



Stabilization/solidification of petroleum drill cuttings: Leaching studies

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ABSTRACT

This work explores the effectiveness of Portland cement (CEM I), with the addition of high carbon fly ash (HCFA), as a novel binder, for the improvement of leachability-related properties of stabilized/solidified (s/s) petroleum drill cuttings. A factorial design experiment was adopted to investigate the effects of waste-to-binder ratio, HCFA addition, and curing time on leachate pH, acid neutralization capacity (ANC), and metal, chloride and hydrocarbon leaching. The leachate pH and ANC of all products suggested successful formation of a calcium–silicate–hydrate-based matrix with good resistance to acid attack, and little detrimental effect from drill cuttings addition. Leaching of amphoteric metals was significantly affected by pH, which was a function of other studied factors. All studied factors also affected leaching of chloride and hydrocarbons. CEM I, without HCFA addition, was more effective in immobilizing chlorides, but the overall chloride immobilization was poor in all runs. HCFA addition significantly reduced the leaching of hydrocarbons. Comparison of milligram of contaminant leached per kilogram of drill cuttings from the s/s products and untreated drill cuttings provided clear evidence of hydrocarbon and chloride immobilization. This work shows that HCFA improved the immobilization of organic contaminants and may represent an inexpensive binder for stabilization/solidification of organic wastes.

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1. Introduction

1.1. Stabilization/solidification (S/S) of organics

Cement-based stabilization/solidification (s/s) is a quick, “low-tech”, and inexpensive waste treatment technique aimed at immobilizing contaminants by converting them into a less soluble form (stabilization); and encapsulating them by the creation of a durable matrix (solidification). Its use for inorganic wastes is to some extent well-accepted and has been widely reported [1]. S/S is considered less compatible with organic wastes, however, because organic compounds may inhibit binder hydration [2] and are generally not chemically bound in binder hydration products. Hence, immobilization of organic contaminants depends mainly on physical entrapment in the binder matrix, and sorption onto the surface of binder hydration products, with the possibility of release of undesirably high concentrations when exposed to environmental leachants.

The leaching of organic contaminants from stabilized/solidified (s/s) products treated with Portland cement alone has been reported in some publications. For example, dynamic leaching (diffusion) test results have shown relatively high release of polycyclic aromatic hydrocarbons (PAHs) [3] and methanol and

2-chloroaniline [4]. In other work [5], leachates from s/s soils contaminated with polychlorinated biphenyls (PCBs) were reported to have concentrations above the regulatory limits for the USEPA toxicity characteristic leaching procedure (TCLP). Another work [6] reported that s/s waste released up to 100% of phenol in the TCLP. In fact, one work [7] reported that increased cement addition to oil refinery sludge containing alkanes and PAHs led to higher concentrations in leachates from batch extraction than were observed prior to S/S treatment.

The foregoing shows that a Portland cement only binder system is not effective for the immobilization of several common organic contaminants. A possible method for improving the effectiveness of S/S for organic wastes is by using binders that increase sorption of organic compounds, thereby improving their immobilization and preventing their detrimental effects on binder hydration. Caldwell et al. [8] reported that activated carbon used with Portland cement was effective in S/S of a range of organic contaminants. Hebatpuria et al. [9] also reported that the use of regenerated activated carbon in S/S of phenol-contaminated sand resulted in a significant reduction in leaching. Activated carbon is however expensive; a less expensive material that could combine sorption and binding characteristics is high carbon power plant fly ash (HCFA), an industrial by-product with pozzolanic properties [10], similar to the pulverized fuel ash (PFA) widely accepted for use in cement-based construction materials [11], but which contains a higher proportion of unburnt carbon that could act as a sorbent for organic compounds. This work therefore aims to investigate the possibility of

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using cement and HCFA for the treatment of a waste type containing organic compounds: oil-based petroleum drill cuttings.

1.2. Petroleum drill cuttings

Petroleum drill cuttings, a mixture of drilling fluids used as lubricants and coolants during crude oil drilling and small pieces of formation rock, are one of the major wastes from crude oil exploration and production. They pose a waste management problem to the petroleum industry because of the volume generated and their content of both organic and inorganic contaminants which include petroleum hydrocarbons, such as aliphatic hydrocarbons, PAHs, and PCBs; heavy metals, including lead, barium, zinc, mercury, chromium, arsenic and nickel; and inorganic compounds including chlorides [12–14]. The level of toxicity of any drill cutting depends on the composition of the formation rock and the type of drill fluid involved, which could be water-based, 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 [14–16]. Oil-based drill fluids are more harmful because of their diesel/mineral oil content but are inevitably the best option for some drilling conditions; hence, there is a continuing need for effective management method of such drill cuttings.

