act-listed hazardous wastes [22,23], and which has been used for 25% of US superfund sites [24]. S/S is a low cost technology that can be applied quickly. The energy requirement is low if industrial by-product binders, such as pulverized fuel ash (PFA) or ground granulated blast furnace slag (GGBS) are used [25–27]. Depending on the characteristics of the resulting s/s product, there is the possibility of reusing it as a construction material. S/S has been reported to be effective in the treatment of inorganic wastes [22], however its effectiveness in treating waste containing substantial quantities of organic compounds remains questionable because of the detrimental effects that organic compounds can have on the hydration of binders [23,28]. Furthermore, there is little potential for chemical uptake of organic contaminants into hydration products. Any immobilization of organic contaminants will therefore depend on physical entrapment in the matrix porosity, and sorption, such that non-polar (insoluble) compounds are more likely to be retained by the solid, whereas polar (soluble) compounds will remain leachable.

Little published work exists on the use of S/S in the treatment of drill cuttings. In a work by Al-Ansary and Al-Tabbaa [21], S/S of synthetic drill cuttings was carried out using different binders; leaching of oil and chloride in the BS EN 12457 batch extraction from some formulations was compliant with the UK acceptance criteria for non-hazardous waste landfills. In another work [29], petroleum drill cuttings were treated with cement, lime and PFA, resulting in improved unconfined compressive strength and permeability, however, the leaching of chlorides was not assessed. Joshi et al. [30] reported on S/S of oil and gas well sludges consisting of drill cuttings and hydrocarbons using Portland cement, PFA, lime, and sodium silicate, but did not investigate hydrocarbon or metal leaching.

Although organic compounds are generally incompatible with cement-based matrices, their treatment using S/S may be improved using binders that can sorb organic compounds, thus preventing their detrimental effect on binder hydration. Previous work by other workers has used activated carbon to increase contaminant sorption in S/S [31,32]. Activated carbon is however expensive; a possible cheap material that could combine sorption and binding characteristics is high carbon power plant fly ash (HCFA), a pozzolanic material [33] similar to the PFA widely accepted for use in cement-based construction materials [34], but which contains a higher proportion of unburnt carbon. This carbon may act as a sorbent for organic compounds. Portland cement is often used as a source of alkalinity and calcium to activate pozzolanic reactions in fly ash. This work therefore aims to investigate the possibility of treating oil-based petroleum drill cuttings using cement and HCFA.

A full factorial experimental design approach, which maximizes the information that can be obtained from experiments by enabling study of the effects and interaction of multiple variables concurrently [35], was adopted. For a given waste type, the main process variables for S/S are the proportions (i.e., relative amounts) of waste, cement-based binder and water [36]. With a binder composed of more than one material, another important factor is the binder formulation. This work therefore investigates the effects of binder formulation: ratio of cement and HCFA, waste-to-binder ratio, and curing time on the S/S of petroleum drill cuttings using a factorial design experiment. It further assesses different management scenarios for the s/s products based on the results from testing and performance criteria adapted from regulatory guidance.

#### 2. Materials and methods

#### 2.1. Drill cuttings

Two buckets of drill cuttings were obtained from an unidentified terrestrial drilling operation and characterized, including determination of moisture content, specific gravity, loss-on-ignition, hydrocarbon, metal and chloride contents, as well as hydrocarbon desorption as a function of pH. The hydrocarbon content was determined by subjecting duplicate samples to USEPA Test Methods for evaluating solid waste, physical/chemical methods [37], including Method 3540C (soxhlet extraction), Method 3611B (alumina column cleanup and separation of petroleum wastes), and Method 8270C (semi-volatile organic compounds by GC/MS).

#### 2.2. Binders

Ordinary Portland cement, CEM I 42.5, conforming to BS EN 197-1:2000, was used; HCFA was provided by an unidentified source. The characteristics of both materials are reported in Table 1.

#### 2.3. Factorial design experiment

Three factors were studied in a full factorial design as summarized in Table 2.

- *Binder formulation*: Experimental runs were carried out at two levels: CEM I only and CEM I:HCFA=1:1 to assess the effectiveness of HCFA as a sorbent and investigate its effects on the properties of the s/s product.
- *Waste-to-binder ratio*: Experimental runs were carried out at three levels of waste-to-binder ratios: 0:1, 1:4 and 3:2, to examine the effect of drill cuttings on binder hydration and other s/s product properties.
- *Curing time*: Tests were conducted on the s/s products after 7, 28 and 56 days, resulting in three levels. While cement-based constructions materials can be relied upon to continue to hydrate over time, leading to a stronger matrix of greater density, addition of waste to a cement-based binder can result in retarded, sometimes completely inhibited, hydration, or even matrix degradation with time. Hence, s/s product properties were determined over time to monitor for such effects.

The water:solid ratio was maintained at 0.45 for all runs; it should be noted that this resulted in a variation in the water:cement and water:binder ratios between runs.

