Oil spills debris clean up by thermal desorption

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Abstract

Oil spills represent a significant environmental issue in Brazil. This paper presents the latest results of a comprehensive experimental programme aimed at understanding how the presence of spilled oil affects the properties of sands and at studying alternatives to remediate the affected shores. Results indicate that oil causes a slight increase in grain size and uniformity, and oiled debris presents a smaller void ratio but a larger unit weight. It was also observed that effective strength parameters for both the natural and oiled debris were the same although the undrained strength of a natural sand is much higher than that of the contaminated sand. At ambient temperature, oiled debris emits methane and ammonia, and these emissions tend to increase with rising temperatures. On the other hand, the oil and grease content from oiled debris decreases with rising temperature and prolonged exposure. Finally, in situ thermal desorption seems to be a promising method for cleaning debris from oil spills. It is simple, fast and avoids all the difficulties associated with digging up the soil for disposal or cleanup.
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1. Introduction

Oil spills have represented a significant environmental issue in Brazil. For example, on 24 November 2001, a ruptured pipeline spilled 100,000 l of crude oil into Guanabara Bay, Rio de Janeiro. In spite of the spill response effort, a large slick was formed on the Bay stretching from Fiscal Island and Santos Dumont Airport, on Rio de Janeiro's side of the Bay, to Flechas Beach, on Niterói's side of the Bay.

Another event occurred on 16 February 2001, when a ruptured pipeline spilled 50,000 l of diesel fuel into the Atlantic Ocean near the City of Curitiba in Brazil's Serra do Mar region. Despite the work of over 200 people to contain the lightweight fuel, a slick stretching 10 km along the coastline of Paraná State was formed and contaminated not only the natural reserve of Mata Atlântica but also five rivers.

Brazil's worst spill in 25 years happened on 16 July 2000, when another pipeline burst at Presidente Vargas Refinery in the State of Paraná and spilled 4 million litres of crude oil. Even with the spill response effort, that contained part of the spill within the refinery, over 3.5 million litres of crude oil escaped into the Barigui River and eventually reached the Iguaçú River.

However, this was the third spill that year. In January 2000, a ruptured pipeline at Duque de Caxias Refinery (REDUC) released 1.3 million litres of oil into Guanabara Bay and a nearby protected mangrove swamp. Also, in June 2000, a much smaller spill took place in Guanabara Bay again. This time, a barge washed its tank out, dumping ca. 400 l. Later in July 2000, a pipeline carrying methyl tertiary butyl ether (MTBE) ruptured, spilling 1000 l near the town of Paracambi in Rio de Janeiro State. Finally, on 7 August 2000, 100 l of crude oil were spilled off the coast of Ceará State. These accidents were not the only oil spills that took place in Brazil over the past 2 years. Other spills have occurred, but with unidentified responsible parties.

According to USEPA [1], shoreline cleanup of inland spills usually involves lighter oils, generally refined petroleum products. Conversely, spills in marine ecosystems often involve crude oils and heavy fuel oils originating from accidents during tanker operations.

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Oil from inland tends to evaporate and degrade very quickly. Generally, such oil spills do not tend to be deposited in large quantities on banks and shorelines. On the other hand, heavier oils form a thick oil-and-water mixture called *mousse*, which clings to rocks and sand. Additionally, heavier oils exposed to sunlight and wave action also tend to form dense, sticky substances known as *tar balls*. These substances are very difficult to remove from rocks and sediments.

When oil reaches the shorelines, it tends to stick to sediments and to the surfaces of cobbles and pebbles. Depending on the efforts of the response team, it might also flow downward in the spaces between cobbles, pebbles, and sand grains, making it difficult to clean up and reducing its ability to degrade.

According to USEPA [1], natural processes and physical methods aid in the removal and containment of oil. Natural processes include evaporation, oxidation and biodegradation, whereas the most common physical processes include wiping with absorbent materials, pressure washing and raking or bulldozing [1].

This study intends to evaluate a promising technique that employs high temperatures to convert compounds, such as oil, into gas and water. Because thermal desorption produces air pollution, its emissions are also evaluated herein. The results presented in this paper are a part of a comprehensive experimental programme that is currently being carried out at the Pontifical Catholic University of Rio de Janeiro (PUC-Rio) and the State University of Norte Fluminense (UENF) to study the consequences of oil spills on shorelines. This programme aims to (1) understand how the presence of oil will affect the geotechnical properties of sands, (2) establish possible alternatives of proper disposal of oiled debris, and (3) evaluate remediation methods for the affected beaches.

2. Geotechnical background

This section describes changes in geotechnical properties of oiled debris that reached the beaches of Anil and Mauá, as a consequence from the January 2000 spill at Guanabara Bay. The oil, referred to as MF 380, has a density $0.985 \, \text{Mg/m}^3$ at $4\,^\circ\text{C}$ and a viscosity of 309.8 cP at $50\,^\circ\text{C}$.

For comparison, oil debris was removed by two different methods: solvent washing and thermal desorption. In the latter case, a clean sand was obtained after mixing the oiled debris with a solvent, and leaving the mixture of sand and oiled debris in solution for at least 7 days. After this period, the solvent was extracted from solution, disposed properly, and the sand was then washed with hot water (ca. $60\,^\circ\text{C}$) for at least 1 h and dried overnight in a conventional geotechnical oven. In the former case, oiled debris was subjected to $270\,^\circ\text{C}$ under a thermal blanket for 100 h. Owing to space limitations, only the effects on the physical indices are discussed here.

