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Leachability of Solidified Petroleum Sludge

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Abstract. Petroleum sludge was solidified in ordinary Portland cement, and the leachability test was performed based on American Nuclear Society 16.1 to produce leachate. The organic in solidified sludge was extracted by micro solid extraction to determine the organic in the sample. Organic in the leachate sample was detected by solid phase micro extraction by head space polydimethyl siloxane fiber using gas chromatography mass spectrometry. The targeted organic compounds in solid sample and leachate were quantified by the benzene, toluene, ethyl benzene, xylene, naphthalene and phenanthrene standards. The organic compounds in solidified sludge consist of aliphatic and ester acid with long carbon chain of Carbon 15 to Carbon 64. The aliphatic group in the leachate was found at the reduced rate of about tenfold of the solid sample. Derivative leachate products mainly composed of cyclic siloxane compounds. The metals leachability in the acidic medium depends on the metal hydroxide solubility value. High lead mobility in the acidic medium was due to its high solubility induced the highest effective diffusion coefficient of 1.59 x 10^{-07} cm^2/s.

Introduction

Crude oil is one of the important resources mostly used in meeting world energy demand. All largest oil and gas stakeholders must comply with the stringent standard in the manufacturing process. One of the European Union requirements known as Restriction of Hazardous Substance Directive (RoHS) adopted in February 2003 is applied to every single substance in electrical and electronic appliance production material. RoHS controls six hazardous materials as shown in Table 1 [1]. The RoHs limit is the upstream control of hazardous material in production line.

Crude oil component listed in Table 2 [2] is formed by three hydrocarbons groups, namely paraffins, aromatic and naphthenes. The paraffins, linear alkanes formed 10 to 30 % of crude oil and branched alkane is highly volatiles. Unsaturated hydrocarbon, cyclic or aromatics formed 2 to 4 % of crude. Naphthenes include parent compound such as saturated hydrocarbon arranged in a ring of 5 to 6 carbon atoms such as cyclopentane and cyclohexane formed 30 to 60 % crude oil. Other components in the crude are non hydrocarbon like sulfur, fatty acid, nitrogen and metals.

Petroleum sludge, residue of crude oil processing, has numerous contaminants such as organics, inorganic metals and other substances. The sludge composed of heavy metals, which includes Hg, As, Pb, Zn, Cu, Cd, Cr, Ni and Al. Most of the metals are toxic found in excess than the regulated standard. Mobile metal ions like Pb and Hg can easily migrate to water reservoir and affect biotic species and other living creatures in contact or consume the water. Organic compounds in the sludge include naphthalene, phenanthrene, anthracene, oil and grease. Typical petroleum waste inorganic and organic components [3, 4] were tabulated in Table 3.

Table 1: RoHs requirement for manufactured substance

Hazardous Material	Regulating Standard
Lead	Maximum concentration of 0.1 % or 1000 ppm for all element except for cadmium 0.01% or 100 ppm
Mercury	
Cadmium	
Hexavalent chromium	
Polybrominated biphenyl, PBB	
Polybrominated diphenyl ether, PBDE	

Source: [1]

Table 2: Crude oil components

Element	Weight Percent (%)
C	84-87
H	11-14
S	< 0.1-8
O	< 0.1-1.8
N	< 0.1-1.6
Ni	Trace to 1000 ppm
V	Trace to 1000 ppm
Se	Trace to 510 ppb

Source: [2]

Table 3: Typical petroleum waste component

Component	Common Ranges (µg/L)
Inorganics:	
Mercury, Hg	< 0.2[1]
Cadmium, Cd	< 5[1]
Lead, Pb	< 50[1]
Zinc, Zn	< 500-1000
Copper, Cu	3-500
Nickel, Ni	6-500
Chromium, Cr (Total)	<500 or <1000 Cr (IV)
Arsenic, As	0.55-100
Cobalt, Co	< 500
Iron, Fe	< 3000-5000
Vanadium, V	< 1000
Organics:	
Naphthalene	1.15[2]
2-Methylnaphthalene	1.71[2]
Phenanthrene	1.11[2]
Anthracene	1.10[2]
Oil	50-5000