#### 2.4. Specimen preparation

Weighed quantities of drill cuttings, CEM I, HCFA and water were homogenized in a Hobart mixer. The freshly prepared mixture was poured into 50 mm × 50 mm steel cube moulds to fill them half way. 70 mm × 70 mm cylindrical specimens were also prepared for hydraulic conductivity testing. The half-filled moulds were compacted using a vibrating table for approximately 15 s, and then completely filled, allowing the top of the samples to extend slightly above the top of the moulds. The moulds were further compacted and the excess mixture scraped off to obtain a flat and smooth surface. The moulds were then sealed in plastic bags to prevent possible carbonation due to exposure to air and cured for 24 h in a humidity chamber with a relative humidity of  $98 \pm 2\%$  and a temperature of  $21 \pm 3$  °C before demoulding. The demoulded spec-

#### Table 1

Characteristics of binders and drill cuttings.

	Values $\pm$ standard deviation of three replicates			
	HCFA	CEM I	Drill cuttings	
Properties				
Moisture content (% wet mass)	$0.6\pm0.1$	-	$10.5\pm0.1$	
Bulk density (g/cm <sup>3</sup> , wet mass)	0.9-1.3	1.3–1.5	1.1–1.6	
Specific gravity	$2.34 \pm 0.01$	$3.58\pm0.01$	$1.98 \pm 0.01$	
pH (L/S of 10)	$12.4\pm0.1$	$13.1\pm0.2$	$8.6\pm0.2$	
Loss-on-ignition (% dry mass)				
Organic carbon (550°C)	$33.1 \pm 0.2^{a}$	$2.1\pm0.4$	$4.3\pm0.2$	
Inorganic carbon (950 °C)	$0.3\pm0.1$	$0.7\pm0.1$	$2.1\pm0.1$	
Gravimetric masses (mg/kg dry mass)				
Soxhlet extracts	_	_	$66700 \pm 400$	
Aliphatic fraction	_	_	44600 + 600	
Aromatic fraction	_	_	$6580 \pm 40$	
Polar fraction	-	-	$5990\pm20$	
Bulk composition analysis (%)				
SiO <sub>2</sub>	25.4	21.8	60.4	
Al <sub>2</sub> O <sub>3</sub>	12.9	4.5	10.4	
Fe <sub>2</sub> O <sub>3</sub>	10	2.5	4.9	
MgO	2.2	0.9	2.0	
CaO	6.5	59.3	2.5	
Na <sub>2</sub> O	0.5	0.3	2.4	
K <sub>2</sub> O	1.1	0.6	1.7	
TiO <sub>2</sub>	0.6	0.4	0.6	
P <sub>2</sub> O <sub>5</sub>	0.6	0.2	0.1	
MnO	0.3	0.04	0.06	
SO4 <sup>2-</sup>	0.68	1.43	1.46	
Elemental composition (mg/kg dry mass)				
As	42	10	5	
Ba	1,520	196	51,500	
Cd	0.1	0.2	21	
Со	23	8	14	
Cr	114	55	106	
Cu	68	35	44	
Mn	1,880	294	345	
Ni	96	23	38	
Pb	32	14	150	
Sr	730	475	930	
Zn	61	52	82	
Sn	3	34	1	
V	131	67	108	
Fe	59,200	18,300	26,400	
CI	1,300	200	6,360	

<sup>a</sup> Strictly elemental carbon.

Table 2	
---------	--

Factorial design experiment.

Runs	CEM I:HCFA	Waste:binder	Curing time (days)	Water:solid	Water:CEM I	Water:binder
1 <sup>a</sup>	1:0	0:1	7	0.45:1	0.45:1	0.45:1
2 <sup>a</sup>	1:0	0:1	28	0.45:1	0.45:1	0.45:1
3 <sup>a</sup>	1:0	0:1	56	0.45:1	0.45:1	0.45:1
4 <sup>b</sup>	1:0	1:4	7	0.45:1	0.56:1	0.56:1
5	1:0	1:4	28	0.45:1	0.56:1	0.56:1
6 <sup>b</sup>	1:0	1:4	56	0.45:1	0.56:1	0.56:1
7 <sup>b</sup>	1:0	3:2	7	0.45:1	1.13:1	1.13:1
8	1:0	3:2	28	0.45:1	1.13:1	1.13:1
9 <sup>b</sup>	1:0	3:2	56	0.45:1	1.13:1	1.13:1
10 <sup>a</sup>	1:1	0:1	7	0.45:1	0.9:1	0.45:1
11 <sup>a</sup>	1:1	0:1	28	0.45:1	0.9:1	0.45:1
12 <sup>a</sup>	1:1	0:1	56	0.45:1	0.9:1	0.45:1
13 <sup>b</sup>	1:1	1:4	7	0.45:1	1.13:1	0.56:1
14	1:1	1:4	28	0.45:1	1.13:1	0.56:1
15 <sup>b</sup>	1:1	1:4	56	0.45:1	1.13:1	0.56:1
16 <sup>b</sup>	1:1	3:2	7	0.45:1	2.25:1	1.13:1
17	1:1	3:2	28	0.45:1	2.25:1	1.13:1
18 <sup>b</sup>	1:1	3:2	56	0.45:1	2.25:1	1.13:1

<sup>a</sup> Control runs. <sup>b</sup> Used for 2<sup>3</sup> factorial analysis.

imens were resealed in plastic bags and transferred back into the humidity chamber for further curing prior to testing.

