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Assessment of alternative management techniques of tank bottom petroleum sludge in Oman

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Abstract

This paper investigated several options for environmentally acceptable management techniques of tank bottom oily sludge. In particular, we tested the applicability of managing the sludge by three options: (1) as a fuel supplement; (2) in solidification; (3) as a road material. Environmental testing included determination of heavy metals concentration; toxic organics concentration and radiological properties. The assessment of tank bottom sludge as a fuel supplement included various properties such as proximate analysis, ultimate analysis and energy content. Solidified sludge mixtures and road application sludge mixtures were subjected to leaching using the toxicity characteristic leaching procedure (TCLP). Tank bottom sludge was characterized as having higher concentrations of lead, zinc, and mercury, but lower concentrations of nickel, copper and chromium in comparison with values reported in the literature. Natural occurring radioactive minerals (NORM) activity values obtained on different sludge samples were very low or negligible compared to a NORM standard value of 100 Bq/g. The fuel assessment results indicate that the heating values, the carbon content and the ash content of the sludge samples are comparable with bituminous coal, sewage sludge, meat and bone meal and petroleum coke/coal mixture, but lower than those in car tyres and petroleum coke. The nitrogen content is lower than those fuels mentioned above, while the sulfur content seems comparable with bituminous coal, petroleum coke and a petroleum coke/coal mixture. The apparent lack of leachability of metals from solidification and road material sludge applications suggests that toxic metals and organics introduced to these applications are not readily attacked by weak acid solutions and would not be expected to migrate or dissolved into the water. Thus, in-terms of trace metals and organics, the suggested sludge applications would not be considered hazardous as defined by the TCLP leaching procedure.

Keywords: Oily sludge; Fuel supplement; Solidification; Heavy metals; TCLP

1. Introduction

Each year Petroleum Development Oman (PDO) generates approximately 18,000 tonnes of oily tank bottom sludge, 53,000 tonnes of petroleum-contaminated soil, and 1000 tonnes of mud cuttings. Disposal of tank sludge is a significant cost item of tank maintenance for producers, refiners and transporters of petroleum materials. The current waste management practice of PDO's oily sludge undergoes two stages: in the first stage oily sludge is held in a receiver pit to enable the draining of free oil and water; then in the second stage, the remaining sludge is mixed with sand in land-farming strips where biodegradation is stimulated with tilling and watering. Biological treatment by land-farming or composting is well-proven in the treatment of municipal sewage sludge [1], and has recently been adopted for treatment of chemical and industrial waste sludges. Although the cost of land farming is low, it has certain limitations [2] such as the large space requirements; the need for proper management and control; the failure in reducing the levels of inorganic contaminants; the limited depth of treatment. PDO is indeed realizing that their land-farming practice is not an effective treatment in reducing the concentration levels of petroleum contaminants. Experimental land strips in Marmul and Fahud have failed to consistently reduce the oil content below 2–3%. As a result, PDO was interested in evaluating other techniques for managing their oily sludge such as a fuel supplement, in solidification, and reuse in engineering construction applications such as roads. Other possible oily sludge management techniques include recycling (recycled through crude oil reclaimers); road spreading;

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on-site burial; off-site commercial facilities; incineration; high temperature reprocessing and chemical treatment with solvents [3–5].

Various oil field wastes may be applied to roads (if permitted by regulations) as dust suppressants, as surface deicers, to provide a better surface, or simply for disposal. API [6] recommends that tank bottoms, crude-contaminated soil, solid filter media, and other materials destined for road spreading be tested for flash point, metals content, and density; that these parameters should be consistent with approved road soils or mixes. Deuel [7] recommended "threshold guidance values" for waste-soil mixtures for land disposal, including road spreading: electro conductivity <4 mS/cm; sodium adsorption ration <12; exchangeable sodium percentage for salinity <15%; oil and grease <1%. From an environmental perspective, there are three important factors in the road application of oily wastes. These include consideration of hazardous constituents in the oily wastes; proper application procedure; protection of the environment from run-off from oiled roadways [8]. Tuncan and Koyuncu [9] recommended that the petroleum sludge which is used in road construction should be tested for flash point, permeability, density, California Bearing Ration (CBR) capacity and leachate. Organic matter content, pH, electrical conductivity and oil content should be also determined.

