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ORIGINAL RESEARCH PAPER

Management of toxic and hazardous contents of oil sludge in Siri Island

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ABSTRACT: Sirri Island is one of the most important islands in Iran where contains massive amounts of crude oil reservoirs and is a crude oil exporting and storage spot. Petroleum sludge wastes produced by the refineries are deposited in outdoor 2-ha open pits. 30 sludge samples from different depot locations were conducted in 3-time intervals and mixed with each other to form one homogenized sample. The sample was treated by solvent extraction method using methyl ethyl ketone as an efficient polar solvent in order to recover the valuable hydrocarbon and oil. About 99.8% of the oil was recovered and determined to reach almost the same quality as the exportable crude oil of Sirri Island. The sediments were also tested for size distribution range and titled as fine-grained soil. Toxicity characteristics leaching procedure test was conducted on the residuals to determine whether the waste is categorized as toxic and hazardous. The industrial waste evaluation model used in the current work suggested different leachate concentrations (10%, 30%, 50%, 70% and 90% of total leachate) based on toxicity characteristics leaching procedure for different probable leaching scenarios. The surface and subsurface regional conditions such as depth to underground water table, climate condition, subsurface pH, soil texture and material were defined to the model as well. Then, the model simulated 10000 possible runs considering the leaching procedure, contaminant concentrations, maximum contaminant limits and surface and sub-surface conditions. The final outcomes regarding heavy metals results showed that nickel, chromium and vanadium were protective under composite liner while cobalt and lead were not safe under such liner and need proper treatment before landfilling. As the final step, the size and details of landfill were designed. The landfill was selected as a square with side and depth of 55m and 3m respectively. The composite liner consisted of 1.5mm high density polyethylene layer with 50cm compacted clay liner of 10^{-7} cm/s hydraulic conductivity underneath.

KEYWORDS: *Heavy metals; Industrial waste management evaluation model (IMEM); Linear; Maximum contaminant level (MCL); Petroleum sludge; Toxic and hazardous management; Toxicity characteristics leaching procedure (TCLP)*

INTRODUCTION

A vast amount of petroleum sludge is produced during exploration, production, transportation, and refining of crude oil in petroleum industry. The oily sludge contains quantitative amount of petroleum hydrocarbons (PHCs), thus being categorized as hazardous waste (Hu *et al.*, 2013). Industrial and hazardous waste management is one of the most significant problems because of the high risk of leaching into environment (Hoveidi *et al.*, 2013; Shams Fallah *et al.*, 2012; Karbassi *et al.*, 2015). The treatment of oily sludge has been a worldwide environmental concern and could result in an environmental disaster due to improper treatment and refining (Da Rocha *et al.*, 2010). Petroleum sludge consists of valuable hydrocarbons and some other compositions such as heavy metals, sand and fine-grained soils, water (Liu *et al.*, 2009). Properties of petroleum sludge can vary