#### 2.5. Testing procedure

The following physical and chemical tests were conducted on the s/s products in accordance with the screening tests for hardened s/s products recommended for treatability testing by Stegemann and Zhou [38], who also discuss the rationale for use of these tests. Unless otherwise noted, tests were conducted in triplicate after a curing time of 7, 28, and 56 days, as recommended in adopted standards and guidance taken from literatures [e.g., 38–40]:

- Measurement of specimen mass and volume (bulk density).
- Unconfined compressive strength (UCS) (according to BS EN 196-1:2005, with a 50 mm cube).
- Moisture content.
- Specific gravity (using a Micromeritics helium pycnometer).
- Porosity (using data obtained from bulk density and specific gravity measurements).
- Hydraulic conductivity (in duplicate according to ASTM D5084-03 method D).
- 24 h batch extraction with distilled water (in duplicate, according to BS EN 12457-2:2002), with the determination of extract pH and leached concentrations for chlorides and hydrocarbons.
- Acid Neutralization Capacity (ANC) (according to DD CEN/TS 15364:2006, after 56 days only), with the determination of pH and metal concentrations in the extracts with zero acid addition.

#### 2.6. Data analysis

A  $2^3$  factorial analysis of selected factorial levels (see Table 2) was carried out using Minitab 15 statistical analysis software. Analyses conducted included the determination of the main and interaction effects of the studied factors and the determination of a feasible region (using surface and overlaid contour plots) within the factorial levels where the s/s product would have predetermined desired properties, i.e., would meet performance thresholds [38]. Minitab uses the Pareto chart of effects to determine the factors that have significant effects (main and interaction) on each response. This is achieved by plotting the absolute value of effects against the various factors and drawing a reference line on the chart. Any factor whose absolute effect value extends beyond the reference line is potentially significant. The position of the reference line is determined using the standard deviation of effects, degree of freedom and *t*-statistics of the experimental data [41] and it corresponds to the level of significance (*p*-value) of the analysis of variance of the experimental results. A significance level of 0.05 was used for all analyses. To determine regions within the studied factorial levels where the s/s products would meet performance thresholds, Minitab plots a contour surface plot of each response and then overlays the plots on each other in a single figure, to show the region in which the performance thresholds can be achieved.

#### 3. Results and discussion

#### 3.1. Drill cuttings

The characteristics of the untreated drill cuttings, including metal concentrations and compositional analysis are summarized in Table 1. They contain predominantly  $C_{12}$  to  $C_{32}$  aliphatic hydrocarbons in concentrations ranging from <1 to 140 mg/kg, which were tentatively identified as shown in Fig. 1, based on a mass spectrometry library search. Analysis for polycyclic aromatic hydrocarbons (PAHs) revealed the presence of only 5 of



Fig. 1. Concentration of aliphatic compounds in drill cuttings (dry mass basis).

the 16 USEPA priority PAHs: phenanthrene,  $(m/z \ 178)$ , fluoranthene/pyrene  $(m/z \ 202)$ , benzo(j)fluoranthene/benzo[a]pyrene  $(m/z \ 252)$ , and indeno[1,2,3-cd]pyrene/benzo[ghi] perylene  $(m/z \ 276)$ , indicating the toxicity of oil drill cuttings [e.g., 42] and the need for treatment. Up to 7% hydrocarbons were present in the drill cuttings, which could have detrimental effects on cement hydration and consequently the properties of the s/s products, especially the unconfined compressive strength as later reported in the test results.

#### 3.2. Test results

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

A high UCS is not necessary for most waste management scenarios, but can be important for waste utilization, and UCS is an excellent indicator of the progress of hydration reactions. Fig. 2a summarizes the UCS results. The Pareto chart in Fig. 2b shows that all factors studied had significant main and interaction effects on the UCS. The UCS values ranged from 1.7 to 36.3 MPa after 7 days, which significantly increased to 4.7 to 44.5 MPa after 56 days. Products with the higher waste:binder ratio have a significantly lower UCS at all ages, possibly indicating a detrimental effect of hydrocarbons on strength development, though this effect is confounded with strength decrease caused by reduced cement content. S/S products containing HCFA also had lower UCS as compared to samples prepared with CEM I only; PFA is known to hydrate more slowly than CEM I and hydration is further retarded in PFA containing a high amount of carbon [33]. It has, however, been reported that blends of up to PFA:CEM I = 1:1 continue to hydrate over time, leading to additional gains in strength [33,43].