2.1. Physical Indices

As Fig. 1 shows, oil coats the individual sand grains, and causes a slight increase in grain size and uniformity of natural sands. As shown by the grain size distribution curves, all sands are poorly graded with virtually no fines. The cleaned sands are classified as SP according to the Unified Soil Classification System. It can also be seen from Fig. 2 that the sand treated by thermal desorption contains more fine sand than the one obtained from solvent extraction. On the other hand, as Table 1 shows, a slight increase in grain size and uniformity due to the mixing of oil is observed for the contaminated material.

The results suggest that the exposure to high temperatures might lead to breaking of sand-sized particles. Fig. 3, which
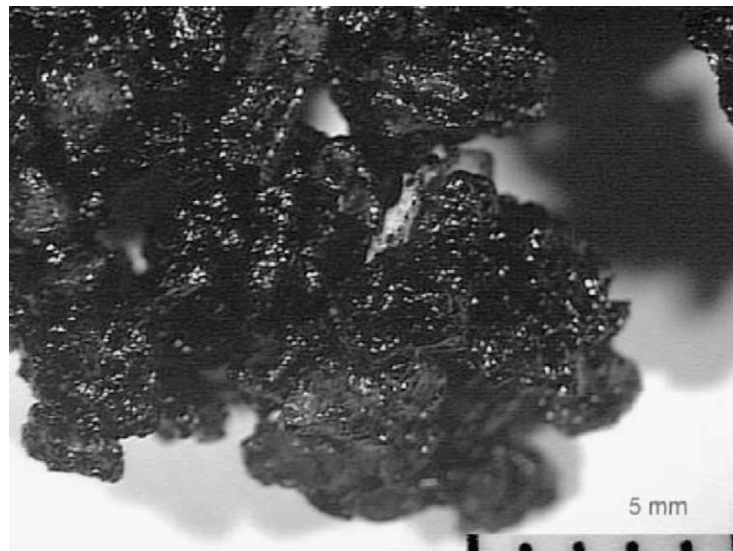

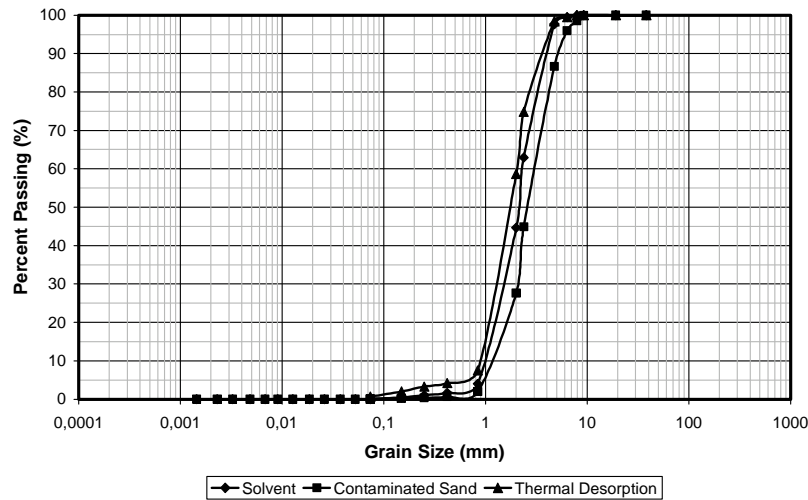Fig. 1. Photograph taken from the contaminated material using an optical microscope.

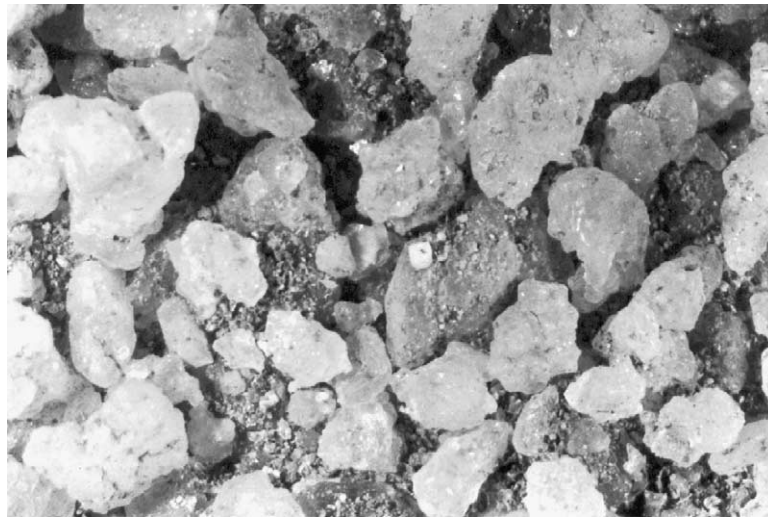Fig. 2. Grain size distribution curves.

Fig. 3. Photograph of the cleaned debris by thermal desorption.

is a photograph taken from oiled debris just after cleaned by thermal desorption using an optical microscope, shows that the finer particles present the same mineralogical composition as the coarse fraction. This indicates that the fines are not transported and supports the aforementioned assumption.

On the other hand, as shown in Fig. 4, the solvent cleaning process washes out all the fines. However, the difference is so small that it can be neglected for practical purposes.

