

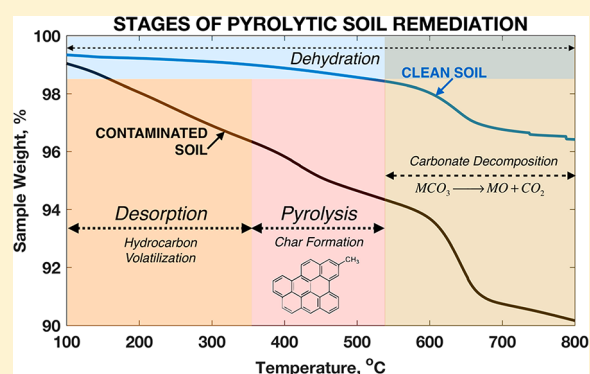
Pyrolytic Remediation of Oil-Contaminated Soils: Reaction Mechanisms, Soil Changes, and Implications for Treated Soil Fertility

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Supporting Information

ABSTRACT: Pyrolysis of hydrocarbon-contaminated soils offers the potential for rapid remediation without destroying soil fertility. Here we elucidate the fundamental mechanisms of pyrolytic treatment and advance understanding of the surface properties of pyrolyzed soils. Using thermogravimetry and evolved gas analysis, we identified the two stages of pyrolytic remediation. Desorption of light hydrocarbons is the dominant process for temperatures between 150 and 350 °C. Pyrolysis reactions dominate in the 400–500 °C range releasing gaseous products (hydrogen, methane, higher alkanes, and olefins) and forming a solid char. XPS analysis and partial combustion revealed that the char forms a layer coating the particles of treated soils. Since pyrolysis can effectively reduce the TPH of contaminated soils at temperatures below 500 °C, it avoids carbonate decomposition reactions that may lead to large soil pH increases and severe loss of fertility. This is a significant potential advantage over competing thermal processes that expose contaminated soil to temperatures above 500 °C.



INTRODUCTION

Thermal treatment technologies are generally very effective for the remediation of soils contaminated with heavy hydrocarbons, with removal commonly over 99%.^{1–7} However, these technologies frequently employ high temperatures and oxidative conditions that may damage soil integrity, ultimately impairing soil fertility.^{2,8} As a result, contaminated soils that have been treated with thermal techniques often cannot sustain vegetation and can only be used as backfill in construction projects or sent to landfills.^{9,10} Thus, full ecosystem restoration of petroleum-contaminated sites is incomplete in these cases.

Most studies on the efficacy of thermal remediation technologies focus on the hydrocarbon removal rather than the resulting soil quality. Therefore, knowledge of the full impacts of these methods on soil performance is limited. Much of the existing fertility research has been done on soils treated with thermal desorption processes. Some studies have concluded that thermally desorbed soils are “fairly environmentally friendly” as a result of qualitative, visual inspection.^{11,12} However, studies that delved deeper into the agricultural value of these soils found mixed results. Thermal desorption studies with PAH-impacted soils was reported to increase genotoxicity to earthworms in one case but experienced successful greening efforts in another.^{13,14} A recent study found that thermally desorbed soils produced the same yield of wheat as unimpacted soils but exhibited a lower grain protein content overall.¹⁵ The variability in these studies may be a result of differences between soil types and thermal desorption methods (varying oxygen levels and

temperatures). Findings for other thermal treatment technologies have been similarly difficult to parse. For example, some studies on incineration/combustion found poor seedling growth and high mortality,^{2,16} while others have found merely a period of stunted growth (5–6 weeks) before plant performance seemed to return to normal.¹⁶ Yet another study found no significant difference in agricultural performance between burning and other (nonthermal) treatments.¹⁷

Due to the high variability of field experiments with soils, some studies have examined the behavior of individual soil constituents under high heat to obtain deconstructed data that can be compiled to predict the thermal behavior of different soil types.¹⁸ Such studies suggest that exposing soils to high heat can result in alteration and decomposition of organic matter and minerals that may drastically change soil properties.^{19–24} For example, exposing soils to the high temperatures encountered in thermal desorption or smoldering remediation can result in drastic changes.¹⁹ The pH of the two soils they considered (initial pH values of 4.2 and 7.4) increased by 20–30% when the soils were heated to 500 °C in air and by 40–55% when the heat treatment temperature reached 1000 °C. Among the geochemical changes reported in that study were significant decreases in both cation exchange capacity (CEC) (up to 85%)