Solidification and stabilization (S/S) techniques are used to prevent or minimize the release of hazardous compounds from the finished asphalt road base into the environment by producing a solid mixture, improving handling characteristics, decreasing surface area for contaminant transport, reducing mobility of the contaminant transport and bonding the contaminate into a non-toxic form [9]. They can be defined as mixing the sludge with some solid additive materials like fly ash, cement, lime, cement kiln dust, sulfur, clay or combinations of them [2]. Joshi et al. [10] recommended the use of fly ash–cement mixtures for solidification of oil and gas sludges, because of their cohesive and adhesive characteristics. Morgan et al. [11] recommended the use of cement kiln dust to solidify tank bottom sludge.

Another option for sludge disposal is to use it as a fuel supplement. Problems associated with the incineration process for generation of fuel are [12]: large volume of effluent gases that needs to be properly treated; the initial organic materials will not be possibly recovered; ashes resulting from the incineration process could contain heavy metals should be disposed safely. Poor energy efficiency and landfill facilities are still needed for the final disposal of ashes.

The main objective of this paper is to examine the environmental aspects of considering alternative techniques for managing tank bottom sludge in PDO. In particular, we will characterize the sludge material in-terms of its content of total heavy metals and toxic petroleum hydrocarbons. Then, the sludge material is tested as a fuel supplement by studying the proximate analysis, ultimate analysis and energy content of the considered sludge. Finally, the leachability characteristics of raw sludge, solidified sludge, and sludge reused in road construction materials are evaluated.

2. Experimental procedure

2.1. Samples collection and preparation

Samples have been collected from the oily sludge disposal site constructed by PDO near the major oil tanks in Mina Al-Fahal, Muscat, which receives crude oil from different parts of Oman. Total often samples have been collected from different depths and different spatial points within the disposal site.

2.2. Separation of phases

The gravimetric method EPA 9071B [13] was used for separating water, oil and solids in sludge samples, thereby, estimating the moisture, hydrocarbons and total heavy metals in each sample. It should be noted that the EPA 9071B is the method recommended for quantifying the concentrations of oil and grease in soil, sediments, oily sludge, and other solid materials amenable to chemical drying and solvent extraction. A separate aliquot of as-received sludge sample, 5 g, was used for calculating the moisture content of the sludge. The aliquot used for this determination was not used for further analyses. Moisture content was determined gravimetrically.

For the petroleum hydrocarbon analysis, another portion of the sludge (10 g) was chemically dried by blending it with 10 g of anhydrous sodium sulfate. The homogenized sample was transferred to an extraction thimble and covered with glass wool. The extraction thimble was allowed to freely drain for the duration of the extraction period. The Soxhlet Apparatus was setup to contain the extraction thimble and sample and attached to a 125-ml boiling flask containing 90 ml of solvent (hexane). The heating control on the heating mantle was adjusted so that a cycling rate of 20 cycles/h was obtained. Then, a rotary evaporator was used to remove the solvent from the extract.

A third portion of the same sludge sample was extracted with the same procedure using the Soxhlet apparatus, but this time without adding the anhydrous sodium sulfate. In this case, the remaining solid phase in the extraction thimble was used for the calculation of total heavy metals in the sludge.

2.3. Total heavy metals

Solids separated from sludge samples were acid digested for heavy metals analysis by atomic absorption according to Method 3050B. Metals analyzed by this method were lead, chromium, nickel, copper and zinc. However, concentration of total mercury in solids was achieved by using Nippon SP-3D Mercury Analyzer. Samples analyzed by this system do not require any pre-treatment (such as digestion, filtration, etc.). The instrument applies the cold vapor atomic absorption method to determine the quantity of total mercury.

2.4. Hydrocarbon analysis

The oil extract obtained from the Soxhlet apparatus as describe in Section 2.2 was first used to gravimetrically determine the total petroleum hydrocarbon (TPH in mg/kg). Then, using Gas Chromatography with mass spectrometers (GS/MS Varian Model), chromatogram plots of the various hydrocarbons in the sludge samples were produced and compared. Concentrations of specific volatile organic compounds (VOC), non-halogenated VOC, and semi-volatile organic compounds (SVOC) listed by EPA were measured using the same GC/MS.