When weight–volume relationships are of concern, it is observed that oiled debris presents a smaller void ratio but a larger unit weight when compared to the cleaned sand.

Regarding maximum and minimum unit weight (γ) and void ratio (e), a significant difference in the values is obtained depending on if the materials are oven-dried or not prior to the determination. As Table 2 shows, the difference in the determined values of unit weight and void ratio for both materials are much closer when they are subjected to oven-dry prior to testing.

The authors believe that the debris was *weathered* due to the exposure to temperatures close to 100 °C. In such an environment, volatile compounds evaporate, leaving just the heavier residues. Such an belief is supported by the fact

Table 1
Summary of physical indices

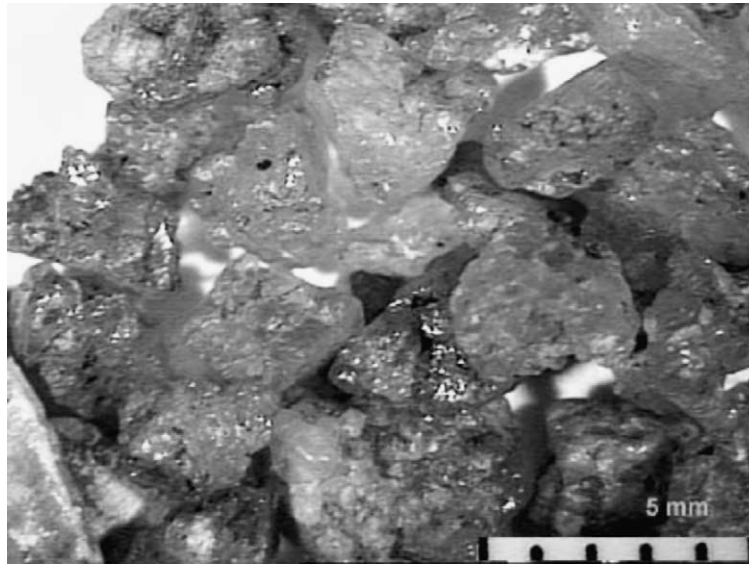| Index	Cleaned sand	Contaminated sand
Particle density (G_s)	2.66	2.65
D_{10} (mm)	1.01	1.20
D_{15} (mm)	1.15	1.43
D_{30} (mm)	1.58	2.05
D_{50} (mm)	2.11	2.67
D_{60} (mm)	2.32	3.24
D_{85} (mm)	3.89	4.66
Uniformity coefficient, C_u	2.3	2.7
Coefficient of concavity, C_c	1.1	1.1
Unified soil classification	SP	Not applicable

Fig. 4. Photograph of the cleaned debris by solvent washing.

that it was much easier to crumble the clods after the contaminated material was removed from the oven than before its exposure to high temperatures. Tests performed on these samples using a small thermal desorption unit also support this belief. On average, the oil and grease content of the debris were reduced from ca. 6% at 25 °C to less than 2% at 100 °C [2].

From the viewpoint of geotechnics, the values determined when the materials are not oven-dried are considered as being more representative, and were those used as reference in the experimental programme.

2.2. Strength characteristics

The entire experimental programme included the determination, at three different densities (maximum, minimum and intermediate one) of: (1) permeability by the constant head method using flexible-wall permeameters, (2) compressibility parameters by the step-loading method using oedometers and triaxial cells, (3) strength parameters using the direct shear test and the triaxial test. Owing to space limitations, only the results of isotropically consolidated, undrained tests, performed using both the natural and contaminated sands at the maximum density, are presented here.

Table 2
Summary of void ratio and unit weight

Index	Oiled debris oven-dried	Oiled debris	Sand oven-dried	Sand
e_{max}	0.95	0.68	0.8	0.94
e_{min}	0.88	0.63	0.68	0.76
γ_{max} (kN/m^3)	13.7	16.3	15.9	15.2
γ_{min} (kN/m^3)	14.1	15.9	14.8	13.7

Note: e_{max}, maximum void ratio; e_{min}, minimum void ratio; γ_{max}, maximum unit weight; γ_{min}, minimum unit weight.

The triaxial tests were performed with pore pressure measurements on both materials, following procedures recommended by Head [3]. The specimens, with a 38 mm diameter and a 76 mm height, were saturated by backpressure, allowed to consolidate at effective stresses ranging from 25 to 200 kPa, and sheared at a constant rate of 0.08%/min.

Test results reveal that the effective stress strength parameters for both the natural and the contaminated sand were the same (i.e., $c' = 0$ and $\phi' = 28.1°$). On the other hand, the undrained strength of the natural sand is much higher than that of the contaminated one.

3. Thermal desorption experiments

This section gives an insight on thermal desorption and presents the results of the experimental programme aimed at identifying the gas emissions performed at the State University of Norte Fluminense and at cleanup experiments by offsite and in situ methods conducted at PUC-Rio.

3.1. Background

Thermal desorption removes pollutants from soil and other materials by using heat to change the chemicals into gases [4]. In a conventional unit, these gases are collected with special equipment, the dust and the harmful constituents are separated and treated adequately.

