Cement-based stabilization/solidification of oil refinery sludge: Leaching behavior of alkanes and PAHs

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Abstract

Stabilization/solidification is a process widely applied for the immobilization of inorganic constituents of hazardous wastes, especially for metals. Cement is usually one of the most common binders for that purpose. However, limited results have been presented on immobilization of hydrocarbons in cement-based stabilized/solidified petroleum solid waste. In this study, real oil refinery sludge samples were stabilized and solidified with various additions of I42.5 and II42.5 cement (Portland and blended cement, respectively) and subject to leaching. The target analytes were total petroleum hydrocarbons, alkanes and 16 polycyclic aromatic hydrocarbons of the EPA priority pollutant list. The experiments showed that the waste was confined in the cement matrix by macroencapsulation. The rapture of the cement structure led to the increase of leachability for most of the hydrocarbons. Leaching of n-alkanes from II42.5 cement-solidified samples was lower than that from I42.5 solidified samples. Leaching of alkanes in the range of n-C_{10} to n-C_{27} was lower than that of long chain alkanes ($>n$-C_{27}), regardless the amount of cement addition. Generally, increasing the cement content in the solidified waste samples, increased individual alkane leachability. This indicated that cement addition resulted in destabilization of the waste. Addition of I42.5 cement favored immobilization of anthracene, benzo[a]anthracene, benzo[b]fluoroanthene, benzo[k]fluoroanthene, benzo[a]pyrene and dibenzo[a,h]anthracene. However, addition of II42.5 favored 5 out of 16, i.e., naphthalene, anthracene, benzo[b]fluoroanthene, benzo[k]fluoroanthene and dibenzo[a,h]anthracene.

1. Introduction

Cement-based stabilization/solidification (S/S) is a widely applied and well-established technique for the immobilization of inorganic hazardous constituents. Many industrial wastes are well treated with this cost-effective technology. However, solidification technology has run into difficulties when trying to solidify organic wastes [1,2]. In a well solidified product, hazardous contaminants are chemically immobilized in the cement hydration products or physically entrapped by encapsulation. The resulting solidified specimen has improved structural integrity and physical characteristics.

Oily materials are the primary source of waste for most refineries and are generated when oil coalesces on solids.

Because the oil acts as an adhesive, 1 kg of crude oil can generate 10–20 g of residue. Oily residues are collected at several points within the refinery, such as oil/water separators, dissolved air flotation units, heat exchanger cleanings, and tank bottom cleanings [3]. The use of cement-based stabilization/solidification as a treatment process can restrain the inorganic species mobility. However, the leaching behavior of organic compounds from treated industrial wastes is still under investigation.

It has been reported that the solidification of organic loaded wastes often produces materials with poor strength characteristics [1]. If organics are admixed with cement (e.g. phenols [4]), they would affect the cement hydration kinetics by retarding the reactions via formation of a protective film around the cement grain, hindering the formation of calcium hydroxide, and accelerating the reaction of modification of the colloidal C–S–H (C: CaO, S: SiO$_2$, H: H$_2$O) gel precipitated at very early stages around the cement grains [5,6]. Some examples have been reported, 3-chlorophenol retards the hydration of cement paste and stabilizes the ettringite phase, slowing its

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conversion to monosulphate. Experiments with ethylene glycol, *p*-chlorophenol and *p*-bromophenol with Portland cement type I revealed that ethylene glycol inhibited the setting of cement and significantly decreased the compressive strength [7]. Chlorophenol was found in crystals in the cement paste which also contained calcium. Chloronaphthalene was immiscible with the inorganic cement matrix and had no effect on hydration [8].

Stabilization of organic contaminants can occur through a number of processes, including sorption. Although there are substantial amounts of surface area in wastes treated by cement-based S/S, the surfaces are polar and are not as suitable for removal of organics as solids with more non-polar surfaces [9]. Another concern aside from the problems associated with cement setting is that organic waste constituents usually do not form the strong chemical bonds within the cement that some inorganics do. Thus, because organic constituents are not chemically bound in the waste, their retention is strongly dependent upon physical entrapment [10]. The presence of organic material causes retarding of setting or hardening of cement.

For example, this was observed when cement was mixed with water, methanol and 2-monochloroaniline in volume ratios of 100/76/4 [11]. The basic cement reactions remained the same, but they became slower. Vipulanandan [7] reported that the presence of 10% phenol caused the final setting time of cement to increase by approximately seven-fold. Another study [12] indicated that the organic components of hazardous wastes interfered with the confinement and strength characteristics of solidified products of wastes. It was concluded that oil, grease and phenol were generally deleterious to the strength and durability of Portland cement, cement-fly ash and lime-fly ash, when used as binders for metal immobilization. Nestle et al. [13] concluded that organic solvents (toluene, cyclooctanol, hexanol) delayed the hydration kinetics. While non-polar organic compounds only lead to a minor delay and qualitatively to the same hydration kinetics compared to the uncontaminated cement mixture, the polar solvents lead to much more pronounced delays in the hydration kinetics. For example, Gussoni et al. [6] reported large liquid pockets formed during first hours and days of hydration in the presence of methanol and 2-chloroaniline using MRI. They also confirmed using XRD analysis that the solution containing these two chemicals behaves as a retarder to the hydration reactions even after 6 months of aging [6]. The use of cement as a binder to stabilize wastes containing hydrocarbons is not a common practice, although it has been reported [14,15] that some polycyclic aromatic hydrocarbons (PAHs) were well stabilized with cement. Although the PAH-molecules cannot be built into the cement matrix, physical encapsulation in the matrix may occur to some extend [16]. In addition, it has been proposed that cement-based S/S could be used under certain conditions for waste (e.g. oily sludge) containing non-polar organics, such as aromatic hydrocarbons, halogenated hydrocarbons and PCBs [17,18].

Experimental data for hydrocarbon leaching from cement-stabilized/solidified refinery oily sludge, in various percentages of cement, do not exist. Oily sludge is usually piled-up untreated on-site, unless its management is forced by regulations. This on-site storage results in various environmental problems, such as potential leaching of organic constituents to soil and possibly to groundwater. Application of cement-based S/S to oily sludge can be significant for two reasons: the potential co-disposal of the treated waste in a sanitary landfill instead of a hazardous waste landfill, and the abated cost of the process against other waste management technologies, such as vitrification and incineration [19,20]. Especially, in countries where infrastructure for alternative management technologies has not been established, S/S for refinery oily sludge could be an economically feasible and ready to use technology.

The present work focuses on the leaching behavior of hydrocarbons from stabilized/solidified refinery oily sludge. Real samples taken from an oil refinery were stabilized using two types of cement, type I42.5 (Portland) and II42.5 (Blended). The samples were subject to leaching and the concentrations of hydrocarbons in the leachate were determined by gas chromatography. The results were used to assess the extent of leaching and understand the leaching mechanism.

2. Materials and methods

2.1. Oily sludge

Sludge samples were obtained from a Greek refinery (R). The R samples originated from a centrifuge unit, which contained a mixture of different kinds of oily sludge, such as API type gravity separator sludge and dissolved air flotation (DAF) sludge. The purpose of the centrifuge unit was to recover and reuse the hydrocarbon fraction contained in the sludge.

2.2. Binding materials and oily sludge characterization

The two kinds of cement, CEM I42.5N and CEM II42.5N, were obtained from TITAN Cement Company SA. These names are effective since 2002 [21] and correspond to previously used names I-45 and II-45, respectively. The I42.5 cement does not contain pozzolanic material, whereas the II42.5 contains natural pozzolanic material (7%, w/w) (Table 1). For the S/S process, ultra-pure water was used in order to minimize contamination of the solidified specimens by constituents contained in the water. Ultra-pure water (18.2 MΩ/cm, ASTM Type 1, ISO 3696) was prepared using a PURELAB UHQ II water purification unit (USF-ELGA, Spain).

The chemical characterization of the sludge was deemed necessary, before the implementation of the stabilization experiments. The determined parameters were: chemical oxygen demand (COD), total solids (TS), volatile solids (VS), fixed solids (FS) and moisture, as is shown in Table 1. The analytical methods used for parameters determination were according to Standard Methods [22].

2.3. Stabilization and solidification

Measured amounts of cement were added to known amount of oily sludge, followed by addition of ultra-pure water at water to sample (wet weight) ratio of approximately 0.4. The slurries were mixed manually, using a plastic bowl and a rubber spatula.