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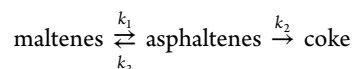
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and total N (40–50%) when the treatment temperatures exceeded 500 °C. Thus, different soil types react quite differently to thermal treatment, and a “one size fits all” approach to thermal remediation is likely to yield inconsistent results.^{25–27}

We recently proposed the use of pyrolysis as a thermal remediation option to facilitate ecosystem recovery of contaminated sites by restoring the agricultural value of soils.² Pyrolysis, or heat treatment in an anoxic environment, is commonly used in the production of charcoal/biochar, which has been linked to positive fertility benefits when added to soil as an amendment.^{28,29} In our earlier study, we pyrolyzed at 420 °C two soils contaminated with petroleum crudes and TPH contents of 16 000 mg/kg and 19 000 mg/kg. TPH is a term generally used to describe the measurable amount of petroleum-based hydrocarbons in the environment. In the context of this study, TPH quantitates the fraction of petroleum hydrocarbons that are solvent-extractable from samples of contaminated or treated soils. Results showed TPH removal well below applicable regulatory levels (<0.1% by weight), as well as increased beneficial agronomic properties compared to untreated or incinerated soils.²⁷ Plants grown in pyrolyzed soils (*Lactuca sativa*, *Arabidopsis thaliana*) also showed better germination and growth metrics than in untreated or incinerated soils. In addition, because of its lower temperature, pyrolysis may use less energy than soil incineration.² These encouraging results suggest that pyrolysis may be a more sustainable option to many current thermal treatment technologies.

The rational development and implementation of pyrolytic soil remediation require mechanistic understanding of the formation, spatial distribution, and chemical composition of the carbonaceous compound or “char” left behind after pyrolytic treatment. Because of its importance to petroleum processing, hydrocarbon pyrolysis and the resulting formation of solid petroleum cokes have been extensively studied over the past 7 decades.^{30–37} Thermal cracking reactions start at about 350 °C

leading to the formation of free radicals. This is the initiation step of a free-radical chain reaction sequence.^{34,38–40} The propagation steps of this sequence involve hydrogen abstraction, β -scission and radical addition reactions, while termination of the chain reaction occurs via radical recombination. While this mechanism cannot exactly predict what will happen in the complex reaction environment of oil crudes that contain hundreds if not thousands of different hydrocarbon molecules, it provides a consistent framework for interpreting experimental data on the pyrolysis of crude oils and residues. Most studies relevant to our work have considered the pyrolysis of homogeneous systems of crudes and their four fractions asphaltenes, resins, aromatics, and saturates. When asphaltenes are pyrolyzed at temperatures between 350 and 560 °C, the primary reactions involve decomposition of asphaltene to its aromatic core, smaller heptane-soluble hydrocarbons (or maltenes), and gas products that include C₁–C₄ hydrocarbons (gas) and H₂S.³¹ Secondary reactions then convert these products to lighter maltenes, more gas, and char. Asphaltenes consist of a core with condensed aromatic and heteroatomic rings, and alkyl chains attached to their periphery. Fission of these peripheral chains is probably the first step in asphaltene conversion and will very likely involve an α - β carbon bond because of the low dissociation energy (317 kJ/mol) of such bonds.^{31,34} Experiments with heavy crudes and residues revealed that maltene pyrolysis produces first asphaltenes and then coke in the following sequential reaction scheme:^{32,33,35}



As noted before, asphaltenes and maltenes will also produce C₁–C₄ hydrocarbons (gas). While paraffinic, naphthenic, and small aromatic molecules can also produce asphaltenes and eventually coke, the reaction rates of these reactions are