Thermal desorption speeds the cleanup of many pollutants from the ground. A faster cleanup generally leads to lower costs. Additionally, thermal methods can work in some soils, e.g. clays, where the majority of the currently available methods do not perform well [5]. On the other hand, when in situ methods are applied, the costs associated with digging up the soil for disposal or cleanup are avoided.
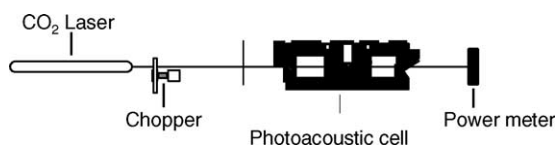
Fig. 5. Experimental arrangement for photoacoustic spectroscopy.

In situ thermal desorption employs electrical resistance heating either on the surface or through wells made of steel. The heat from the current converts groundwater and the water in the soil to steam, which evaporates the harmful chemicals [5]. These gases are then collected and properly treated.

According to the USEPA [5], cleaning soil and groundwater using thermal methods may take from only a few months to several years. The length depends on three major factors that are site specific:

- type and amounts of chemicals present,
- size and depth of the polluted area, and
- type of soil and conditions present.

Since marine shoreline areas are important public and ecological resources, and oil tends to evaporate very quickly, it seems reasonable to employ thermal methods to restore their cleanliness and beauty.

However, there are some complicating factors. First, when oil reaches sandy banks, it tends to flow downward into the sand, making it difficult to clean up and reducing its ability to degrade. Second, sand minerals (i.e. quartz and feldspars) do not possess good thermal conductivity. Finally, resulting emissions are greenhouse gases.

3.2. Gas emissions

The composition of gas emissions was determined by the use of two different techniques at both 25 and 50 °C. The first method to determine the gas composition employed an infrared gas analyser (URAS 14 from Hartman and Braun), which allowed for the detection of small molecules such as those for CO, CO_2, SO_2, CH_4 and NH_3. The second method of determination is based on the photoacoustic method. This technique, shown schematically in Fig. 5, is based on pressure changes around the sample that are induced by vibrational–rotational excitation of molecules and, subsequent, relaxation by collisions. The pressure change is detected by one microphone placed inside a resonator pipe of a photoacoustic cell through which the air sample, containing the molecules under consideration, flowed. An acoustic signal is produced by modulation of the excitation laser beam at the pressure frequency of 1600 Hz of the cell. A continuous CO_2 wave infrared laser, tuneable over about 80 different lines between 9 and 11 μm, was employed as the excitation source. Within this spectral region, many small molecules show an unique fingerprint.

Infrared gas analysis (URAS) detected concentrations for CH_4 and NH_3 of 1.2 and 43 ppm, respectively, at 25 °C. With
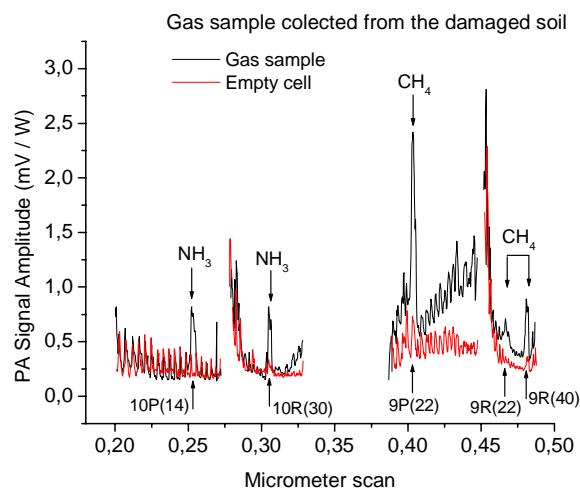

Fig. 6. Photoacoustic absorption spectrum.

an increase of temperature to 50 °C, the rate of gas emission was activated resulting in an increase of the concentration of methane to 4.8 ppm and of ammonia to 126 ppm, showing a differential increase of the emission rate for each gas species.

Photoacoustic absorption also detected methane and ammonia as shown in Fig. 6. Strong absorption lines can be seen at 949.5 cm^{-1} (10P14), 982.1 cm^{-1} (10R30), 1045.1 cm^{-1} (9P22), 1080.0 cm^{-1} (9R22) and 1090.0 cm^{-1} (9R40). The absorption lines 10P14 and 10R30 are associated with NH_3 whereas the absorption lines 9P22, 9R22 and 9R40 are associated with CH_4, showing thus a very good agreement with those results obtained by URAS technique.

3.3. Offsite thermal desorption

Offsite experiments were performed in a small unit shown in Fig. 7. This unit, described in Araruna et al. [6], was used to assess two important parameters for cleanup: temperature and time of exposure. Tests were conducted on 50 g samples of oiled debris subjected to temperatures ranging from 100 to 500 °C and times of exposure ranging from 2 to 8 h. The unit was installed inside a hood in a temperature-controlled room.