Source: [1][3], [2][4]

Water soluble compound of crude oils and refined products include a wide variety of toxic compound to plant and animal. Aromatic compound is more toxic than aliphatic and middle molecular weight constituents are more toxic than high molecular weight tars. Low molecular weight compounds are generally unimportant because there are volatile and rapidly lost to the atmosphere. Some of the hydrocarbons are toxic to human and have a carcinogenic effect like polycyclic aromatic hydrocarbon (PAH) which enters into the human body through the food chain. EQA (Scheduled Waste) 2005 coded oily waste based on its sources as SW308, SW310, SW311 and SW314 for oil tanker, oil storage tank, wastewater treatment residue and plant maintenance operation accordingly [5].

The BTEX compounds after treatment in the final effluent are in the range of < 0.001 to 0.1 mg/L as shown in Table 4 [4] and the drinking water standard use as a comparison [6]. The objective of the current study was to investigate the organic compounds present in the solidified sludge, and in the leachate generated by American Nuclear Society (ANS) 16.1. Stabilization and solidification (S/S) of sludge was used to immobilize the contaminant in the sludge for final disposal. The leaching test was conducted to produce leachate to investigate the migration of contaminant in the solidified sludge.

Table 4: BTEX in the final effluent wastewater and drinking water

Volatiles Compound	Wastewater (mg/L)[1]	Drinking Water Standard (mg/L)[2]
Benzene	< 0.001-0.1	0.005
Toluene	total	2.0
Ethyl benzene		0.66
Total xylene		0.44

Source: [1][4], [2][6]

Materials

Binder Materials. The binder used in the study was ordinary Portland cement (OPC) based on Malaysian Standard 522 Part 1 2003 supplied by Lafarge Malaysia. The main compounds of the cement include calcium oxide, CaO and silica oxide, Si_2O with 64.96 and 21.41 % weight accordingly.

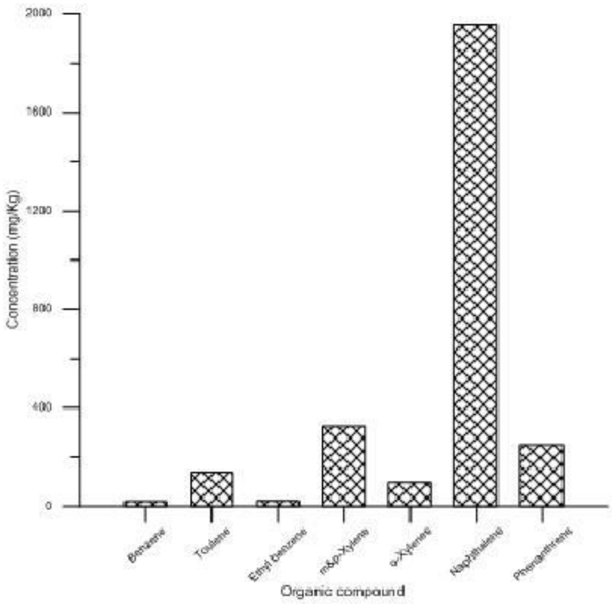

Fig. 1: Organic compounds in the sludge

Waste Materials. Petroleum sludge in form of semisolid containing 53.8 % moisture and significant amount of volatile solid of 92.0 % [7] used for S/S process was retrieved from a local refinery wastewater treatment plant. Oil and grease in the sludge attributed to 39.23 % weight [8]. Significant amount of BTEX, naphthalene and phenanthrene were found in the sludge as depicted by Figure 1 determined by USEPA 8260b [9]. Metals concentration in the OPC, waste sludge and solidified OPC & waste were determined by nitric acid digestion method APHA 3030E [10] as depicted in Figure 2.