Table 1

Chemical composition of I42.5 Portland cement (PC), II42.5 blended cement (BC) and oil refinery sludge

Component	I42.5 PC (wt.%)	II42.5 BC (wt.%)
SiO_2	19.79	28.31
Al_2O_3	4.50	8.73
Fe_2O_3	3.85	3.61
CaO	64.52	50.79
MgO	1.90	2.15
K_2O	0.71	1.97
SO_3	2.91	3.15
Total	98.18	98.71

Oil refinery sludge characterization

COD^a (mg O_2/g)	1150 (18)	
TS^b (%)	88.8 (0.11)	
VS (%)^a	23.5 (0.36)	
FS (%)^a	76.5 (0.36)	
Moisture^b (%)	11.2 (0.11)	

Numbers in parentheses are standard deviations.

　^{a} On dry weight basis.
　^{b} On wet weight basis.

After mixing, the slurries were poured into plastic cylindrical molds. Air bubbles in the paste were removed by tapping the mold with approximately 40 hits (for about 1 min). The molds then were exposed to ambient air (62–66% relative humidity). The samples were cured at approximately 24 °C in the laboratory for 28 days. The cured samples were demolded and ground to pass through a 500 μm sieve before used in the leaching test. The total weight of a solidified sample is given by $T = W + B + W_a$, where T is the total weight (g) of the S/S specimen, W is the waste wet weight (g) which has been used for every S/S specimen, B is the weight (g) of the binder and W_a is the added water (g). The value of B is given by $B = [(B\%)W]/100$ and $(B\%)$ is the

percentage of the binder added with respect to the sludge wet weight. The amount of cement used in all S/S experiments varied from 10 to 70% with respect to the wet weight of sludge, as it is shown in Table 2.

2.4. Materials

Trace analysis dichloromethane (CH_2Cl_2) (SupraSolv), *n*-hexane (C_6H_{14}) (SupraSolv) and acetone (C_3H_6O) (SupraSolv) and silica powder (230 × 400 mesh) were obtained from Merck (Darmstadt, Germany).

Aliphatic hydrocarbon standards (*n*-C_{10} to *n*-C_{40} all even and uneven, including pristane and phytane) and polycyclic aromatic hydrocarbons (PAHs) standards, containing naphthalene, acenaphtylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenzo[*a,h*]anthracene, benzo[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene, were obtained from Chiron Laboratory, Norway. 5α-Androstane was used as internal standard for aliphatics, and 1-phenylhexane, 2,3-dimethylnaphthalene, 3,6-dimethylphenanthrene and 2,2-binaphthyl as internal standards for PAHs analysis. All internal standards were also purchased from Chiron Laboratory. For method control and recoveries, surrogate compounds were used. For *n*-alkanes, 1-chlorooctadecane and for PAHs analysis a mix of 2-fluorobiphenyl and 1-fluoronaphthalene were used as surrogates.

All re-usable glassware used for the experiment was first sonicated for 15 min with hexane (in order to flush off non-polar compounds), washed with detergent and tap water, rinsed several times with ultra-pure water, dried at 100 °C for 1 h and then wrapped with aluminum foil and heated at 500 °C for 6 h. Vials were sonicated for 15 min with acetone, washed with ultra-pure water, sonicated with ultra-pure water for additional 15 min, dried at 100 °C in an oven for 1 h and finally wrapped with

Table 2

Detailed description of sample mixtures

Mixture name	Oily sludge sample (g)	I42.5 PC addition (g)	II42.5 BC addition (g)	Water addition (g)	Actual % of cement in the specimens
R	100	–	–	–	–
I42.5 CS^a	–	100		40	100
II42.5 CS	–	–	100	40	100
R I42.5 10%^{b}	100	10	–	33	9.09
R I42.5 20%	100	20	–	37	16.66
R I42.5 30%	100	30	–	41	23.07
R I42.5 40%	100	40	–	45	28.57
R I42.5 50%	100	50	–	49	33.33
R I42.5 60%	100	60	–	53	37.50
R I42.5 70%	100	70	–	57	41.17
R II42.5 10%	100	–	10	33	9.09
R II42.5 20%	100	–	20	37	16.66
R II42.5 30%	100	–	30	41	23.07
R II42.5 40%	100	–	40	45	28.57
R II42.5 50%	100	–	50	49	33.33
R II42.5 60%	100	–	60	53	37.50
R II42.5 70%	100	–	70	57	41.17

　^{a} CS: cement sample.
　^{b} 10% = (10 g cement/100 g waste) × 100.

aluminum foil and baked at 500 °C for 6 h. Tweezers, spatulas, chromatographic column stopcocks and screw cap vials were sonicated for 15 min with methanol (to remove polar compounds), and then for additional 15 min with dichloromethane (to remove medium to non-polar compounds) and let to dry in a clean container.

2.5. Sample preparation

2.5.1. Leaching procedure

A static leaching test was used for the interpretation of aliphatic and aromatic leaching behavior from stabilized/solidified oil refinery sludge. Ultra-pure water was used as leachant. About 80 g of solidified sample were weighed and placed into borosilicate glass bottles. About 800 mL of ultra-pure water, at a solid to leachant ratio 1:10, was added. The samples were mixed at 30 ± 2 rpm in a rotary agitator at room temperature for 18 h. At the end of the extraction, the solid sample was let to settle overnight.

Our leaching test was inspired by TCLP, which is applicable for semi-volatiles and non-volatiles, but was modified in terms of leaching fluid composition and L/S ratio. We used ultra-pure water instead of acetic acid solution, because disposal of oily sludge frequently takes place *on-site*, in landfills for hazardous waste or in landfills for non-hazardous waste, which accept treated hazardous waste, but segregated, from municipal waste. The L/S ratio of 10 was used to simulate the earlier leaching period and this is in agreement with the European leaching protocol for hazardous waste [23] and other investigators [24–26]. Nevertheless, regulatory leaching tests specific for S/S wastes for hydrocarbons do not exist and usually standard leaching tests targeting leaching of inorganic constituents are used for both inorganic and organic compounds.

2.5.2. Liquid–liquid extraction and silica fractionation

The supernatant leachate was used for liquid-to-liquid extraction. Five-hundred millilitres of leachate was extracted three times with aliquots of 30 mL CH_2Cl_2. The volume of dichloromethane fraction was measured (dichloromethane recovery varied from 80 to 89%) and poured into a 100 mL peer-shaped flask. Concentration to volume of 1 mL was accomplished with at a rotary evaporator. An aliquot of 1 µL was analyzed by gas chromatography for total dichloromethane extractables. Afterwards, silica clean up and fractionation took place. For the fractionation a 1 cm in diameter column was used. A glass cotton wool plug was placed in the column, followed by 3 g silica powder (230×400 mesh ASTM) and Na_2SO_4 to form a 0.5 cm thick layer at the top of the silica column. Silica gel was purified in Soxhlet with a mixture of hexane:CH_2Cl_2:acetone, 1:1:1 (v/v/v) for 24 h and activated for 3 h to 150 °C. The glass cotton wool was also purified in Soxhlet with CH_2Cl_2 for 24 h. Na_2SO_4 was purified by baking at 150 °C for 3 h. The packed column was rinsed with 15 mL of CH_2Cl_2 and then with 15 mL of hexane. The first fraction (F1) of aliphatics was collected with 13 mL of hexane in a 25 mL peer shaped flask. The second fraction of aromatics (F2), was collected with 15 mL, using a mixture of solvents hexane:ethyl acetate (9:1, v/v) at average flow rate of 0.8 mL/min for both fractions in a 25 mL peer shaped flask. Concentration of the two fractions to final volume of 1 mL each was done using a rotary evaporator. The 1 mL aliquot was put into a 4 mL vial and was blown-down to dryness using a N_2 stream. The samples were diluted with internal standard solution (5 µg/mL in hexane) to a final volume of 200 µL prior to analysis. Additional dilutions were conducted with hexane as needed.

2.5.3. Ultrasonic extraction

The methylenechloride (CH_2Cl_2)-extractable hydrocarbons from sludge samples were extracted using ultrasonic sequential extractions with CH_2Cl_2 as the extractant. One gram of sludge was homogenized with 3 g anhydrous Na_2SO_4 (heated at 150 °C for 3 h) and placed into a cotton wool thimble (pre-extracted in Soxhlet with CH_2Cl_2 for 24 h). The thimble was placed into a 100 mL beaker and an aliquot (30 mL) of CH_2Cl_2 was added. The beaker was covered with aluminum foil and placed into an ultrasonic bath. The sample was sonicated for 15 min and then the volume of the extract was collected and measured. The extraction took place three additional times. All CH_2Cl_2 extracts were combined and homogenized and the volume was recorded. Afterwards, silica gel fractionation was conducted, as described previously.