2.5. Leachibility test

The toxicity characteristic leaching procedure (TCLP) as developed by the U.S. Environmental Protection Agency [14] was designed to simulate the leaching of metals and organic compounds from the sludge samples and their solidified and road applications considered in the study. An appropriate extraction fluid for each application was determined based on the pH of sample as described in TCLP, such that, if the pH of the sample is less than 5, extraction fluid #1 (5.7 ml glacial acetic acid and 64.3 ml 1N NaOH are diluted in 1 l reagent water) was used, otherwise, extraction fluid #2 (5.7 ml glacial acetic acid is diluted with 1 l reagent water) was used. Control of pH was carried out during the tests. Sludge samples and their applications were slightly alkaline (pH < 5), so U.S. EPA extraction fluid #1 was used. A 10 g dry sample and the appropriate extraction fluid were put with a 20:1 ratio of liquid to dry sample into polypropylene extraction bottles for metals and borosilicate glass bottles with Teflon-lined caps for hydrocarbons. The extraction bottles were sealed and then rotated on a specially designed rotator for 18 h. This time is theoretically long enough to allow steady-state dissolution and mobilization to occur for small diameter samples. All samples in this study were ground to <0.85 mm, which is sufficiently small to assume that steady-state conditions were met. At the end of 18 h extraction period, liquid in each bottle was separated from solid phase by vacuum filtration through 0.8 μm glass fiber filter paper. The solid phase was discarded and the pH of the separated TCLP extracts was then measured and all extracts were acidified to a pH less than 2 for long-term preservation. At the end, metal concentrations in the extract were analyzed using inductively coupled plasma optical emission spectrometry (Perkin–Elmer Model 3300 DV ICP-OES). Concentrations of Cd, Ni, Pb, Cr, Cu and Zn were measured by ICP using the method described in standard methods [15]. The concentration levels were compared with the TCLP limits [16].

2.6. Radiological measurements

gamma-ray spectrum analyses were conducted in the Department of Clinical and Biomedical Physics at Sultan Qaboos University.

3. Tank bottom sludge characteristics

Chemical and physical parameters of the sludge can provide useful guidelines for selecting alternative management methods. They can also serve as an assessment tool for any process or management performance. This section presents detailed discussion on oil, water, and solids content; heavy metals and toxic organics concentration; radiological levels of the considered sludge samples.

Table 1
General composition of 10 tank bottom oily sludge samples collected from Petroleum Development Oman

Sample	% Moisture	% Oil	% Solids	Sulfur (wt.%)	Micro-carbon residue (wt.%)
S_1	26	54	20	0.75	17.3
S_2	33	59	8	0.81	13.3
S_3	26	57	17	0.83	15.4
S_4	36	51	13	0.57	15.6
S_5	32	54	14	0.71	15.5
S_6	37	58	5	NA[a]	NA[a]
S_7	20	64	16	1.17	16.7
S_8	22	64	14	0.96	14.7
S_9	21	64	15	0.81	16.4
S_{10}	24	62	14	0.51	15.5

[a] Data not available.

3.1. Oil, water, and solids composition

The results of the general composition of 10 sludge samples are shown in Table 1. Sulfur and micro-carbon residue were also determined for all 10 sludge samples. All the experiments were performed in duplicates to ensure their reproducibility. The results clearly indicate that tank bottom sludge has a high percentage of hydrocarbon (approximately 55–65%). The remaining is 25–35% moisture, and just 5–20% solids. These percentages are very typical of oily sludge samples [4]. Ideally, the oily sludge will have a high concentration (>50%) of oil and a relatively low solids concentration (<30%) [4].

The other important observation that could be obtained from this analysis is that there are relatively small variations in the contents of the collected samples. The oil content is about 55% for the first six samples and around 65% in the last four samples. Moisture content for Samples S_1 and S_3 are the same; Samples S_2, S_4, S_5 and S_6 have moisture content around 35%; the last four samples have a similar moisture content ranging from 20 to 24%. The same observation could be applied to the solids content.