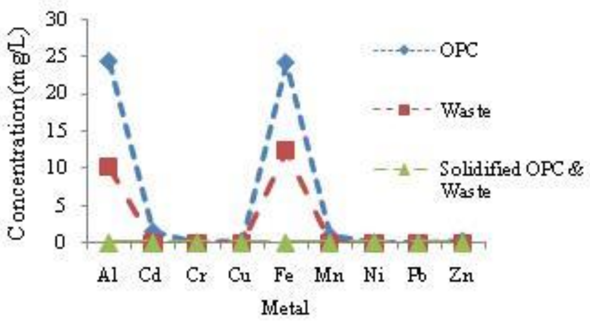

Fig. 2: Metals in OPC, waste and solidified OPC & waste

Method

The sludge was mixed with OPC at cement to sludge ratio of 8, and water to cement ratio of 0.45 to form solidified sludge. The simplified flowchart of S/S process is illustrated in Figure 3. Solidified sludge organic compounds were extracted by the microscale solvent extraction (MSE) according to USEPA SW-846 method 3570 [11]. The solid sample was extracted into Fluka analytical methylene chloride solvent with solid to the liquid ratio of 0.20. The sample was agitated by end-to-end rotation for 4 hours using rotary agitator. The solvent containing organic compounds was separated from solid by glass fiber filter. The solvent was preconcentrated using a 25 mL Supelco Kuderna Danish (KD) concentrator by water bath heating at temperature of 60 to 65ºC until the final volume of 1 to 2 ml remains in the receiving vessel. The heating was conducted in the fume hood to prevent any spillage of solvent. Schematic diagram of solid sample extraction is illustrated in Figure 4.

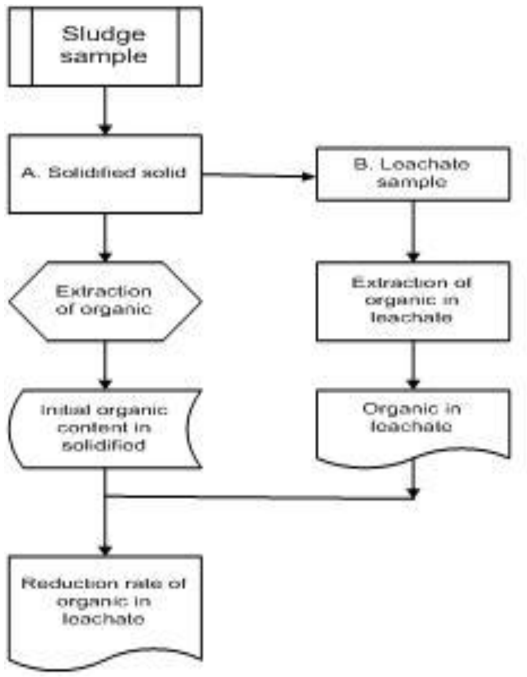

Fig. 3: Simplified flowchart of solidified sludge organic extraction

The leachability sample was performed by ANS/ANSI 16.1 [12]. Solid phase micro extraction (SPME) was developed by Pawliszyn and Belardi [13]. SPME was conducted based on two steps, the extraction and desorption of extracted compound as in Figure 5. Solid phase micro extraction (SPME) was used to extract the organic compounds from leachate of solidified sludge. SPME principles are based on the extraction of organics by fiber layer coated on the surface of a fused silica needle. The SPME optimization can be made by controlling contact time, agitation and temperature of extraction parameters [14, 15]. Suitable polydimethyl siloxane (PDMS) fiber with thickness of 100 µm was used for targeted analyte extraction of non polar hydrocarbons. Optimum SPME parameters are listed in Table 5 for the organic compounds determination. Inorganic metals were determined by Perkin Elmer ICP-OES.

