

# Effect of temperature on the release of hexadecane from soil by thermal treatment

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Received 30 January 2006; received in revised form 16 September 2006; accepted 18 September 2006

Available online 22 September 2006

## Abstract

A natural organic soil (2.5% of total organic carbon) was artificially contaminated with hexadecane, and thermally treated under an inert medium up to different final temperatures (150–800 °C) for 30 min to simulate *ex situ* thermal process conditions. The experiments were conducted using a complete organic soil, instead of the clays or isolated soil fractions that are commonly used. Neat and contaminated samples were separately heated to understand the impact of the soil itself and the contaminant in the release of volatiles. The soil quality as well as the quality and amount of volatile compounds generated during the process were monitored. More than 80–88% of the initial hexadecane content in the soil matrix was recovered in liquids traps after the thermal treatment, therefore the contaminant could be recovered for further recycling. The high amount of hexadecane collected without suffering chemical transformations indicated that the main mechanism for the hexadecane removal was evaporation. The analysis of the light gases released from contaminated samples indicated negligible or null hexadecane pyrolysis reaction rates, confirming that the evaporation/desorption of the contaminant are the processes that governed the removal of the contaminant from the soil. For the soil tested, of a relatively low surface area, good removal efficiencies (higher than 99.9%) were detected at about 300 °C, being higher temperatures not necessary to significantly improve the contamination removal.

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**Keywords:** Hexadecane; Temperature effect; Thermal remediation; Soil treatment; Hydrocarbon contamination

## 1. Introduction

There are soils contaminated with hydrocarbons in many industrial sites and oil refineries. Several technologies can be used for the remediation of these sites. Thermal treatments are the most popular and versatile techniques because they can be effectively applied to a wide range of organic contaminants. According to their operational temperature, thermal treatments can be classified into desorption and destruction techniques. In the former, the contaminated soil is generally heated between 150 and 500 °C, and a physical separation that transfers the pollutants to a gas stream is produced. On the other hand, the latter involves working at high temperatures, usually 600–900 °C or greater, and the contaminants often suffer chemical modifications.

Several independent analyses to understand the fundamentals of contaminant release from soils have been performed [1–10]

and different laboratory and pilot-scale devices have been used to obtain data. Recently, Mechatí et al. [11] have studied the thermal desorption process using an industrial pilot-scale unit. Important studies about the fundamentals of hydrocarbon thermal desorption and destruction have been reviewed by Pershing et al. [12] and Saito et al. [13].

Based on the systematic parametric studies above mentioned, the properties of the contaminant, the characteristics of the soil, and the operating conditions have been recognized as the key parameters for thermal decontamination processes. However, in most cases the studies were limited to clay soils, and it is assumed that soils behave as inert media throughout the thermal treatment. Moreover, the fate of the contaminants during the decontamination process and the quality of the generated gases are relevant aspects that have not been simultaneously addressed in depth to date.

Relatively few results have been reported in the literature about the effect of the nature of the soil on thermal decontamination. Bucalá et al. [14] have studied how soil decomposition itself may affect thermal cleanup. They have quantified the total weight loss and the yields of several volatile products from rapid

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pyrolysis of an U.S. EPA synthetic soil matrix. These authors presented data and kinetics models that should be useful in better understanding the contributions of soil decomposition itself during soil thermal decontamination processes performed at very high heating rates. Merino et al. [15] showed that temperature can significantly modify the chemical and physical structure of the soil itself, strongly depending on its nature and constituents, especially when soils contain enough organic matter to be pyrolyzed.

In studies associated to the mechanisms of pollutant removal and the effect of operating conditions, Bucalá et al. [8], using a U.S. EPA synthetic inorganic soil contaminated with fuel oil, showed that at 500 °C, heating at 1000 °C/s, the contaminant undergoes non-negligible chemical modifications. Piña et al. [16], using two different organic soils contaminated with gasoil, found that soil composition and temperature strongly influence the quantity and composition of volatile compounds. These authors have determined that the operating conditions analyzed (temperatures from 200 to 900 °C and heating rates as high as 300 °C/min) prevent the pollutant from suffering significant chemical transformations and practically eliminate the gasoil from the soil matrices. The above-mentioned work was based on the study of gasoil removal on lumped concentrations measured gravimetrically after solvent extraction with dichloromethane.