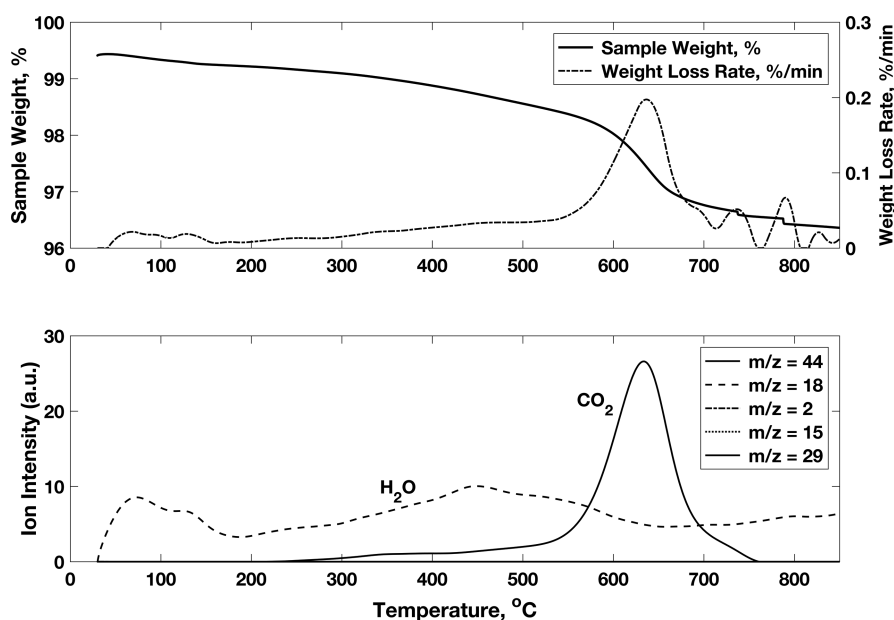


Figure 1. TG–MS analysis of uncontaminated (background) soil used to generate contaminated soil 1. This figure shows the weight loss of an uncontaminated (background) soil as it is heated in an inert atmosphere and the corresponding rates of (a) water release due to dehydration of clay minerals and (b) CO₂ release due to decomposition of carbonate minerals above 500 °C. No hydrocarbons or hydrogen were detected for runs with background soil. Top panel: Thermogravimetry (TG) and differential thermogravimetry (DTG) curves showing the weight loss and weight loss rate vs temperature. Bottom panel: Evolved gas analysis (EGA) curves showing ion intensities vs temperature of selected fragments: $m/z = 44$ for CO₂, $m/z = 18$ for H₂O, $m/z = 2$ for H₂, $m/z = 15$ for CH₃, and $m/z = 29$ for C₂H₅.

very small.^{31,32} We expect, therefore, that these hydrocarbons will evaporate before the pyrolytic remediation temperatures reach values high enough to reach appreciable rates for these cracking reactions.

All the previously mentioned studies considered the pyrolysis of homogeneous mixtures of petroleum hydrocarbon mixtures. Our pyrolytic remediation process, however, involves thermal treatment of contaminated soils that contain mostly soil and only a few weight percent of petroleum hydrocarbons.² Very few studies have considered the effect of soil minerals on pyrolysis and coke formation. One study found that clay components of reservoir formations can catalyze oxidation and encourage deposition of coke.⁴¹ Another study on in situ thermal recovery reported that the total surface area and surface properties of soil minerals may affect coke formation and type.⁴² Still, other investigators have concluded that surfaces of materials like quartz do not significantly enhance coke formation,⁴³ and a recent study on the pyrolysis of an Indonesian oil sand also reported that the residual sand did not influence the kinetics of the bitumen pyrolysis.⁴⁴

In order to provide a theoretical foundation for the soil remediation process that we recently introduced, this paper explores the mechanisms leading to the formation of the carbonaceous compound or “char” during thermal treatment of soils contaminated with heavy hydrocarbons under anoxic conditions. Using

thermogravimetry and evolved gas analysis, we characterize the stages of the pyrolysis process, compare our observations to the previously described literature results, and quantify the effect of soil minerals. Finally, we use XPS analysis to study the surface properties of remediated soils and characterize the spatial distribution of the char produced during pyrolysis to advance fundamental understanding of the resulting soil quality.

EXPERIMENTAL SECTION

Contaminated Soil Samples. This study considers two soils (soil 1 and soil 2) contaminated with heavy hydrocarbons. Soil 1 was created by spiking an Arizona topsoil with oil sludge from a crude oil well site. The contaminated soil had a TPH value of 19 000 mg/kg. On the basis of X-ray diffraction (Table S1 in Supporting Information), the composition of this soil was 12% clays, 10% carbonates, 31% quartz, 20% K-spar, 26% plagioclase, and 1% pyrite.²

Soil 2 had a TPH of 16 000 mg/kg and was taken from a crude oil spill at an oil well. X-ray diffraction showed that soil 2 was composed of 4% clays, 3% carbonates, 79% quartz, and 14% other minerals (Table S1 in Supporting Information). Contaminated soil 2 had a TPH of 16 000 mg/kg and was taken from a crude oil spill at an oil well. The crude oil contaminating this soil was lighter in composition than the oil found in soil 1.