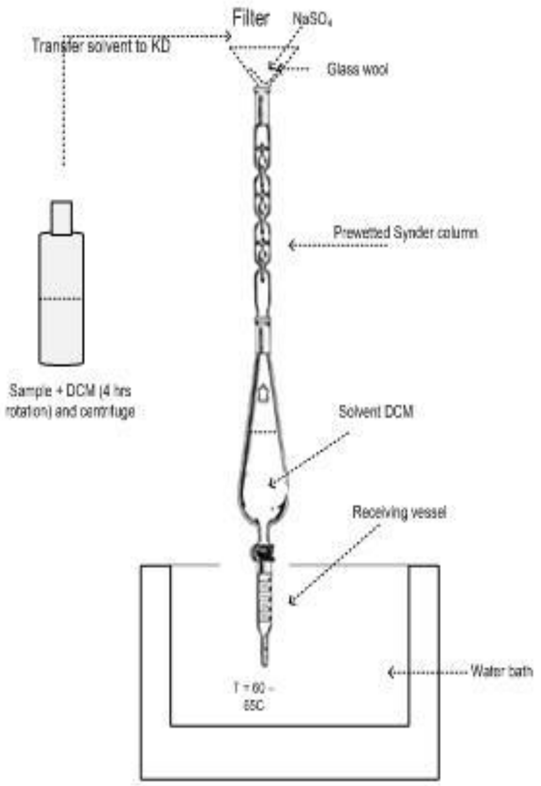

Fig. 4: Solid sample extraction and preconcentration

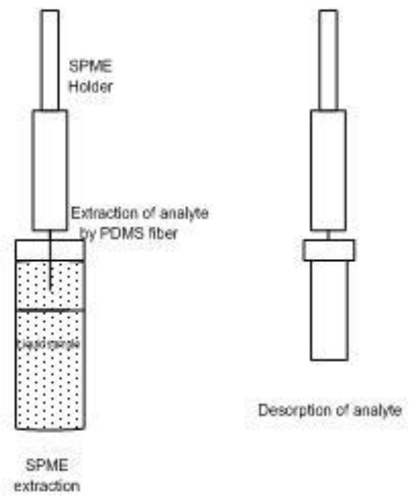

Fig. 5: Absorption and desorption of organic compounds in the sample

Table 5: Operating parameters for GCMS

Operating parameter	Values
Column oven temperature (°C)	50 (4 min) - 150 (8°C/min) - 280 (12°C/min), 310 (5°C/min, 5 min)

Injection temperature (°C)	250
Injection mode	Splitless
Absorption time (min)	25
Desorption time (min)	7
Incubation time (min)	5
Ion source	Electron ionization
Extraction agitation (rpm)	250

The extracted organic compounds in the solvent were measured by Shimadzu QP2010 GCMS. The solidified sludge and leachate were analyzed for the organic compounds based on modification of method 8270d [16] and 8260c [17], USEPA SW-846, according to the amended method for determination of extractable petroleum hydrocarbon [18]. Column used was Rtx-5MS with 30 m length x 25 µm diameter. Post run of 30 minutes for conditioning the fiber was conducted prior to sample analysis.

Results

Organic Compounds in the Solidified Sludge. Organic compounds in the solidified sludge were determined by the total-ion chromatogram (TIC) of the GCMS and external standard calibration curves [19] for the targeted compounds. The targeted compounds are benzene, toluene, ethyl benzene, xylenes, naphthalene and phenanthrene. None of the targeted aromatic compounds present in the solid sample since the aromatic form only 5 percent of the hydrocarbon content which already vaporized during the mixing process. Non targeted organic compound in the samples was determined based on Eq. 1 using the internal USEPA standard based on Method AK 102 for the determination of diesel range organics [20]. The concentration of organic compound found in the OPC-sludge is shown in Table 6.

$$C_s = \frac{(A_x)(C_{st})(D)(V_t)}{(A_{st})(RF)(V_s)} \quad (1)$$

Where,
C_S = concentration of sample, mg/kg
A_x = response of sample, area
C_{st} = concentration of standard, µg/mL
RF = response factor of standard
A_{st} = response of standard, area
V_t = volume of final extract, mL
V_s = volume of sample extracted, L or Kg
D = dilution factor, if no dilution use D = 1

Hydrocarbons found in solidified sludge mainly the aliphatic groups and ester acids consist of Carbon 15 to Carbon 64. The main component includes tetracosane, hexatriacontane, hexadecane and octadecane; all are straight chain alkanes and 1, 2-benzenedicarboxylic acid, diisooctyl ester. Branched alkanes were also found in the solidified sludge such as pentadecane, 2, 6, 10-trimethyl.