The 56-day UCS of the CEM I:HCFA control mix without waste (30.1 MPa) was not significantly different from that of the CEM I:HCFA s/s product with waste:binder = 1:4 (29.8 MPa). Since these UCS values were significantly lower than that of the CEM I only control mix (44.5 MPa), the main factor negatively influencing 56 days strength at the lower waste:binder ratio seems to be the presence of HCFA rather than drill cuttings. Since there was a significant difference in the UCS of the CEM I control (44.5 MPa) and the CEM I s/s product with waste:binder = 1:4 (33.3 MPa), it can be inferred that the presence of HCFA was able to impede the detrimental effect of hydrocarbons on 56 days strength at the lower waste:binder ratio. Though strength development of products containing HCFA was slower, this main effect of HCFA addition was less important than the interaction effect from the combination of waste:binder ratio and curing time.



Fig. 2. (a) Summary of UCS results, (b) Pareto chart for UCS, (c) summary of hydraulic conductivity results, (d) Pareto chart for hydraulic conductivity, (e) summary of porosity results, (f) Pareto chart for porosity, (g) summary of leachate pH, and (h) Pareto chart for Leachate pH. (\*measurements were recorded for 7 and 56 days samples only).



Fig. 2. (Continued).

The strengths obtained in this work are similar to those obtained by Al-Ansary and Al-Tabbaa [21], who stabilized synthetic drill cutting using Portland cement, GGBS, and micro-silica. However, they reported no significant difference in the UCS for the cement control mix and cement/drill cuttings mix at 30% binder content, which is contrary to the result obtained here. This could be due to the fact that the characteristics of actual drill cuttings may differ significantly from those of laboratory synthesized drill cuttings.

#### 3.2.2. Hydraulic conductivity and porosity

The hydraulic conductivity of a s/s product controls whether leaching occurs by advection or diffusion. Fig. 2c and d respectively shows the bar and Pareto charts for the hydraulic conductivity, which was measured at 7 and 56 days only (on different specimens). The Pareto chart reveals that the hydraulic conductivity was influenced by all factors studied, with the interaction between binder formulation and curing time having the dominant effect. Hydraulic conductivities ranged from 0.5 to  $9.7 \times 10^{-9}$  m/s after 7 days and  $0.05-23.5 \times 10^{-9}$  m/s after 56 days. It was noted that the CEM I s/s products show a lower (i.e., more desirable) hydraulic conductivities of CEM I products increased substantially with time while those of CEM I:HCFA products decreased, with the sample containing HCFA at waste:binder ratio = 3:2 having the lowest hydraulic conductivity after 56 days.

The hydraulic conductivity is a function of the pore structure [44], hence the porosity, but this relationship is complicated [45]. Porosity values are summarized in Fig. 2e. The Pareto chart for porosity (Fig. 2f) shows that the studied factors did not have similar effects on porosity as on hydraulic conductivity, with effects of waste:binder and binder formulation, but no effect of curing

time or interaction effects. A correlation analysis of the porosity and hydraulic conductivity yielded a negative and poor correlation (-17%); Morin [46] reported a similar result.

Hydraulic conductivity would be expected to decrease with time, as a consequence of matrix densification by continued hydration, as was observed for the CEM I:HCFA products. The observed increase in hydraulic conductivity of the CEM I products could result from matrix disruption reaction, such as delayed ettringite formation, due to the presence of sulphates in the drill cuttings. Sulphate-induced expansion has been reported to increase with increased cement content but can be inhibited by fly ash addition [47,48]. However, such reactions would be expected to manifest also in increased porosity and decreased UCS, which were not observed. Thus, it is more likely that the increase in hydraulic conductivity of the CEM I products is an experimental artifact, caused by difficulties in achieving the same degree of compaction during specimen preparation, which can affect the connected porosity and therefore fluid flow.

#### 3.2.3. Leachate pH and acid neutralization capacity (ANC)

Matrix pH and ANC are important in understanding the stability of the chemical environment in an s/s product. Since the conditions provided by the ANC test extract without acid addition are similar to those in BS EN 12457-2, the pH values measured in these two tests are expected to be similar. Either value can be used, along with strength development, to assess the progress of binder hydration [38]. Fig. 2g shows the BS EN 12457-2 pH values. The corresponding Pareto chart (Fig. 2h) shows significant effects caused by all three main factors and the interaction between the binder formulation and curing time, with the binder formulation having the dominant effect. All leachates without acid addition had pH values above 12.3, indicating the likely formation of physically stable



Fig. 3. Acid neutralization capacity (ANC) plots for s/s products cured for 56 days.

C-S-H, which is responsible for the physical integrity of the matrix [38], in equilibrium with lime.