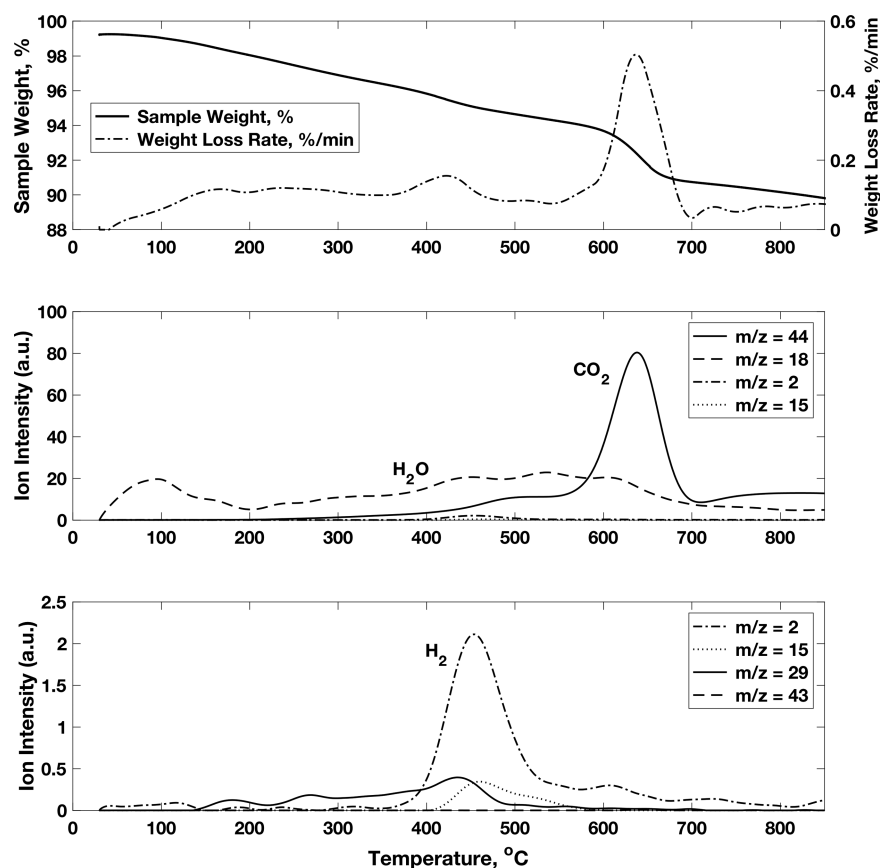


Figure 2. TG–MS analysis of contaminated soil 1. This figure highlights the behavior of petroleum-contaminated soil as it is heated in inert atmosphere. Since the sample consists primarily of soil, we observe (middle panel) water and CO₂ release patterns similar to those of Figure 1. The intensities of ions corresponding to desorbed hydrocarbons or pyrolysis products are much lower and are barely visible in the scale of the middle panel. The scale of the bottom panel is adjusted to highlight the ions corresponding to desorbed hydrocarbons or pyrolysis products that were barely visible in the middle panel. Top panel: Thermogravimetry (TG) and differential thermogravimetry (DTG) curves showing the weight loss and weight loss rate vs temperature. Middle panel: Evolved gas analysis (EGA) curves showing ion intensities vs temperature of selected fragments: $m/z = 44$ for CO₂, $m/z = 18$ for H₂O, $m/z = 2$ for H₂, and $m/z = 15$ for CH₃. Bottom panel: Evolved gas analysis (EGA) curves showing ion intensities vs temperature of selected fragments: $m/z = 2$ for H₂, $m/z = 15$ for CH₃, $m/z = 29$ for C₂H₅, and $m/z = 43$ for C₃H₇.

Note that uncontaminated background soil was not available for soil 2. Table S2 provides the carbon content, pH, and selected agronomic properties of all the uncontaminated, contaminated, and treated soils used in this study.

