



## Thermal treatment of soils contaminated with gas oil: influence of soil composition and treatment temperature

Juliana Piña, Jerónimo Merino, Alberto F. Errazu, Verónica Bucalá\*

*PLAPIQUI (UNS — CONICET), Camino La Carrindanga, Km 7 (8000), Bahía Blanca, Argentina*

Received 5 December 2001; received in revised form 13 March 2002; accepted 22 March 2002

### Abstract

Samples of two soils containing different organic matter contents, neat or contaminated with gas oil (diesel fuel oil) at 2.5 wt.% were heated from room temperature to different final temperatures (200–900 °C). The experiments, performed in an anaerobic media, simulate conditions pertinent to ex situ thermal desorptive and thermal destructive treatments. The products generated during the heating were collected and light gases were analyzed by gas chromatography. The results indicate that the chemical composition of the soil is a key factor since it strongly influences the quantity and composition of the off-gases. According to the liquid and light gas yields, the gas oil does not affect appreciably the generation of pyrolysis products of the own soil constituents and the gas oil does not suffer significant chemical transformations even at high operating temperatures (e.g. 900 °C). With surface areas of 16 000 cm<sup>2</sup>/g (Soil A) and 85 000 cm<sup>2</sup>/g (Soil B) based on the monolayer adsorbed model, 4 and 20%, respectively, of the original gas oil can be adsorbed. These values are in good agreement with experimental data. Even for high temperatures, the employed thermal treatment is capable to practically remove the gas oil from the soil bed without changing appreciably the original chemical composition of the contaminant.

© 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Soils; Gas oil contamination; Thermal desorption; Soil cleanup; Thermal destruction

### 1. Introduction

Contaminated soils exist in many industrial sites, gas plants, oil refineries, etc. To date, thermal processes have been the primary means for decontaminating such solid wastes [1,2]. In particular, thermal treatment of waste soil in anaerobic conditions has been suggested as an environmentally acceptable method for decontamination [3–5]. Adequate treatment

\* Corresponding author. Tel.: +54-291-4861700x265; fax: +54-291-4861600.

E-mail address: vbucala@plapiqui.edu.ar (V. Bucalá).

times and temperatures can provide enough energy to desorb or crack the pollutants. The contaminants and the cracking products generated by the contaminated soil can be subsequently recovered by condensation.

Several studies have been performed to understand the fundamentals of the contaminant release from soils. Full-scale performance predictions require a combination of small-scale data and computer modeling [6]. Different treatability test equipment, such as thermogravimetric analyzers [5,7], quartz tube furnaces [8], rotary reactors [6,9], modified gas chromatographs [10,11], among many other devices, has been used to obtain data that can be scaled up to predict residual concentrations in large units. Based on systematic parametric studies, the operating conditions for the equipment, the contaminant, and the soil characteristics have been found as key factors that affect the performance of thermal treatment systems. The soil temperature, treatment time, and heating rate have been recognized to influence the decontamination processes [12–15]. The effects of contaminant type and contamination level on the removal efficiency have been studied by several authors [13,16,17]. Particle size, moisture content, organic and inorganic carbon contents influence the application of thermal treatments [12,17]. Pershing et al. [6] and Saito et al. [15] have reviewed important studies concerning the fundamentals of hydrocarbon thermal desorption and destruction.

Although significant advances in understanding soil thermal decontamination have been achieved, needs still exist in the areas of: (a) experimental information on thermal treatments of different soil/contaminant systems and (b) the influence of the treatment operating conditions on the removal efficiency and mechanism, and on the rate and yields of gaseous and liquid products. Particularly, systematic studies about the role of the soil in the generation of volatiles derived from thermal treatment of contaminated soils (i.e. products of pyrolysis and/or oxidation of soil substances or contaminants) and the fate of complex mixtures can enhance our current knowledge relating to thermal remediation. The present work focuses on the thermal treatment of soils with different organic matter contents impacted with commercial gas oil (diesel fuel oil). The decontamination process involves soil thermal treatment from room temperatures up to different final temperatures.

The overall goal of this study is to evaluate the chemical and physical processes relevant to thermal removal of gas oil from soils, simulating conditions pertinent to *ex situ* anaerobic thermal desorption and thermal destruction treatments. The specific objectives are to: (1) elucidate effects of treatment conditions on the decontamination efficiency and the quality and quantity of the products generated during thermal treatment; (2) to evaluate the influence of the soil on the product yields and (3) to understand the primary mechanisms that govern contaminant removal from the soil matrix, particularly at high temperatures.

## **2. Methods and materials**

Two types of soil were used in the present work: (a) natural soil obtained from the north zone of Bahía Blanca-Argentina (Soil A) and (b) a biohumus soil (Soil B). These samples were selected to represent two soils with different organic matter contents. Total carbon contents (TOCs) of 0.47 and 15.13 wt.%, and organic carbon contents of 0.30 and 14.69 wt.% were determined for Soils A and B, respectively. TOC were determined, elsewhere, by total oxidation of the samples and measurement of the CO<sub>2</sub> generated. The organic carbon content

was determined in a similar way as the TOC, using soil samples previously treated with HCl 1:1 to remove the carbonate carbon. Samples of both soils were size fractionated, and particles in the 210–297  $\mu\text{m}$  sieve diameter range were selected for the present study. The soils were conditioned during 15 days in a desiccator, at room temperature and at a constant relative humidity of 8.24% provided by a saturated solution of sodium hydroxide. Moisture contents of 0.73 and 5.5 wt.% for Soils A and B, respectively, were determined by drying at 110 °C until they reached a constant weight. Samples of neat soils were artificially contaminated with commercial gas oil (diesel fuel oil) at 2.5 wt.%. The density and boiling range for the gas oil used in the experiments are shown in Table 1. The distillation data are in good agreement with the boiling ranges at atmospheric conditions reported in the literature for gas oil from different sources [18,19].

Fig. 1 shows the apparatus employed for the soil heating experiments. The main section of this equipment is an insulated electric oven (Fig. 1a). In a typical experiment, a soil mass around 10 g is placed in the central 16 cm of a quartz tube (length = 85 cm, internal diameter = 0.8 cm) (Fig. 1b). At 77 cm from one end of the quartz tube, a small piece of porous refractory brick (1 cm long) is located to prevent soil spilling during the loading process. A type-K thermocouple is axially inserted through the quartz tube up to the middle of the soil bed. A thimble of stainless steel mesh is securely located in the thermocouple at approximately 8 cm from its free end. This thimble and the porous refractory brick plug, which allows the gases to flow, prevent particle movement through the bed. Once the soil is loaded, the quartz tube is connected to a movable arm that introduces the soil bed into the oven. To collect the liquid products, a quartz tube was welded to the main tube joined to a collector vial (Fig. 1b). The liquid vial is maintained at 0 °C to allow the condensation of the off-gases. The low boiling point gases (light gases), which pass through the liquid trap, are trapped in a 5000  $\text{cm}^3$  glass flask for the duration of the soil thermal treatment (Fig. 1a).