In the present work, the thermal treatment of a whole soil (i.e., not an isolated soil fraction) contaminated with hexadecane is studied. The use of a pure chemical instead of a fraction of petroleum permits to keep track of the contaminant more accurately. The objectives of the present work are: (a) to analyze the influence of the treatment temperature on the *n*-hexadecane removal from a soil with relatively high organic carbon content (2.5 wt%) in order to find optimal treatment operating conditions (i.e., high removal efficiencies and low energy requirements), (b) to study the role of the soil itself on the decontamination process, and (c) to elucidate the fate and removal mechanism of the contaminant.

## 2. Materials and methods

### 2.1. Soil sample

A soil from Sierra de la Ventana (Argentina) was used in the present work. After the sample was collected, it was air dried, homogenized and size-fractionated. For this research, the chosen range of particle size was 105–210 μm, to represent samples with relatively high surface area. Surface area measurements for different particle size ranges indicated that the surface area of the soil particles increased as the particle mean diameters were lower. This fact suggested that the main contribution to the total surface area is given by the external area of the particle [17]. As the soil surface area increases significant soil-contaminant interactions are expected, for this reason particles of small size have been selected for the present study. Besides, the humic substances predominate in the smaller size fractions of the soil. The presence of humic substances increases, as the surface area, the interactions between the pollutant and the soil itself. The BET surface area of the samples was 3.45 m<sup>2</sup>/g. The

hygroscopic moisture content (2.17 wt%) was determined by drying the sample at 110 °C until constant weight. A total carbon content of 2.68 wt% was determined in a LECO instrument (model CR-12); elsewhere, by total oxidation of the samples and measurement of the generated CO<sub>2</sub>. An organic carbon content (TOC) of 2.48 wt% was determined in a similar way to total carbon contents, using samples previously treated with HCl 1:1 to remove the carbonate carbon. The inorganic carbon content of 0.20 wt% was calculated by difference and also corroborated by analyzing (by GC) the CO<sub>2</sub> generated during treatment of the soil sample with HCl. Diffraction and fluorescence X-ray measurements (using a Philips PW1710 X-ray diffractometer and a Philips PW 1400 spectrometer) were performed to detect metals and crystalline structures in the soil. The following crystalline structures were found: quartz, albite ordered, iron oxide, γ-alumina, sodium hydrogen carbonate hydrate, trona and magnesium silicate. The elements Ca, Ti, Fe, Cu, Zn, Sr, Rb, P, Si, Al and Cl were detected.

### 2.2. Contamination of the soil sample

The soil samples were artificially contaminated with *n*-hexadecane, C<sub>16</sub>H<sub>34</sub> (+98% purity, olefins-free), which was obtained from Fluka-Chemica (Switzerland) and used with no further purification.

The contamination of the soil matrix was performed gradually by adding the pollutant with a syringe to a pre-specified amount of uncontaminated soil (200–300 g, with a hygroscopic moisture content of 2.17 wt%). Immediately after, the sealed recipient was shaken in order to achieve the homogenization of the contaminated sample. The level of contamination (*L<sub>c</sub>*) was determined gravimetrically by the weight increase exhibited by the sample after the contamination procedure, which was verified by 24-h Soxhlet extraction and subsequent GC/FID analysis.

### 2.3. Thermal treatment

The thermal treatment of neat and contaminated soil samples was carried out in an improvement of the unit reported by Piña et al. [16]. It consisted of an adiabatic electric oven and traps of liquids and gases. An amount of approximately 10 g of soil, either of neat soil or contaminated soil, was placed in the center of a quartz tube (length: 85 cm, internal diameter: 0.8 cm). A small piece of porous refractory brick (0.5 cm long) was located at 77 cm from one end of the quartz tube to prevent the soil spill during the loading stage. A type-K thermocouple was axially inserted up to the middle of the soil bed. It had a thimble of stain steel mesh welded at around 8 cm from its free end. This thimble together with the small brick prevented the soil particle from moving through the bed. Once the oven reached the desired temperature, the soil bed (even outside the oven) was purged with helium for 20 min to ensure an inert atmosphere throughout the thermal treatment, after which the quartz tube was located inside the oven for the thermal treatment of the soil.

Clean and contaminated soil samples were separately subjected to treatments at selected different final temperatures. The range of temperature was between 150 and 800 °C. A constant

helium flow of 56 cm<sup>3</sup>/min STP, fixed by a mass flow controller, was established through the bed during the experiment. The experimental procedure was designed to simulate a sudden discharge of soils in a heated inert environment. This experimental setup can mimic a section of bed solids as they move through a rotary indirectly fired kiln, replacing the variable of distance (or residence time) with time.