Organic Compounds in the Leachate. On the other end, leachate of OPC-sludge contained mainly organic acid and cyclic siloxane compounds. Siloxane compound is a dissolution product of chemical reaction between silica in cement and organic compound by carboxylic acid. The organic compounds found in the leachate sample are tabulated in Table 7.

Organic leachate products from solidified sludge are in form of reduced hydrocarbon ring such as Carbon 14 and Carbon 18 as a result of hydrocarbon reaction with acetate ions, or the chemical reaction of hydrocarbon with carbonic acid and silane, forming cyclic siloxane hydrocarbon. The aliphatic hydrocarbon was also found in the leachate, but the value was found at reduced rate of about tenfold of the solidified sludge, for instance, heneicosane. Heneicosane remains due to limited free ions available in the solution. Hydrocarbon molecular structures in the leachate are represented in Figure 6 based on mass spectral library of NIST08s.Lib.

Table 6: Concentration of organic compounds in the solidified sludge

Concentration (mg/L)	Organic Compound	Formula
38.95	Pentadecane	$C_{15}H_{32}$
55.97	Hexadecane	$C_{16}H_{34}$
14.90	Pentadecane, 2,6,10-trimethyl	$C_{18}H_{38}$
135.31	Octadecane	$C_{18}H_{38}$
89.28	Nanodecane	$C_{19}H_{40}$
140.90	Hexadecane, 2,6,10,14-tetramethyl	$C_{20}H_{42}$
87.47	Eicosane	$C_{20}H_{42}$
86.08	Heneicosane	$C_{21}H_{44}$
84.81	Docosane	$C_{22}H_{46}$
120.07	1,2-Benzenedicarboxylic acid, diisooctylester	$C_{24}H_{38}O_4$
149.59	Tetracosane	$C_{24}H_{50}$
23.30	Decanedioic acid, bis(2-ethylhexyl) ester	$C_{26}H_{50}O_4$
43.46	Dotriacontane	$C_{32}H_{66}$
69.94	Tetratriacontane	$C_{34}H_{70}$
145.22	Hexatriacontane	$C_{36}H_{74}$
11.13	Tetrapentacontane	$C_{64}H_{110}$

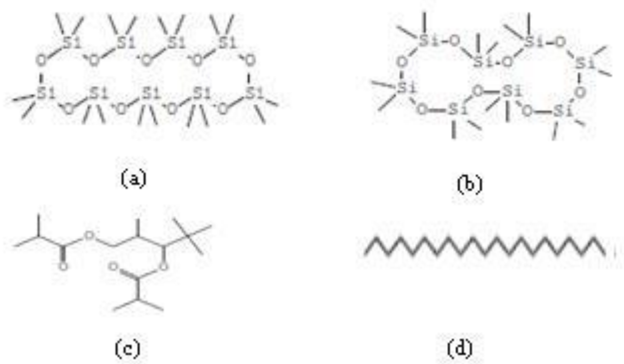

Fig. 6: Molecular structure of leachate organic compounds (a) cyclonanosiloxane octadecamethyl, (b) cyclooctasiloxane hexadecamethyl (c) propanoic acid, 2-methyl, 1-(1,1-dimethyl)-2-methyl-1,3-propanedyl ester and (d) heneicosane

Table 7: Concentration of organic compounds in the leachate

Concentration (mg/L)	Organic compound	Formula
2.15	Cycloheptasiloxane, tetradecamethyl	$C_{14}H_{42}O_7Si_7$
2.10	Tetradecanoic acid	$C_{14}H_{28}O_2$
12.18	Propanoic acid, 2-methyl, 1-(1,1-dimethyl)-2-methyl-1, 3-propanedyl ester	$C_{16}H_{30}O_4$
1.09	Cyclooctasiloxane, hexadecamethyl	$C_{16}H_{48}O_8Si_8$
4.26	Cyclononasiloxane, octadecamethyl	$C_{18}H_{54}O_9Si_9$
1.88	Heneicosane	$C_{21}H_{44}$
2.47	Squalane	$C_{30}H_{50}$