ANC was measured for all products at 56 days; the resulting plots of pH as a function of acid addition in mequiv. of HNO<sub>3</sub>/g of dry binder are shown in Fig. 3. The plateaus in an ANC plot represent different hydrated phases which are able to resist acid attack [49] and their absence or lack of distinct presence (steep slope) in an ANC plot indicates the inhibition of their formation. Relative to the CEM I control, the plots show that drill cuttings did not visibly affect the ANC of CEM I s/s products at acid additions below 8.0 mequiv./g, but the plots for the CEM I s/s products became steeper at higher acid additions, indicating a relatively minor detrimental effect of drill cuttings on the ANC provided by the binder. By contrast, for the CEM I:HCFA s/s products, drill cuttings addition seems to have improved the ANC, especially for the products with higher waste:binder ratio. For example, while the cement/HCFA control had an ANC of ~5.2 mequiv./g of binder at pH 9, the s/s products with the same binder formulation had ANCs of approximately 6.3 and 6.8 at the same pH. Since the drilling mud has a poor ANC (pH 1.3 after addition of 3 mequiv./g), this may be evidence of formation of new phases by reaction of the drilling mud with the binder.

#### 3.2.4. Chloride, hydrocarbon and metal leaching

Chloride, hydrocarbon, and metal leaching from the s/s products range from 26 to 170 mg/L, 0 to 0.6 mg/L, and 0.001 to 12.7 mg/L, respectively. Detailed discussion on these is reported in Ref. [50]; however, the assessment of the s/s product management options discussed in the next section makes reference the results.

#### 3.3. Assessment of s/s product management options

Using available information on performance thresholds, an approach for assessing management options for the s/s products was demonstrated using contour plot overlays developed using Minitab. Performance thresholds were taken from a variety of sources having different degrees of formalization, i.e., while some are regulations or standard specifications, others are simply proposals under discussion. The adoption of these thresholds in this work is for illustrative purposes only, and it is recommended that the appropriateness of values applied be carefully considered in practice.

Contour plot overlays for the various responses were used to assess potential management options for the s/s products. All analyses were done based on the characteristics measured at 28 days. The ranges of values shown on the *x* and *y* axes represent the limits of the experimental conditions investigated. The upper and lower performance thresholds are represented by dashed and solid colored lines, respectively, as identified in the figure legends. Where a performance threshold is not shown on the plot, this indicates that such threshold is outside the plot, i.e., that it is satisfied by the experimental conditions investigated. The white area in the plots represents the range of binder formulation and waste-to-binder ratios where the proposed performance thresholds are satisfied. Five management options were assessed and discussed.

#### 3.3.1. Controlled low-strength materials (CLSM)

CLSM, also referred to as flowable fills, are self-compacting cement-based materials used as alternatives to conventional compacted fills [51]. They find application as backfills, structural fills, pavement (bases, sub-bases, and sub-grades), conduit bedding, and in erosion control and bridge reclamation works. CLSM consist of water, cement, fly ash, and fine aggregates; however, ACI recommends the use of non standard materials if they meet desired properties including strength, hydraulic conductivity, density, excavatability, and flowability. Recommended UCS values range between 0.3 and 8.4 MPa depending on the type of application. Hydraulic conductivities between  $10^{-6}$  and  $10^{-9}$  m/s and densities between 1.4 and 2.3 g/cm<sup>3</sup> are acceptable. The excavatability refers to the ease of removal at a later age and is related to the UCS. The main environmental protection consideration is contaminants leaching from the s/s products. In the absence other guidance. the Dutch intervention value of 0.6 mg/L for mineral oil in groundwater was adopted [52]. For chlorides, the USEPA drinking water limit of 250 mg/L [53] was adopted. A combination of the USEPA preliminary remediation goals [54] and the Dutch intervention values [52] were adopted for metals. The overlaid plot is shown in Fig. 4a. The ANC was not considered as all s/s products satisfy the recommended value of 1 mequiv./g at pH 9 for unrestricted utilization [55]. The white area in the plot indicates that CLSM can be prepared from a mixture drill cuttings, CEM I and HCFA within the studied factorial levels.

#### 3.3.2. Landfill liners

The most important property for a landfill liner is the hydraulic conductivity, for which an upper limit of  $10^{-9}$  m/s is often recommended, e.g., [55,56] and has been applied here. Fig. 4b shows the



Fig. 4. Overlaid contour plot for: (a) the use of S/S products drilling cuttings as CLSM, (b) the use of S/S drilling cuttings as landfill liner, (c) the use of S/S drilling cuttings as landfill daily cover, and (d) the disposal of S/S drilling cuttings as hazardous waste.

overlaid plot. A minimum of 4 MPa; to provide a fourfold safety margin over the 1 MPa for landfill disposal of s/s products recommended in [57] was applied for UCS. For other properties, the same performance thresholds were used as for CLSM. The white area in Fig. 4b shows that only a small range of binder formulation and waste-to-binder ratio can meet the hydraulic conductivity threshold value for use of s/s drilling cuttings as landfill liner.

#### 3.3.3. Landfill daily cover

The UCS and hydraulic conductivity performance thresholds applied for application of s/s drilling muds as daily cover material in landfills were a minimum of 1 MPa and maximum of  $10^{-8}$  m/s, respectively, based on the proposals for acceptance for landfill disposal [55,57]. The threshold values adopted above for landfill liners were applied for the other properties of interest. The overlaid plot (Fig. 4c) indicates that most s/s products in the experimental range could be utilized as landfill daily cover.