The soil bed temperature, for a given time, was practically constant along its length [16]. For a given oven temperature the solids underwent a relatively rapid heating. Thus, the soil temperature increased initially in a linear way with time and then achieved an equilibrium temperature, being the total heating time of around 30 min (close to the minimum value recommended for indirectly heated desorber units [18]). Finally, after completing the procedure, the soil bed was removed from the oven and cooled down by natural convection. The pressure downstream of the soil bed varied initially from 0.25 atm (25.325 kPa) to around 0.6 atm (60.78 kPa) at the end of the experiment, using pressure below atmospheric pressure to mimic the vacuum conditions commonly used in pyrolytic furnaces in order to prevent fugitive emission of contaminants.

In order to collect the liquids, two 10-ml vials arranged in series, located downstream of the oven, were used. The former was maintained at room temperature and the latter was kept at 0 °C (using an ice-bath). Thus, the amount of total liquids collected included the products that can be condensed at the mentioned temperatures. The gases generated during the thermal treatment that did not condense in the liquid traps were accumulated in a 5-liter glass flask throughout the experiment. It is worth mentioning that the liquid traps were purged while the soil bed was subjected to a purge with helium. On the other hand, the purge of the light gas trap was performed independently. It was flushed with helium several times to remove the original air.

#### 2.4. Analysis of the samples

The weight loss of the soil was determined as the weight difference between the loaded soil and the soil residue (after thermal treatment) collected from the quartz tube. The residual contamination levels of the soil samples after the thermal treatment were determined by Soxhlet extraction using hexane (120 ml) as solvent during 24 h followed by quantitative gas chromatographic analyses of the resulting solutions. The accumulated liquids in the trap were determined gravimetrically as the weight increase of the liquid vials.

An HP 4890D Gas Chromatograph, equipped with a Flame Ionization Detector (FID) was used in order to determine the amount of hexadecane in both the Soxhlet extract obtained and the liquid waste samples. The capillary column employed was HP-5 MS (5% diphenyl–95% dimethylsiloxane copolymer; length: 15 m; diameter: 0.53 mm; film thickness: 1.5 μm—Part Number 19095J-321). The extracts obtained were submitted to GC/FID analysis three times, using *n*-tetradecane as internal standard. The analysis was performed at 140 °C, being the FID and injector temperatures 300 and 250 °C, respectively. The split relationship was 4:1, and the analysis duration was 8 min.

The same model of the HP chromatograph, but equipped with an HP PLOT Q capillary column (length: 30 m; diameter: 0.53 mm; film thickness: 40 μm—Part Number 19095P-QO4), and a TCD and an FID, arranged in series, were used to quantify the yields of light gases. The initial GC oven temperature was established at 40 °C and held for 3 min, after that the temperature was increased at 20 °C/min up to a final temperature of 200 °C, which was kept constant for 9 min. The FID, TCD and injector temperatures were 250 °C. The light gases quantified were: CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. For all the GC analysis, the carrier gas flow was helium. The light gases were also analyzed by triplicate.

The *n*-hexadecane Destruction and/or Removal Efficiency (DRE) is calculated as the hexadecane mass removed during the thermal treatment (based on the GC analysis of the liquid extract obtained from Soxhlet extraction of treated soil samples) divided by the initial contaminant mass in the untreated contaminated samples.

### 3. Results and discussion

#### 3.1. Hexadecane removal

The influence of temperature on the thermal decontamination of a soil polluted with *n*-hexadecane at 2.93 wt% and the liquids and gaseous products generated during the process were studied. The temperature was in the range of 150 and 800 °C and the total time of the treatment was 30 min. In the present study, the weight loss of the soil, the yields of liquids and light gases, the Destruction and/or Removal Efficiency (DRE), and the residual concentration of the pollutant after the treatment were evaluated.