Little published work exists on the application of S/S for drill cuttings treatment. One work [17], on the S/S of oil and gas well sludges consisting of drill cuttings and hydrocarbons, reported that a combination of Portland cement and fly ash treatment resulted in improved hydraulic conductivity and reduced micro-toxicity; but did not investigate the leaching of hydrocarbon, metal, or chloride contaminants. In another work [18], petroleum drilling wastes were treated with Portland cement, lime and PFA and the resultant

monolith was subjected to dynamic leaching using rainwater. It was reported that metal leaching was satisfactory; however, hydrocarbon and chloride leaching were not investigated. Al-Ansary and Al-Tabbaa [19] also worked on the S/S of synthetic drill cuttings using different binders and reported that products from some formulations were compliant with the UK non-hazardous waste landfill acceptance criteria based on the BS EN 12457 batch leaching test. They, however, did not investigate metal leaching; more so, the properties of s/s products prepared from synthetic drill cuttings might vary considerably from those prepared with the real waste. It is therefore apparent that further study on the leaching of contaminants from s/s drill cuttings is still needed.

1.3. Aims and objectives

This work is therefore aimed at investigating the leaching behavior of metals, chloride and hydrocarbon contaminants present in a real oil-based petroleum drill cuttings treated with Portland cement and HCFA, and to determine whether HCFA addition results in any improvement in immobilization of these contaminants. A factorial experimental design approach, which maximizes the information that can be obtained by enabling study of the effects and interaction of multiple variables concurrently [20] was adopted.

2. Materials and methods

2.1. Drill cuttings

Two buckets of drill cuttings obtained from an unidentified terrestrial drilling operation were homogenized in a Hobart mixer and characterized as described in previous work [21], including deter-

Table 1
Characteristics of binders and drill cuttings.

Properties	Values \pm standard deviation of three replicates			Elemental Composition (mg/kg dry mass)	Values		
	HCFA	CEM I	Drill cuttings		HCFA	CEM I	Drill cuttings
Moisture content (% wet mass)	0.6 \pm 0.1	–	10.5 \pm 0.1	As	42	10	5
Bulk density (g/cm ³ , wet mass)	0.9–1.3	1.3–1.5	1.1–1.6	Ba	1520	196	51,500
Specific gravity	2.34 \pm 0.01	3.58 \pm 0.01	1.98 \pm 0.01	Cd	0.1	0.2	21
pH (L/S of 10)	12.4 \pm 0.1	13.1 \pm 0.2	8.6 \pm 0.2	Cl	1300	200	6,360
Loss-on-ignition (% dry mass)				Co	23	8	14
Organic carbon (550 °C)	(33.1 \pm 0.2) ^a	2.1 \pm 0.4	4.3 \pm 0.2	Cr	114	55	106
Inorganic carbon (950 °C)	0.3 \pm 0.1	0.7 \pm 0.1	2.1 \pm 0.1	Cu	68	35	44
Gravimetric masses (mg/kg dry mass)				Fe	59,200	18,300	26,400
Soxhlet extracts	–	–	66,700 \pm 400	Mn	1880	294	345
Aliphatic fraction	–	–	44,600 \pm 600	Ni	96	23	38
Aromatic fraction	–	–	6580 \pm 40	Pb	32	14	150
Polar fraction	–	–	5990 \pm 20	Sn	3	34	1
Organic contaminants (mg/kg dry mass)				Sr	730	475	930
				V	131	67	108
				Zn	61	52	82
				Bulk composition analysis (% dry mass)			
Dodecane C ₁₂	–	–	14.1	SiO ₂	25.4	21.8	60.4
Tetradecane C ₁₄	–	–	55.5	Al ₂ O ₃	12.9	4.5	10.4
Hexadecane C ₁₆	–	–	138	Fe ₂ O ₃	10	2.5	4.9
Octadecane C ₁₈	–	–	41.5	MgO	2.2	0.9	2
Eicosane C ₂₀	–	–	34.1	CaO	6.5	59.3	2.5
Docosane C ₂₂	–	–	37.5	Na ₂ O	0.5	0.3	2.4
Tetracosane C ₂₄	–	–	1.5	K ₂ O	1.1	0.6	1.7
Hexacosane C ₂₆	–	–	1.1	TiO ₂	0.6	0.4	0.6
Octacosane C ₂₈	–	–	0.6	P ₂ O ₅	0.6	0.2	0.1
Triacosane C ₃₀	–	–	0.6	MnO	0.3	0.04	0.06
Dotriacontane C ₃₂	–	–	0.4	SO ₄ ²⁻	0.68	1.43	1.46