3.2. Levels of heavy metals

The concentration of total heavy metals in solids isolated from sludge samples are shown in Table 2. The table presents metals that are of most importance with regard to oily sludge [17]. It should be noted that most of these metals have a cumulative effect, and are of particular hazard [18,19]. The table shows that all sludge samples contain relatively high concentrations of zinc (Zn) and lead (Pb), followed by relatively lower concentrations of copper (Cu), nickel (Ni), chromium (Cr), and mercury (Hg). Except for Sample S_3, which showed very high levels of zinc compared to others, the variations of measured metal concentrations from one sample to another is relatively small. The literature reported metals concentration for oily sludge obtained from a refinery [6] are: 7–80 mg/kg of zinc, 0.001–0.12 mg/kg of lead, 32–120 mg/kg of copper, 17–25 mg/kg of nickel, and

Table 2
Concentrations of zinc, lead, copper, nickel, chromium, and mercury in collected sludge samples

Sample	Zn (mg/kg)	Pb (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Cr (mg/kg)	Hg (mg/kg)
S_1	366	206	33.4	18.8	17.7	2.7
S_2	300	67.4	12.4	6	3.9	3.3
S_3	759	70	13.9	5.5	12.8	2.6
S_4	334	42.3	12.9	ND	9.6	6.2
S_5	289	97.3	10.9	0.6	11.4	4.9
S_6	74	33.5	2.4	0.4	4.7	2.2
S_7	233	114.5	12.2	6.6	14.8	3.7
S_8	122	44.6	7.3	ND	10.2	3.6
S_9	186	147.9	26.2	14.2	16.6	2.6
S_{10}	110	86.5	11.98	6.8	17.4	2.1

27–80 mg/kg of chromium. When comparing these ranges with sludge samples under consideration, it can be concluded that they have higher concentrations of lead and zinc and lower concentrations of the other metals.

3.3. *Toxic hydrocarbons*

The organic content is of great importance when considering alternative management techniques of oily sludge. However, unlike inorganic compounds, organics are usually less soluble in water [20]. This indicates that organic compounds may persist in the sludge unless they are destroyed during treatment. As indicated in Table 1 by % oil, the total petroleum hydrocarbon (TPH) present in the analyzed 10 samples ranges from 510,000 to 640,000 mg/kg. This much of oil in the considered samples is considerably large. The concentrations of specific volatile organic compounds (VOC), non-halogenated VOC, and semi-volatile organic compounds (SVOC) listed by EPA and present in the extracts of oil sludge sample S_2 soils were also measured using GC/MS as reported as μg/l in Table 3. Most of the considered organic compounds were not detected. The only four detected compounds of the list were: naphthalene, 2-methylnaphthalene, phenanthrene, and anthracene. However, the concentrations of the specific compounds are very low (<1.8 μg/l).

3.4. *Radiological analysis*

The results of gamma-ray spectrum analyses are presented in Table 4. The activity values obtained for indicated sludge samples were very low or negligible compared to a natural occurring radioactivity mineral (NORM) value of 100 Bq/g.

4. Sludge assessment as a fuel supplement

In order to evaluate the suitability of tank bottom sludge as a fuel, it is essential to know its chemical composition. The most important properties that must be investigated when sludge is to

Table 3
Concentrations of specific volatile organic compounds (VOC), non-halogenated VOC, and semi-volatile organic compounds (SVOC) present in the extract of the sludge sample S_2 in μg/l