Metal Leaching. Solidified waste constitutes of porous matrix and has void portion. The leaching of metal was induced by dissolution, diffusion or wash-off of the exposed surface matrix to the leaching agents. In ground water, the leaching rate is controlled by the molecular diffusion. But in acidic condition, the supply of H^+ limits the leaching rate but after hydrogen ions depleted, the molecular diffusion is controlling the leaching rate. Molecular diffusion is driven by the concentration gradient of the constituent in solution and solid. The flux of constituent location is described by first Fick's law. The leaching rate, *l* of metals in the solidified sludge was determined based on Eq. 2 [21]. The effective diffusion coefficient, D_e of metals was determined by Eq. 3.

$$Leaching\ rate\ (l) = \frac{a_n}{A_0}\frac{V}{St_n} \quad (2)$$

$$D_e = \pi \left[\frac{a_n/A_0}{\Delta t_n}\right]\left[\frac{V}{S}\right]\left[\frac{1}{2}(t_n^{1/2} + t_n^{1/2})\right]^{1/2} \quad (3)$$

Where D_e = effective diffusion coefficient, cm^2/s, a_n = contaminant loss during leaching period n, mg, A_0 = initial amount of a contaminant present in the specimen, mg, S = surface area of the specimen, cm^3, V = volume of the specimen, cm^3 and Δt_n = duration of the leaching interval, t_n-t_{n-1}.

Table 8: Diffusion coefficient of metals in acidic medium

Metal	Diffusion Coefficient (cm^2/s)
Al	7.81×10^{-15}
Mn	1.2×10^{-14}
Zn	1.08×10^{-12}
Pb	1.59×10^{-07}

The leaching rates of nine metals namely, Cu, Fe, Mn, Al, Cd, Cr, Ni, Pb and Zn leached from solidified sludge via acetic acid (HA) and deionized water (DI) are depicted in Figure 7. Leaching of metal occurs immediately, but significant metal leached was observed after few days until about two months before equilibrium at pH 9.5 whereby acetate ions are dominating the solution while free hydronium ions are depleting. The H^+ ions have facilitated Cd, Cr, Mn, Ni and Pb to reach a maximum leaching rate. The significant metal diffusion rate was observed for selected metals as tabulated in Table 8. Pb has the highest leaching rate compare to other metals since it is one of the mobile metals with the D_e of $1.59 \times 10^{-07} cm^2/s$. The high solubility of lead hydroxide of 20 mg/L [22] has contributed to its mobility. Lead found in the sample was originated from OPC binder as lead is ubiquitous element in the environment. Iron has the lowest diffusion coefficient, 7.81×10^{-15} cm^2/s in acetic acid solution due to its low hydroxide solubility of 5×10^{-4} mg/L [22].