^a 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 ^a	1:0	0:1	7	0.45:1	0.45:1	0.45:1
2 ^a	1:0	0:1	28	0.45:1	0.45:1	0.45:1
3 ^a	1:0	0:1	56	0.45:1	0.45:1	0.45:1
4 ^b	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 ^b	1:0	1:4	56	0.45:1	0.56:1	0.56:1
7 ^b	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 ^b	1:0	3:2	56	0.45:1	1.13:1	1.13:1
10 ^a	1:1	0:1	7	0.45:1	0.9:1	0.45:1
11 ^a	1:1	0:1	28	0.45:1	0.9:1	0.45:1
12 ^a	1:1	0:1	56	0.45:1	0.9:1	0.45:1
13 ^b	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 ^b	1:1	1:4	56	0.45:1	1.13:1	0.56:1
16 ^b	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 ^b	1:1	3:2	56	0.45:1	2.25:1	1.13:1

^a Control runs.

^b Used for 2³ factorial analysis.

mination of moisture content, specific gravity, loss-on-ignition, metal, chloride and hydrocarbon contents, as well as hydrocarbon desorption as a function of pH. The characteristics are summarized in Table 1. The drill cuttings contain predominantly C₁₂–C₃₂ aliphatic hydrocarbons in concentrations ranging from <1 to 140 mg/kg, which were tentatively identified as indicated.

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 experiment as summarized in Table 2, and described in previous work [22] including (1) *binder formulation*, studied at two levels: CEM I alone and CEM I:HCFA = 1:1, to assess the effectiveness of HCFA in immobilizing hydrocarbon; (2) *waste-to-binder ratio*, studied at three levels: 0:1, 1:4 and 3:2, to assess the effect of drill cuttings quantity on contaminant leaching; and (3) *curing time*, studied at three levels: 7, 28, and 56 days. The water-to-solid ratio was maintained at 0.45 for all runs; it should be noted that this resulted in a variation in the water-to-CEM I and water-to-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 × 50 mm steel cube moulds to fill them half way. 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 the exposure to air and cured for 24 h in a humidity chamber with a relative humidity of 98 ± 2% and a temperature of 21 ± 3 °C before demoulding. The demoulded specimens were resealed in plastic bags and transferred back into the humidity chamber for further curing prior to testing. The various formulations and preparation procedure resulted in specimens having weights and specific gravities ranging from 198 to 238 g and 1.7 to 1.9, respectively.

2.5. Testing procedure

The following tests were conducted on the s/s products:

- *Acid neutralization capacity (ANC)* (according to DD CEN/TS 15364:2006), which involves extraction of 11 subsamples of s/s product ground to <150 μm for 48 h with a range of concentrations of nitric acid, followed by the determination of pH, and metal concentrations in the extracts with zero acid addition using inductively coupled plasma/mass spectrometry (ICP/MS).
- *De-ionized water batch extraction* (in duplicate, according to BS EN 12457-2:2002), of s/s product ground to <4 mm at a liquid-to-solid ratio of 10:1 for 24 h, with determination of extract pH and leached concentrations (expressed as mg/kg of dry solid sample) for:
 - *Chloride*, using a Jenway chloride meter which works based on the coulometric principle (measurement of the solution potential when all the chloride in solution has complexed with silver released by a cathode).
 - *Hydrocarbons*, by GC/MS using adapted USEPA Method 8270C (as further described in Ref. [21]). The crushed samples were not dried before the test to prevent loss of hydrocarbons, but the mass of sample used in the test was corrected for the moisture content. Batch leaching was conducted by mixing 500 mL of de-ionized water with 50 g of samples in a Teflon sealed glass bottle at ambient temperature (21–25 °C). The mixture was agitated end-over-end using a rotary extractor rotating at 30 rpm. At the end of the agitation, the mixture was vacuum filtered using a 0.7 μm Fisher-brand glass microfiber filter paper, followed by liquid–liquid extraction of hydrocarbons (USEPA Method 3510C).
- *Other tests*, including bulk density, specific gravity, moisture content, porosity, unconfined compressive strength, and hydraulic conductivity were also conducted on the samples and reported in Ref. [22].

2.6. Data analysis

A 2³ factorial analysis of selected experimental runs (see Table 2) was carried out to determine the main and interaction effects of the studied factors using Minitab 15 statistical analysis software. 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

Table 3
Metal leaching from s/s products (48 h batch extraction; ANC leachates at zero acid addition).