2.6. Capillary GC

Hydrocarbon analyses were performed on an Agilent 6890N gas chromatograph equipped with a flame-ionization detector and split/splitless injector. For the analyses, a HP-5 (5% phenyl-95%methylpolysiloxane) (30 m × 0.32 mm i.d. × 0.25 µm film thickness) (J&W Scientific) capillary column was used. Samples were injected in splitless mode (splitless time: 0.80 min, flow: 20 mL/min). The oven temperature program was at initial temperature of 70 °C (1 min) then, at 15 °C min^{-1} to 150 °C and then at 6 °C min^{-1} to a final temperature of 300 °C, which was held for 22 min. Inlet and detector temperature was held at 300 and 290 °C, respectively. Helium was used as the carrier gas at a flow rate of 1.2 mL/min (linear velocity 23 cm/s). System control and data acquisition were calculated with the Agilent ChemStation (G2070AA ver. A.10.02). A 5-point calibration curve was created for *n*-alkanes, using standards containing *n*-alkanes from *n*-C_{10} to *n*-C_{40}, pristane and phytane. Quantification of *n*-alkanes was based on the internal standard compound 5α-androstane (Chiron Laboratory, Norway). For PAHs analysis a 16-priority pollutant standard, recommended by US EPA, was used to construct a 5-point calibration curve. The quantification was based on four internal standards 1-phenylhexane, 2,3-dimethylnaphthalene, 3,6-dimethylphenanthrene and 2,2-binaphthyl. All the results, including those from the solidified samples, were expressed as mg/kg dry weight of oily sludge contained in the sample.

Qualitative analysis of standards and unknown samples was conducted using GC–MS. For this reason a Hewlett-Packard (HP) 5890 gas chromatograph equipped with a mass-spectrometer detector VG-trio 1000 and split/splitless injection port was employed. The gas chromatograph was oper-

ated in the splitless mode and the injection port temperature was set at 290 °C. The column used was a 60 m DB-5MS (phenyl arylene polymer virtually equivalent to the 5%-phenyl-methylpolysiloxane) (0.25 mm i.d. and 0.25 μm film thickness). Helium was used as a carrier gas, and the column head pressure was set at 15 psi. The ionization was carried out in the electron impact (EI) mode (70 eV). The electron multiplier voltage and automatic gain control target were set automatically. The transfer line and source were set at 300 °C. The mass range scanned was from 15 to 650 amu under full scan mode. The MS system was tuned to m/z 69, 219, 502 and 614 for EI corresponding to perfluorobutylamine (PFTBA). The initial oven temperature program was 60 °C (1 min), then raised at 10 °C min^{-1} to 80 °C and then at 7 °C min^{-1} to a final temperature of 290 °C, which was held for 37 min.

2.7. Description of petroleum hydrocarbon groups

In the present study, in addition to characterization of the individual hydrocarbons, the determination of six additional groups was deemed necessary for the interpretation of leaching behavior of hydrocarbons contained in the oily sludge and in the stabilized/solidified oily sludge. The definitions of these groups are described below:

Total n-alkanes (TAlk). It was defined as the sum of all resolved and calibrated (with internal standard calibration method) n-alkanes (n-C_{10} to n-C_{40}) including pristane and phytane (expressed as mg/kg of dry oily sludge contained in every sample). The calculation of concentration of total n-alkanes was based on the internal standard 5α-androstane. The resolved and calibrated n-alkanes peaks were integrated as shown in Fig. 1A.

Total 16 PAHs (TPAH). it was defined as the sum of all 16-target polycyclic aromatic hydrocarbons (based on internal standard calibration method) (expressed as mg/kg of dry oily sludge contained in every sample). The calculation of total 16 PAHs was based on the internal standards 1-phenylhexane, 2,3-dimethylnaphthalene, 3,6-dimethylphenanthrene and 2,2-binaphthyl.

Total aliphatics (TAL). It was defined as the sum of all resolved and unresolved aliphatic hydrocarbons determined in the aliphatic fraction (F1), including calibrated and uncalibrated peaks (expressed as mg/kg of dry oily sludge contained in every sample). This fraction includes total n-alkanes, branched alkanes cycloalkanes and compounds recovered after silica fractionation with hexane in fraction F1. The calculation of concentration of total aliphatics was based on the procedure described below.

For the quantification of TAL fraction the following procedure was developed: the chromatogram was divided into a number of sections equal to the number of resolved and calibrated n-alkane peaks (those contained in the aliphatic standard) (Fig. 1). Each n-alkane was located approximately in the middle of the respective section. Then, the areas of all resolved and unresolved peaks were summed-up as one, including the area of the known n-alkane peak of the specific section of the chromatogram (Fig. 1B). The total area of each such section was quantified based on the external standard calibration curve of the known n-alkane (known response factor), which existed in
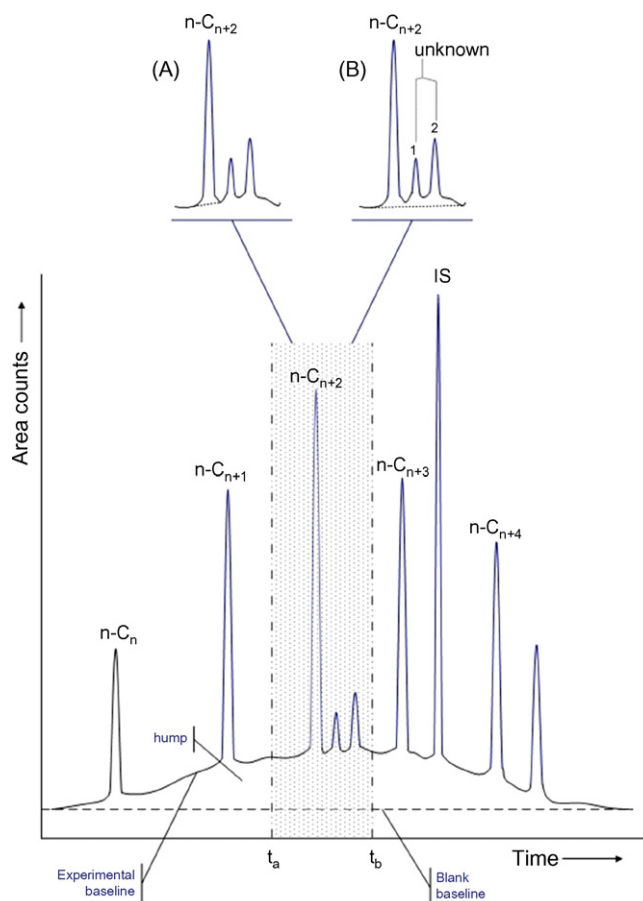

Fig. 1. Hypothetical chromatogram of petroleum hydrocarbons. Quantification modes: (A) total n-alkanes (TAlk) and (B) total aliphatics (TAL). IS: internal standard.

the particular section. The sum of all such concentrations, calculated from every section, equalled the concentration of the TAL fraction.

Total aromatics (TAR). It consisted of all resolved aromatic hydrocarbons determined in the aromatic fraction (F2), including calibrated and uncalibrated peaks (expressed as mg/kg of dry oily sludge contained in every sample). Total aromatics includes total substituted and unsubstituted polycyclic aromatic hydrocarbons, and all compounds extracted after silica fractionation with hexane:ethylacetate in the fraction F2. The calculation of total aromatics was based on the internal standards 1-phenylhexane, 2,3-dimethylnaphthalene, 3,6-dimethylphenanthrene and 2,2-binaphthyl.

TPHs (total petroleum hydrocarbons, GC-detectable) was defined as the sum of total aliphatics (resolved and unresolved, calibrated and uncalibrated peaks) and total aromatics (expressed as mg/kg of dry oily sludge contained in every sample): TPH = TAL + TAR.

MCE (methylenechloride extractable fraction) was defined as the sum of all resolved and unresolved (calibrated and uncalibrated peaks) peaks (expressed as mg/kg of dry oily sludge contained in every sample). The samples originated from either liquid–liquid extraction or extraction with sonication, but without previous fractionation or clean-up. Therefore, it is

likely that the extracts contained not only hydrocarbons, but also additional compounds extracted by methylene chloride. Therefore MCE ≥ TPH. The resolved compounds appeared as peaks and the unresolved as a hump area between the blank baseline and the curve defining the base of resolved peaks [27].

3. Results and discussion

3.1. Leaching of MCE, TPH, TAL, TAR, TAlk and TPAH fraction

All the results were expressed as mg/kg dry weight of oily sludge contained in the solidified sample. The MCE fraction of the oily sludge was almost 5% on dry weight basis, as it is shown in Table 3. Only a small part (0.18%) of MCE fraction was transferred to the water when aqueous leaching was applied. The reason for that is that hydrocarbons are hydrophobic compounds, which prefer to stay in the oil phase of the sludge.