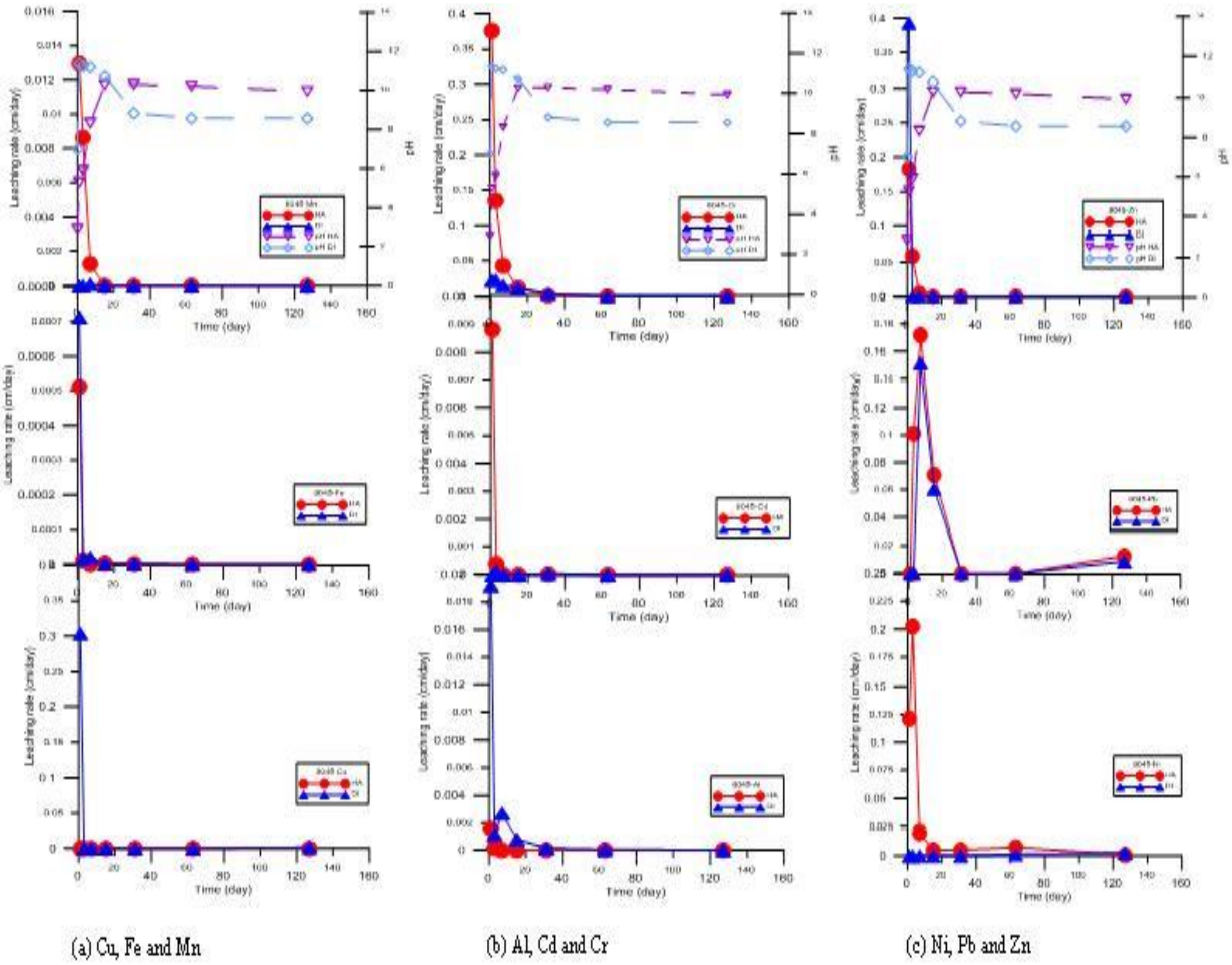

Fig. 7: Metal leaching rate (a) Cu, Mn and Fe (b) Al, Cd and Cr and (c) Ni, Pb and Zn

Conclusions

As a conclusion the organic compounds found in the solidified sludge were in form of linear or branched aliphatic hydrocarbons with long carbon chain of Carbon 15 to Carbon 64, which was quite resistant to decomposition due to heavier hydrocarbon group origin. The leachate of solidified petroleum sludges were composed of cyclic siloxane or acid ester as a derivative product of leached silica reaction with hydrocarbons since silica has high affinity toward reverse charges and carboxylic acid reaction on hydrocarbons. Abundant silica from cement hydration products facilitates the formation of cyclic siloxane.

Metal leachability in acid medium depends on its metal hydroxide solubility. Lead has high mobility for leaching activity as shown by higher effective diffusion coefficient compared to other metals due to its high hydroxide solubility. Metals in the sludge were immobilized by OPC with minimum leachability values released into acidic medium.

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