The effectiveness of the method was assessed via the total oil and grease (TOG) content of the samples exposed to the different temperatures. Analyses were performed by an Infracal Total Oil and Grease/Total Petroleum Hydrocarbon Analyser (TOG/TPH). This analyser measures the absorption of an extract at two wavelengths, one wavelength that is strongly absorbed by hydrocarbons (the analytical wavelength) and another wavelength at which there is very little absorption (the reference wavelength). The logarithm of the ratio of the energy at the reference wavelength to that at the analytical wavelength is the absorbance, which is proportional to the concentration and pathlength of the absorbing sample. Since the pathlength is held constant by the analyser, the calculated absorbance varies only with the oil
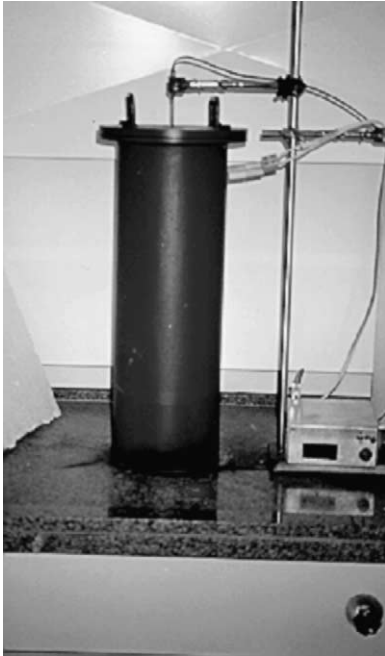
Fig. 7. Offsite thermal desorption unit.

Fig. 9. In situ thermal desorption unit.

concentration. Measurements were carried out by employing a simplified extraction method, using perchloroethylene (PCE) as the extraction solvent, followed by a rapid and convenient evaporation and infrared measurement.

Fig. 8 shows that the oil and grease content decreases markedly with increasing temperature. When comparisons are made on the basis of time of exposure, a decrease in oil and grease content is expected with increasing exposure. However, the results were somewhat erratic indicating that sample heterogeneity is likely to have caused some deviations from this pattern.

It is clear from Fig. 8 that the exposure to temperatures above 450 °C virtually eliminates any trace of oil from the debris.

3.4. In situ thermal desorption

In situ thermal desorption experiments were performed by the system described in Portes [2]. This system, shown in Fig. 9, consists of a thermal blanket positioned on the top of a refractory masonry tank.

The mini thermal blanket, 415 mm wide by 425 mm long, consists of a metal container made of 316 stainless steel sheets, each 1 mm thick, where two heating elements are placed on riveted hinges. As Fig. 10 shows, a 15 mm opening is left between the elements to allow gas emissions to flow through the 25 mm exhaust tube and filter system. Two 316 stainless steel holders were riveted at opposite ends to improve the mobility of the blanket.
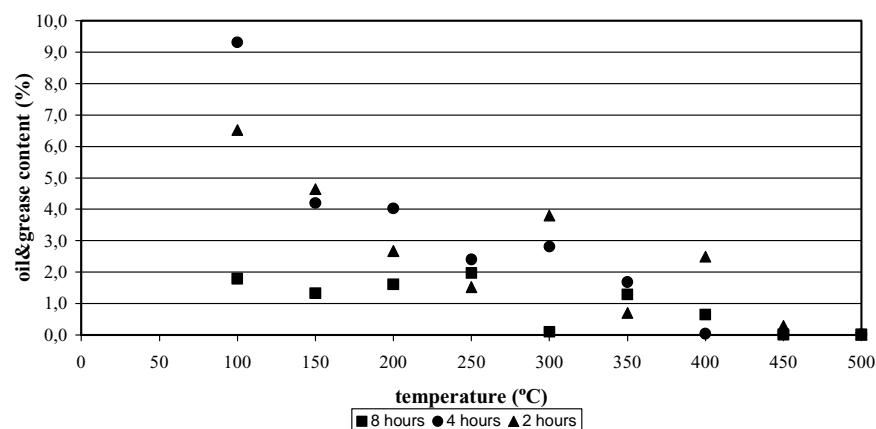

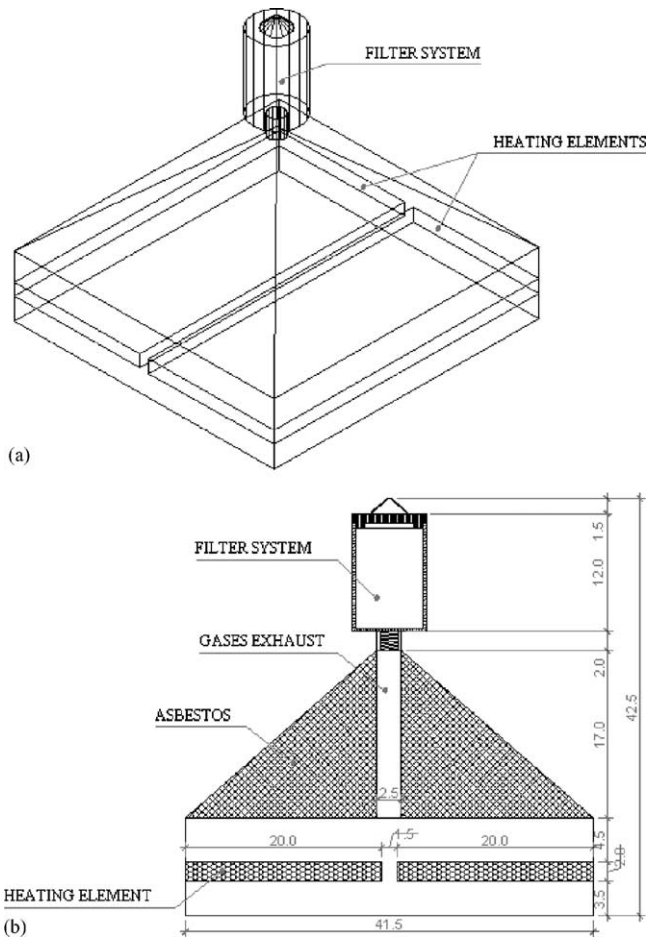Fig. 8. Offsite thermal desorption results.