Leaching of TPHs from the solidified/stabilized sludge with I42.5 cement was generally at the oily sludge leaching level except for R I42.5 30% specimen, which was about half the leached amount of the sludge alone (16.7 mg/kg versus 41.5 mg/kg) (Table 3). R I42.5 40 and 70% showed leaching reduction, compared to the untreated sludge (31.7 and 29.8 mg/kg, respectively, versus 41.5 mg/kg). As shown in Table 3, solidified samples with 10, 20 and 40% II42.5 cement exhibited remarkably high leachability, 3.5, 1.6 and 2.6 times higher than that of oily sludge (144, 68.5 and 109 mg/kg, respectively). Samples with 30 and 70% cement addition leached almost the same amount with the sludge, whereas the 50 and 60% showed a small leaching reduction.
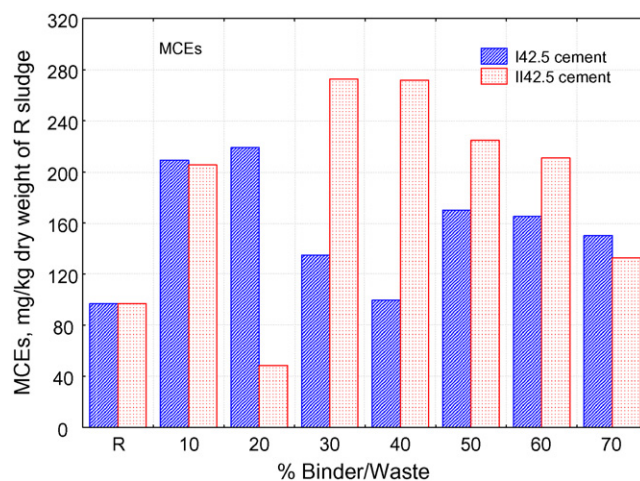

Fig. 2. Leaching of MCEs from oily sludge and solidified/stabilized oily sludge with I42.5 and II42.5 cement.

With regard to % leaching of hydrocarbons from S/S specimens, the aliphatic fraction showed bigger leachability than the aromatic fraction (Table 3). In the case of S/S samples with type I of cement the aliphatic fraction resulted in almost 50% release, whereas S/S samples with type II blended cement showed bigger leachability <69% (Table 3). In contrast, aromatic compounds were better contained in the cement matrix than aliphatics by showing maximum % leaching of 29 and 34.5 for S/S samples with type I and II cement, respectively (Table 3).

The presence of cement in the solidified oily sludge, in general increased MCE fraction leaching (Fig. 2). In most cases leaching increased by 1.4–2.8 times with addition of II42.5 cement, and by 1.2–2.4 times with addition of I42.5 cement.
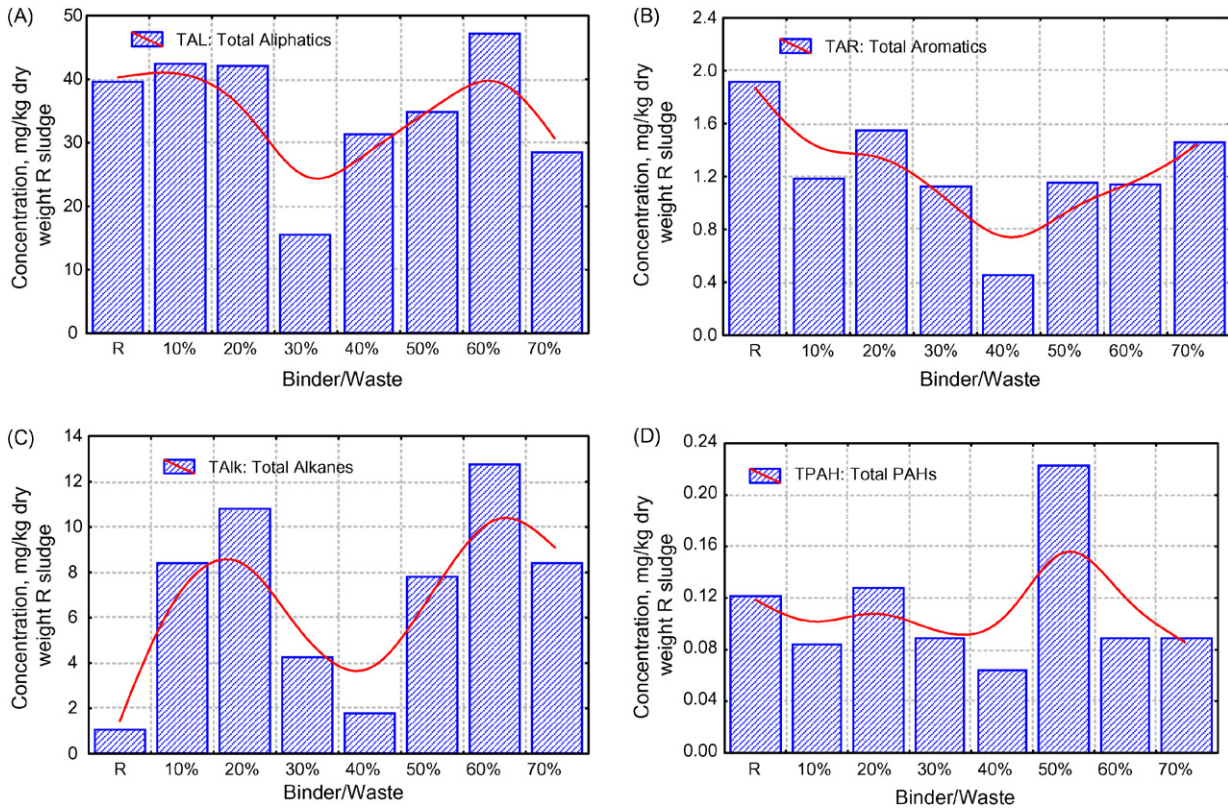
Table 3
Hydrocarbon content of and hydrocarbon leaching from oily sludge and its S/S specimens

	Hydrocarbon content of oily sludge (mg/kg dry weight R sludge)				
	MCEs[a]	TAL[b]	TAR[c]	TAlks[d]	TPAHs[e]
R sludge	53,377	2743	181	925	27.6

	Hydrocarbon leaching from oily sludge and its S/S specimens (mg/kg dry weight R sludge)													
	R[f]	I42.5 PC solidified samples							II42.5 BC solidified samples						
		10%[g]	20%	30%	40%	50%	60%	70%	10%	20%	30%	40%	50%	60%	70%
TPHs[h]	41.5	43.7	43.7	16.7	31.7	36.1	48.2	29.8	144	68.5	35.2	109	30.8	25.1	46.8

	% Leaching of hydrocarbons from S/S specimens with cement content varying from 10 to 70% (calculation based on dry weight oily sludge)	
	S/S samples with I42.5 PC	S/S samples with II42.5 BC
TAL	18–44	35.5–69
TAR	8–29	13.5–34.5
TAlk	7–50	6–38.5
TPAHs	7–27	9–26.6

[a] Methylenechloride extractable hydrocarbons.
[b] Total aliphatic fraction.
[c] Total aromatic fraction.
[d] Total alkanes.
[e] Total 16 PAHs.
[f] R: oil refinery sludge.
[g] 10% = (10 g cement/100 g waste) × 100.
[h] Total petroleum hydrocarbons.