Experimental runs	pH (no acid addition)	Concentration leached (mg/kg of dry solid)											
		Ba	Cd	Co	Cr	Cu	Mn	Ni	Pb	Sn	Sr	Zn	
Waste:binder = 1:4; CEM I:HCFA = 1:0	13.0	19.4	nd	0.01	0.6	0.03	0.02	0.03	0.03	0.03	0.01	28.8	0.8
Waste:binder = 1:4; CEM I:HCFA = 1:1	12.7	1.3	0.005	0.02	1.4	0.01	0.01	0.08	0.08	0.08	0.21	0.5	0.4
Waste:binder = 3:2; CEM I:HCFA = 1:0	12.6	5.3	nd	0.01	1.3	0.03	0.01	0.07	0.07	0.07	0.26	7.8	0.5
Waste:binder = 3:2; CEM I:HCFA = 1:1	12.3	1.4	0.005	0.005	0.9	0.08	0.01	0.07	0.03	0.17	0.17	2.0	0.7
Waste:binder = 0:1; CEM I:HCFA = 1:0	12.5	10.4	0.01	0.02	0.2	nd	0.02	0.03	0.01	0.45	0.45	87.7	0.9
Waste:binder = 0:1; CEM I:HCFA = 1:1	12.2	10.7	nd	0.005	0.7	0.01	0.01	0.04	0.01	0.26	0.26	40.1	0.6
Untreated drill cuttings	8.55	3.4	0.004	0.05	0.01	0.4	0.1	0.24	0.02	0.31	0.31	9.1	0.9
Unhydrated CEM I	12.5	24.0	0.001	nd	0.01	0.3	0.09	0.06	0.16	0.01	0.01	127	1.0
Unhydrated HCFA	12.4	0.2	0.004	0.02	0.7	0.07	0.04	0.01	0.03	0.11	0.11	60.2	1.0

nd = not detected.

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 [23] and it corresponds to the level of significance (*p*-value) of the analysis of variance (ANOVA) of the experimental results. A separate ANOVA was also performed to determine the statistical significances of the effects of leachate pH, binder formulation, and waste-to-binder ratio on metal leaching. A significance level of 0.05 was used for all analyses.

3. Results and discussion

3.1. Leachate pH and acid neutralization capacity (ANC)

Leachate pH and matrix ANC are important in understanding the stability of the chemical environment in a s/s product, and in assessing the immobilization of metals, many of which tend to become soluble at both low and high pH values. The statistical analysis of the pH measurements for the BS EN 123457-2:220 extracts are shown and discussed in more detail in Ref. [22]. All of the s/s product leachates without acid addition had pH values above 12.3 (between 12.3 and 13.0), indicating the likely formation of physically stable calcium-silicate-hydrate (C-S-H), which coexists at approximately pH 12.3 with portlandite (calcium hydroxide), the most alkaline hydration product in a cement-based system [24]. Generally, s/s products containing HCFA had lower leachate pH values (between 12.3 and 12.7), which were attributed to the consumption of portlandite in the pozzolanic reaction between the HCFA and Portland cement.

ANC was measured for all s/s products at 56 days; drill cuttings had a relatively minor detrimental effect on the ANC provided by CEM I, and improved the ANC of s/s products containing HCFA, suggesting formation of new phases by reaction of the drilling mud with the binder. The ANCs of the s/s products were between 6.3 and 12 at pH 9, indicating good resistance to acid attack [25]. These s/s products are likely to be able withstand reaction with carbon dioxide from the atmosphere or acidic leachates in a landfill, during utilization or disposal, without disintegrating or reaching a pH value below 9, where metals become more soluble [24–26].

3.2. Toxic metals content and leaching

Comparison of the concentrations of toxic metals in the drill cuttings and CEM I (Table 1) shows more than 200 times enrichment of Ba, 100 times enrichment of Cd and 10 times enrichment of Pb in the drill cuttings. The HCFA was also somewhat enriched in Ba (though only 8 times the concentration in CEM I). The remaining metals of concern were present in comparable concentrations within all three materials.

Concentrations of all metals investigated were above detection in the leachates from the s/s products and their raw materials in most instances, even for the binder materials. Metal concentrations measured in mg/L have been multiplied by the liquid-to-solid ratio to convert them to milligram of contaminant leached per kilogram of dry sample, as specified by BS EN 12457-2 (Table 3). ANOVA (Table 4) indicated that leaching from the s/s products of all of the metals except Ba and Sr was strongly affected by leachate pH. As discussed above, leachate pH was increased by drill cuttings addition; therefore waste-to-binder ratio also significantly affected metal leaching. Although leachate pH was seen to decrease as a result of addition of HCFA to the binder, the effect of binder formulation was not found to be significant at the chosen significance level of 0.05; the decrease in pH may have been insufficient to result in highly significant changes in leachability in this region of the pH-solubility curve.