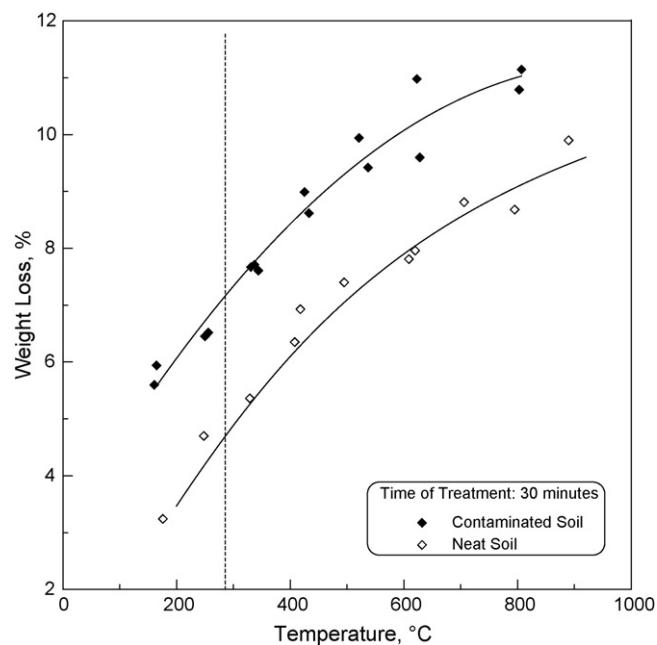


Fig. 1. Effect of temperature on the weight loss exhibited by both neat and contaminated soils. The dashed line represents the *n*-hexadecane normal boiling point.

Fig. 1 shows how the temperature affects the weight loss of both the neat and the contaminated samples of soil. To compare the results between neat and contaminated matrix, the neat soil data were multiplied by 0.9707 to properly represent the contribution of the neat soil to the total weight loss of contaminated samples. As observed in Fig. 1, the contaminated soils exhibited a higher weight loss than the neat samples at a fixed temperature. Furthermore, the difference of weight loss between both soils was approximately constant in all the range of temperature studied. This difference (calculated by fitting the experimental data to mathematical functions) ranged from 2.5 to 2.75 wt%, which is close to the initial contamination level, and represents a removal of approximately 83–92% of the initial *n*-hexadecane. This suggests that a significant removal of the contaminant from the soil bed can be reached even at low temperatures of treatment, as it was also suggested by Piña et al. [16] for diesel oil contaminated samples. For example, for a maximum temperature of 200 °C, the difference between the weight losses exhibited by the contaminated and neat samples was around 2.5 wt%. This value is indicative of a good hexadecane removal well below the hexadecane normal boiling point, which is represented with a dashed vertical line in Fig. 1.

The real *n*-hexadecane removal efficiency of the decontamination process was evaluated by submitting the treated samples to Soxhlet extraction for 24 h, using hexane as solvent, and to subsequent analysis of the obtained extract by GC/FID. These chromatographic analyses also permitted to determine the remaining concentration of hexadecane after the thermal treatment.

Fig. 2 presents the results of the hexadecane DRE obtained at different temperatures of treatment. At around 160 °C, 85–92% of the initial contaminant was released from the soil matrix. In fact, these values are coincident with the difference between the weight losses of neat and contaminated samples at a similar

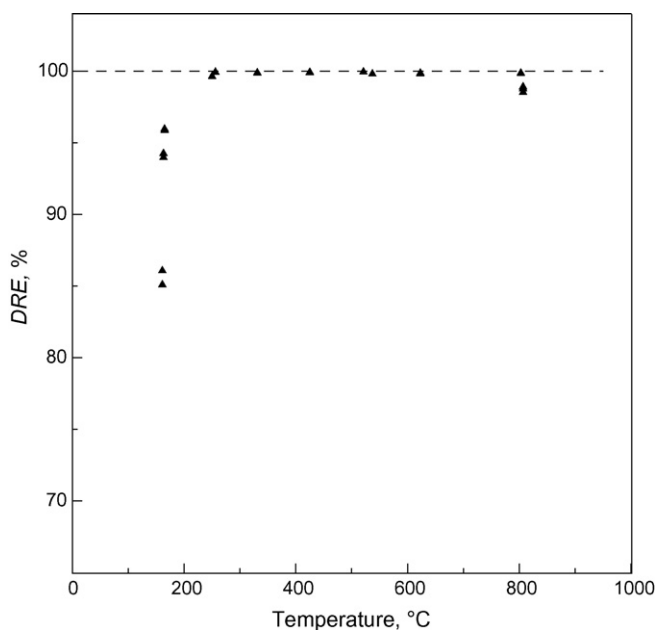


Fig. 2. Destruction and/or removal efficiency as a function of temperature.