Compounds	S_2	Compounds	S_2	Compounds	S2
Bis(2-chloroethyl) ether	0.000	2,4,5-Trichlorophenol	0.000	Indeno[1,2,3-*cd*]pyrene	0.000
2-Chlorophenol	0.000	2-Chloronaphthalene	0.000	Dibenz[*a*,*h*]anthracene	0.000
1,2-Dichlorobenzene	0.000	2-Nitroaniline	0.000	Benzo[*ghi*]perylene	0.000
1,3-Dichlorobenzene	0.000	Dimethyl phthalate	0.000	Hexachlorobenzene	0.000
1,4-Dichlorobenzene	0.000	2,6-Dinitrotolunene	0.000	Phenanthrene	1.117
2-Methylphenol	0.000	Acenaphthylene	0.000	Anthracene	1.104
4-Methylphenol	0.000	3-Nitroaniline	0.000	Carbazole	0.000
Hexachloroethane	0.000	Acenaphthene	0.000	Dibutyl phthalate	0.000
Nitrobenzene	0.000	Dibenzofuran	0.000	Fluoranthene	0.000
Isophorone	0.000	2,4-Dinitrotoluene	0.000	Pyrene	0.000
2-Nitrophenol	0.000	Diethyl phthalate	0.000	Benzyl butyl phthalate	0.000
2,4-Dimethylphenol	0.000	Fluorine	0.000	Benz[*a*]anthracene	0.000
Bis(2-chloroethomethane)	0.000	4-Chlorophenyl phenyl ether	0.000	Chrysene	0.000
2,4-Dichlorophenol	0.000	4-Nitroaniline	0.000	Bis(2-ethylhexyl) phthalate	0.000
1,2,4-Trichlorobenzene	0.000	Azobenzene	0.000	Di-*n*-octyl phthalate	0.000
Naphthalene	1.157	4-Bromophenyl phenyl ether	0.000	Benzo[*b*]fluoranthene	0.000
4-Chloroaniline	0.000	Chrysene	0.000	Benzo[*k*]fluoranthene	0.000
Hexachlorobutadiene	0.000	Bis(2-ethylhexyl) phthalate	0.000	Benzo[*a*]pyrene	0.000
4-Chloro-3-methylphenol	0.000	Di-*n*-octyl phthalate	0.000	Indeno[1,2,3-*cd*]pyrene	0.000
2-Methylnaphthalene	1.712	Benzo[*b*]fluoranthene	0.000	Dibenz[*a*,*h*]anthracene	0.000
Hexachlorocyclopentadiene	0.000	Benzo[*k*]fluoranthene	0.000	Benzo[*ghi*]perylene	0.000
2,4,6-Trichlorophenol	0.000	Benzo[*a*]pyrene	0.000		0.000

Table 4
Gamma-ray spectrum analysis on tank bottom sludge

	S_2	S_4	S_5	S_6	S_7	S_9
Ra-226 (Bq/g)	0.228 ± 0.013	0.254 ± 0.021	0.201 ± 0.012	0.264 ± 0.014	0.297 ± 0.030	0.173 ± 0.006
Pb-210 (Bq/g)	<0.35	0.521 ± 0.224	0.610 ± 0.222	0.560 ± 0.210	<0.70	0.231 ± 0.088
Ra-228 (Bq/g)	0.0547 ± 0.0031	0.0465 ± 0.0037	0.0457 ± 0.0027	0.0545 ± 0.0028	0.0572 ± 0.0061	0.0371 ± 0.0013
Th-228 (Bq/g)	<0.22	<0.32	<0.19	<0.18	0.437 ± 0.186	0.153 ± 0.069
K-40 (Bq/g)	0.0420 ± 0.0077	0.0509 ± 0.0102	0.0267 ± 0.0075	0.0441 ± 0.0082	0.0704 ± 0.0173	0.0182 ± 0.0036
Calc. Max. activity Conc.[a] (Bq/g)	1.48	3.18	313	3.37	4.96	2.88
44A CPS to K40[b] (Bq/g)	0.0	0.1	0.0	0.0	0.1	0.0

The '<' sign indicates that the activity is below the specified minimum detectable level under the measurement conditions. *Note*: The calculated maximum activity is now determined according to BS-2000.

[a] Calculated maximum activity concentration = 6 × Ra-226 + 3 × Pb-210 + 2 × Ac-228 + 7 × Th-228.

[b] Expected count rate (CPS) to PDO mini monitor with 44A probe.