Fig. 10. Thermal blanket: (a) aerial view and (b) cross-section dimensions are in centimetres (not to scale).

Each heating element, shown in Fig. 11, is capable of heating up to 1200 °C and has 200 mm in width and 400 mm in length. It is ceramic insulated in order to operate in the radiant temperature region thereby minimising heating time. Its properties are presented in Table 3.
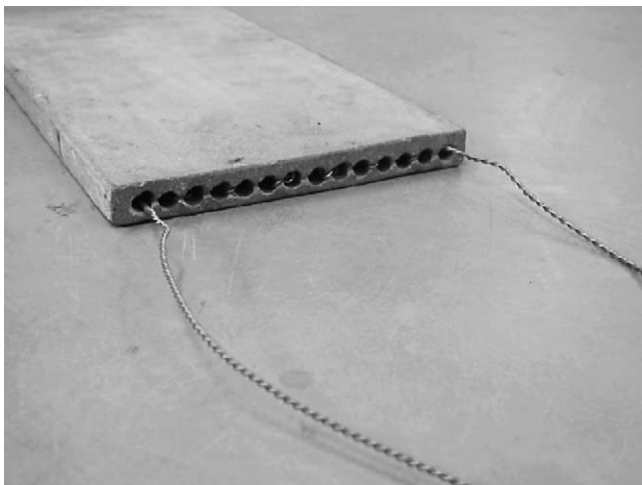
Table 3
Heating element properties

Resistance (Ω)	20
Voltage (V)	220
Current (A)	11
Power (W)	2420

Thermal insulation is provided by loose asbestos particles housed in a chamber located between the heating elements and the filter system. The chamber is airtight due to environmental concerns associated with the nature of asbestos.

The filter system consists of an aluminium chamber that is screwed to the top of the blanket. Inside the chamber, four layers of a hydrophilic paper are placed at its bottom to filter any particulate matter. Above the filter, loose activated carbon particles adsorb emitted gases. Electrical power is supplied to the heating elements, linked in a parallel configuration, at ordinary 60 Hz power-line frequencies with three-phase configuration.

Temperature is set and controlled by a unit that receives information through a thermocouple (K-type) positioned at any desirable location in the tank. This set up helps with overcoming problems associated with the relatively low thermal conductivity properties of sands. During tests, as Fig. 12 shows, temperature is monitored by a set of five thermocouples (K-type) positioned 14 cm (point A), 20 cm (point B), 28 cm (point C), 34 cm (point D) and 41 cm (point E) from the surface of the tank. At convenient time intervals, a portable logger scans and stores the readings of all five thermocouples, which are subsequently downloaded to a personal computer through a RS 232-C communication port.

Fig. 13 shows the temperature profile during a typical experiment where the control thermocouple is positioned right below the surface of the debris. At early stages, the temperature is increased to 60 °C to burn all organic matter and to reduce moisture, and then it is increased incrementally in steps to avoid carbonisation of sand particles. This
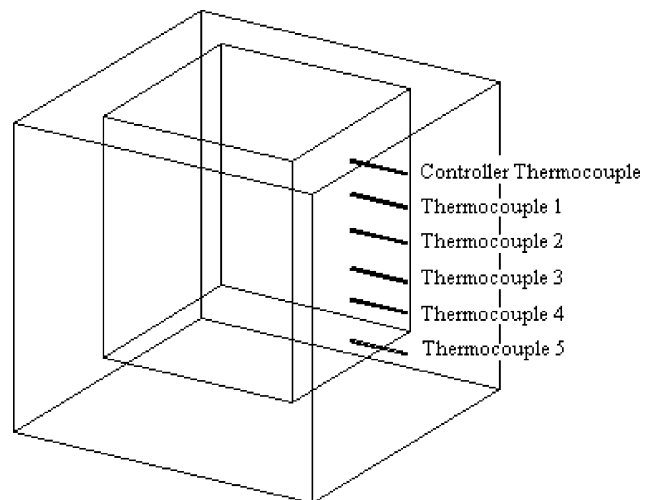

Fig. 11. Heating element.
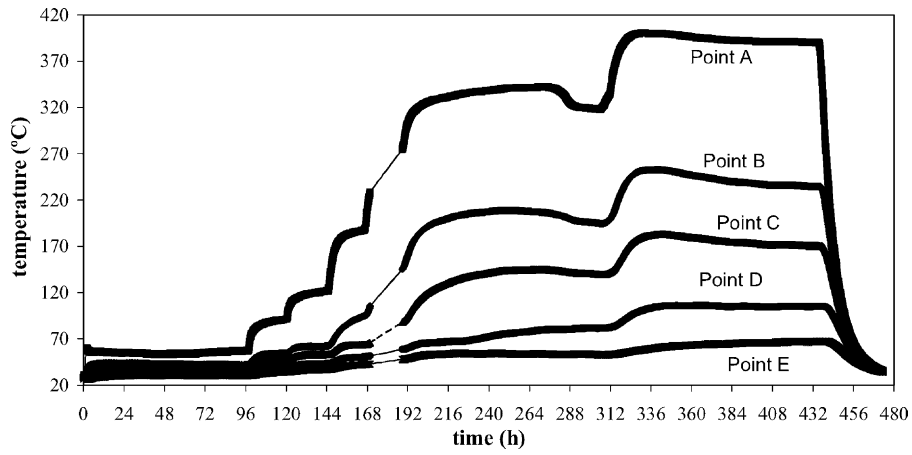

Fig. 12. Schematic diagram of temperature monitoring during tests.