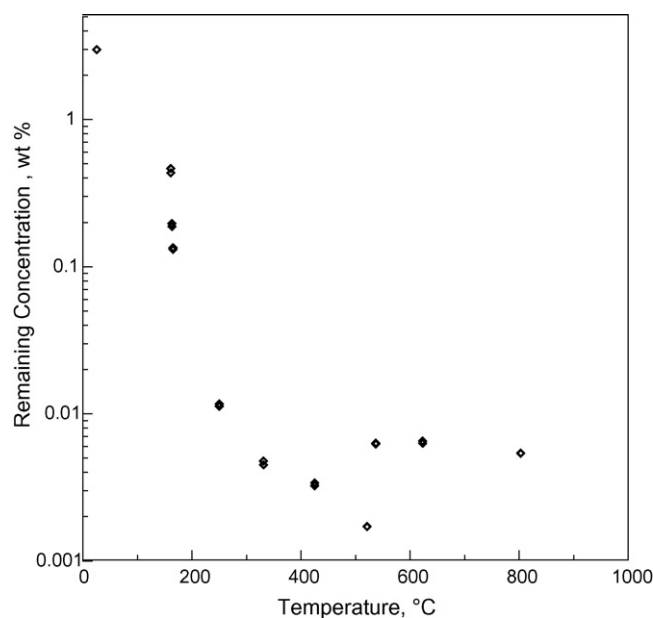


Fig. 3. Residual concentration of hexadecane after the thermal treatment as a function of temperature.

thermal level (see Fig. 1). The data illustrate that a removal of 99.6–99.8% was reached at temperatures higher than 250 °C. At temperatures close to 350 °C, the decontamination level was larger than 99.9%. Thermal treatment at temperatures beyond 350 °C did not allow a more noticeable removal.

Fig. 3 shows the remaining concentration of pollutant in the soil after the thermal process. At 160 °C a 10-fold reduction of the contamination level was obtained, and at around 250 °C a significant removal of the hexadecane was reached. The residual concentration of pollutant can be reduced to around 0.004% (40 ppm) at temperatures close to 350 °C. A dispersion of data can be observed after 400 °C. This can be explained from the fact that the level of the residual pollutant is consequence of two effects that occur simultaneously. The contaminant level decreases when the temperature rises. However, there is another opposite effect that is related to the soil weight loss during the heating treatment, especially at higher temperatures, i.e. the reduction of the soil mass due to soil pyrolysis causes a non-desired effect: the residual concentration may rise owing to the reduction of soil mass. This is an important aspect for those soils that undergo important chemical modifications throughout thermal treatments, especially soils of high organic matter content. This behavior was not reported before, since usually the soil itself is considered as an inert medium. Consequently, the increase of residual concentration of pollutant beyond 400 °C is due to the loss of soil mass, in fact the DRE remains almost constant while the weight loss rises (see Figs. 1 and 2).

### 3.2. Fate of the pollutant

A fundamental aspect that must be considered in a decontamination process is the fate of the pollutant, which can desorb, evaporate or be pyrolyzed. This analysis should be useful in a better insight of the mechanisms of contaminant release from



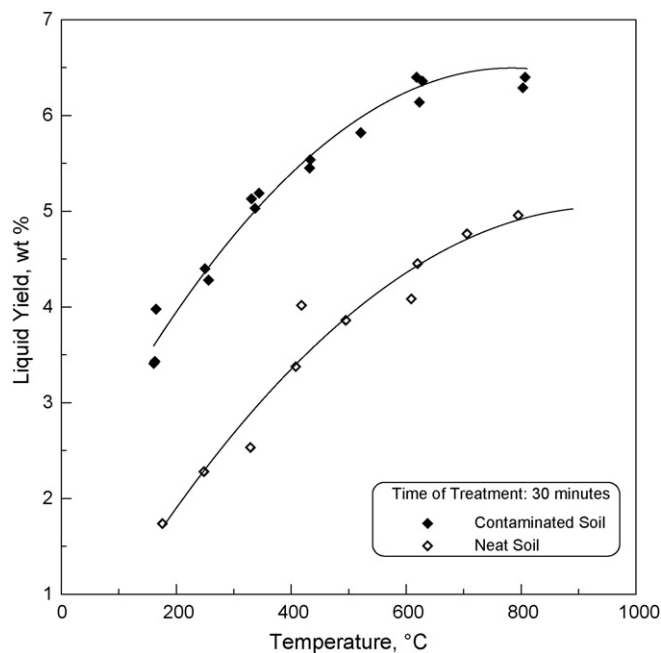


Fig. 4. Effect of the temperature on liquid yield of both neat and contaminated soils.