Table 5
Chemical composition of selected sludge samples from Petroleum Development Oman (PDO)

Sample ID	Gross calorific value (MJ/kg)	C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)	O (wt.%)	H_2O (wt.%)	Ash (wt.%)	Solids (wt.%)
S_1	21.4	56.4	9.58	0.10	1.98	31.94	26	11.49	20
S_2	22.4	59.9	10.03	0.14	2.13	27.8	33	12.31	8
S_3	19.9	59.2	10.05	0.15	2.21	28.39	26	9.94	17
S_5	19.2	54.3	9.42	0.13	2.26	33.89	32	11.59	14
S_8	23.4	60.6	9.74	0.17	2.15	27.34	22	12.94	14
S_{10}	20.2	57.3	9.81	0.15	2.05	30.69	24	11.72	14

Table 6
Mole ratios and molecular weight of six selected sludge samples

	S_1	S_2	S_3	S_5	S_8	S_{10}
Carbon	657.9	499.1	460.4	487.2	415.8	445.6
Hydrogen	1870.4	1511.8	1291.3	1589.1	1007.4	1231.7
Oxygen	452.5	358.5	290.0	445.1	181.6	274.6
Nitrogen	1.0	1.0	1.0	1.0	1.0	1.0
Sulfur	8.65	6.65	6.44	7.60	5.53	5.97
Molecular weight	17323	13485	11693	14836	9108	11195

be used as a fuel source are: (a) proximate analysis; (b) ultimate analysis; (c) energy content.

The results of proximate analysis, ultimate analysis, and energy content of the sludge samples are presented in Table 5. The lower heating value (LHV) for the sludge is not available, but according to the literature the difference between higher heating value (HHV) and LHV is between 4 and 6%.

Table 5 shows that the majority of sludge mass is composed of carbon. Furthermore, significant levels of sulfur and ash are present. This indicates that the use of sludge as a fuel source will be accompanied by some environmental concerns in the form of air pollution due to gaseous and particulate emissions. It should be noted that the percent of oxygen reported in Table 5 is obtained by the difference between 100 and the sum of all other constituents.

Approximate elemental analysis and the molecular weight for the organic portion of the six sludge samples are presented in Table 6. The molecular weights are significantly high. Additionally, the number proportion of hydrogen to carbon is reasonable, and in the vicinity of 3.0. It should be noted that fuels that have

Table 7
Properties of fuels of interest to the cement industry

	HHV (MJ/kg)	LHV (MJ/kg)	C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)	O (wt.%)	H_2O (wt.%)	Ash (wt.%)
Bituminous coal	26.2	25.3	66.6	3.99	1.07	1.22	8.85	2.35	18.4
Petroleum coke	ND[a]	33.7	89.5	3.08	1.71	4.00	1.11	1.50	0.50
Sewage sludge	ND[a]	15.8	42.9	9.00	1.84	0.12	27.2	5.20	17.9
Car tire rubber	37.3	35.6	87.0	7.82	0.33	0.80	1.81	0.73	2.20
Coal–petroleum coke mix	29.7	28.9	75.1	4.20	1.70	3.00	4.90	1.3	11.1
Meat and bone meal	ND[a]	16.2	42.1	5.83	7.52	0.38	15.3	8.09	28.3

[a] Not determined.

Table 8
Trace metal concentrations (mg/l) of the TCLP extracts from various oily sludge applications along with the MCL and TCLP established limits

Application	Cd	Ni	Pb	Cr	Cu	Zn
Sludge:QF (1:4)	<0.0005	0.11–0.12	0.025–0.026	0.02	0.0036	0.80–0.92
Sludge:cement (1:4)	<0.0005	<0.001	0.020–0.025	0.29–0.35	<0.001	0.001–0.004
Sludge:CBPD						
1:3	<0.0005	<0.001	0.027–0.028	0.048–0.086	<0.001	0.001–0.002
1:2	<0.0005	<0.001	0.016–0.020	0.008–0.009	<0.001	0.0005–0.002
Sludge:CBPD:QF						
1:1.5:1.5	<0.0005	<0.001	0.024–0.028	0.03–0.037	<0.001	0.003–0.006
1:1.0:1.5	<0.0005	<0.001	0.023	0.014–0.016	<0.001	0.004–0.006
Sludge:cement:CBPD (1:0.5:1.5)	<0.0005	<0.001	0.02–0.03	0.01–0.04	<0.001	0.001–0.002
Sludge:cement:QF (1:0.5:1.5)	<0.0005	0.05–0.08	0.02	0.06–0.08	<0.001	0.04–0.07
TCLP	1		5	5		
MCLs	0.01		0.015	0.05	1	5

a higher proportion of carbon will generally: (a) be denser than fuels which have a low proportion of carbon; (b) have lower enthalpy change and lower exhaust velocity than fuels which have a low proportion of carbon; (c) have a higher combustion temperature than fuels which have a low proportion of carbon.