Clean and contaminated soil samples were separately subjected to treatments at different preselected final temperatures. A constant flow of helium was used during the experiment. The experimental procedure was designed to simulate a sudden discharge of soils in a heated

Table 1  
Gas oil properties

Contaminant property	Value
Density ( $\text{g}/\text{cm}^3$ )	0.8354
Boiling range (°C)	
IBP	169
10%	200
20%	220
30%	241
40%	260
50%	278
60%	297
70%	316
80%	337
90%	362
EBP	392

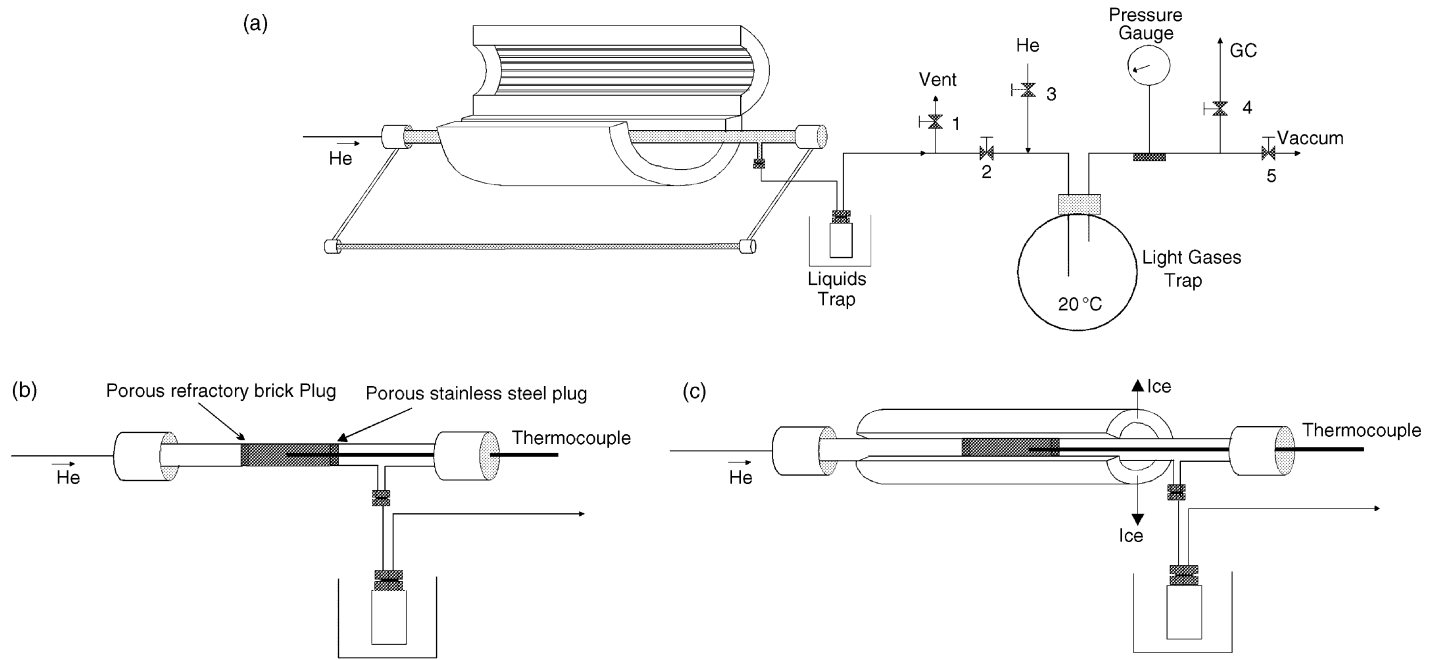


Fig. 1. Schematic representation of the experimental apparatus.

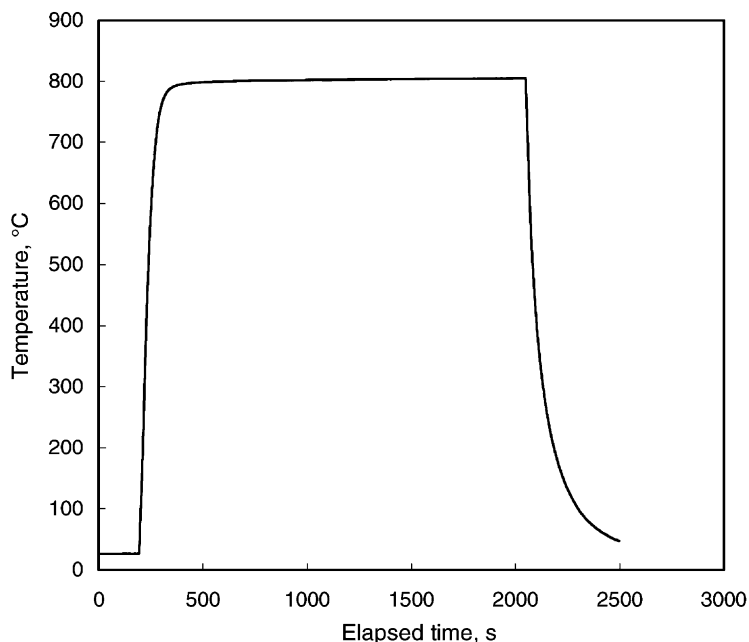


Fig. 2. Typical temperature–time profile obtained in the experimental apparatus.

inert environment. This experimental setup, which has similar features to the Quartz Tube Furnace [2], can mimic a section of bed solids as they move through a rotary indirectly-fired kiln by correlating the distance (or residence time) in the rotary kiln equipment with the treatment time in this experimental setup. In fact, the experimental soil residence times and the solid temperature profiles (see Fig. 2) are very close to those reported for a pilot-scale rotary kiln [20].

In a typical experiment, the soil bed (at room temperature, i.e. outside the oven) is purged with helium at  $0.933 \text{ cm}^3/\text{s}$  (STP) (fixed by a mass flow controller) for 900 s to ensure good air removal. For contaminated samples, the quartz tube is cooled to minimize evaporation of gas oil during the purging. The cooling is performed by using an annular insulated tube filled with crushed ice (Fig. 1c). The collector for light gases is flushed several times to remove the original air. A flush involves filling the glass flask to a pressure of 149.6 kPa and then evacuating the collector to 4.8 kPa using a mechanical vacuum pump. After purging, ice is added to the liquid trap Dewar flask, the valve (#2) connecting the liquid and light gas traps is opened (Fig. 1a), and steady helium flow is established through the soil bed. The downstream pressure varies from initially 4.8 kPa to approximately 149.6 kPa after completion of the treatment. By using the movable arm, the soil bed is introduced into the oven for thermal treatment.

The soil bed temperature, for a given time, is practically constant along its length. The axial thermal profile of the bed was measured for different oven temperatures. In all cases, temperature deviations relative to the temperature measured in the center of the soil bed

were less than 1.1%. For a given temperature, the solids undergo a relatively rapid heating where the temperature increases initially linearly with time and then achieves an equilibrium temperature, for a total heating time of approximately 35 min (close to the minimum value recommended for indirect-heated desorber units [2,21]). Finally, the soil bed is removed from the oven and cooled by natural convection.

An example of the temperature histories achieved in the thermal treatment system is shown in Fig. 2. A wide range of temperatures (200–900 °C) was selected for final treatment temperatures. This temperature range, which may be considered high relative to the boiling range of the contaminant, was chosen because there is limited information about the adsorption/desorption kinetics of the gas oil on the studied soils, and because many sites are contaminated with complex mixtures that require high temperatures to improve the removal efficiency of all the compounds (especially the heavier ones). Moreover, the results for the clean soil samples (i.e. without contaminant) can be extended to those processes for which the removal of other contaminants from similar soil matrices is required.