the soil matrix. In the present work, the fate of the contaminant was assessed analyzing the liquids and light gases yielded throughout the thermal treatment. Fig. 4 illustrates the amount of liquids produced from both neat and contaminated soils when they were subjected to thermal remediation at different temperatures. The data obtained from uncontaminated samples were multiplied by  $(1 - L_c)$  to appropriately quantify the contribution of the soil itself to the total liquid yield of the contaminated samples. Throughout the range of temperature studied, the difference between the mass of liquid trapped from both contaminated and clean samples (calculated by fitting the experimental data with mathematical functions) was about 2%, which corresponds to around 70% of the original contamination level. This suggests that most of the hexadecane could be collected unaltered downstream of the primary thermal unit. This assumption is correct if the pollutant does not restrict or promote the generation of liquids from the soil itself. In order to evaluate the amount of hexadecane present in the liquid fraction collected from polluted samples, it was quantified by GC/FID. From this examination about 80–88% of the original contaminant was found in liquid fraction. Therefore, the main mechanism for *n*-hexadecane removal from the soil matrix is evaporation, even at severe treatment temperatures (e.g. 800 °C). This means that most of the *n*-hexadecane did not undergo chemical modifications even under pyrolysis conditions (i.e. high temperatures). This is in agreement with a previous work, in which a complex mixture of contaminant (gasoil) was used [16]. Data presented in Fig. 2 show that at temperatures higher than 300 °C the removal efficiency was above 99%. However, it does not agree with the amount of pollutant quantified in the liquid fraction. This could be associated to the fact that 12–20% of hexadecane undergoes chemical reactions. As it will be explained below, the main products of pyrolysis of hexadecane were not found throughout the

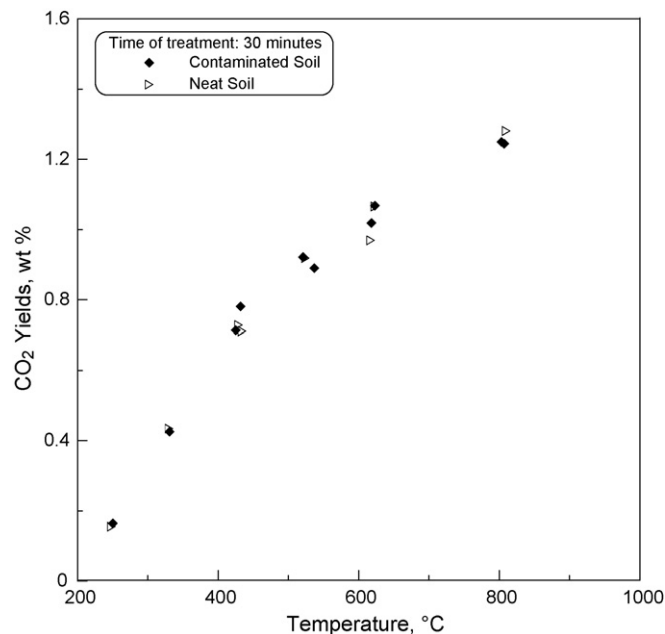


Fig. 5. CO<sub>2</sub> yield from both neat and contaminated soils as a function of temperature.

measurement of light gases by GC/TCD and GC/FID. Thus, the difference found can be attributed to the fact that the collection with liquid traps during the thermal process was not completely efficient. In fact, hexadecane was observed on the walls of the quartz tube and the Teflon<sup>®</sup> pipeline between the two traps of liquids.

Several studies about the cracking of *n*-hexadecane have been performed by different authors [19–24]. Depeyre et al. [20] detected, for operating conditions close to the thermal treatments reported in this work, the following light gases: H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub>, butanes, butadiene, among others. The ethylene, for different operating conditions, reported the highest yield. In the soil thermal treatment experiments carried out in the present work, the following gases were monitored: CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> to detect pyrolysis of hexadecane or thermal decomposition of the soil itself.

In Figs. 5–7 the yields of light gases (CO<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>, respectively), quantified after heating both clean and contaminated soil samples, are presented. These data indicate that the light gases generated during the thermal treatment of the polluted soil with respect to the uncontaminated soil were very similar. The C<sub>2</sub>H<sub>6</sub> yields show the same behavior (data not shown). Neither a significant increase in the generation of light gases (particularly for C<sub>2</sub>H<sub>4</sub> and CH<sub>4</sub> which are important gaseous products from hexadecane cracking [20]) nor new components from those found in the clean soil were detected (even for higher treatment temperatures). Therefore, poor chemical interaction between the contaminant and the soil components, and little or negligible chemical modifications of the hexadecane during the heating of the contaminated samples can be assumed. In other words, if the *n*-hexadecane pyrolyzed, the ethylene yield would increase significantly. This fact is confirming that, in the range of temperatures studied, the *n*-hexadecane release from the soil