A comparison (Table 7) between the values presented in Table 6 with a number of fuels used by the cement industry reveals that the heating values, the carbon content and the ash content of the sludge samples are comparable with bituminous coal, sewage sludge, meat and bone meal and petroleum coke/coal mixture, but lower than those in car tires and petroleum coke. The nitrogen content in the sludge is lower than those of all of the fuels listed in Table 7. The sulfur content is comparable with bituminous coal, the petroleum coke/coal mixture and petroleum coke. The water content seems to be high which might need some pre-treatment.

Based on the chemical analysis of the sludge samples investigated, we believe that it is feasible to use the sludge as an alternative fuel in the cement industry given that the sludge is diluted to a level where it is easily pumped, and the emissions of sulfur, heavy metals and particulate matter are monitored to ensure compliance with regulatory standards [21].

5. Solidification of oily sludge

In this section, we present the analysis obtained from considering solidification of oily sludge as a possible management option. Tank bottom sludge mixtures were solidified using various combinations of selected additives such ordinary Portland cement (OPC), cement by-pass dust (CBPD) and quarry fines (QF). The latter two additives are considered by-product materials of cement manufacturing and aggregate crushing processes, respectively. Mixtures were subjected to leachability-based tests namely the toxicity characteristic leaching procedure (TCLP). Ordinary Portland cement was brought from Oman Cement Company (OCC). It primarily consists of silicon, aluminum, iron and calcium oxides. CBPD is a fine powder that is off-white to light brown in color. Quarry fines exist in a powder form that is off-white to light brown in color. The material is produced during crushing and screening of aggregates. It is considered a waste material. It was provided from the Oriental Company crushers.

The toxicity characteristic leaching procedure (TCLP) is selected for this study to be the only extract procedure. The

Table 9
TCLP extract analysis for raw sludge and cold mix (cold aggregates + 6.5% sludge)

Mix type	Raw sludge	Cold mix (cold aggregates + 6.5% sludge)	U.S. EPA threshold limits
Metals (mg/l)			
Arsenic	<0.0118	<0.0118	5
Selenium	<0.0217	<0.0217	1
Mercury	2	<1	0.2
Barium	0.72	0.065	100
Cadmium	0.005	0.0006	1
Chromium	0.0107	<0.0107	5
Lead	0.0108	<0.0107	5
Silver	0.0038	<0.0038	5
Volatile organic compound (VOC) I (μg/l)			
Benzene	<0.01	<0.01	5
Carbon tetrachloride	<0.01	<0.01	5
Chlorobenzene	<0.01	<0.01	6
Chloroform	<0.01	<0.01	7.5
1,4-Dichlorobenzene	<0.01	<0.01	0.5
1,2-Dichloroethane	<0.01	<0.01	0.7
1,1-Dichloroethylene	<0.01	<0.01	5
Trichloroethylene	<0.01	<0.01	0.5
Vinyl chloride	<0.01	<0.01	0.2
Non-halogenated (VOC)			
Pyridine	<0.02	<0.02	5
Methyl ethyl ketone	<0.02	<0.02	–
Hexachlorobenzene	<0.02	<0.02	0.13
Hexachloroethane	<0.02	<0.02	3
Nitrobenzene	<0.02	<0.02	2
2,4-Dinitrotoluene	<0.02	<0.02	0.13
Phenols (mg/l)			
o-Cresols	<0.02	<0.02	200
m-Cresols	<0.02	<0.02	200
p-Cresols	<0.02	<0.02	200
Pentachlorophenol	<0.02	<0.02	<100
2,4,5-Trichlorophenol	<0.02	<0.02	400
2,4,6-Trichlorophenol	<0.02	<0.02	<0.02