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widely. For instance physical properties of petroleum sludge of a specific spot as storage tank differs clearly in two different days with two different temperatures (Mater *et al.*, 2006, Mrayyan and Battikhi, 2005). Considering the complexity and unknown compositions of different sludge from different spots, there is not any distinctive formula to estimate the composition of the sludge. Thus, chemical, physical and Physico-chemical analyses must be conducted to assess the exact compositions and elements present in the waste (Xu *et al.*, 2009). An average of 30,000 tons of petroleum sludge is produced annually in United States. According to EPA reports, annually, China produces 3 million tons of petroleum sludge by all refining plants (Wang *et al.*, 2012). Reports indicate that 1 ton of petroleum sludge is produced out of 500 tons of crude oil (Van Oudenhoven *et al.*, 1995). It is reported that over 60 million tons of sludge are produced every year and it is estimated that more than 1 billion tons of sludge are accumulated worldwide (Hu Li and Zeng, 2013). Defects in petroleum sludge management in form of releasing the waste into the environment is the current most attended concern (Mazlova and Meshcheryakov, 1999). Recovery is the most desirable manner for petroleum sludge management since it lets the petroleum industry to recover some of the costs on the waste treatment and also lessens the negative impact on the environment (USEPA, 1991). Moreover, recovering decreases the mass of residual waste for disposal and minimizes the area for landfilling .The reduction in oil production and consumption of non-renewable resources are the next reasons for recovery. Oil sludge is generally a thermal valuable substance which can produce 3900 kcal per 1 kg (Hou *et al.*, 2013). The use of sludge as material in road construction has been discussed in past papers (Al-Futaisi *et al.*, 2007). Land treatment is one of the most suitable methods of petroleum sludge treatment after pre-treatment (*Pazoki et al.*, 2012; Pazoki *et al.*, 2014). In Iran, methods like pyrolysis, freeze/thaw, incineration and microwave irradiation are expensive and not efficient enough in oil-producing regions which generally have dry and hot climate conditions. For instance using freeze-thaw method in the extreme hot weather of southern parts of Iran will cost a vast amount of money and energy just to reach a freezing point and this method is absolutely not applicable in such region and climate condition (Da Silva *et al.*, 2012, Pinheiro and Holanda, 2009). Among all the methods used, solvent extraction is an experienced, suitable and not expensive way to separate constituents and is reported as a very successful method to separate PHCs from petroleum sludge (Taiwo and Otolorin, 2009). After separation, the valuable hydrocarbon phase is recycled and returned to the fuel cycle in order to compensate a portion of treatment costs. The residues then need further treatments. These residuals contain solid particles such as sand, gravel, etc., moisture and heavy metals (Raab and Feldmann, 2003). Although the concentration of heavy metals for recycling are not generally as high as making the recovery economically profitable, the hazardous and toxic nature of these compositions make the treatment essential in order to prevent leaching of wastes into the water and food chain of consumers (Shen *et al.*, 2005). It is discussed in the literature that high value of TPH and heavy metal are potential sources of contaminated sites (Adeniyi and Afolabi, 2002). In case of being in a land covered by vegetation, negative impact on biodegradation will cause by existence of heavy metals (Businelli *et al.*, 2009, Thavamani*, et al.*, 2012). At the opposite point of view heavy metals concentrations below limits can enhance metabolism of microorganisms due to increase in catalytic activity (Zukauskaite *et al.*, 2008). Sludge sediments form at the bottom of reservoirs and storage tanks which consist of heavy compositions like asphaltene and wax while the lighter hydrocarbons float on top. The sludge at the bottom of storage tank is a stable emulsion (Saeedi and Amini, 2007). Formation of sludge will reduces the effective volume of the storage tank and also accelerates erosion. The accumulated layer at the bottom of the tank can become more dense with time (Pereira *et al.*, 2014). If the evacuation of storage tanks doesn't happen regularly, the accumulated sludge will probably increase in height and overflow with the crude oil and damage the further processes (Pazoki *et al.*, 2010; Takdastan and Pazoki, 2011). Sludge management is expensive and one of the most challenging issue in environmental studies. To clean the sediments, some physical and chemical methods are generally used such as digging with mechanical equipment, steaming and using chemical solvents. All the named techniques are time-consuming, dangerous and expensive and also result in crude oil contamination by sludge (Hu, Li and Zeng, 2013).

In the present study, some of petroleum sludge physical properties and heavy metals concentrations have been conducted. Secondly, solvent extraction method has been used to recover hydrocarbon from sludge. The method is advantageous because of lower treatment process and available plant and facility near the disposal site in Sirri Island and efficiency of the method for particular type of sludge (petroleum sludge). For this purpose Methyl ethyl ketone (MEK) has been selected as the solvent for solvent extraction process. MEK is reported to be an efficient solvent since polar solvents are more useful and compatible with petroleum sludge which is generally a polar composition (Rincon *et al.*, 2005; Wang, *et al.*, 2014; Zubaidy and Abouelnasr, 2010). Then the concentration of heavy metals has been measured and it was revealed that some of the elements in residual are in a dangerous limit to leach and need further treatment. Landfilling as the compatible solution for residual disposal is suggested and the size of required landfill for waste is estimated. The industrial waste management evaluation model (IWEM) was used to predict the risk of subsurface water contamination. Finally, the standard liners based on the leachate concentration and subsurface environment and conditions were suggested. The sampling has been carried out in Sirri Island in Persian Gulf during November, 2015 at the disposal site on approximate geographical coordinate; 25°54'40.0"N as the longitude and 54°31'56.5"E as the latitude.