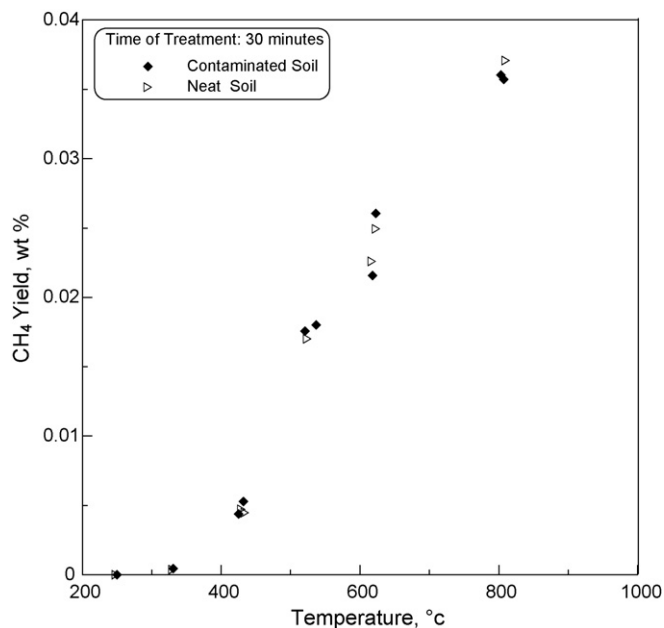


Fig. 6. CH<sub>4</sub> yield from both neat and contaminated soils as a function of temperature.

bed occurs through a mechanism of evaporation/desorption with non-noticeable chemical transformations.

In Fig. 8 the thermal profile of a soil sample heated from room temperature to 800 °C is presented. This figure also shows the corresponding vapor pressure of pure hexadecane and the behavior of the total pressure during the thermal treatment. Fig. 8 shows that at temperatures close to 250 °C the vapor pressure equals the total pressure. Then, at this thermal level, hexadecane is at boiling condition. Moreover, the soil bed is continuously purged with helium, favoring evaporation by carrying the contaminant at lower temperatures. If we suppose that evaporation

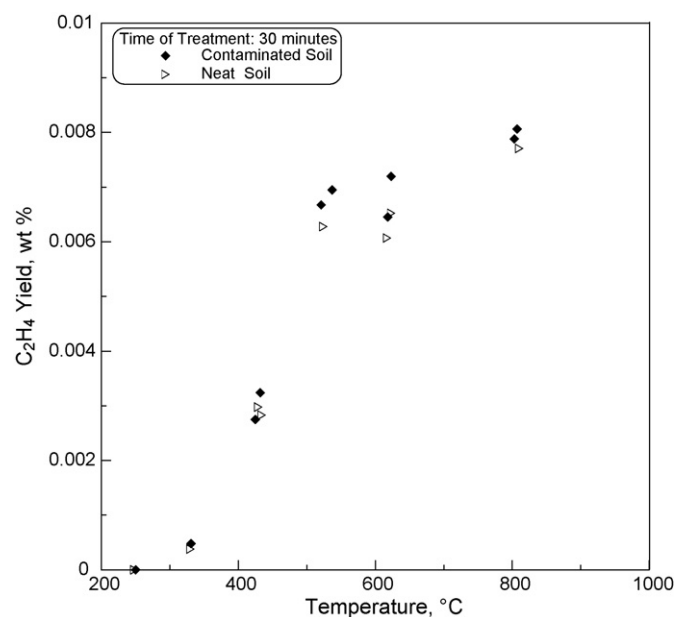


Fig. 7. C<sub>2</sub>H<sub>4</sub> yield from both neat and contaminated soils as a function of temperature.

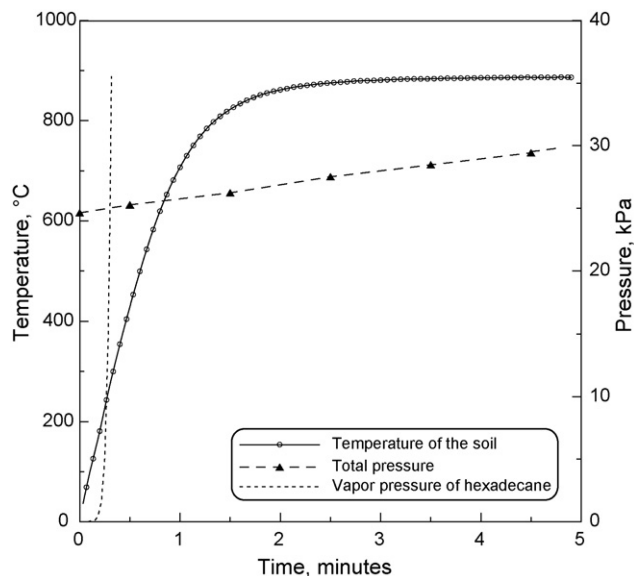


Fig. 8. Thermal profile, total pressure, and vapor pressure of hexadecane as a function of treatment time.