Soil pyrolysis was conducted in a 0.5 L fixed-bed reactor heated at 420 °C in a split-tube furnace (Thermo Scientific Lindberg/Blue M) for 3 h. Nitrogen flowed through the reactor at 1 L/min. The exhaust gas passed first through a trap to condense the moisture and liquid pyrolysis products, and the gases were vented to a fume hood. Temperature was monitored and logged throughout the experiment, with thermocouples placed in the center of the soil chamber and on the side of the reactor. Although a much shorter pyrolysis time could be used to meet cleanup standards, this long reaction time was chosen to obtain complete conversion of our petroleum hydrocarbons to pyrolysis products. This would allow us to measure the maximum amount of char remaining in the soil after pyrolysis and to accurately characterize the char's chemical composition and spatial distribution.

In addition, contaminated soils were incinerated under air in a muffle furnace (Thermo Scientific Lindberg/Blue M) at 650 °C for 3 h. This temperature was chosen to represent low temperature incineration (incineration can range from 600 to 1200 °C in the field), in the hopes that this would present one of the least-destructive scenarios for incinerated soils.

Evolved Gas Analysis (EGA) with Thermogravimetry–Mass Spectrometry (TG–MS). Thermogravimetric analysis–mass spectrometry (TG–MS) experiments were performed using a Q500 thermobalance (TA Instruments, New Castle, DE) equipped with evolved gas analysis furnace and connected with a heated capillary transfer line to a Discovery quadrupole mass spectrometer (TA Instruments, New Castle, DE). The mass spectrometer was operated in electron impact ionization mode with 70 eV electron energy. All TG–MS experiments were carried out using argon purge gas with a flow rate of 100 mL/min and started with a 90 min purge at room temperature to flush the

air entering the system when the samples are loaded. After the purge, the samples were heated at 10 °C/min to a final temperature of 900 °C. To improve the signal-to-noise ratio, we used the selected ion monitoring technique for all TG–MS experiments by limiting the number of ions scanned during each run to 10 or fewer. Using multiple scans for each sample, the mass spectrometric intensities of ion fragments that are the main fingerprints of aliphatic, aromatic, and unsaturated hydrocarbons were recorded together with the sample weight and temperature. Ions with $m/z = 15$ and $m/z = 16$ were used to detect (or eliminate) the presence of methane, since the $m/z = 16$ ion also comes from the fragmentation of carbon dioxide and oxygen. Ions with $m/z = 2$ and $m/z = 44$ were monitored to detect the evolution of hydrogen and carbon dioxide, respectively. Finally, the intensity of the main oxygen fragment ($m/z = 32$) was always recorded, and its level was checked to ensure there were no leaks in the instrument. Each intensity curve was normalized by the “dry” sample weight, which was taken here to be the weight recorded at 120 °C. Ion intensities were corrected using baselines obtained with clean, empty pans in the thermobalance.

Partial Combustion of Treated Soils. Partial oxidation or combustion experiments of soils treated with our pyrolysis process were carried out in a thermogravimetric analyzer (Q500, TA Instruments, New Castle, DE) connected to a nondispersive infrared (NDIR) gas analyzer (LI-840A, LI-COR, Lincoln, NE). The NDIR analyzer allowed for continuous measurement of the CO₂ and H₂O concentrations in the gaseous stream exiting the thermogravimetric analyzer (TGA). In order to flush the air entering the system when the samples are loaded on the thermobalance, all experiments started with a 15 min purge at room temperature under nitrogen flowing at 100 mL/min. The sample was then rapidly heated to the final reaction temperature under nitrogen and held there for 15 min. At that point, the furnace gas stream (40 mL/min) was switched to air and the sample was allowed to react with oxygen for 90 min.