The soil weight loss was determined as the weight difference between the soil loaded and the soil residue (after thermal treatment) collected from the quartz tube. The accumulated liquids were determined gravimetrically as the weight increase of the liquid vials. Yields of light gases (CO<sub>2</sub>, and C<sub>1</sub>–C<sub>3</sub> hydrocarbons) were quantified by using a HP 4890D gas chromatograph.

### 3. Results and discussion

The effect of final temperature on the weight loss of neat and contaminated samples of Soils A and B is shown in Fig. 3. To compare the weight loss values, the neat soil data were multiplied by 0.975 to properly represent the contribution of the neat soil to the total weight loss of contaminated samples (i.e. 100 wt.% contaminated soil = 97.5 wt.% neat soil + 2.5 wt.% gas oil).

Neat Soil A, even for high final treatment temperatures, shows relatively low weight loss. The low moisture, organic and inorganic carbon contents of this sample justify the limited generation of volatiles found even for high temperatures. Due to the presence of gas oil, the contaminated samples exhibit higher weight loss than the uncontaminated soil for the entire temperature range studied. For Soil A, the neat and contaminated soil data show the same increasing trend as the temperature augments. In fact, the weight loss difference between both curves is almost constant for final temperatures in the range of 300–900 °C, and very close to the contamination level.

Fig. 3 indicates that Soil B shows high weight loss percentages even at low and moderate temperatures. The high generation of volatiles from this soil can be explained in terms of its elevated organic matter content. The humic substances can be cracked even at moderate temperatures, releasing liquid and gaseous products. In fact, for heating rates around 0.2–100 °C/s, the evaporation and thermal degradation of different humus types occur approximately in the temperature range of 200–650 °C [22–26]. Greater quantities of organic material are evolved for temperatures and treatment times lower than 500 °C and 600 s, respectively [23,24]. Soil B exhibits a weight loss of approximately 25 wt.% for a treatment temperature of 500 °C. Taking into account the organic nature of this soil and the knowledge

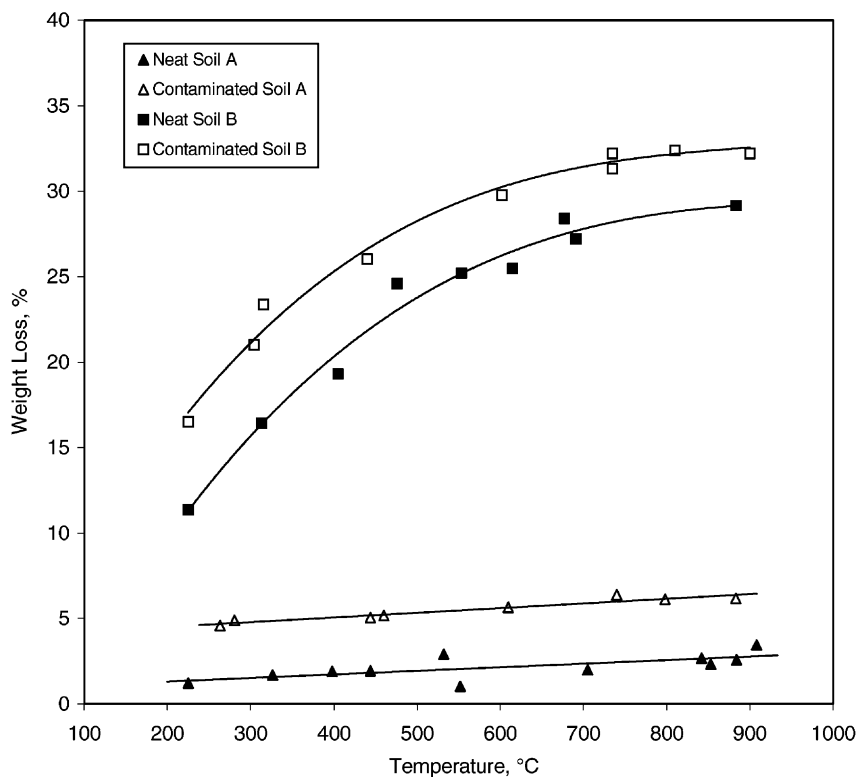


Fig. 3. Weight loss exhibited by Soils A and B as function of temperature. Curves are trend lines.

that common soil carbonates can not decompose at temperatures lower than 500 °C, Soil B may lose as high as 19.5 wt.% as a consequence of thermal degradation of organic substances (the soil moisture content is 5.5 wt.%). Considering that the ratio of soil organic matter to organic carbon content can be assumed close to a factor of 2 [27,28], the organic matter content of Soil B could be approximately 29.4 wt.%. The ratio  $19.5/29.4 = 66\%$  represents the organic matter decomposition level achieved for temperature lower than 500 °C. This result is in good agreement with the percentages found for thermal degradation of humic substances subjected to similar operating conditions [24,25].

The contaminated Soil B presents higher weight losses than those obtained for the neat soil as a consequence of the gas oil removal (Fig. 3). For Soil B, both curves follow the same increasing trend with temperature, differing by almost a constant factor close to the contaminant level. This observation suggests, as it happens for Soil A, high removal of gas oil even for relatively low temperatures.

Analysis of the light gases collected from thermal treatments of Soils A and B using GC indicates the generation of CO<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>2</sub>H<sub>4</sub>, respectively. The components found for both soils are recognized as pyrolysis products of humic substances and products originated by thermal decomposition of carbonates [29–31]. The yields of these

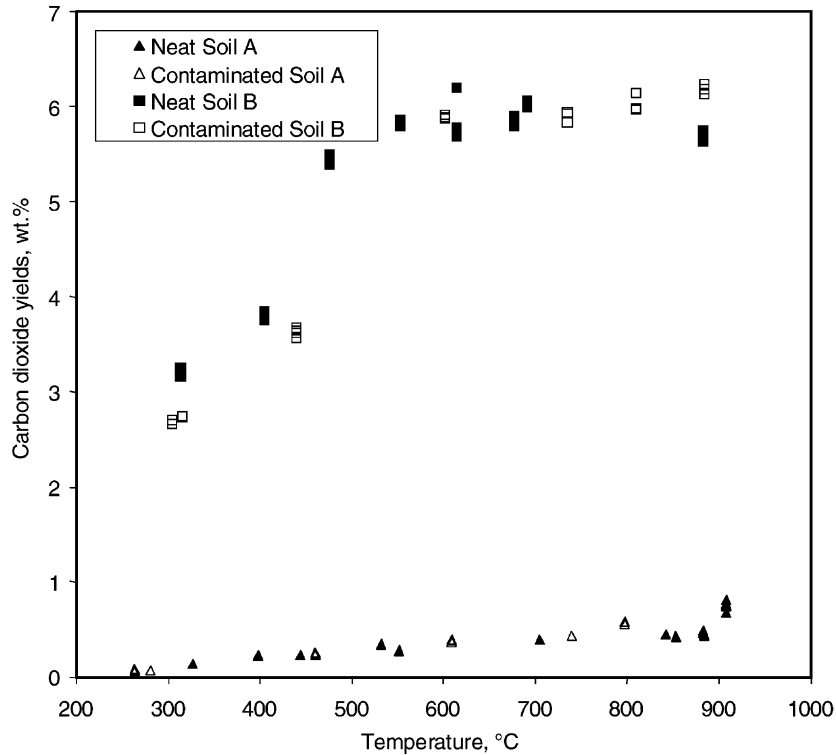


Fig. 4. CO<sub>2</sub> production from Soils A and B as function of treatment temperature.

compounds (i.e. the ratio of the light gas accumulative mass to the initial soil mass) are shown in Figs. 4–7. To compare the production of light gases from neat and contaminated soil, the yields in light gases produced by clean soil samples were corrected by a factor of 0.975.