#### 3.3.4. Landfill disposal as inert waste

Under the UK guidance for waste landfilling, a waste is considered inert if it does not produce leachates with significant ecotoxicity [57]. A comparison of the guidance values (not shown) and the leaching results for metals [50] shows that chromium leaching exceeds the threshold of 0.5 mg/kg dry waste. Furthermore, the mineral oil ( $C_{10}$  to  $C_{40}$ ) concentration of the untreated drill cuttings exceeds the 500 mg/kg threshold allowable for land-filling; hence the s/s drilling muds cannot be accepted as inert waste.

# 3.3.5. Landfill disposal:hazardous waste (to be disposed in a non-hazardous landfill)

Under the UK guidance [57], chloride leaching must not exceed 15,000 mg/kg (i.e., 1500 mg/L at L/S = 10). Comparison of the UK guidance values for metal leaching and leaching from the s/s products [50] shows that concentrations were below guidance values. The guidance does not set limits for hydrocarbons leaching; therefore the Dutch guidance value was adopted. The overlaid plot (Fig. 4d) is the same as that of landfill daily cover even though the set chloride limits were different. This is because the highest chloride leaching from the s/s products was below the 250 and 1500 mg/L set for landfill daily cover and non-hazardous landfills respectively.

#### 4. Further remarks and recommendations

The assessment of management options was based on tested properties of the s/s products. A complete assessment would require taking other factors such as economic and social aspects into consideration. Furthermore, a more rigorous technical assessment of the civil engineering properties of the S/S products would be required for utilization. Many other potential reuse scenarios, such as concrete bricks and blocks, footpaths and light weight concretes remain to be explored.

#### 5. Conclusion

In this work, cement-based S/S of petroleum drill cuttings and possible management options for the s/s products was studied using a factorial design experiment. The following conclusions can be drawn for the results obtained:

- Factorial analysis shows that the binder formulation, waste-tobinder ratio, and the curing time affected the tested properties of the S/S products.
- Although the presence of drill cuttings significantly decreased the strength of the s/s products, their UCS values indicate that hydration of the binder has taken place. Samples treated using HCFA were less affected by the drill cuttings and show better hydraulic conductivity than those treated with CEM I only.
- The leachate pHs were above 12.3, confirming the likelihood of binder hydration to form C–S–H. Furthermore, the ANC plots indicate that drill cuttings do not significantly affect the matrix ANC; instead, the addition of drill cuttings seems to improve the ANC of s/s products prepared from CEM I with HPFA.
- Assessment of management options for the s/s drill cuttings indicates that they could find potential application as CLSM, landfill liners, and landfill daily cover. The s/s products also satisfy the UK non-hazardous landfill acceptance criteria but cannot pass as inert waste due to their chloride and oil contents.
- The work demonstrates how a systematic treatability study can be used to develop an operating window for S/S of a particular waste type and illustrates the possibility of utilizing an industrial by-product (HCFA) in cement-based S/S; hence, a sustainable management method.

#### References

- A.B. Doyle, F.V. Jones, S.S.R. Pappworth, D. Caudle, Drilling and production discharges in the marine environment, in: S.T. Orszulik (Ed.), Environmental Technology in the Oil Industry, Blackie Academic & Professional, London, UK, 1997, pp. 181–206.
- [2] OGP, Environmental Aspects of the Use and Disposal of Non-aqueous Drilling Fluids Associated with Offshore Oil and Gas Operation, International Association of Oil & Gas Producer, 2003.
- [3] E. Breuer, A.G. Stevenson, J.A. Howe, J. Carroll, G.B. Shimmield, Drill cutting accumulations in the northern and central North Sea: a review of environmental interactions and chemical fate, Mar. Pollut. Bull. 48 (2004) 12–25.
- [4] J.M. Neff, Composition, Environmental, Fates, and Biological Effects of Water Based Drilling Muds and Cuttings Discharged to the Marine Environment, Prepared for Petroleum Environmental Research Forum and American Petroleum Institute, 2005.
- [5] ICF Consulting, Overview of Exploration and Production Waste Volumes and Waste Management Practices in the United States, American Petroleum Institute, 2000.
- [6] P.W. Page, C. Greaves, R. Lawson, S. Hayes, F. Boyle, SPE 80583: options for the recycling of drill cuttings, in: Proceedings of the SPE/EPA/DOE Exploration and Production Environmental Conference, San Antonio, TX, USA, 2003.
- [7] A.K. Wojtanowicz, Environmental control technology in petroleum drilling and production, in: S.T. Orszulik (Ed.), Environmental Technology in the Oil Industry, Blackie Academic & Professional, London, UK, 1997, pp. 73–170.
- [8] UKOOA, Drill cuttings initiative final report—compilation of reports, research & development phases 1 and 2, Science Review Group, in: Stakeholder Dialogue Meetings, 2001.
- [9] OLF, Guidelines for characterization of offshore drill cuttings piles, Final Report, Norwegian Oil Industry Association, 2003.
- [10] A.F. Meinhold, Framework for a Comparative Environmental Assessment of Drilling Fluids, Prepared for National Petroleum Technology Office, Office of Fossil Energy, United States Department of Energy, BNL-66108, 1998.
- [11] OSPAR Commission, Discharges, Waste Handling, and Air Emissions from Offshore Oil and Gas Installations in 2000 and 2001, Offshore Industry Series, 2003.
- [12] R. Minton, Strategic management of waste streams generated by exploration and production drilling operations, in: Business Briefing: Exploration & Production: The Oil & Gas Review, 2004.