Leachability of Ba and Sr was found to be pH independent because these metals are not amphoteric. Despite the high Ba content of the drill cuttings, Ba shows poor leachability even in the untreated drill cuttings; this is because it is present as relatively insoluble barium sulfate (barite). In fact, the highest Ba and Sr leachability was observed for the CEM I binder, indicating that these metals are present in the binder in a more soluble form, possibly oxides or carbonates.

3.3. Chloride leaching

Chlorides have high solubility and their dissolution when a s/s product comes into contact with water can increase porosity, leading to increased hydraulic conductivity and compromising matrix integrity. Concentrations leached in a batch test such as BS EN 12457-2, applied in this work, will depend first on sorption/mineral uptake, then the solubility limit, and finally dilution,

Table 4
ANOVA: effect of leachate pH, binder formulation, and waste-to-binder ratio on metal leaching.

Element	<i>p</i> -Value (probability that the observed effect on metal leaching is due to chance)		
	pH	Binder formulation	Waste-to-binder ratio
Ba	0.09	0.37	0.218
Cd	9.8E-11	0.13	0.022
Co	9.8E-11	0.14	0.022
Cr	3.8E-10	0.36	0.050
Cu	1.1E-10	0.14	0.024
Mn	1.1E-10	0.14	0.023
Ni	9.9E-11	0.14	0.024
Pb	9.8E-11	0.14	0.023
Sn	1.0E-10	0.16	0.030
Sr	0.29	0.32	0.097
Zn	2.1E-10	0.24	0.050