The CO<sub>2</sub> yields as a function of treatment temperature are presented in Fig. 4. For contaminated and neat samples of Soil A, the CO<sub>2</sub> production achieves a maximum yield of 0.7 wt.% for a treatment temperature of 900 °C. This value is very close to the CO<sub>2</sub> yield expected from the thermal decomposition of the carbonates (i.e. 0.17 wt.% (inorganic carbon content)  $\times$  44/12 = 0.62 wt.%).

The CO<sub>2</sub> yields for samples of neat Soil B show high decomposition rates for temperatures around 450 °C, substantially lower than the decomposition temperatures for the carbonates that are commonly found in soils. The maximum CO<sub>2</sub> yield for contaminated and neat soil is around 6 wt.%, a value that surpasses the weight loss due to carbonates decomposition (0.44 wt.%  $\times$  44/12 = 1.61 wt.%). Therefore, the CO<sub>2</sub> produced by Soil B can be associated to the pyrolysis of humic soil fractions. In fact, Bonneau and Souchier [32] and Rupert et al. [33], among others, have verified the production of carbon dioxide by heating humic substances.

Fig. 5 shows the methane yields obtained for both soils. The CH<sub>4</sub> and CO<sub>2</sub> yields generated by Soil B for high treatment temperatures are one order-of-magnitude higher than



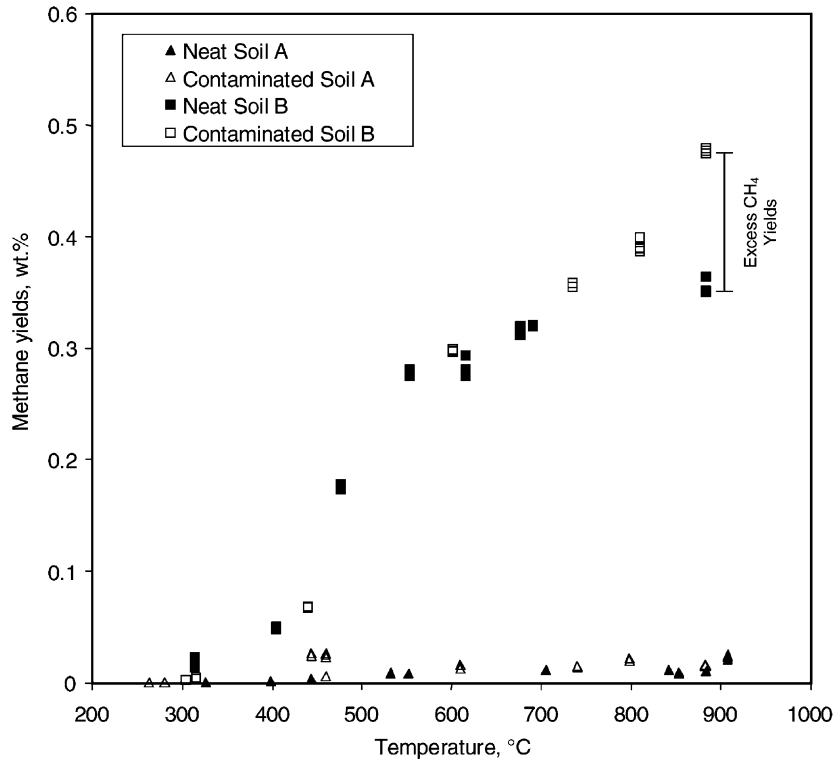


Fig. 5. Methane yields from Soils A and B as function of treatment temperature.

those produced by Soil A. The results in light gases indicate that the chemical composition of the soil is a key factor since it strongly influences the quantity and composition of the off-gases. Moreover,  $C_2H_4$  and  $C_2H_6$  only were detected during the thermal treatment of Soil B. These yields, which are very low, are shown in Figs. 6 and 7, respectively.

For atmospheric pressure and short exposure times, pure gas oil can be cracked under the pyrolysis temperature ranging between 650 and 900 °C. In addition,  $CH_4$  and  $C_2H_4$ , among other compounds, were reported as pyrolysis products of gas oil [18]. However, for Soil A,  $CH_4$  and  $CO_2$  yields for neat and contaminated samples are similar for the entire range of treatment temperatures. Since neither a significant increase in the generation of light gases nor new components relative to those found for the clean soil were detected (even for high treatment temperatures), poor interaction between the contaminant and the soil components and little or negligible chemical modifications of the gas oil during the heating of the contaminated samples can be assumed.

Under typical conditions, evaporation of relatively volatile compounds, such as the gas oil used in this study is a well-known removal mechanism for treatments performed at low temperatures. Conversely, when contaminated soil samples are subjected to high temperatures (e.g. 700–900 °C), pyrolysis reactions involving the contaminant are expected [14],

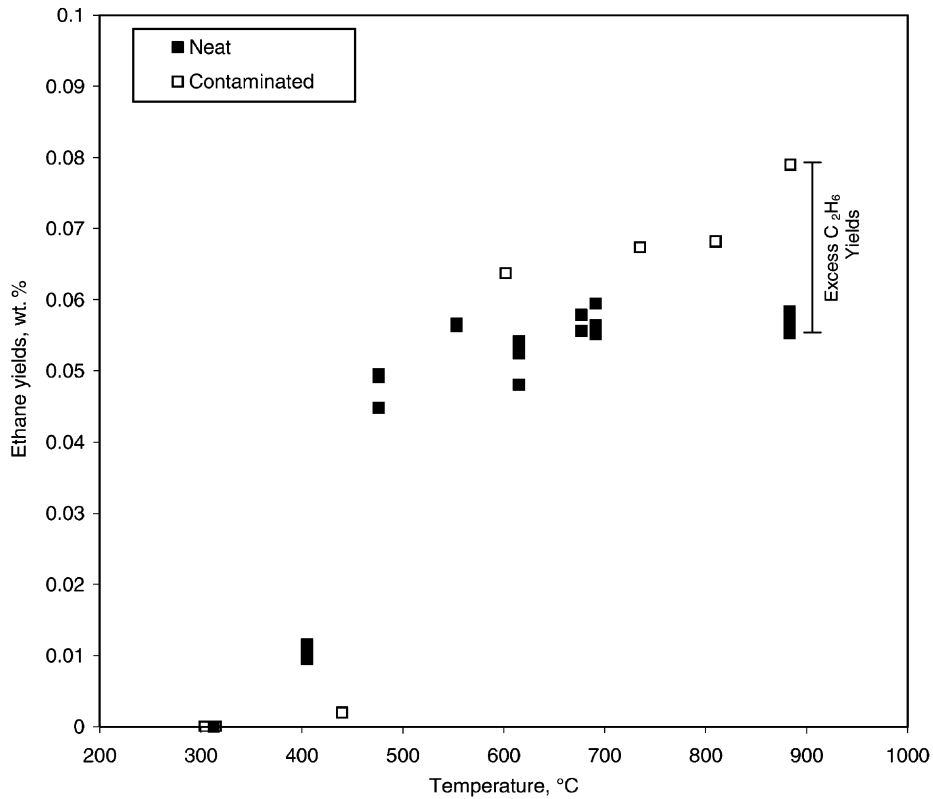


Fig. 6.  $C_2H_6$  yields from Soil B as function of treatment temperature.

although this was not encountered during the present study. Rather, the evolution of the gas oil from Soil A without suffering significant cracking reactions is explained based on the following issues.