MATERIALS AND METHODS

Formation and location of accumulated sludge

Sirri is a non-residential island and is just used for crude oil production, storage and exportation. Thus, there is no landfill or disposal facility availabe within the whole Island and all of the wastes are deposited in outdoor open pits. The petroleum sludge is sedimentated when the oil impurities, rusts formed by surface-oxidation of pipe and storage tanks, heavy hydrocarbon such as long-chain paraffin (wax), asphaltene, mineral compositions and water are deposited altogether at the bottom of storage tank. The sludge composition is a stable emulsion and too viscous. Over time, the pressure of upper-layer oils and emulsified sediments has converted the bottom sludge into solid and semi-solid form. Hot steam and physical drilling is used to discharge the bottom tank sludge. After the discharge, the sediments are pile up as pits in a 2 ha area in the environment. The sludge depots have been accumulated since 20 years ago, therefore the moisture content, volatile and semi-volatile compositions and lighter hydrocarbons have been released and evaporated from the remained sediments. The petroleum sludge depot region in Sirri Island located in the Persian Gulf of Iran is shown in Fig. 1.

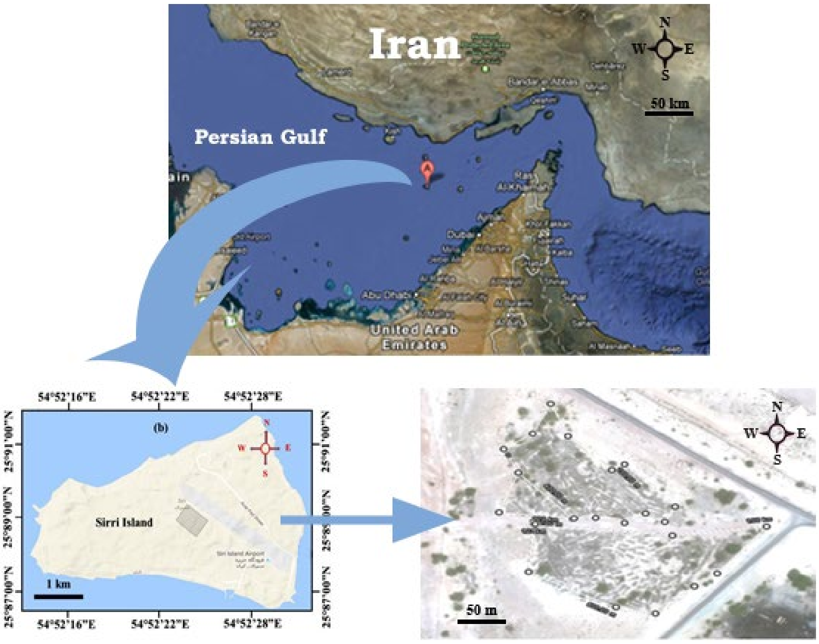

Fig. 1: The petroleum sludge depot region in Sirri Island located in the Persian Gulf of Iran

Climate conditions of Sirri Island

Average relative moisture content during the year is 70 percent with highest value of 84 percent during the summer. The precipitation and evaporation rates are absolutely low and high equal to 0.11 and 1.2 m per year, respectively. During the rainy seasons, heavy metals constituents are solved into runoff, washed through the sludge and percolated into the ground or flow on the ground surface. Therefore, the solution shall impair and contaminate resources such as groundwater or surface vegetation. Refereeing to two parameters of precipitation and evaporation rates, the present study could find an equal condition to Sirri Island which leads us to Pheonix city in USA (USEPA, 2015).