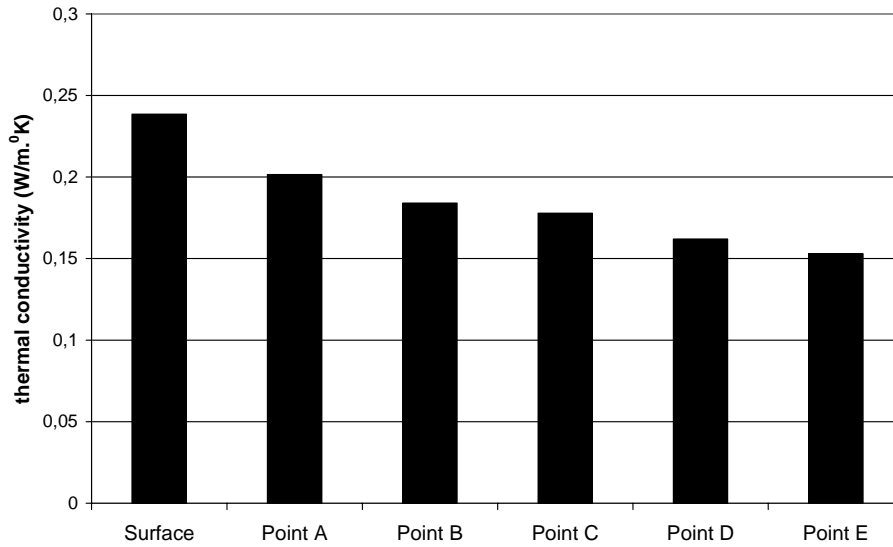Fig. 13. Temperature profile of a typical in situ experiment.

Fig. 14. Thermal conductivity at the end of the test.

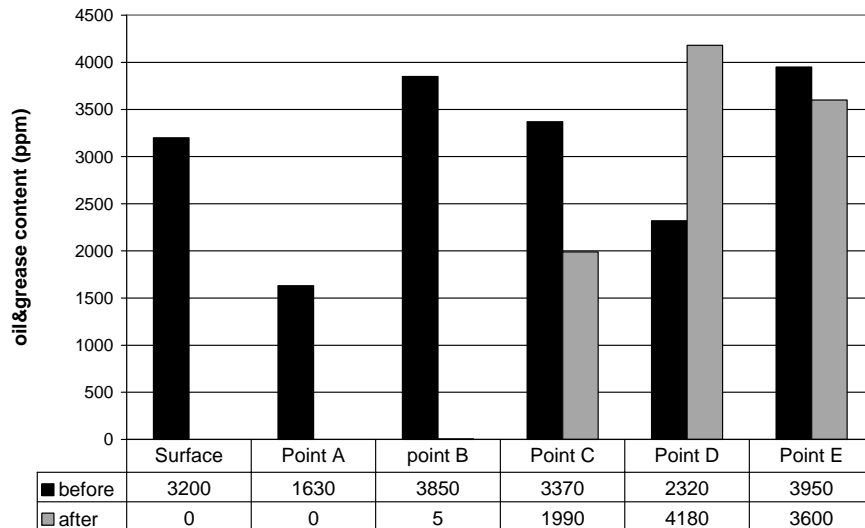|	Surface	Point A	point B	Point C	Point D	Point E
before	3200	1630	3850	3370	2320	3950
after	0	0	5	1990	4180	3600

Fig. 15. Oil and grease content from samples collected at different depths in the masonry tank.

procedure is rather time consuming, but necessary for restoring not only the cleanliness of sands but also their beauty.

As Fig. 13 shows, temperature is drastically dissipated through the debris. Temperature falls from ca. 400 to less than 80 °C through a layer of only 27 cm of sand. This behaviour could well be associated to the thermal conductivity of the debris that is varying during the test.

To investigate this possibility, a series of five tests on samples at different depths was carried out using a thermal conductivity probe FP A437-1 from ALMEMO®. This device employs a heatable probe that feeds a constant heat flow into the material until a balance is established between thermal energy being passed into and thermal energy dissipating from the material. The resulting difference in temperature is a measure for the thermal conductivity.

As Fig. 14 shows, the thermal conductivity obtained from the average results from the five tests decreases with depth. This trend suggests that the oil coating is responsible for some reduction of this property.

The effectiveness of the in situ experiment was assessed via the TOG content employing the same methodology of the *offsite* experiments. It can be seen from Fig. 15 that the oil coating was virtually removed from a depth of up to 20 cm. Below this point, the results indicate in general that the test was not as effective as near the surface since, as shown in Fig. 13, the temperature in the masonry tank sharply decreased. As a result of the non-uniform distribution of temperature inside the tank, only the debris that is subjected to temperatures above 300 °C is cleaned up.