- Gas oil evaporation

Evaporation can be the primary mechanism for contaminant release if a small fraction of the total gas oil is present on the soil surface as the first monolayer [5]. The contaminant fraction ( $f$ ) that can be adsorbed on the surface can be expressed as follows [17]:

$$f = \frac{M_c S_{BET} (100 - CL)}{N_a CL S_{mol}} \quad (1)$$

where  $M_c$  is the contaminant molecular weight,  $S_{BET}$  the soil surface area ( $cm^2/g_{neat\ soil}$ ),  $N_a$  is Avogadro's number,  $CL$  is the contamination level ( $g_{contaminant} \times 100/g_{contaminated\ soil}$ ), and  $S_{mol}$  is the projected surface area of the contaminant molecule ( $cm^2$  per molecule). The BET surface area for Soil A is  $16\ 000\ cm^2/g_{neat\ soil}$  and the contamination level is 2.5 wt.%. Since the *n*-hexadecane adequately represents the mean molecular formula for the gas oil [18], its projected surface was used in Eq. (1). For a hexadecane

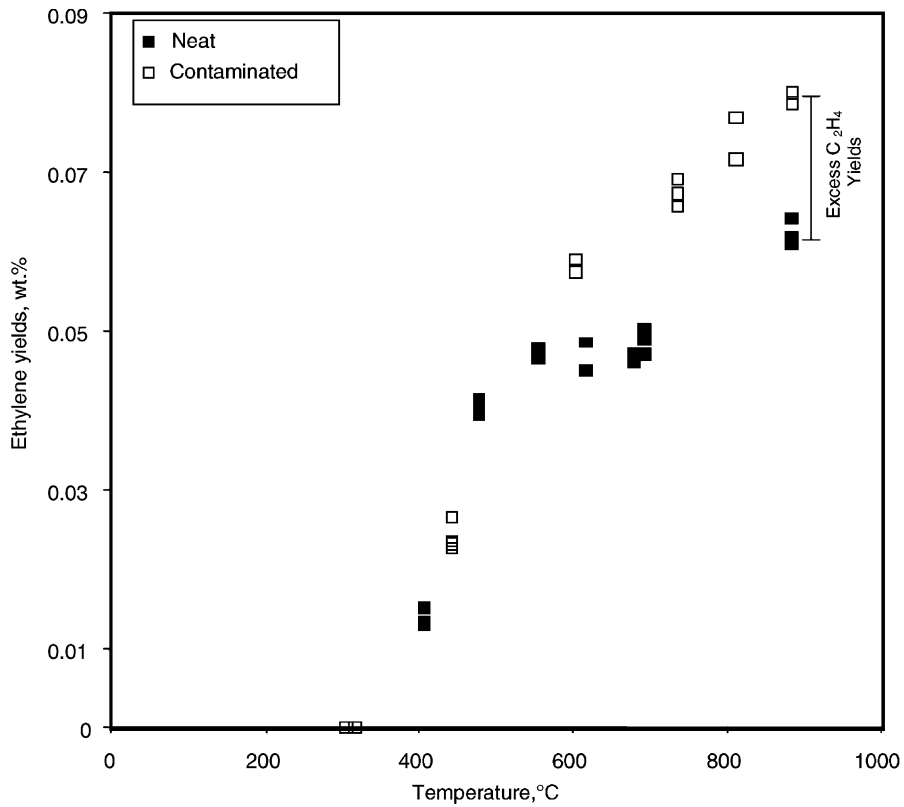


Fig. 7.  $C_2H_4$  yields from Soil B as function of treatment temperature.

molecule ( $M = 226.45 \text{ g}_{\text{contaminant}}/\text{g-mol}$ ), a projected surface area of  $6.21 \times 10^{-15} \text{ cm}^2$  per molecule (computed by the hexagonal close-packing model [19]) was used. Thus, based on Eq. (1), about 4% of the contaminant content can be adsorbed on the soil surface. Therefore, evaporation can be considered as the primary process for the release of most of the gas oil.

- Gas oil residence time

For a helium flowrate of  $0.933 \text{ cm}^3/\text{s}$  (measured at STP conditions) and a cross-sectional area equal to the tube area, the calculated gas velocity is about  $1.86 \text{ cm/s}$ . The gases should travel along  $46 \text{ cm}$  before leaving the quartz tube, then the spatial time is about  $24.7 \text{ s}$ . This is a conservative value in that the residence time should be lower than the time based on spatial considerations, due to: (1) bed temperatures higher than  $21.1 \text{ }^\circ\text{C}$ ; (2) lower cross-sectional area restricted by the solid particles; (3) higher volumetric flow rate due to the generation of gases during the soil thermal degradation and (4) operating pressures from vacuum to atmospheric conditions. Therefore, any fraction of evaporated gas oil (if the mass transfer resistances are negligible) may exit the reactor in a period less than  $24.7 \text{ s}$ .

- Gas oil boiling range

Distillation data indicate a boiling range between 169 and 392 °C at atmospheric conditions. In a typical run, the soil bed pressure initially varies from vacuum to atmospheric conditions, therefore, the gas oil evaporation could proceed for lower temperatures than the normal initial boiling point (IBP) and end boiling point (EBP) [17].

- Gas oil pyrolysis

At atmospheric pressure, the cracking of gas oil can occur at temperatures ranging from 650 to 900 °C [19]. Since the soil bed is treated under vacuum to atmospheric conditions and the carrier stream dilutes the gas oil concentration in the gas phase, the partial pressure of the gas oil compounds are expected to be low. To maintain equivalent pyrolysis rates, the reaction temperatures could be higher than those reported for pure gas oil at atmospheric conditions.