Sample preparation

The accumulated sludge has been deposited since 1995 in an open area under severe circumstances such as direct and intense sunlight. Therefore, the texture is almost dry and needs pretreatment before being fed into extractor. Due to Heterogeneity within the sludge depot, 30 samples have been collected from different depths and locations of deposition zones. Every 10 samples have been collected in 8 hours interval within a full day. 100 grams of each sample was taken and mixed with the other 29 samples. Then, the mixed matrix of samples was heated and agitated in an oven in 12ºC for 1 h.

Hydrocarbon phase recovery by solvent extraction method

For the recovery process, ASTM-D5369 has been applied. Sludge samples were divided into smaller segments and 500 g. It was then fed into the extractor. The extractor was a 2 L cellulose timble. 1,000 g of MEK was used as the solvent for extraction. 5 consecutive cycles of reflexes at 50ºC temperature for extraction was conducted in the laboratory process. Thereafter, extraction was stopped since the solvent was completely stripped off hydrocarbon due to the solvent color stabilization. Then, the cellulose timble was located under a hood in room temperature and pressure conditions to ensure that all of the solvent evaporated from residue. The remaining solids were then weighted and the mass of hydrocarbon extracted from sludge were calculated by subtracting the remaining solids at the end of the process and mass of solvent used from sludge which was fed into the extractor at the beginning of extraction process. Gas chromatography analysis were carried out to determine the number of carbon atoms according to ASTM-D7169 and ASTMD-2887 standards.

Size and characteristics determination of Sediment

ASTM-D6913 was used to determine size distribution of extracted sediments. Sieve mesh sizes were selected as 0.5, 1, 1.7, 2.36 and 4 mm. The sieves were placed in the sieve shaker. 100 g of sediments were poured on the most coarse-grained mesh sieve and shook for 20 min with 80 rounds per min. The mass of grains on every sieve was calculated afterward. The results are shown in Table 1. The soil sediment is fine-grained since more than 90% of particles have passed through the sieve with 4mm mesh size (4.75mm mesh size is the boundary of coarse-grained and fine-grained soils).

Heavy metals analysis in residuals

Some of the physical properties and concentrations of heavy metals have been also analyzed according to Table 1. After determining the concentrations of heavy metals, the classification of the elements based on their concentrations as a hazardous or non-hazardous waste must be carried out according to standards and regulations. The classification of the waste specifies the method of treatment process.

Table 1: Physical and concentrations data for sludge samples

Specification	Unit	Result	Test method
Specific gravity (@15.56/15.56°c)	-	0.9051	ASTM-D4052
Specific gravity (@60/15.56°c)	-	0.8622	ASTM-D4052
Sulphur content (Total)	Weight (%)	2.00	ASTM-D2622
Asphaltene	Weight (%)	2.85	SIP 143
Nickel	mg/kg	11	UOP 800
Vanadium	mg/kg	51	UOP 800
Chromium	mg/kg	22.5	UOP 800
Cobalt	mg/kg	80	UOP 800
Lead	mg/kg	55	UOP 800

Toxicity and hazardousness determination of heavy metal constituents in sludge

In Table 2, heavy metals concentrations in sludge are compared with the toxicity standard limits suggested by EPA, California State and Office of Environmental Health Hazard Assessment (OEHHA) regulations. Leaching concentrations on the residuals and sediments of sludge samples were conducted by following toxicity characteristic leaching procedure (TCLP) test method (USEPA, 1992). To produce the leachate for heavy metal analysis, 100 g of sample was acidified with 2000 mL of acetic acid (sample to solvent ratio of 1:20). Then, the mixture was tumbled for 18 h with 30 rpm to simulate leaching procedure in an actual landfill over time. The final leachate solution was filtered through a high density polyethylene (HDPE) filter with effective pore size ranging from 0.6 to 0.8 µm. It should be noted that the filters shall be acid-washed prior to use by rinsing with 1L rinse of nitric acid followed by three consecutive rinses with deionized distilled water. The filtered solution was analyzed with atomic absorption spectroscopy to determine heavy metals concentrations according to Table 2 results. The sludge waste was categorized as toxic and hazardous since lead, cobalt and chromium concentrations were higher than the standard limit. Maximum contaminant level (MCL) shows the ability of heavy metals to contaminate the environment. MCL considers the level values based on standards for potable water, being carcinogenic, and expenditure on treating the affected people under named parameters.