Fig. 3. Leaching of TAL, TAR, TAlk and TPAH from oily sludge R and solidified/stabilized sludge with I42.5 cement. The solid line is a least square fitting and shows the leaching trend for each parameter.
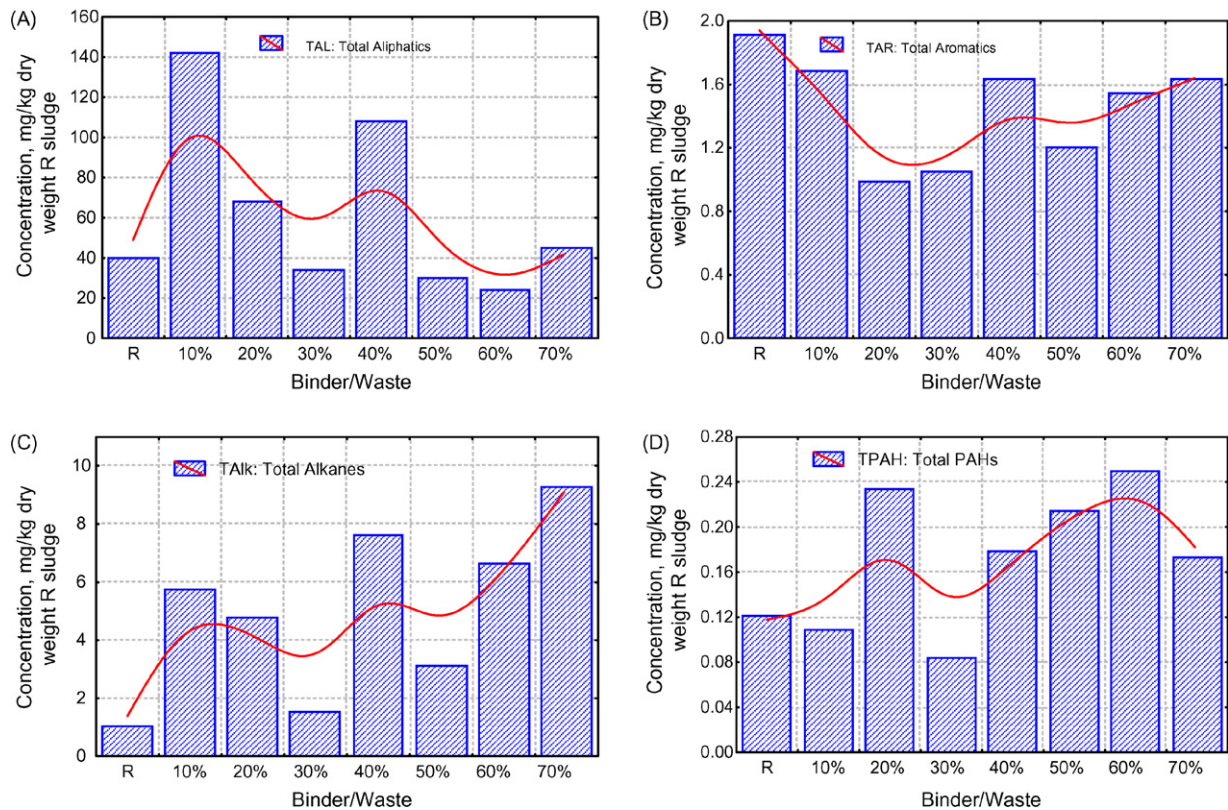

Fig. 4. Leaching of TAL, TAR, TAlk and TPAH from oily sludge R and solidified/stabilized sludge with II42.5 cement. The solid line is a least square fitting and shows the leaching trend for each parameter.

An exception was the sludge sample solidified with 40% I42.5 cement, in which the leached amount did not increase and the sample solidified with 20% II42.5 cement, in which the leached amount decreased by half (Fig. 2). The highest leachability observed, was for the II42.5 30% and the I42.5 20% solidified samples.

The reason of increased leaching with increasing amount of cement was that the polar cement resulted in a more hydrophilic environment and, therefore, a better contact between water and the stabilized/solidified specimen. Specifically, macroencapsulation of the sludge into the cement matrix was achieved and small spherical cavities filled with waste were formed. These cavities were smaller in size, but more abundant in solidified samples with higher percent of cement addition, resulting in

significant increase of contact area. This was observed with an optical stereomicroscope equipped with digital camera. In addition, the hydrophobicity of the sample decreased with increasing addition of the hydrophilic cement. In performing the leaching test, particle size reduction and consequently cavity destruction took place. When mixed with the leaching medium, the material with lower cement content tended to form clots, thus reducing its interphase contact area. The higher cement content samples did not form clots, thus maintaining higher interphase contact area. Therefore, larger concentrations of MCEs were measured for stabilized/solidified waste with higher addition of cement.

The leached amount of MCEs was many times higher than the leached amount of total aliphatics and total aromatics together
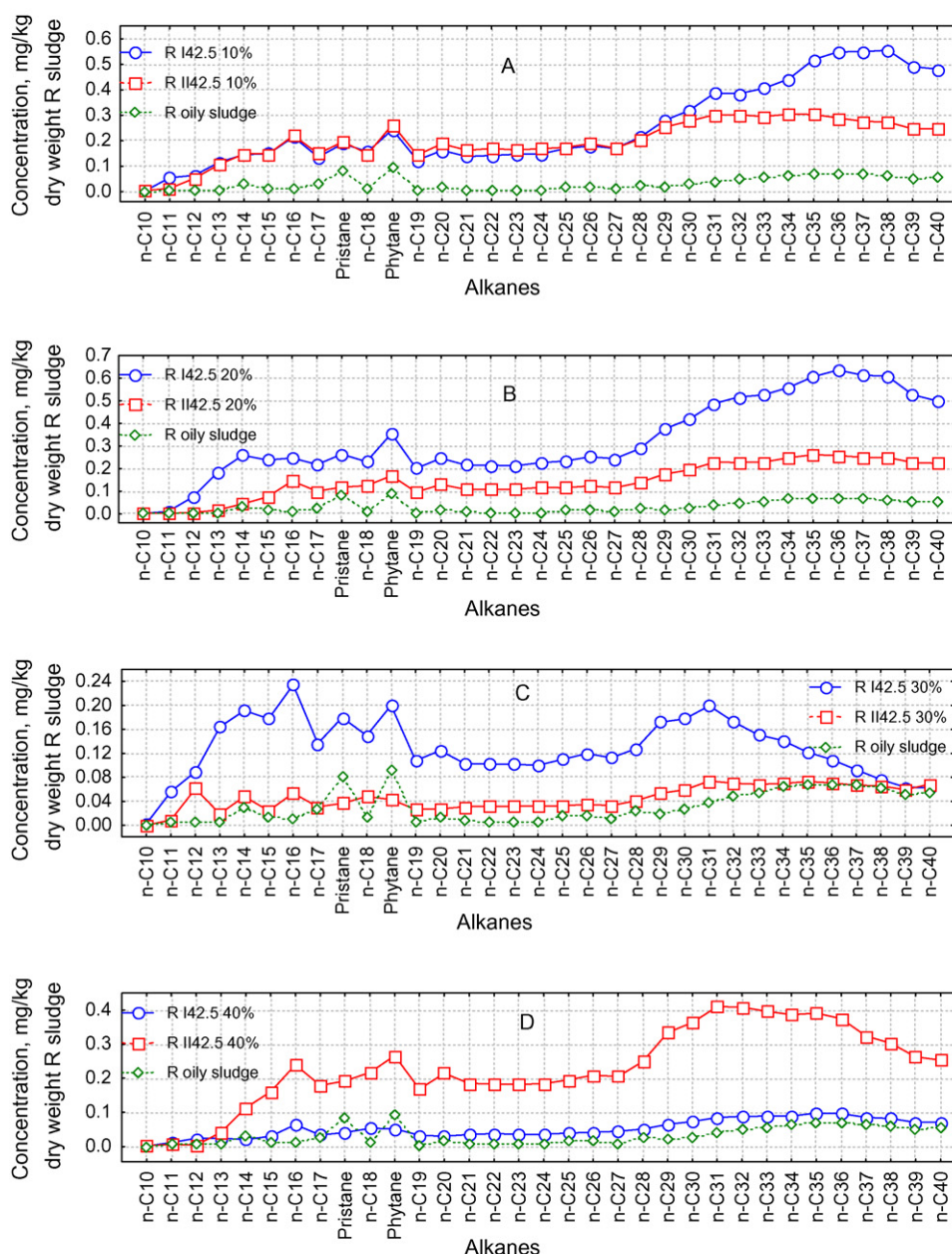

Fig. 5. Leaching of individual *n*-alkanes, pristane and phytane from oily sludge and its stabilized/solidified samples with I42.5 and II42.5 cement.

(i.e., TPHs). This is justified, because during column fractionation and clean up only the aliphatic and aromatic fractions were recovered, whereas a significant fraction of polar compounds (e.g., esters, ketones, ethers) remained on silica gel. The amount of total aliphatics (TAL) and total alkanes (TAlk) in the leachate was in every case larger than the amount of total aromatics (TAR) and TPAHs, respectively. The total aliphatics varied from 15.6 to 47.1 mg/kg for stabilized/solidified sludge with I42.5 cement and from 34.1 to 142 mg/kg for stabilized/solidified sludge with II42.5 cement (Fig. 3A and 4A).

Leaching of total alkanes (TAlks) (Fig. 3C and 4C) from solidified specimens with either I42.5 or II42.5 cement was much higher compared to leaching from untreated sludge. In general, leaching of TAlks increased with increase of cement addition. For the I42.5 solidified samples the leaching trend observed was that, for low and high percent of stabilizing agent, the leaching was high, whereas in samples with medium percent of cement addition (e.g. 30 and 40%) the leaching was lower, but still higher than this of the oily sludge (Fig. 3C). Also, for samples solidified with 30 and 50% II42.5 cement, decreased leaching was observed but still higher than this of the oily sludge (Fig. 4C).