Table 10
Gamma-ray spectrum analysis for road mixtures

	Petroleum contaminated soil with 12% sludge	Cold mix with 6.5% sludge	Oil sludge
Ra-226 (Bq/g)	0.0700 ± 0.0061	0.0906 ± 0.0072	0.203 ± 0.011
Pb-210 (Bq/g)	<0.20	<0.19	<0.30
Ra-228 (Bq/g)	0.0185 ± 0.0017	0.00942 ± 0.00146	0.0636 ± 0.0023
Th-228 (Bq/g)	<0.11	<0.13	<0.15
K-40 (Bq/g)	0.154 ± 0.007	0.0492 ± 0.0062	0.0581 ± 0.0073
Calc. Max. activity Conc. (Bq/g)	0.457	0.562	1.35
44A CPS to K40 (Bq/g)	0.2	0.0	0.1

concentrations of the trace metals resulting from these extractions are given in Table 8 along with the TCLP maximum limits and the primary and secondary maximum concentration limits (MCLs) in drinking water for the sake of comparison. All reported concentrations are in mg/l. The results of the TCLP analyses reveal that no extracts exceeded the established TCLP maximum limits set by U.S. EPA. In fact, for several extracts, the metal concentrations are much below the MCLs.

The apparent lack of leachability of metals from these sludge applications suggests that metals introduced to these applications are not readily attacked by weak acid solutions and would not be expected to migrate or dissolved into the water. Thus, in-terms of trace metals, the suggested sludge applications would not be considered hazardous as defined by the TCLP leaching procedure.

6. Sludge assessment as a road material

This section presents the results obtained on the use of the sludge in mixes with aggregates for paving layer applications. The application is similar to an asphalt concrete mixture, with the exception that the sludge is treated as the binding material instead of asphalt cement. After establishing an appropriate blend of aggregates, three mixes were prepared. The first mix was prepared by heating both the aggregate and the sludge for a period of 2 h at 150 °C. The second mix was prepared by heating only the sludge and using cold aggregate. The third mix was prepared by mixing both the aggregate and sludge at room temperature.

The TCLP results are reported in Table 9. The data indicate that no extracts exceeded the established TCLP maximum limits set by U.S. EPA, except mercury content in raw sludge.

Raw sludge, conventional road bitumen and selected asphalt concrete mixtures were subjected to radiological analysis. The results are presented in Table 10. The activity values obtained for all these materials were very low or negligible compared to a natural occurring radioactive mineral (NORM) value of 100 Bq/g.

7. Conclusions

The data indicate that the considered sludge has substantial hydrocarbon content since its value of TPH is greater than 500,000 mg/kg. Tank bottom sludge was characterized as having higher concentrations of lead and zinc but lower concentrations of nickel, copper and chromium in comparison with values reported in the literature. Also, mercury concentration appears to be high. The activity values obtained for all these materials were very low or negligible compared to a natural occurring radioactivity mineral (NORM) value of 100 Bq/g.

To assess the use of tank bottom sludge as a fuel supplement, various properties such as proximate analysis, ultimate analysis and energy content were determined. The results indicate that the heating values, the carbon content and the ash content of the sludge samples are comparable with bituminous coal, sewage sludge, meat and bone meal and petroleum coke/coal mixture, but lower than those in car tyres and petroleum coke. The nitrogen content is lower than those fuels mentioned above, while the sulfur content seems comparable with bituminous coal, petroleum coke and a petroleum coke/coal mixture. The water content seems to be high which might need some pre-treatment. Based on the chemical analysis of the sludge samples investigated, it is feasible to use the sludge as an alternative fuel in the cement industry given that the sludge is diluted to a level where it is easily pumped and the emissions of sulfur, heavy metals and particulate matter are monitored to ensure compliance with regulatory standards.

The results of the TCLP analyses reveal that no extracts of the solidified oily sludge or even sludge applied in road exceeded the established TCLP maximum limits set by USEPA. In fact, for several extracts, the metal concentrations are much below maximum concentration limits (MCLs) and toxic organic compounds are undetected. The activity values obtained for all mixtures of sludge in road applications (with one or two additives) were very low or negligible compared to a natural occurring radioactivity mineral (NORM) limit value of 100 Bq/g.

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