- [13] R.L. Stephenson, S. Seaton, R. McCharen, E. Hernandez, P.R. Benson, Thermal desorption of oil from oil-based drilling fluids cuttings: processes and technologies, in: Proceeding of SPE Asia Pacific Oil and Gas Conference and Exhibition, APOGCE, 2004, pp. 323–330.
- [14] J.A. Veil, Drilling waste management: past, present, and future, in: Proceedings of the SPE Annual Technical Conference and Exhibition, San Antonio, TX, United States, 2002.
- [15] J.P. Robinson, S.W. Kingman, O. Onobrakpeya, Microwave-assisted stripping of oil contaminated drill cuttings, J. Environ. Manage. 88 (2008) 211–218.
- [16] C.H. Chaineau, J.L. Morel, J. Oudot, Microbial degradation in soil microcosms of fuel oil hydrocarbons from drilling cuttings, Environ. Sci. Technol. 29 (1995) 1615–1621.
- [17] G.D. Ji, Y.S. Yang, Q. Zhou, T. Sun, J.R. Ni, Phytodegradation of extra heavy oilbased drill cuttings using mature reed wetland: an in-situ pilot study, Environ. Int. 30 (2004) 509–517.
- [18] J. Veil, D. Elcock, M. Raivel, D. Caudle, R.C. Ayers, B. Grunewald, Disposal of nonhazardous oil field wastes into salt caverns, in: Proceedings of the International Conference on HSE in Oil and Gas Exploration and Production, vol. 2, 1996, pp. 767–768.
- [19] CORDAH, Research on the re-use of drill cuttings onshore, Anne Manning and Marianne Lang, Report No: Cordah/COR012/1999, CORDAH Research Limited, 1999.
- [20] BMT Cordah Limited, Use of oily drilling wastes in civil engineering applications, Report No. BMT Cordah Ltd/COR.027/2002, 2002.
- [21] M.S. Al-Ansary, A. Al-Tabbaa, Stabilisation/solidification of synthetic petroleum drill cuttings, J. Hazard. Mater. 141 (2007) 410–421.
- [22] J.R. Conner, Chemical Fixation and Solidification of Hazardous Waste, Van Nostrand Reinhold, New York, 1990.
- [23] J.R. Conner, S.L. Hoeffner, A critical review of stabilisation/solidification technology, Crit. Rev. Environ. Sci. Technol. 28 (1998) 397–462.
- [24] USEPA, Treatment Technologies for Site Cleanup: Annual Status Report, eleventh edition, 2004 (EPA-542-R-03-009).
- [25] C.C. Wiles, A review of solidification/stabilization technology, J. Hazard. Mater. 14 (1987) 5–21.
- [26] Environmental Agency, Guidance on the use of stabilization/solidification for the treatment of contaminated soil, Environmental Agency, UK, Science Report: SC980003/SR1, 2004.
- [27] S. Paria, P.K. Yuet, Solidification-stabilisation of organic and inorganic contaminants using portland cement: a literature review, Environ. Rev. 14 (2006) 217-255.
- [28] S. Trusell, R.D. Spence, A review of solidification/stabilisation interferences, Waste Manage. 14 (1994) 507–519.
- [29] A. Tuncan, M. Tuncan, H. Koyuncu, Use of petroleum contaminated drilling wastes as sub-base material for road construction, Waste Manage. Res. 18 (2000) 489–505.
- [30] R.C. Joshi, R.P. Lohtia, G. Achari, Fly ash cement mixtures for solidification and detoxification of oil and gas well sludges, Trans. Res. Rec. 1486 (1995) 35–41.
- [31] R.J. Caldwell, P. Cote, C.C. Chao, Investigation of solidification for the immobilization of trace organics contaminants, Hazard. Waste Hazard. Mater. 7 (1990) 273–281.
- [32] V.M. Hebatpuria, H.A. Arafat, H.S. Rho, P.L. Bishop, N.G. Pinto, R.C. Buchanan, Immobilization of phenol in cement-based solidified/stabilized hazardous wastes using regenerated activated carbon: leaching studies, J. Hazard. Mater. 70 (1999) 117–138.
- [33] C.S. Poon, X.C. Qiao, Z.S. Lin, Pozzolanic properties of reject fly ash in blended cements pastes, Cement Concrete Res. 33 (2003) 1857–1865.
- [34] L.K.A. Sear, Should you be using more PFA? in: Dundee University Conference, Global Construction, Ultimate Concrete Opportunities, 2005.
- [35] G.E.P. Box, W.G. Hunter, J.S. Hunter, Statistics for Experimenters: Design, Innovation, and Discovery, John Wiley & Sons, Inc, New Jersey, 2005.
- [36] J.A. Stegemann, Q. Zhou, Development of process envelopes for cement-based stabilisation/solidification of metal treatment filtercakes, in: M. Zamorano, V. Popov, A.G. Kungolos, C.A. Brebbia, H. Itoh (Eds.), Waste Management and the Environment IV (Waste Management 2008), WIT Transactions on Ecology and the Environment, vol. 109, WIT Press, 2008.
- [37] USEPA, SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, available on the internet at http://www.epa.gov/sw-846/main.htm (last accessed January, 2009).
- [38] J.A. Stegemann, Q. Zhou, Screening tests for assessing treatability of inorganic industrial wastes by stabilization/solidification with cement J. Hazard. Mater. 161 (2009) 300–306.
- [39] USEPA, Stabilization/Solidification of CERCLA and RCRA Wastes: Physical Tests, Chemical Testing Procedures, Technology Screening, and Field Activities, Office of Research & Development, U.S. Environmental Protection Agency, Cincinnati, OH, US, 1989.
- [40] A.S.R. Perera, A. Al-Tabbaa, J.M. Reid, J.A. Stegemann, State of practice reports, UK stabilization/solidification treatment and remediation—testing and performance criteria, in: A. Al-Tabbaa, J.A. Stegemann (Eds.), Stabilization/Solidification Treatment and Remediation, Advances in S/S for Waste and Contaminated Land, A.A. Balkema Publishers, London, UK, 2004, pp. 415–436.
- [41] LB. Barrentine, An Introduction to Design of Experiments: A Simplified Approach, ASQ Quality Press, Milwaukee, USA, 1999.
- [42] ATSDR, Agency for Toxic Substances & Disease Registry, ToxFAQs, Available at http://www.atsdr.cdc.gov/toxfaq.html (last accessed July, 2009).
- [43] M.D.A. Thomas, J.D. Matthews, Performance of PFA concrete in a marine environment—10-years results, Cement Concrete Comp. 26 (2004) 5–20.