Total aromatics (TAR) varied from 0.45 to 1.54 mg/kg dry weight sludge for specimens solidified with I42.5 cement (Fig. 3B) and from 0.98 to 1.63 mg/kg for II42.5 cement addition (Fig. 4B). In all cases the amount of total aromatics leached from the solidified samples was lower than the amount leached from the oily sludge. However, leaching of TPAHs measured, did not

show the same behavior as in the case of total aromatic fraction (Fig. 3D and 4D). TPAHs from solidified specimens with I42.5 Portland cement seemed to be unaffected by the presence of the binder and released almost the same amount as the sludge itself, except for the R I42.5 50% sample, which leached two-fold more (Fig. 3D). TPAHs leached from solidified samples with II42.5 cement showed an increasing leachability as the cement addition increased, except for the R II42.5 30% sample, which released 33% less than the oily sludge itself. Concentrations of TPAHs were low, ranging from 0.063 mg/kg to 0.23 mg/kg for solidified specimens with I42.5 cement (Fig. 3D). For solidified specimens with II42.5 cement the concentration values varied from 0.85 to 0.25 mg/kg on dry weight sludge basis (Fig. 4D). Some discrepancies in the leaching behavior of aromatic hydrocarbons could be explained on the basis of sample heterogeneity (existence of hot spots) and the low levels of individual aromatic hydrocarbon concentration (<0.25 mg/kg dry weight).

3.2. Alkanes

In general, leachate concentrations of individual n-alkanes from the cement-based S/S samples were higher, in every case, than those from untreated oily sludge (Figs. 5 and 6). The addition of II42.5 cement resulted in lower leaching of individual alkanes than the addition of I42.5 cement. This was indicated by the higher n-alkane concentration in the leachate of specimens stabilized/solidified with I42.5 (Fig. 5A–C and 6E and F).
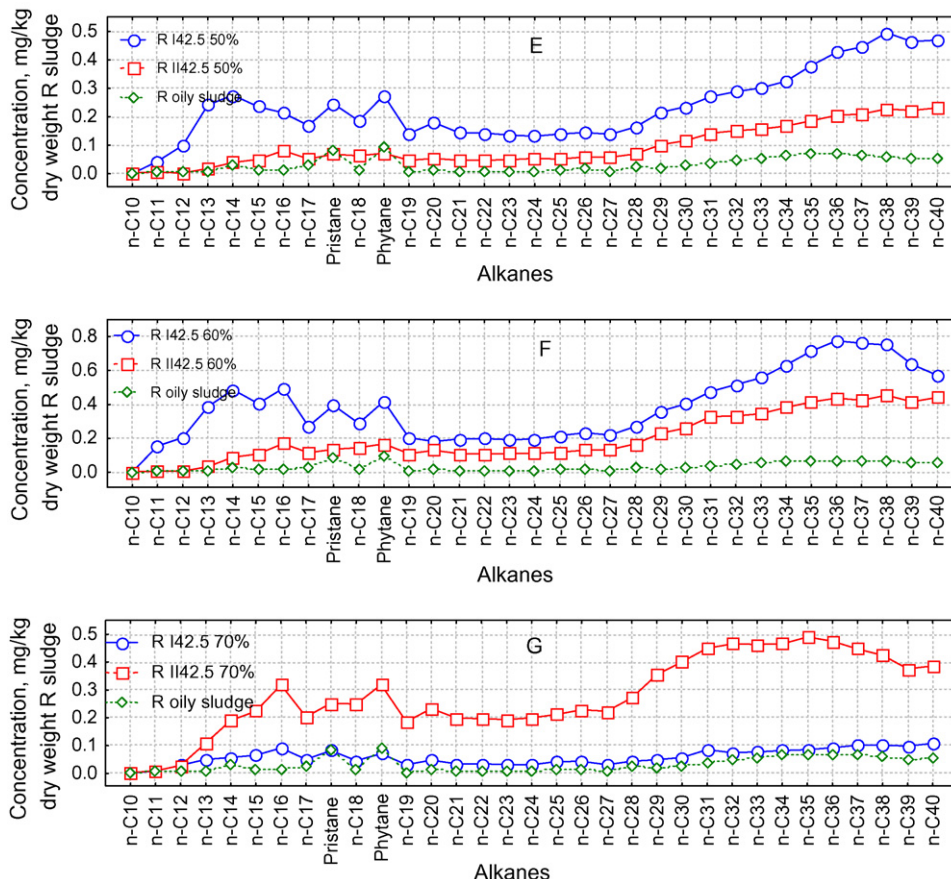

Fig. 6. Leaching of individual n-alkanes, pristane and phytane from oily sludge and its stabilized/solidified samples with I42.5 and II42.5 cement.

This trend was not observed for samples solidified with 40 and 70% cement (Fig. 5D and 6G). Generally, the figures showed that when the alkane chain increased, from *n*-decane to *n*-tetracondane, the leaching of *n*-alkanes increased as well.

A remarkably similar leaching behavior was observed for alkanes in the range *n*-C$_{10}$ to *n*-C$_{30}$ for either I42.5 or II42.5 cement-solidified specimens with 10% binder addition. Only for *n*-alkanes with higher molecular weight (more than 30 carbon atoms in the molecule), a different binder effect was observed. Apparently, the amount of cement (10%) was very low to cause a significant difference in the leaching behavior of stabilized/solidified oily sludge. With increasing cement addition (>20%), the difference in leaching behavior, because of the two types of cement addition, was obvious (Figs. 5B–D and 6E–G). Concentrations of *n*-alkanes in the leachate from untreated oily sludge were lower by one order of magnitude, than those leached from the solidified specimens. This is due to clot formation during the leaching, as previously explained.

3.3. Polycyclic aromatic hydrocarbons

As it is shown in Figs. 7–9, I42.5 cement addition was more effective than II42.5 in stabilizing acenaphthylene, acenaphthene, fluorene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*a*]pyrene and indeno[1,2,3-*c,d*]pyrene. In contrast, II42.5 cement seemed better stabilizer for naphthalene, phenanthrene and dibenzo[*a,h*]anthracene, whereas immobilization of anthracene and benzo[*k*]fluoranthene seemed unaffected by the addition of either I42.5 or II42.5 cement. The addition of cement to the oily sludge usually increased the leachability of PAHs compared to the leaching amounts of the oily sludge itself. Unlike the leaching behavior of *n*-alkanes, where the II42.5 cement addition showed better immobilizing characteristics, in the case of PAHs I42.5 cement performed better for 10 PAH compounds out of 16 which were measured, whereas in 2 cases the difference between the two types of cement was negligible.

The S/S process resulted in formation of cavities containing encapsulated waste. This macroencapsulation, which was observed by optical stereomicroscope in the cement-solidified matrix implies that the leaching behavior of PAHs might be controlled by this mechanism of immobilization. The particle size reduction of the oily sludge and the solidified samples required by the leaching protocol revealed that increasing the amount of cement, led to the formation of smaller and more abundant clots and therefore increased the interphase area of the waste with the extract. Therefore, increased amount of cement resulted in increase in leaching.