Table 2: Determination the toxicity and hazardousness of heavy metals (Values are expressed as mg/kg)

Parameters	Leachate Concentration (TCLP test method)	MCL (Corresponding to 1/10 concentration)
Nickel	1.15	3.5 (California)
Vanadium	2.6	4.2 (California)
Chromium	6.8	5 (EPA)
Cobalt	5.5	5.7 (OEHHA)
Lead	7.67	5 (EPA)

Locating the landfill site

After the extraction process, most of the hydrocarbon phase were recovered and the remained residuals composed of heavy metals and sediments were prepared to be treated or disposed (Karbassi and Pazoki, 2015). Sirri Island owns an unbearable climate conditions (very low precipitation, high humidity and extreme temperature up to 60°*C*) during most of the months of the year which makes it a probable alternative to manage the wastes in form of landfilling. The incineration method is not economically efficient in this weather condition in comparison to landfilling since the humidity will enhance the moisture absorption of waste mass and reduce incineration efficiency. Heavy metals were less soluble and motive in alkaline condition (pH>7) and were also more soluble and leachable in acidic form (pH<7). On the other hand the texture of local subsurface environment composed of limestone, coral and luma shale resulting in an alkaline condition (pH was assumed to be 7.5) making Sirri Island a suitable place for disposal of heavy metals in a landfill since the leaching speed will hinder because of more alkaline-based condition. The dominant wind direction was from west to east, thus it was more desirable to locate the landfill site in the eastern blocks of the island in order to prevent lighter compositions from evaporating and being transported through the lands. The groundwater level in the north of Island was about 12 m deep and about 20m deep in the southern part of the Island. The surface water and vegetation were distributed through west, center and north-west of the Island. Thus, it is the best option to locate the landfill site in the south-east of the island to satisfy all above constraints and maximize the protection distance from surface water and vegetation.

Introducing a landfill using IWEM

IWEM uses a probabilistic Monte Carlo approach and a ground water fate and transport model to calculate a distribution of estimated ground water concentrations at a wellbore resulting from the release of leachate containing dissolved constituents at entered concentrations. IWEM then compares the 90th percentile of the distribution of estimated groundwater concentrations to reference groundwater concentration (RGC). RGC is adjusted by other standards such as maximum contaminant level and health-based numbers (HBN). Monte Carlo simulation determines the probability distribution of predicted ground water concentrations as a function of the variability of modeling input parameters (Bao and Mays, 1990). The Monte Carlo technique is based on the repeated random sampling of input parameters from their respective frequency distributions, and executing the fate and transport model for each combination of input parameter values (Beck, 1987). At the conclusion of the Monte Carlo analysis, it is then possible to construct a probability distribution of ground water concentration values and associated ground water dilution and attenuation factors. IWEM suggests that results are based on Monte Carlo analyses of 10,000 realizations. However, the number of iterations can be changed. IWEM evaluation uses site-specific data such as distance from surface water, distance from nearest wellbore, subsurface condition like soil texture, rock properties and their corresponding hydraulic conductivity, subsurface pH, depth of water- table, hydraulic gradient, determination of climate center based on regional evaporation and infiltration rates. In case of incapability of natural subsurface environment to deplete the contamination level, IWEM suggests specific liner scenarios for leachate protection in three different categories (USEPA, 2015):

1. *No liner*
2. *Single clay liner (simple liner)*

A clay liner with 90cm thickness with low hydraulic conductivity (1×10^{-7} cm/s)

3. *Composite liner*

A composite liner composed of a 1.5mm high-density polyethylene layer at the bottom of landfill and a synthetic clay liner with maximum hydraulic conductivity of 5×10^{-7} cm/s or a compacted clay liner with hydraulic conductivity of 1×10^{-7}cm/s underneath.