- [44] J.P. Ollivier, M. Massat, Permeability and microstructure of concrete: a review of modelling, Cement Concrete Res. 22 (1992) 503–514.
- [45] A.E. Scheidegger, The physics of flow trough porous media, in: J.P. Ollivier, M. Massat (Eds.), Permeability and Microstructure of Concrete: A Review of Modelling, Cement Concrete Res., vol. 22, 1992, pp. 503–514.
- [46] R.H. Morin, Negative correlation between porosity and hydraulic conductivity in sand and gravel aquifers at Cape Cod, Massachusset, J. Hydrol. 316 (2005) 43–52.
- [47] G.L. Kalousek, L.C. Porter, E.J. Benton, Concrete for long-time service in sulfate environment, Cement Concrete Res. 2 (1972) 79–89.
- [48] C. Ouyang, A. Nanni, W.F. Chang, Internal and external sources of sulfate ions in portland cement mortar: two types of chemical attack, Cement Concrete Res. 18 (1988) 669–709.
- [49] G.K. Glass, N.R. Buenfeld, Differential acid neutralization capacity, Cement Concrete Res. 29 (1999) 1681–1684.
- [50] S.A. Leonard, J.A. Stegemann, Stabilization/solidification of petroleum drill cuttings: Leaching studies, J. Hazard. Mater. 174 (2010) 484– 491.

- [51] ACI, Controlled Low Strength Materials (CLSM), Reported by ACI Committee 229", American Concrete Institute, Detroit, Report WSRC-TR-97-0100, 1999.
- [52] MHSP&E, Ministry of Housing, Spatial Planning and Environment Circular on Target Values and Intervention Values for Soil Remediation, Dutch Department of Soil Protection, 2000, DBO/1999226863.
- [53] USEPA, Drinking Water Regulations and Health Advisories, Washington, D.C., United States Environmental Protection Agency, Office of Water, 1996, EPA 822-B-96-002.
- [54] USEPA, USEPA Region 9 Preliminary Removal Goals (PRGs), available on the internet at http://www.epa.gov/region09/superfund/prg/files/04prgtable.pdf (last accessed January, 2009).
- [55] J.A. Stegemann, P.L. Cote, A proposed protocol for evaluation of solidified wastes, Sci. Tot. Environ. 178 (1996) 103–110.
- [56] D.E. Daniel, C.H. Benson, Water content-density criteria for compacted soil liners, J. Geotechnol. Eng. 116 (1990) 1811–1830.
- [57] Environmental Agency, Guidance for Waste Destined for Disposal in Landfills, Version 2: Interpretation of the Waste Acceptance Requirements of the Landfill (England and Wales) Regulations 2002 (as amended), Environmental Agency, UK, 2006.