This problem can be overcome, to some extent, by placing the control thermocouple at the desired depth. The costs associated with this assemblage will certainly increase since the temperature of the soil above will be higher than the desired temperature. This is a serious shortcoming for this
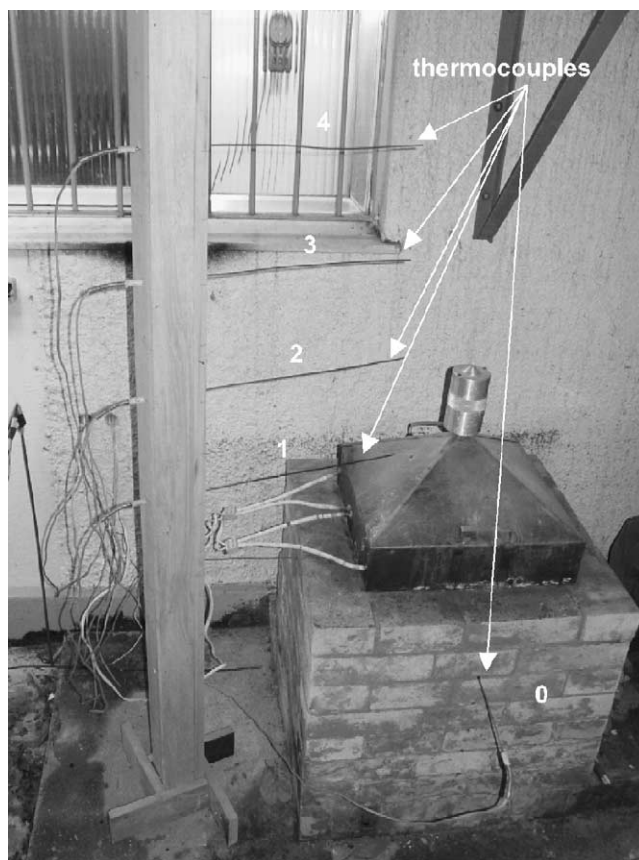

Fig. 17. Insulation assessment test set up.

kind of system, limiting its application for cleaning up subsurface contamination.

Nonetheless, this system appears to be unique for cleaning debris from oil spills. It is clear from Fig. 16 that all traces of oil have disappeared from the debris. Fig. 16 also shows

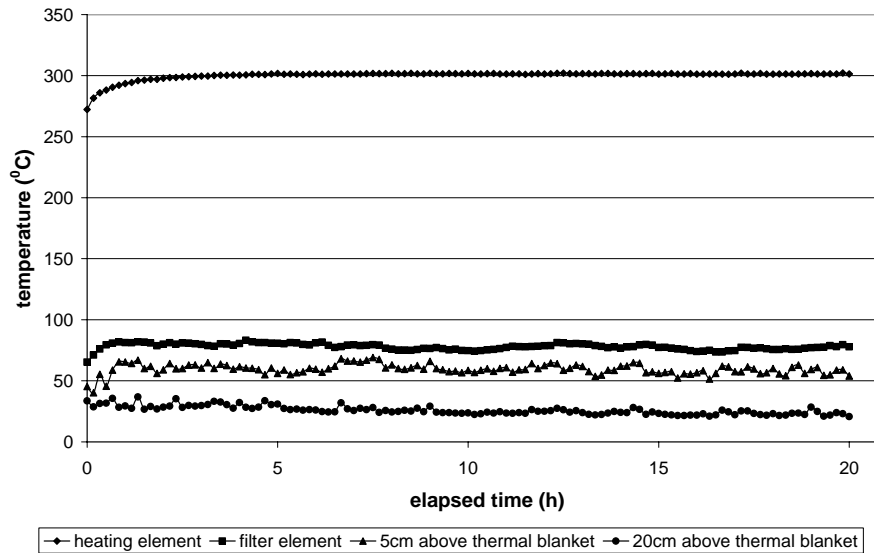Fig. 16. Cleaned debris by in situ thermal desorption.

Fig. 18. Temperature profile on a typical insulation assessment test.

that the natural colour of the sand was not fully restored, but rather the sand became more reddish due probably to heat excess exposure. However, when we compare the results of cleaned debris from thermal desorption (Fig. 3) to solvent washing (Fig. 4), we find that the latter process is more appropriate for restoring the sand to its natural appearance.

Finally, a series of tests was performed in order to assess the insulation provided by asbestos employing a set up shown in Fig. 17. Tests results show on average an increase of 20 °C in ambient temperature at a position 5 cm above the blanket as indicated in Fig. 18. On the other hand, no elevation in ambient temperature was measured by the three thermocouples positioned above 20 cm of the blanket, e.g. thermocouples 2, 3 and 4. The temperature inside the filter system was also measured. As Fig. 18 shows, average temperatures were around 80 °C, and do not compromise either the integrity of the filter papers nor the activated carbon particles.

4. Conclusions

This paper presents the latest results of an experimental research programme that is being carried out at PUC-Rio and UENF to assess in situ remediating methods for cleaning up debris from oil spills.

Oil causes a slight increase in grain size and uniformity of natural sands since it coats individual sand grains and the sand develops an apparent cohesion. It was also observed that oiled debris has a lower void ratio but a higher unit weight when compared to uncontaminated natural sands.

Oiled debris emits methane and ammonia at ambient temperature, and these emissions tend to increase with increasing temperatures. On the other hand, the oil and grease content from oiled debris decreases with increasing temperature and prolonged exposure.

Finally, based on bench tests performed with controlled conditions, thermal desorption is a promising technique for cleaning debris from oil spills. The technique is simple and fast and, when applied in situ, will avoid all the difficulties associated with digging up oiled debris for disposal or cleanup.

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