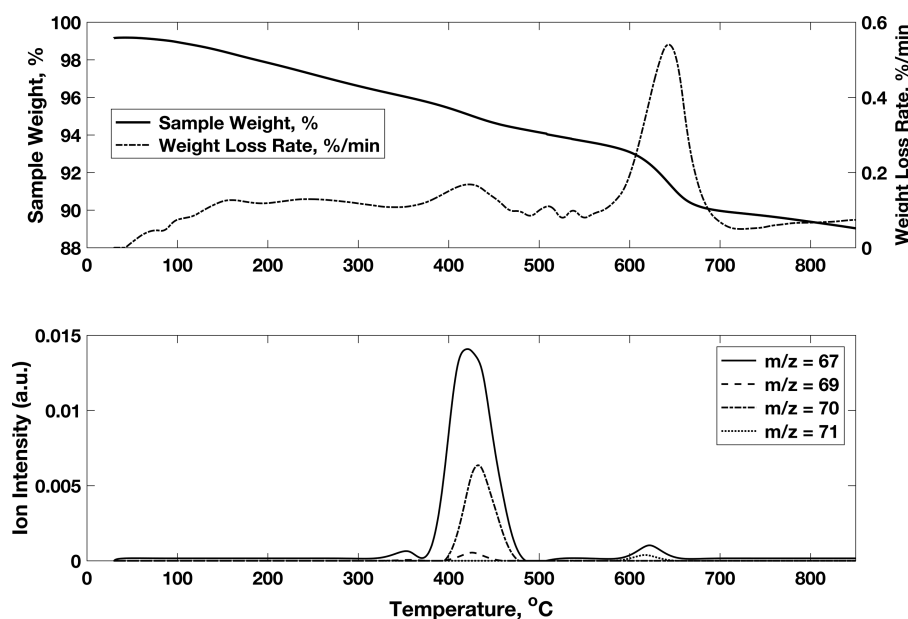


Figure 3. TG–MS analysis of contaminated soil 1. The detection of fragments indicating release of unsaturated or cyclic hydrocarbons supports the hypothesis that pyrolysis reactions (like β -scission) are occurring at temperatures between 350 and 500 °C. Top panel: Thermogravimetry (TG) and differential thermogravimetry (DTG) curves showing the weight loss and weight loss rate vs temperature. Bottom panel: Evolved gas analysis (EGA) curves showing ion intensities vs temperature of selected fragments indicating the presence of unsaturated or cyclic hydrocarbons: $m/z = 67$ for C₅H₇, $m/z = 69$ for C₅H₉, $m/z = 70$ for C₅H₁₀, and $m/z = 71$ for C₅H₇.

To detect char combustion, the CO_2 and H_2O concentrations in the gas stream exiting the TGA were continuously monitored together with the weight and temperature of the sample. Since a very small amount of char (usually less than 1 mg) will react with oxygen over the 90 min duration of the partial combustion experiment, we can safely neglect the contribution of combustion gases to the overall flow rate. The transfer line between the TGA and the NDIR analyzer introduces a time delay in the measurement of. This time delay depends on the flow rates of the carrier gases and was measured with several calibration experiments. The line connecting the TGA instrument to the NDIR analyzer is not heated, and water may very well condense in this line. Thus, the H_2O concentrations detected by the NDIR analyzer will only be used as qualitative indications that combustion is indeed taking place when oxygen is introduced into the TGA.

Determination of Soil Surface Characteristics Using XPS. X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic technique that measures the elemental composition of the surface of a material. XPS spectra are obtained by irradiating a material with a beam of X-rays and simultaneously measuring the kinetic energy and number of electrons that escape from the top 1–10 nm of the material. We used a PHI Quantera X-ray photoelectron spectrometer (Physical Electronics, Inc., Chanhassen, MN) to analyze the surface properties of soil

particles. Samples were shifted using 284.5 eV as the standard carbon binding energy. An aluminum anode served as the X-ray source. The pass energy was 26 eV. Carbon was examined from 280 to 290 eV, and 30 sweeps were conducted. Silicon was measured from 98 to 108 eV with 30 sweeps, aluminum from 70 to 78 eV with 50 sweeps, calcium from 341 to 361 eV with 50 sweeps, and oxygen from 526 to 536 with 10 sweeps. MultiPak software was used for analysis of data.

RESULTS AND DISCUSSION

Heating Triggers Significant Changes in the Mineral Components of Soil 1. To better understand the mechanisms of hydrocarbon pyrolysis in oil-contaminated soils and the effects of soil minerals, we first performed TG–MS experiments with uncontaminated (background) soil 1. Soil samples were heated at $10\text{ }^\circ\text{C}/\text{min}$ to $900\text{ }^\circ\text{C}$ under flowing argon. Figure 1 presents the evolved gas analysis (EGA) results from a run with background soil. First, the soil loses its moisture at around $100\text{ }^\circ\text{C}$ (peak for $m/z = 18$). Another broad H_2O peak appears after about $200\text{ }^\circ\text{C}$ with a maximum around $450\text{ }^\circ\text{C}$. The rate of H_2O release decreases after that point and starts increasing again when the temperature exceeds $700\text{ }^\circ\text{C}$. This pattern of H_2O release is associated with structural changes of clay minerals. Dehydration of clays takes place at temperatures