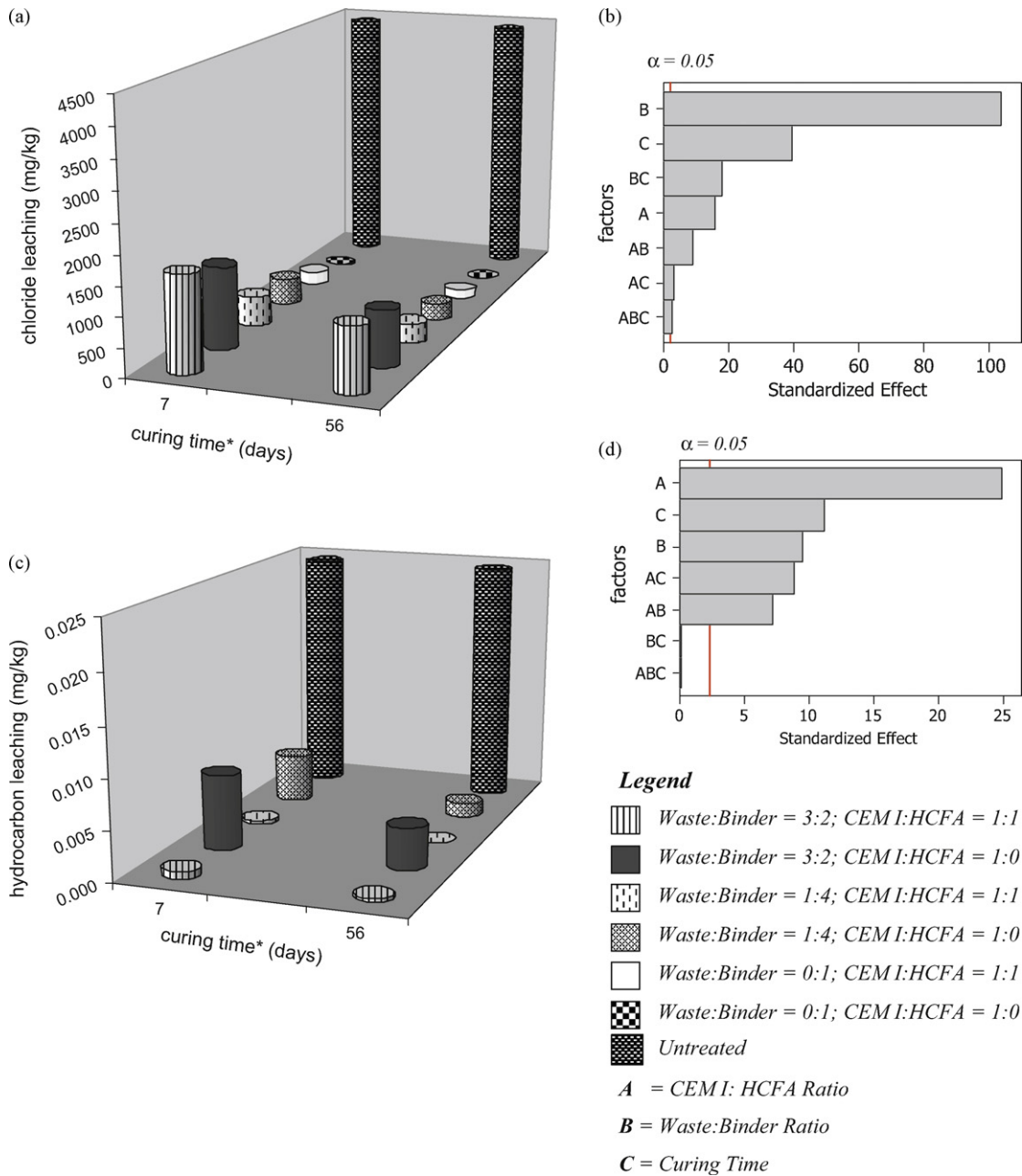


Fig. 1. (a) Summary of chloride leaching results (*measurements were recorded for 7 and 56 days samples only). (b) Pareto chart for chloride leaching. (c) Summary of hydrocarbon leaching results (measurements were recorded for runs containing drill cutting at 7 and 56 days samples only). (d) Pareto chart for hydrocarbon leaching.

when the solubility limit exceeds the amount of chloride in the sample. Fig. 1a shows a decrease in the amount of chloride leached from the s/s products, as compared to the untreated drill cuttings, expressed as mg/kg of dry solid sample. The results also suggest that chloride leached from s/s products with the same waste:binder ratio were similar, and the Pareto chart (Fig. 1b) confirms that the waste:binder ratio is the dominant effect. While this is not surprising, as dilution will affect leaching of such a soluble ion (see Section 3.5 for further discussion), research [e.g., [27–29]] has also shown that chloride concentration is an important factor affecting the binding of chlorides with cement. Interestingly, the Pareto chart also showed all other factors and interactions to have a significant effect on chloride leaching. It was observed that the CEM I:HCFA products released more chlorides than the CEM I products, which may be due to:

- *chloride content of binders*: HCFA has a higher concentration of chlorides than CEM I (Table 1), thereby contributing to the amount of chlorides that will be available for leaching;
- *the chloride binding mechanisms*: chlorides can either react with tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) to form Friedel's salt ($3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$) or can be physically sorbed onto the C–S–H surface [30,31] in a hydrated cement. Physical sorption may be greater in fly ash systems due to the increased C–S–H content from pozzolanic reactions, but is more reversible [32];
- *pore solution alkalinity*: low pore solution alkalinity tends to decrease binding capacity and increase the solubility of Friedel's salt [31,33]. The lower leachate pH for products containing HCFA demonstrates that they will also have a lower porewater pH.

The results obtained here are similar to those reported by Al-Ansary and Al-Tabbaa [19], in which chloride leaching from synthetic drill cuttings treated with a Portland cement binder was less than that from cuttings treated by other binder types, including PFA.

It was also noted that chloride leaching decreased with curing time. This could be because the reactions of chlorides with C_3A and C_4AF are in competition with sulfates which are known to be both thermodynamically more stable and kinetically favored [31], hence chloride binding would be slower and might only occur after all sulfate binding has been achieved. Also, the sorption of chlorides is dependent on CSH formation, which occurs over a period of time, particularly in a system containing pozzolan (e.g., HCFA).

3.4. Hydrocarbon leaching

For most organic contaminants, the procedure in BS EN 12457-2 can be adapted for measuring sorption, i.e., partitioning between the water and inorganic and organic phases of the s/s product, which can be used to assess the risk of contaminant leaching in the environment. Hydrocarbon leaching, expressed as total milligram of C_{12} – C_{32} aliphatic compounds leached per kilogram of dry s/s product (Fig. 1c), was considerably lower than the total hydrocarbon concentration in the untreated drill cuttings, indicating that sorption was taking place in the s/s products. Initial work [21] on untreated drill cuttings also showed poor leaching of hydrocarbons, but the amount leached from the s/s product was lower than that leached from the untreated sample. However, before concluding that s/s was effective for immobilizing hydrocarbons, it is important to differentiate between immobilization and dilution (see Section 3.5).

The Pareto chart (Fig. 1d) shows that the binder formulation had the most significant effect on hydrocarbon leaching; less hydrocarbon was leached from the CEM I:HCFA products than from the CEM I only products. HCFA was chosen for this work because of its high unburnt carbon content, which was expected to act as a sorbent for organic contaminants. Preparatory work by the authors [34] on its sorption properties confirmed a high affinity between aliphatic hydrocarbons and HCFA. It must however be noted that the coefficient for sorption of aliphatic hydrocarbons to HCFA determined in the preparatory work is much greater than the leaching (i.e., desorption) coefficient calculated from the BS EN 12457-2 leaching data for the CEM I:HCFA samples (Table 5). The preparatory work was carried out with water spiked with only three hydrocarbons, whereas the drill cuttings contained a mixture of numerous hydrocarbons; it is possible that the hydrocarbons in this mixture were co-eluted, reducing sorption. Also, the differences in the L/S ratios employed for the sorption ($L/S=40$) and leaching ($L/S=10$) could also influence the desorption/leaching properties [35].