Considering the previous discussion about the gas oil evaporation, residence time, boiling range and pyrolysis, the evolution of the gas oil from the soil matrix is discussed. Fig. 8 shows the soil bed temperature profile for a final temperature of 900 °C. This thermal profile was selected to analyze the contaminant evolution from the soil matrix because it

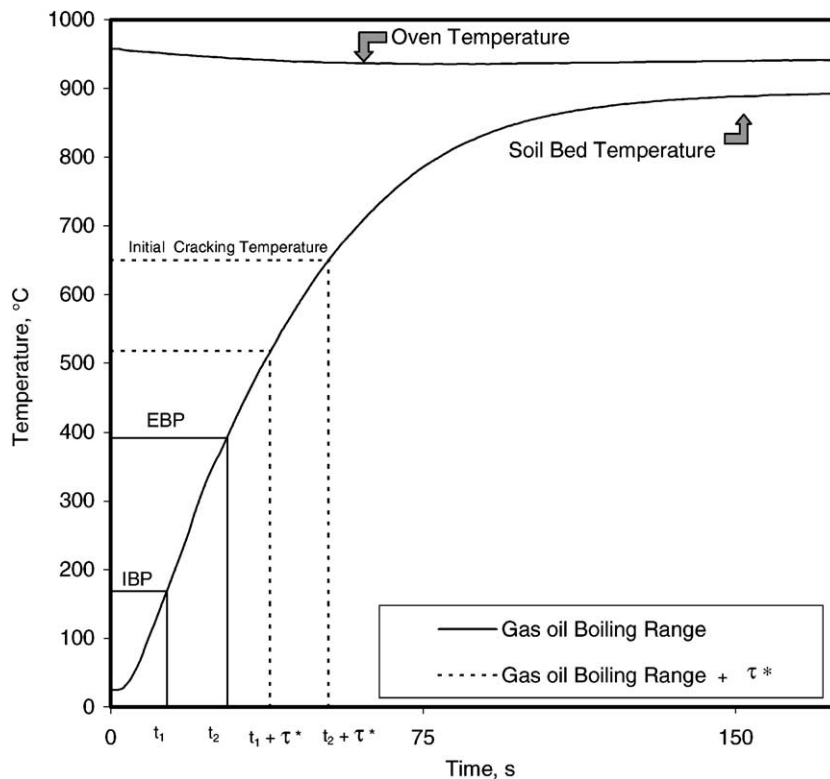


Fig. 8. Conceptualization of gas oil removal from the solid bed.

corresponds to the experiment performed at the highest heating rate. In Fig. 8, the soil bed reaches the gas oil IBP and EBP after 13.5 and 28 s, respectively. Any evaporated gas oil fraction should leave the quartz tube and, therefore, the heated section before 24.7 s ( $\tau^*$ ). If this spatial time is added to the time for which the IBP and EBP points are reached, it can be concluded that the gas oil could leave the hot tube section before 52.7 s. For this time, the soil bed should be at around 650 °C (temperature value coincident with the initial cracking temperature for atmospheric conditions) and, therefore, the gas oil would not be subjected to temperatures high enough to produce its cracking. All calculations are conservative such that the gas oil in the gas phase could leave the heated bed before the calculated times. This conceptualization introduces evaporation, even at high treatment temperatures, as the primary mechanism for the removal of most of the gas oil. In addition, in this removal step, this hypothesis assumes that the evaporation rate and the internal contaminant transport are relatively fast compared with the gas residence time.

The liquids yields for Soil A as function of temperature are shown in Fig. 9. The liquid fractions collected for samples of uncontaminated soil were affected by a factor of 0.975 to

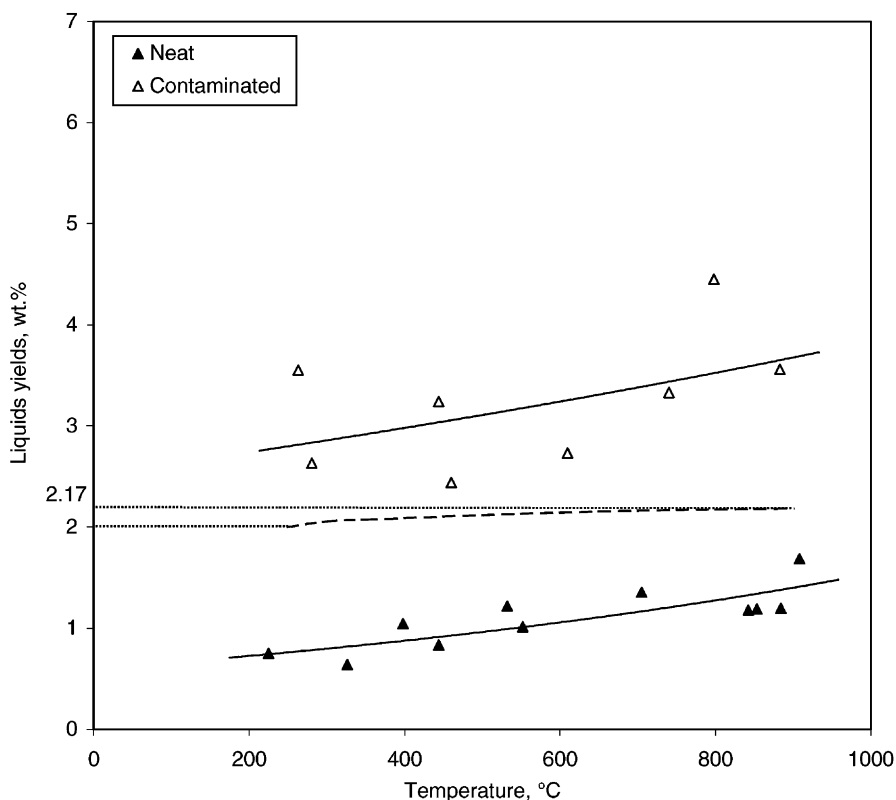


Fig. 9. Liquids fraction generated by Soil A as function of treatment temperature.

correctly represent the contribution of the soil itself. The fraction of liquids obtained for neat soil at low temperatures (around 200 °C) is very close to the moisture content of the samples. The solid curves shown in Fig. 9 are trend lines obtained by fitting the experimental data. The dashed line represents the difference between the trend lines for contaminated and neat soils. As can be seen for treatment temperatures close to 300 and 900 °C, the differences between the yields in liquids from contaminated and uncontaminated soils are 2 and 2.17 wt.%, respectively. Considering a contamination level of 2.5 wt.%, the yields in liquids together with the similar production of light gases from the neat and contaminated samples of Soil A suggest that a high mass fraction of gas oil does not suffer thermal degradation. Moreover, additional experiments were performed with the same heating rate as observed in Fig. 8, but the treatment times were reduced to 50 s (soil bed temperature ~600 °C). The difference between the yields in liquids from contaminated and neat samples of Soil A was about 2.13 wt.%, which is very close to the value obtained for longer residence times. This fact indicates that a high fraction of the original gas oil leaves the hot zone before it can reach high temperatures, and supports the aforementioned hypothesis. For all the experiments, visual observations indicate that condensable volatile compounds were collected during the first minutes of the treatment.

Solvent extractions of treated samples were performed to evaluate the residual gas oil content. For a given treatment temperature, treated samples of neat and contaminated soil were separately extracted to distinguish the extractable material from the soil itself and the residual contaminant. Fig. 10 shows the residual gas oil as function of temperature. For Soil A at 400 °C, the removal efficiency is close to 89%, while for high temperatures (900 °C) the removal efficiency increases to approximately 98%. Although an 89% removal is achieved for relatively low temperatures (e.g. 400 °C), more energy is required to remove the residual fraction (~11%). Eq. (1) indicated that as much as 4% of the original gas oil can be adsorbed onto the soil as the first monolayer. The residual gas oil found for low temperatures is higher than this value, suggesting that the surface area of Soil A may be potentially underestimated. The residual contaminant found for low temperatures can be associated to the gas oil fraction adsorbed onto the soil surface. The removal of the remaining gas oil can be impacted by the desorption kinetics (related to the contaminant removal from the first monolayer) that are affected by the treatment temperature. For Soil A, calculations indicated that the global mass balance is closed within 98.7–99.7 wt.% and within 98–99.2 wt.% for neat and contaminated samples, respectively.