RESULTS AND DISCUSSION

Hydrocarbon recovery using solvent extraction method

Table 3 shows some of physical and chemical characteristics of sludge. Parameters such as specific gravity, sulfur content, asphaltene content, carbon residue conradson, base sediment, water, H_2S and ash contents of the recovered oil are desirable and under the acceptable limit comparing to the exportable Sirri Island crude oil. Comparing Sirri Island's crude oil to recovered oil, the American Petroleum Institute (API) has fallen from 32.6 to 24.6. It shows that during oil storage process in storage tanks, heavier hydrocarbons settle down at the bottom of tanks and sedimentation happens. Therefore, the sludge contains more of heavier hydrocarbons than lighter compositions which show its effect through API index reduction. The wax content has been increased significantly from 4.6 to 49.7. The wax content increase leads to pour point rising from -11°*C* to 70°*C* which indicates the presence of heavier rather than lighter hydrocarbons in sludge. Separated soil and sand in sludge samples which were stripped off hydrocarbon had a light cream color which is the exact same color as the regional soil in Sirri Island indicating the place where the sediments are formed from. The crude oil of Sirri (excluding sludge) contains carbon atoms in range of C7 to C20 and less than 5 percent extends up to C50. The range of abundant carbon atoms of extracted hydrocarbon after petroleum sludge refinement varies from C38 to C50 .These two ranges reveal that during the formation of petroleum sludge at the bottom of the storage tanks, more of molecules with higher molecular weight are precipitated and accumulated in sludge while lighter molecules evaporate and are released to the environment.

Finally, the values in Table 4 were measured as weight percentage of total mass of samples. The separation process was successful and about 99.8% of hydrocarbons were separated from sludge. Solid

Table 3: Physical and concentrations data for recovered oil, sediment and residue

Specification	Unit	Sirri exported crude oil	Recovered oil from sludge	Test method
Specific gravity (@15.56/15.56°c)	-	0.8622	0.9051	ASTM-D4052
Water content	Vol.%	< 0.1	< 0.01	ASTM-D4006
Salt content	P.T.B	5	32	ASTM-D3230
API	-	32.6	24.61	ASTM- D1298
Sulphur content (Total)	Weight (%)	1.81	2.00	ASTM-D2622
Wax content	Weight (%)	4.6	49.7	BP 237
Asphaltene	Weight (%)	1.7	2.85	SIP 143
H_2S content	mg/g	< 1	< 1	RIPI
Pour point	°c	-11	70	ASTM-D5853
Carbon residue Conradson	Weight (%)	3.2	6.10	ASTM-D189
Base sediment and water	Vol. (%)	< 0.1	< 0.01	ASTM-D1796
Ash content	Weight (%)	< 0.02	< 0.02	ASTM-D489

Table 4: Recovered hydrocarbon properties from the sludge sample

Material Content	Hydrocarbons	Solids (% wt)	Water (% wt)
Oil sludge	18.5 (% wt)	75	6.5
Recovered oil	99.80 (% wt)	0.12	0.08
Separated solids	40 (mg/g)	99.9	0.08

Table 5: Surface, subsurface and landfill data

Item	Type/value
Source type	Landfill
Landfill depth	2 m
Distance to well	150 m
Landfill area	3025 m^2
Subsurface environment	Solution limestone
Ground water pH	7.5
Soil type	Coarse-grained soil (sandy loam)
Depth to water-table	12.5 m

Table 6: Contaminant composition and their maximum contaminant level (Values are expressed as mg/kg)

Reference	Constituents list	MCL list
California state	Nickel	0.1
OEHHA	Vanadium	0.0147
California state	Cobalt	0.15
EPA	Chromium	0.1
EPA	Lead	0.015

content in the recovered oil was low under 1%. The majority of hydrocarbons were recovered in 3 steps; stripping of sludge, recovered oil and separated solid.