Compared to untreated waste, the presence of I42.5 cement in the samples increased the leachability of naphthalene, by many times, in specimens R I42.5 20, 30 and 60% (Fig. 7A). Naphthalene leaching decreased slightly in specimens with 10, 40, 50
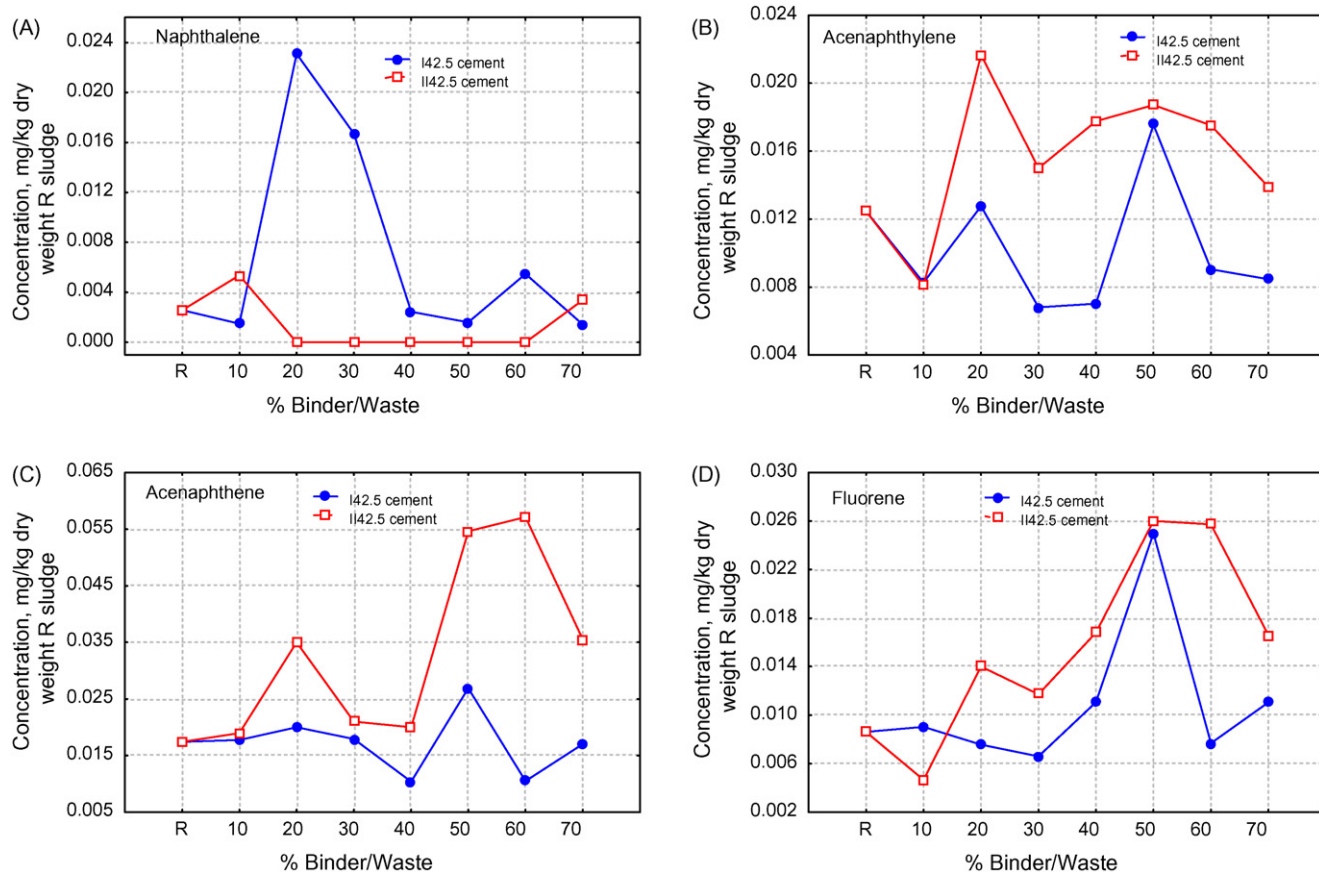

Fig. 7. Leaching behavior of individual PAHs (mg/kg dry weight of R sludge) from samples solidified with two different types of cement (I42.5 and II42.5). (A) Naphthalene, (B) acenaphthylene, (C) acenaphthene and (D) fluorene.
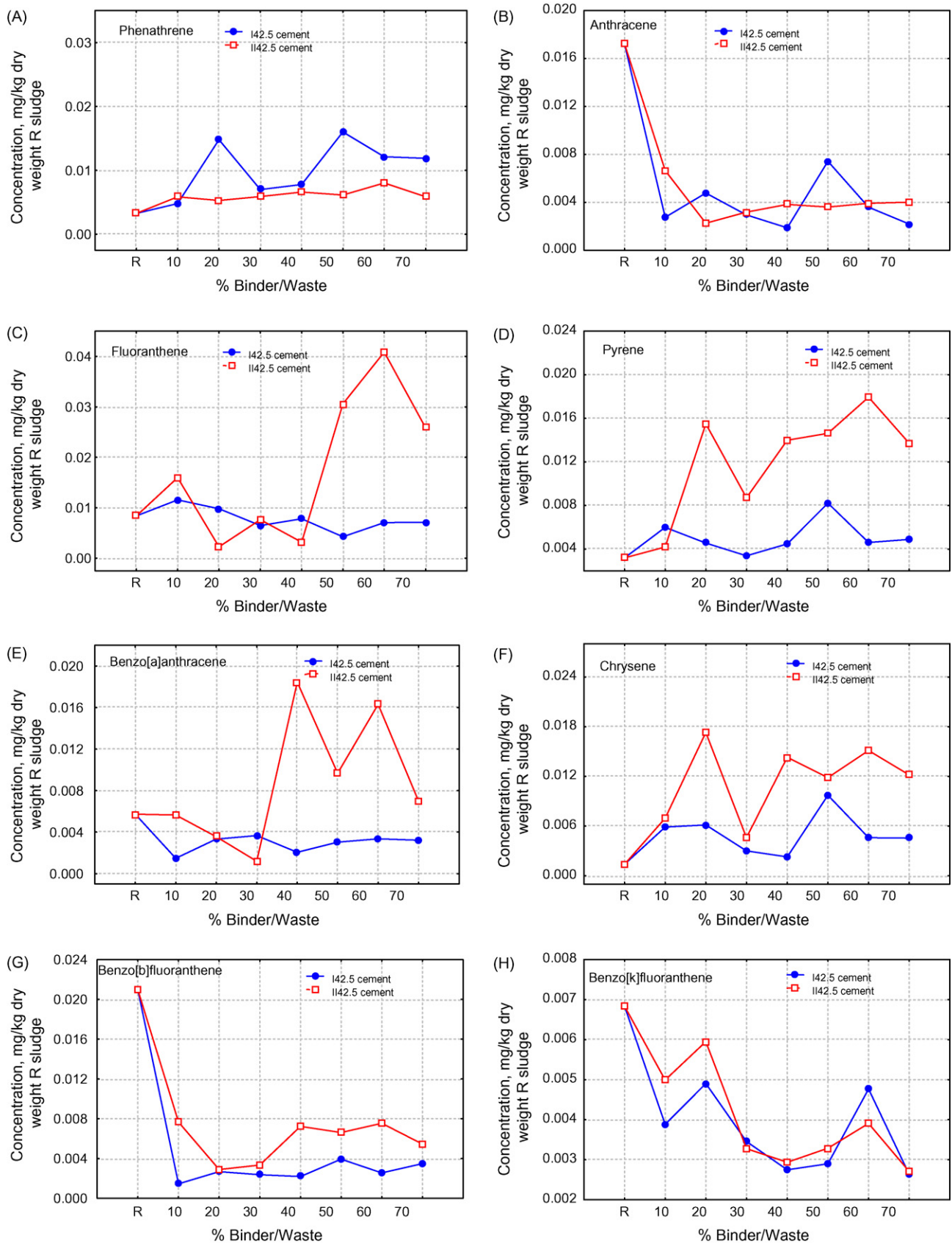
Fig. 8. Leaching behavior of individual PAHs (mg/kg dry weight of R sludge) from samples solidified with two different types of cement (I42.5 and II42.5). (A) Phenathrene, (B) anthracene, (C) fluoranthene, (D) pyrene, (E) benzo[a]anthracene, (F) chrysene, (G) benzo[b]fluoranthene and (H) benzo[k]fluoranthene.
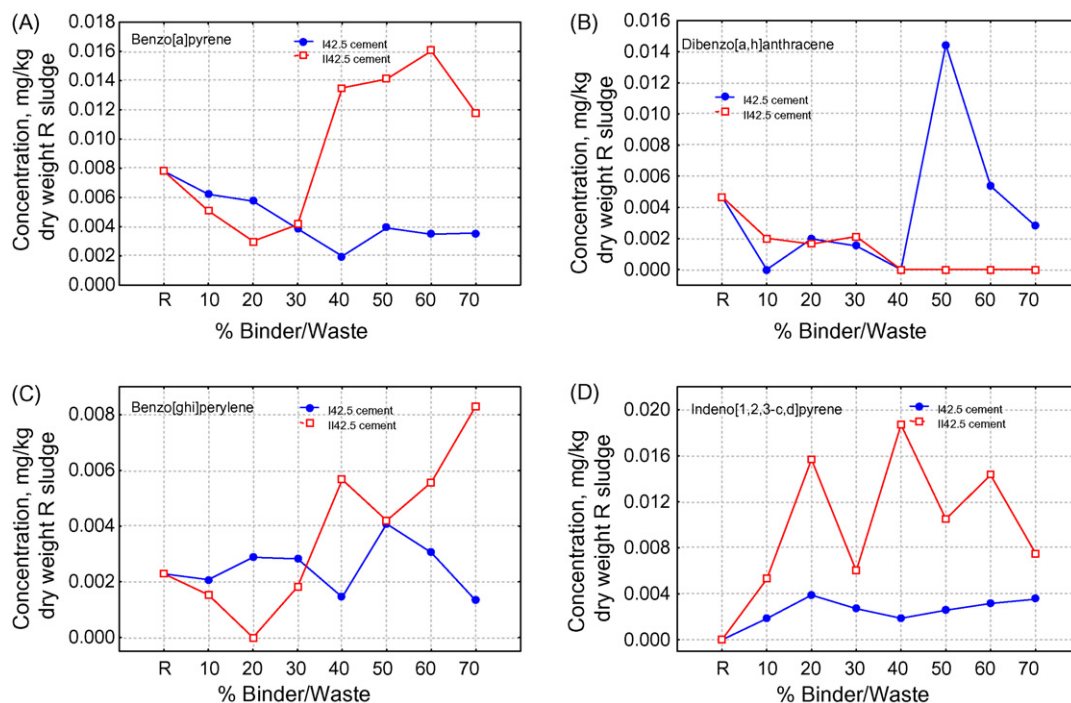
Fig. 9. Leaching behavior of individual PAHs (mg/kg dry weight of R sludge) from samples solidified with two different types of cement (I42.5 and II42.5). (A) Benzo[*a*]pyrene, (B) dibenzo[*a,h*]anthracene, (C) benzo[*ghi*]perylene and (D) indeno[1,2,3-*c,d*]pyrene.

and 70% I42.5 cement. In contrast, II42.5 acted as a stabilizer and decreased naphthalene leaching.