For Soil B, the CO<sub>2</sub> yields obtained for contaminated and uncontaminated samples do not differ significantly (Fig. 4). However, for final temperatures higher than 600 °C, the CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> yields from contaminated samples (Figs. 5–7) are greater than the corresponding neat soil samples. At 900 °C, the sum of the differences between the yields in light gases from contaminated and neat samples (i.e. excess yields, see Figs. 5–7) account for approximately 0.16 wt.% ( $(g_{\sum \text{excess yields}}/g_{\text{untreated contaminated soil}}) \times 100$ ). This value indicates that only about 6% of the original gas oil undergoes chemical transformations at elevated temperatures.

A surface area of 85 000 cm<sup>2</sup>/g<sub>neat soil</sub> was measured for clean and untreated Soil B. Based on Eq. (1), as much as 20% of the original gas oil content can exist as a monolayer. Fig. 10 shows the residual gas oil found in the treated samples of Soil B as function of the final treatment temperature. For low temperatures (460 °C), the residual fraction is close to 20%

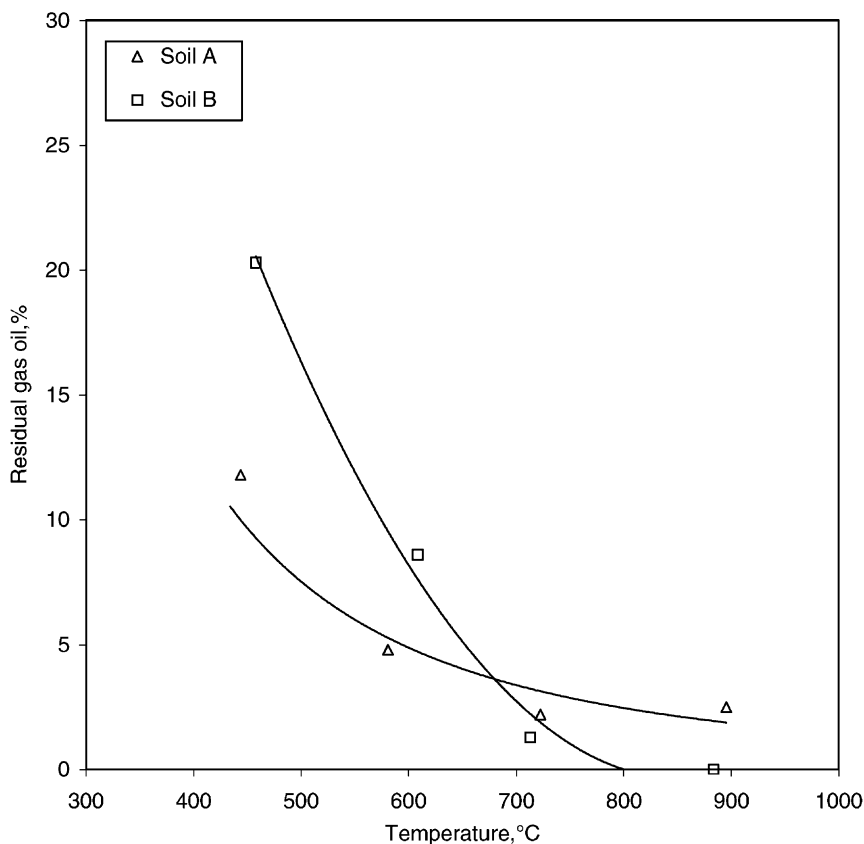


Fig. 10. Residual gas oil for Soils A and B as function of temperature with trend lines.

of the original gas oil content, indicating good agreement with the gas oil fraction estimated by Eq. (1). The adsorbed gas oil fraction requires higher thermal levels to increase the removal of the contaminant. As before, the removal mechanism at low temperatures can be associated with an evaporation process but, as the temperature increases, the kinetics of desorption/adsorption can play a more important role. Finally, for high temperatures, the gas oil may undergo, in a limited extension, cracking reactions. Soil B retains more gas oil than Soil A for final temperatures around 600 °C, similar fractions for treatment temperatures around 710 °C and higher removal efficiency at extreme temperatures (900 °C). For Soil B at 600 °C, the residual gas oil is close to 8% of the original content. This residual gas oil (after a treatment at 600 °C) may be associated to the gas oil fraction that suffers cracking reactions when the temperature is raised. In fact, the summation of excess yields at 900 °C represents about 6% of the initial gas oil content.

The yields in liquids for neat and contaminated Soil B as function of the treatment temperature are shown in Fig. 11. The yield in liquids for low temperatures tends to be close to the soil moisture content (5.5 wt.%), but for temperatures higher than 600 °C, the scatter in

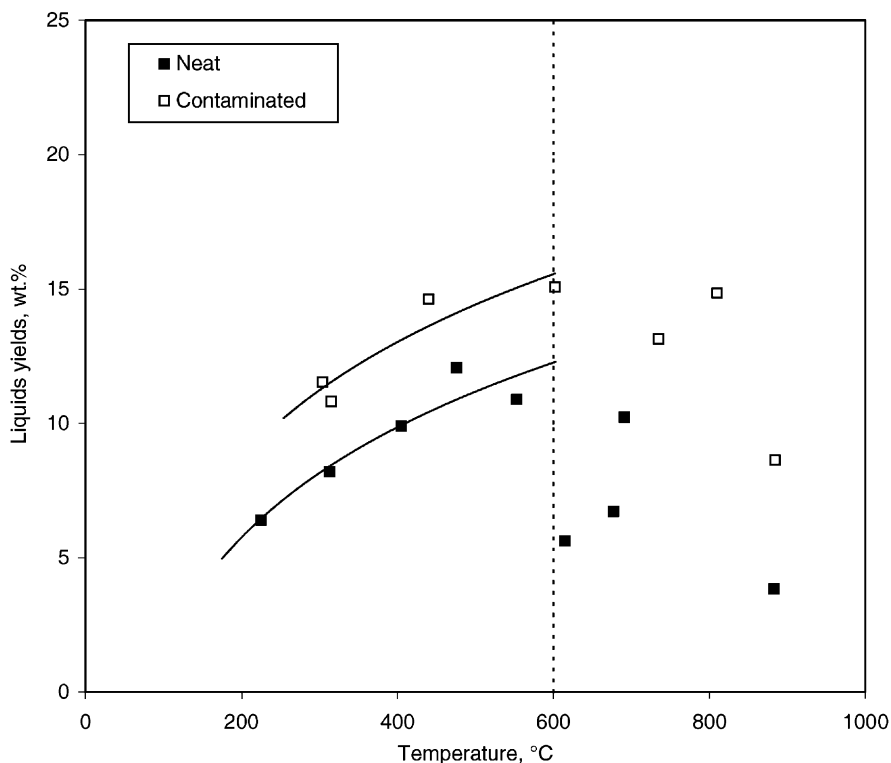


Fig. 11. Liquids fraction generated by Soil B as function of treatment temperature.

the experimental data is significant. This observation coincides with the visual observation performed at those temperatures, wherein high rates in the generation of volatiles were detected after few minutes of heating. The trap efficiency for liquids at these thermal levels was poor. The global mass balances were closed within 92.7–95.7 and 91.6–94.2 wt.% for neat and contaminated samples, respectively. Since CO, among probably other species, was not quantified, the mass balance closures are considered satisfactory.