Disposal scenarios of sludge residuals using IWEM

Determination of the landfill size, area and properties

As shown in Fig. 1, the occupied area by sludge is about 19698 m^2. The average height for 24 spots has been measured and obtained 55.19cm. Based on these numbers, volume of total accumulated sludge was calculated 3850.959m^3. Density of sludge sample was measured and obtained 1039 kg/m^3. Thus the total weight of accumulated sludge blocks was 4002 tons. The volume of deposited sludge (3850.959 m^3) belongs to a 20 year period. Assuming that the production of crude oil remains constant (therefore production of sludge waste remains constant), total mass of 8004 tons is calculated. This total amount includes the sludge production in next 20 years and deposited sludge from previous 20 years. Therefore the metric volume of total sludge to estimate the size of required landfill will be 7704 m^3. At last, the landfill is determined as a square with side of 55m and depth of 3m. Soil texture was solution limestone and the pH was 7.5. Soil size type was coarse-grained as sandy loam and the depth to water-table was 12.5m. The summary of environmental conditions and landfill properties are presented in Table 5.

Liner selection based on heavy metals concentration and leachate

The maximum contaminant level of metals shows the ability of heavy metals to contaminate the environment. MCL considers the level values based on standards for potable water, being carcinogenic, and expenditure on treating the affected people under named parameters. The scenarios for different leachate concentration are shown in Table 6. Heavy metals leaching have been assessed under leachate concentrations to initial concentration of 10, 30, 50, 70, and 90% (Table 7). It is assumed that leachate concentration of zero and 100 percent are not really possible and naturally realistic.

Knowing that leachate concentration leads to assigning suitable liners for different heavy metals, leachates in IWEM are shown in Table 8.

Table 7: Different leachate concentration of heavy metals (Values are expressed as mg/kg)

Element	Initial concentration Mg/g	Leachate (10%)	Leachate (30%)	Leachate (50%)	Leachate (70%)	Leachate (90%)
Nickel	11.5	1.15	3.45	5.75	8.05	10.35
Vanadium	41.56	4.156	12.468	20.78	29.092	37.404
Cobalt	5.5	0.55	1.65	2.75	3.85	4.95
Chromium	68	6.8	20.4	34	47.6	61.2
Lead	76.7	7.67	23.01	38.35	53.69	69.03

Table 8: Final liner scenarios for different leachate concentrations and elements

Elements	Leachate (10%)	Leachate (30%)	Leachate (50%)	Leachate (70%)	Leachate (90%)
Nickel	Single liner	Composite liner	Composite liner	Composite liner	Composite liner
Vanadium	Composite liner	Composite liner	Composite liner	Composite liner	Composite liner
Cobalt	No liner	Single liner	Single liner	Composite liner	Composite liner
Chromium	Composite liner (not protective)	Composite liner (not protective)	Composite liner (not protective)	Composite liner (not protective)	Composite liner (not protective)
Lead	Composite liner (not protective)	Composite liner (not protective)	Composite liner (not protective)	Composite liner (not protective)	Composite liner (not protective)

As shown in Fig. 2, for nickel the single liner was protective only up to 10 percent leachate fraction but composite liner was protective for highest leachate fraction (90%). Vanadium leachate protection just happens when the composite liner exists. Cobalt did not need any liner for protection when leachate fraction was 10%. Up to 50% leachate, single liner was protective for cobalt whereas for the maximum leachate (90%), composite liner must be used to prevent cobalt from leaching. Chromium and lead were unprotected under any liner scenario and no liner could obstruct leaching. As a summary, the conservative liner design for sub-surface water protection in any leachate concentration for nickel, vanadium and cobalt was selected as composite liner. However, for chromium and lead, further treatments are needed to be conducted. A useful further treatment is solidification/stabilization (S/S) process using cement which is reported to give promising results for preventing leaching (Karamalidis and Voudrias, 2008) and can be used for treatment of chromium and lead in the present study. Cement and fly ash have been reported as acceptable alternatives to treat and prevent leaching of heavy metals categorized as toxic and hazardous (Dermatas and Meng, 2003, Park, 2000). Further researches on lead and chromium solidification/ stabilization in the present study are under investigation by the authors and will be presented in future works.