Leaching of acenaphthylene, acenaphthene and fluorene increased with II42.5 cement addition, more than with I42.5 (Fig. 7B–D). That is I42.5 cement-solidified samples showed better immobilizing behavior than II42.5 cement-solidified specimens. Only the R I42.5 50% sample leached 4 times larger amount of fluorene and double the amount of acenaphthylene and acenaphthene, compared to those of the oily sludge alone (Fig. 7D, B and C, respectively).

Leaching of phenanthrene from the stabilized/solidified specimens was almost unaffected by addition of both types of cement (Fig. 8A). On the other hand, anthracene was well immobilized by both I42.5 and II42.5 cement, by decreasing the amount leached from the oily sludge more than 60%. In the case of R I42.5 40% and R II42.5 20% the decrease was 90% compared to the untreated sludge (Fig. 8B).

Addition to sludge of I42.5 cement stabilized fluoranthene, pyrene and benzo[*a*]anthracene at the leaching levels of the untreated waste (Fig. 8C–E). Fluoranthene showed slight leaching reduction as the amount of the added I42.5 increased (Fig. 8C). The leaching behavior of pyrene did not change with addition of I42.5, compared with untreated oily sludge (Fig. 8D), except for R I42.5 50% sample. I42.5 cement showed good stabilizing characteristics for the benzo[*a*]anthracene by reducing the leachability by 84% for R I42.5 10% sample (Fig. 8E) and to about 50% for the rest of the specimens. As an overall leaching trend for these three compounds, the addition of II42.5 cement to the waste increased the leachability five-fold in the case of fluoranthene at the R II42.5 60% sample (Fig. 8C) and three-fold in the case of benzo[*a*]anthracene, in R II42.5 40% sample

(Fig. 8E). Increased leachability was observed for pyrene in all solidified samples with II42.5 cement (Fig. 8D).

Chrysene leaching increased with addition of both types of cement (Fig. 8F). Specimens with I42.5 Portland cement leached lower amounts of the compound than those with II42.5.

I42.5 cement seemed to be a better stabilizing agent than II42.5 in the case of benzo[*b*]fluoranthene. However, the addition of both types of cement resulted in reduction of leaching compared to the untreated sludge, by about 63% for solidified specimens with II42.5 cement and 81% for solidified specimens with I42.5 cement (Fig. 8G). A similar behavior was observed for benzo[*k*]fluoranthene (Fig. 8H). The overall leaching reduction of this compound in S/S specimens with 70% cement, both types, was 57%.

Benzo[*a*]pyrene was stabilized well with I42.5 cement but not with II42.5 cement. The I42.5 addition decreased the initial amount leached from the sludge as the addition of cement increased in the samples. Addition of II42.5 cement had the opposite effect (Fig. 9A).

Compared to untreated sludge, leaching of dibenzo[*a,h*] anthracene decreased with addition of I42.5 cement except for the 50 and 60% samples (Fig. 9B). The addition of II42.5 cement to the waste showed significant reduction of leachability. Specifically, in R II42.5 40–70% samples no dibenzo[*a,h*]anthracene was detected. The R II42.5 10, 20 and 30% specimens leached about 0.002 mg/kg, half the amount leached from the sludge alone (Fig. 9B).

Leaching of benzo[*ghi*]perylene was unaffected by the I42.5 cement addition. Most of the solidified samples leached the same amount as the sludge did. In the case of II42.5 cement addition the specimens R II42.5 10, 20 and 30% showed a slight reduction

in leachability, but the rest of the samples increased it to the level of 0.008 mg/kg (Fig. 9C). This means that the S/S process not only was ineffective in reducing, but in contrast significantly increased benzo[*ghi*]perylene leaching.

Indeno[1,2,3-*cd*]pyrene was not detected in the leachate of the oily sludge (Fig. 9D), but, it showed great leachability in both I42.5 and II42.5 solidified/stabilized specimens. The I42.5 cement was better stabilizer than II42.5 cement. For higher percent of II42.5 cement addition, a higher leachability was observed. Leaching of indeno[1,2,3-*cd*]pyrene was unaffected by the amount of I42.5 cement addition, in the range of 10–70%. The leached amount of solidified samples with I42.5 cement leveled off at 0.002–0.004 mg/kg, regardless of the percent of cement addition in the samples (Fig. 9D).

4. Conclusions

A leaching test was developed by modifying existing standard leaching tests and was applied to study the leaching behavior of hydrocarbons from refinery oily sludge S/S with cement. On the basis of this test, the following conclusions were drawn. Macroscopic observation of the stabilized/solidified samples revealed macroencapsulation of the oily sludge into cavities, formed in the cement matrix. For higher cement addition, smaller and more abundant cavities were formed. The breakage of these cavities for the leaching test resulted in increased hydrocarbon leaching with cement addition. Specifically, cement addition resulted in destabilization of the oily sludge and yielded leaching of methylene chloride extractables from 5 to 186% in excess of those observed from oily sludge alone. Similarly, excess leaching for total alkanes (TAlk) ranged from 70 to 1140% for I42.5 cement addition and from 46 to 800% for II42.5 cement addition.

All II42.5 cement-solidified samples, except for 40 and 70% stabilized/solidified specimens, showed lower leaching of *n*-alkanes compare to I42.5 cement-solidified specimens. *n*-Alkanes in the range *n*-C_{10}–*n*-C_{27} showed better immobilizing behavior than heavier *n*-alkanes. However, cement addition to the oily sludge resulted in higher leached amounts of *n*-alkanes, in every case, compared to those from untreated waste.

In general, I42.5 cement addition to the oily sludge reduced the leachability of most PAHs compared to the leaching amounts of solidified samples with II42.5 cement. I42.5 cement proved to be better stabilizer than II42.5 cement. Namely, I42.5 cement addition was more effective than II42.5 cement for acenaphthylene, acenaphthene, fluorene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*a*]pyrene and indeno[1,2,3-*c*,*d*]pyrene. The stabilized/solidified samples with II42.5 leached higher amounts of PAHs. Only 4 PAHs out of 16 compounds measured in this study showed leaching reduction with the use of II42.5 cement as stabilizing agent. These compounds were naphthalene, phenanthrene, benzo[*k*]fluoranthene and dibenzo[*a*,*h*]anthracene. Anthracene leaching was reduced by the addition of both types of cement (I42.5 and II42.5) to the oily sludge. Both types of cement showed similar leaching behavior with respect to anthracene.

Comparison of the leached PAHs between oily sludge and stabilized/solidified samples, revealed that I42.5 cement favored immobilization of acenaphthene, fluoranthene, benzo[*a*]anthracene and benzo[*a*]pyrene. Anthracene, benzo[*b*]fluoroanthene and benzo[*k*]fluoroanthene leachability were reduced by solidification of oily sludge with both types of cement, I42.5 and II42.5. Addition of II42.5 cement reduced the leachability of naphthalene and dibenzo[*a*,*h*]anthracene compared to that of the untreated sludge. However, acenaphthylene, fluorene, pyrene, chrysene, benzo[*a*]pyrene, benzo[ghi]perylene and indeno[1,2,3-*c*,*d*]pyrene escaped immobilization with the addition of both types of cement to the oily sludge. S/S process was ineffective in reducing the leachability of these compounds compared to that leached from the oily sludge itself, and in contrast significantly increased it.

Several recommendations for further research arose from this study. Due to macroencapsulation of the oily sludge into cavities, additional leaching tests must be considered, in order to understand the leaching behavior of organic constituents from solidified samples. For this case, a static leaching test applied to monolithic specimens or a flow-through leaching test would be more realistic with respect to organic compounds mobility in the environment, rather than leaching tests which destroy the cement admixture structure.

Acknowledgement

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