occurs without significant diffusional resistance and that desorption is not a controlling step (a proper hypothesis for soils with low surface area, due to the limited interactions between the soil and the contaminant [16]), any fraction of evaporated hexadecane will have (as maximum) an additional residence time inside the quartz tube of 0.42 min. This conservative value (spatial time) was calculated by using the helium STP flowrate and the cross-sectional area defined by the tube area. In fact, the residence time should be much lower than the time based on spatial considerations, due to:

- bed temperatures higher than standard temperature conditions,
- lower cross-sectional area restricted by solid particles,
- higher volumetric flowrate due to the generation of gases during the soil itself thermal degradation, and
- operating pressure from vacuum to atmospheric conditions.

Therefore, any fraction of evaporated hexadecane may exit the soil bed in a period shorter than 0.42 min. For the experiment with the highest maximum treatment temperature (800 °C), when this conservative residence time is achieved, the soil bed temperature reaches 400 °C. Consequently, the evaporated hexadecane cannot be exposed to very high temperatures.

It is well known that paraffins cracking at low conversion follow first-order kinetics [19,20]. That is the reason why the first-order apparent kinetic constant for hexadecane cracking is commonly found in the literature. The activation energy for hexadecane vary from 50 to 60 kcal/mol [20,22,23], and the pre-exponential factor can be either reported or calculated from data presented in the literature. Supposing that: (a) the kinetics *n*-hexadecane decomposition in the soil treatment experiments can be represented by a pseudo-first-order kinetics, (b) the maximum residence time available for pyrolysis of this contaminant is about 0.42 min, and (c) the soil bed is isothermal and operates

at the maximum temperature of 400 °C (this assumption leads to the highest reaction rate value); a maximum hexadecane cracking conversion of 0.08% can be expected. Thus, the extension of the pyrolysis reactions is negligible. Finally, it can be concluded that the main removal process should be the contaminant evaporation. Based on the calculated conversions, the 12–20% of the initial hexadecane content not accounted in the liquid fraction cannot be associated to pyrolysis reactions. Moreover, if only the real temperature (400 °C) is taken into account to calculate the volumetric helium flow, the conversion level drops to values close to 0.04%. The additional consideration of the sub-atmospheric operating conditions and the gases released during the thermal treatment of the soil should lead to even lower residence times and consequently lower conversion values. The lack of cracking reactions found for these experiments are in good agreement with other hexadecane cracking studies [19,20].

Depeyre et al. [20], for operating conditions close to the thermal treatments reported in this work, detected aromatic compounds for hexadecane conversion levels higher than 50%. Therefore, the increase in the ethylene yields should be observed before any aromatic compound is generated. Based on the light gases results obtained in the present work, the presence of aromatic compounds in the residual soil should not be expected for the tested experimental conditions.

#### 4. Conclusions

The results obtained at different temperatures (150–800 °C) showed that at about 300 °C the hexadecane can be removed almost completely from the soil matrix (99.9% DRE), and that temperatures above this value do not improve the removal efficiency noticeably.

By monitoring the light gases and liquid products, together with the hexadecane residual concentrations in the treated samples, evaporation became the main mechanism for the contaminant removal. The hexadecane is mainly collected in the liquids without undergoing chemical modifications. There was no evidence of pyrolysis reactions, indicating that the hexadecane leaves the soil bed rapidly before high temperatures are achieved. The contaminant desorption and the mass transport from the soil have to be fast steps, otherwise the hexadecane would have been exposed to severe treatment conditions and consequently pyrolysis products would have been detected. The observed poor soil-contaminant interactions can be explained by the low soil surface area. In fact, a small fraction of the initial contaminant can be adsorbed onto the soil as a monolayer, most of the hexadecane is located as multilayers around the soil particles. All the experimental results reveal evaporation as the key mechanism for hexadecane removal, even at high treatment temperatures.

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