#### 4. Conclusions

Two different mechanisms for the removal of the studied complex mixture were detected. The first mechanism corresponds to a rapid evaporation of the contaminant, and the second one involves a contaminant desorption mechanism.

The soil composition and the treatment temperature strongly influence the quantity and composition of the volatile compounds generated during thermal treatment. For Soils A and B, the light gases CO<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub> were detected respectively. These light gases were products of the pyrolysis of humic substances and thermal decomposition of soil carbonates.



For the experimental conditions used in this study, the nature of the two soils studied did not modify the primary decontamination processes. Thermal treatments at relatively low heating rates (12.5 °C/s as maximum) avoid significant chemical transformations of the contaminant, and practically eliminate the gas oil from the soil matrices. A high fraction of gas oil can be eliminated at moderate temperatures, but higher temperatures are required to achieve high removal efficiencies.

Experimental observations indicated that most of the condensable volatile compounds evolved during approximately the first 2 min of the treatment. This observation together with the gas oil residuals measured for different temperatures indicate that the removal is not only a matter of time but also the temperature level to allow the contaminant desorption.

The experimental results indicate that the gas oil could be collected as liquid product together with those generated by pyrolysis of clean soil. Therefore, similar thermal treatments, which are efficient to clean up the soil, may generate liquid products that could be used as fuel. However, a chemical analysis of this fraction should be performed to allow evaluation of its heating value.

## References

- [1] E.T. Oppelt, *Environ. Sci. Technol.* 20 (4) (1986) 312–318.
- [2] W.L. Troxler, S.K. Goh, L.W.R. Dicks, *J. Air Waste Manage. Assoc.* 43 (1993) 1610–1619.
- [3] L. Yang, B. Farouk, *J. Air Waste Manage. Assoc.* 47 (1997) 1189–1196.
- [4] P.R. De Percin, *J. Hazard. Mater.* 40 (1995) 203–209.
- [5] P. Gilot, J.B. Howard, W. Peters, *Environ. Sci. Technol.* 31 (2) (1997) 461–466.
- [6] D.W. Pershing, J.S. Lighty, G.D. Silcox, M.P. Heap, W.D. Owens, *Comb. Sci. Technol.* 93 (1993) 245–276.
- [7] T.-F. Lin, J.C. Little, W. Nazaroff, *Environ. Sci. Technol.* 28 (1994) 322–330.
- [8] C. Borkent-Verhage, C. Cheng, L. de Galan, E.W.B. de Leer, *Contaminated soil*, in: J.W. Assink, W.J. van den Brink (Eds.), Martinus Nijhoff Publishers, The Netherlands, 1986.
- [9] F.S. Larsen, G.D. Silcox, B.R. Keyes, *Comb. Sci. Technol.* 101 (1994) 443–459.
- [10] Y.G. Wu, J.W. Bozzelli, *Hazard. Waste Hazard. Mater.* 11 (1) (1994) 227–236.
- [11] C. Cabbar, G. Dogu, T. Dogu, B.J. McCoy, J.M. Smith, *Environ. Sci. Technol.* 28 (7) (1994) 1312–1319.
- [12] J.S. Lighty, D.W. Pershing, V.A. Cundy, D.G. Linz, *Nucl. Chem. Waste Manage.* 8 (1988) 225–237.
- [13] J.S. Lighty, G.D. Silcox, D.W. Pershing, V.A. Cundy, D.G. Linz, *Environ. Sci. Technol.* 24 (5) (1990) 750–757.
- [14] V. Bucalá, H. Saito, J.B. Howard, W.A. Peters, *Environ. Sci. Technol.* 28 (11) (1994) 1801–1807.
- [15] H. Saito, J.B. Howard, W.A. Peters, V. Bucalá, in: R.A. Meyers (Ed.), *Soil Thermal Decontamination: Fundamentals*, *Encyclopedia of Environmental Analysis and Remediation*, Wiley, New York, 1998, pp. 4554–4589.
- [16] V. Risoul, C. Pichon, G. Trouvé, W.A. Peters, P. Gilot, G. Prado, *J. Hazard. Mater. B* 64 (1999) 295–311.
- [17] V. Maguire, W.Y. Svrcek, A.K. Mehrotra, M. Razzaghi, *The Can. J. Chem. Eng.* 73 (1995) 844–853.
- [18] M. Hirato, S. Yoshioka, *Int. Chem. Eng.* 13 (2) (1973) 347–354.
- [19] J.F. Campagnolo, A. Akgerman, *J. Hazard. Mater.* 37 (1994) 415–430.
- [20] W.D. Owens, G.D. Silcox, J.S. Lighty, X.X. Deng, D.W. Pershing, V.A. Cundy, C.B. Leger, A.L. Jakwayal, *Combustion and Flame* 86 (1991) 101–114.
- [21] W.L. Troxler, J.J. Cudahy, R.P. Zink, J.J. Yezzi, S.I. Rosenthal, *J. Air Waste Manage. Assoc.* 43 (1993) 1512–1525.
- [22] R. Hempfling, H.-R. Schulten, *Org. Geochem.* 15 (2) (1990) 131–145.
- [23] R. Hempfling, H.-R. Schulten, R. Horn, *J. Anal. Appl. Pyrolysis* 17 (1990) 275–281.
- [24] H.-R. Schulten, *J. Anal. Appl. Pyrolysis* 12 (1987) 149–186.
- [25] R. Hempfling, H.-R. Schulten, *J. Anal. Appl. Pyrolysis* 13 (1988) 319–325.
- [26] H.-R. Schulten, G. Abbt-Braun, F.H. Frimmel, *Environ. Sci. Technol.* 21 (1987) 349–357.

- [27] F.E. Broadbent, in: C.A. Black, D.D. Evans, J.L. White, L.E. Ensminger, F.E. Clark (Eds.), *Methods of Soil Analysis, Part 2*, American Society of Agronomy, Madison, WI, 1965, pp. 1397–1400.
- [28] M. Schnitzer, in: M. Schnitzer, S.U. Khan (Eds.), *Soil Organic Matter*, Elsevier, New York, 1978.
- [29] C. Saiz-Jimenez, J.W. de Leeuw, *J. Anal. Appl. Pyrolysis* 9 (1986) 99–119.
- [30] H.-R. Schulten, *J. Anal. Appl. Pyrolysis* 25 (1993) 97–122.
- [31] T.R. Ingraham, P. Marier, *The Can. J. Chem. Eng.* 41 (1963) 170–173.
- [32] M. Bonneau, B. Souchier, in: V.C. Farmer (Ed.), *Constituents and Properties of Soils*, Academic Press, New York, 1982.
- [33] J.P. Rupert, W.T. Granquist, T.J. Pinnavaia, in: A.C.D. Newman (Ed.), *Chemistry of Clays and Clay Minerals*, Wiley, New York, 1987 (Chapter 6).