Final landfill design

For the composite liner, 1.5mm high density polyethylene layer as a type of geotextile and 50cm compacted clay liner with hydraulic conductivity of 10^{-7}cm/s was selected based on IWEM output. For the cover layer, 30cm of fine-grained soil at the top and 15cm of medium-grained soil was used at the middle. Fine-grained soil can be used at the top of cover layer and a medium-grained soil layer was used underneath to keep the flexibility of the geotextile layer. 1mm high density polyethylene layer was used in the cover layer. The rain drainage conduits were placed at both sides. The slope degree on the walls was 45° for the slope stability. The final details of landfill are shown in Fig. 3. The landfill is a square with side and depth of 55m, 3m, respectively. It must be noted that drainage layer and collection pipes were not considered in the design since the disposable waste nature was not capable of producing leachate when contacting with moisture unlike the usual municipal solid waste. Extremely low precipitation rate is also

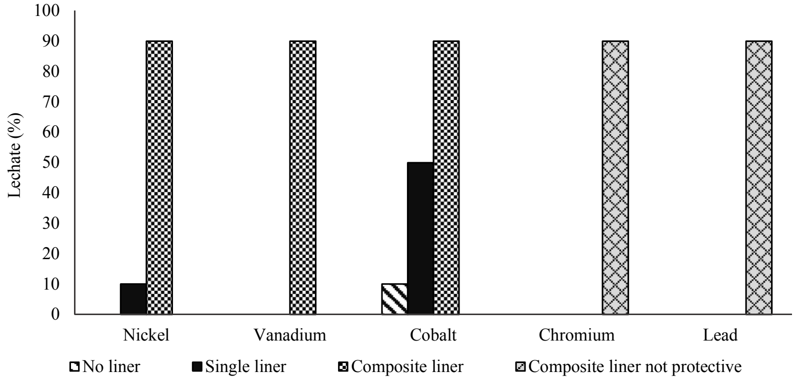

Fig. 2: Liner scenarios under different leachate concentrations

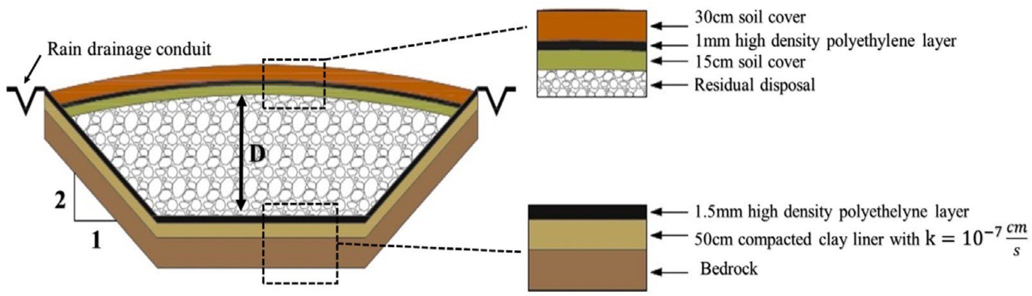

Fig. 3: Cross section of the final designed landfill

another reason for making the collection and drainage designing uneconomical and illogical.

CONCLUSION

Accumulated petroleum sludge of Sirri Island has been analyzed in this research. It is proved that the sludge is classified as hazardous and toxic waste under EPA regulation. For instance, concentration of lead in the sample indicates that this element is classified as toxic according to Basel Convention. About 20 percent of total mass of sludge was hydrocarbon phase. Solvent extraction method was used to separate hydrocarbon phase from sludge by methyl ethyl ketone as an organic polar solvent and results showed that about 99.8% of oil recovered from sludge. The recovered oil was under acceptable limit comparing to Sirri Island crude oil. The residuals after separation need further management. To achieve this, required area for landfilling was estimated by different leachate concentrations and reported to be a square with 55m length and 3m depth and composite liner. At the end, liner scenarios were assessed under different leachate concentrations, using IWEM. The final output indicated that chromium and leads leach under any leachate scenarios and needed proper and further treatment, while cobalt, vanadium and nickel were protective under composite liner.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript

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