The Pareto chart also shows that curing time significantly affects hydrocarbon leaching, which accords with findings in Ref. [9] where it was reported that increased curing time resulted in a reduction in TCLP leaching of phenol. As previously noted, contaminant sorption to hydration products can be expected to increase over time, due to increase hydration, particularly in pozzolanic binders.

3.5. Dilution or immobilization

To differentiate between immobilization and dilution during the S/S treatment, the amounts of chloride and hydrocarbons leached from the treated and untreated drill cuttings were compared by converting the leaching results from mg leached/kg total dry s/s product to mg leached/kg drill cuttings. In the absence of immobilization, the mass leached per mass of treated drill cuttings should equal or exceed the mass leached per mass of untreated drill cuttings. Fig. 2a and b shows the results obtained. In all cases,

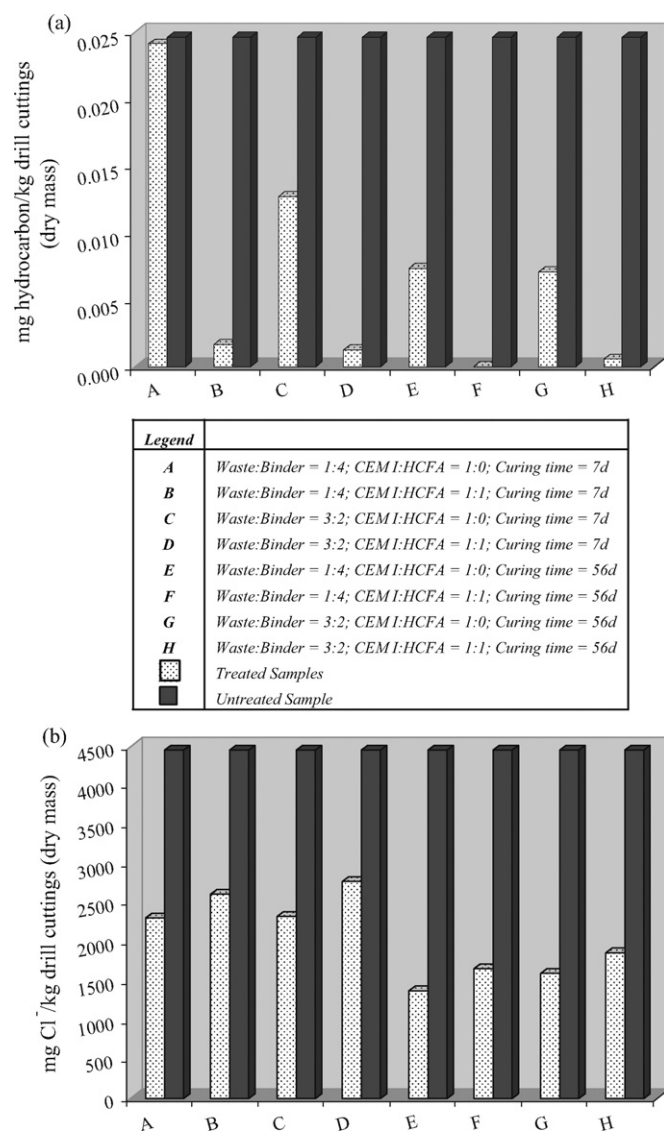


Fig. 2. (a) Comparison of amount of chloride leached from treated and untreated samples. (b) Comparison of amount of hydrocarbon leached from treated and untreated samples.

immobilization was observed to have taken place, i.e., the mass leached per equivalent mass of drill cuttings in the s/s products was lower than that leached from the untreated drill cuttings. ANOVA to determine the statistical significance of the difference in leaching from the treated and untreated drill cuttings yielded p -values of 3.8×10^{-6} and 1.7×10^{-4} for chloride and hydrocarbons, respectively. Thus, the differences are highly significant, and strongly confirm that S/S has indeed resulted in contaminant immobilization.

Although the results show that chloride immobilization was statistically significant, the degree of immobilization achieved by either binder system was unsatisfactory from a practical perspective. In all treatment runs, more than the 30% of the chloride leachable from the untreated samples remained available for leaching, even after 56 days of curing. It must be noted, however, that chloride leaching from the treated products after 56 days was below the UK landfill acceptance criteria for non-hazardous waste, although it was above the criteria for acceptance to landfill as inert waste [36].

Whereas Fig. 2b and the leaching coefficients calculated in Table 5 show that hydrocarbon leaching from the CEM I only s/s

Table 5
Leaching coefficients calculated from BS EN 12457-2 results.

Runs	pH	Leaching coefficient K_d (mL/g)	
		Hydrocarbons	Chlorides
Waste:binder = 1:4; CEM I:HCFA = 1:0; curing time = 7 days	12.8	100	22
Waste:binder = 1:4; CEM I:HCFA = 1:1; curing time = 7 days	12.7	1470	29
Waste:binder = 3:2; CEM I:HCFA = 1:0; curing time = 7 days	12.7	190	19
Waste:binder = 3:2; CEM I:HCFA = 1:1; curing time = 7 days	12.6	1910	17
Waste:binder = 0:1; CEM I:HCFA = 1:0; curing time = 7 days	12.9	nd	90
Waste:binder = 1:1; CEM I:HCFA = 1:1; curing time = 7 days	12.8	nd	24
Waste:binder = 1:4; CEM I:HCFA = 1:0; curing time = 56 days	12.9	330	44
Waste:binder = 1:4; CEM I:HCFA = 1:1; curing time = 56 days	12.7	∞	51
Waste:binder = 3:2; CEM I:HCFA = 1:0; curing time = 56 days	12.8	340	32
Waste:binder = 3:2; CEM I:HCFA = 1:1; curing time = 56 days	12.6	4280	31
Waste:binder = 0:1; CEM I:HCFA = 1:0; curing time = 56 days	12.9	nd	190
Waste:binder = 1:1; CEM I:HCFA = 1:1; curing time = 56 days	12.8	nd	40
Untreated drill cuttings	8.5	99	4
Untreated drill cuttings (with pH adjusted using NaOH)	12.4	21	4
HCFA sorption tests ^a	12.3	28,900	–

nd: not determine because control samples does not contain hydrocarbons.

^a Calculated from data in Ref. [33].

product with waste:binder ratio = 1:4 after 7 days curing was only slightly less than that from the untreated sample, the s/s product with less CEM I (waste:binder ratio of 3:2) showed better hydrocarbon immobilization. Increased mobility of hydrocarbons with higher Portland cement content has been reported previously in Ref. [7]. This observation may be caused by the higher porewater pH in products with higher cement content. A more alkaline porewater could decrease the surface area of clay in the drill cuttings by dissolving silica [37], thereby reducing its sorptivity for hydrocarbons. This mechanism is consistent with the observed improvement in immobilization after 56 days, as the dissolved silica would gradually react with portlandite to produce more C–S–H. Addition of HCFA to the binder system also reduces hydrocarbon leaching (Fig. 2a), resulting in leaching coefficients that are more than an order of magnitude greater than for the CEM I only products (Table 5). In products containing HCFA samples, the carbon content provides an increased surface area for sorption, and less silica will dissolve at the lower porewater pH.

Because of the higher leachate pH after 56 days, it was expected that the 56 days leaching test would have lower leaching coefficients (increased leaching) relative to the 7 days test. This was however not observed, suggesting that, although increased porewater pH may destabilize the drill cuttings, other factors such as formation of binder hydration products and, particularly, the carbon content of HCFA, which could serve as sorbent for hydrocarbons had a more significant effect on the leaching of hydrocarbons.

4. Conclusions

In this work, the leaching of metals, chloride and hydrocarbons from cement-based s/s petroleum drill cuttings was studied using a factorial design experiment. The following conclusions can be drawn from the results obtained:

- Metal leaching from the s/s products in a distilled water batch extraction was not significantly affected by HCFA addition, but was significantly affected by pH and waste-to-binder ratio, apart from Ba and Sr. ANC results show that drill cuttings addition is not detrimental to matrix ANC, indicating that that the s/s products could potentially withstand exposure to acid attack without disintegrating or reaching a pH value below 9; situations that could lead to easy release of contaminants or increased metal solubility.
- Factorial analyses show that HCFA addition, waste-to-binder ratio, and the curing time significantly affected chloride and hydrocarbon leaching. The addition of HCFA significantly reduced

the leaching of hydrocarbons. The CEM I only products show less chloride leachability relative to the CEM I:HCFA products. Overall, the immobilization of chlorides remained poor in all products.

- Increased cement addition seems to increase the amount of hydrocarbon leached at early curing, possibly due to reactions of the clay content of the drill cuttings at high pH, which affects its sorptivity. This effect was however mitigated by HCFA addition and binder hydration with time, both of which provided increase surface area for sorption. The addition of HCFA was the most effective factor in hydrocarbon leaching reduction as evidenced by leaching coefficients more than 10 times higher than those determined for the other s/s products.

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