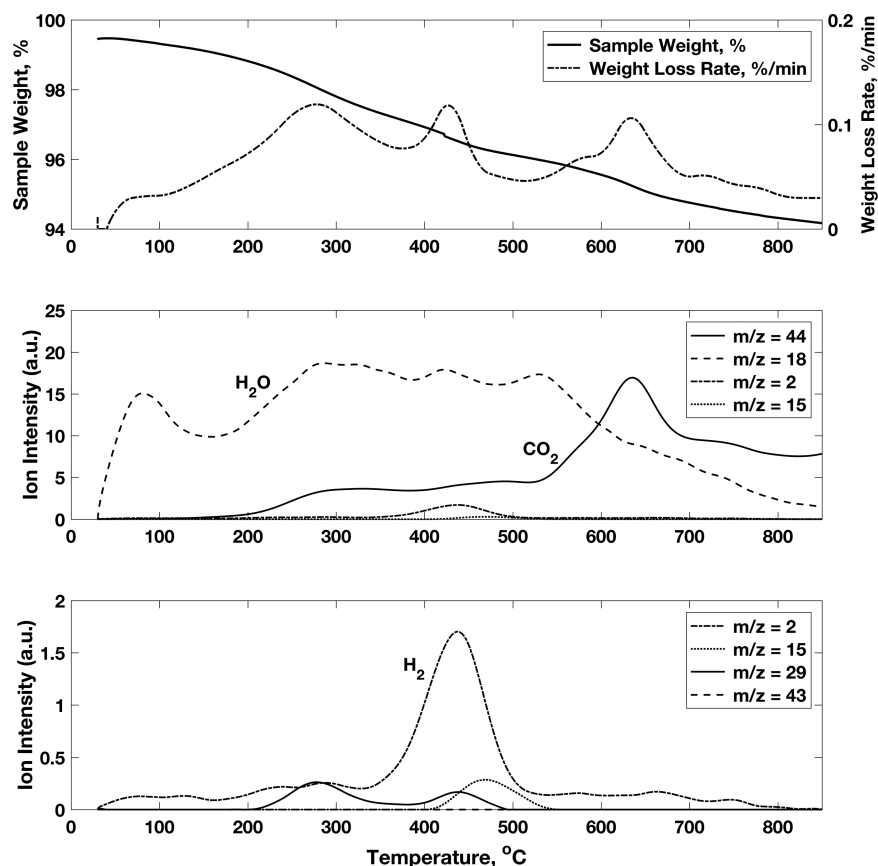


Figure 4. TG–MS analysis of contaminated soil 2. While contaminated soil 2 shows a response similar to that of contaminated soil 1 (Figure 2), it exhibits a smaller CO_2 peak due to its lower carbonate content. This observation emphasizes the potentially significant differences between soils and the need for careful analysis when developing thermal treatment strategies. A comparison of the ion intensities presented in the bottom panels to those of Figure 2 demonstrates that the pyrolytic remediation of both contaminated soils involves the same two processes (desorption and pyrolysis) that occur over very similar temperature ranges. Top panel: Thermogravimetry (TG) and differential thermogravimetry (DTG) curves showing the weight loss and weight loss rate vs temperature. Middle panel: Evolved gas analysis (EGA) curves showing ion intensities vs temperature of selected fragments: $m/z = 44$ for CO_2 , $m/z = 18$ for H_2O , $m/z = 2$ for H_2 , and $m/z = 15$ for CH_3 . Bottom panel: Evolved gas analysis (EGA) curves showing ion intensities vs temperature of selected fragments: $m/z = 2$ for H_2 , $m/z = 15$ for CH_3 , $m/z = 29$ for C_2H_5 , and $m/z = 43$ for C_3H_7 .

below 500 °C as water on the external surfaces and between the clay mineral layers is lost.^{45–47} Dehydroxylation takes place between 500 and 800 °C as structural hydroxyl groups react with each other producing water that is then released.^{45–47} For some clays, dehydration is at least partially reversible if they are not exposed to temperatures higher than 410 °C but irreversible after heating to 570 °C.⁴⁶

Much more important for the agricultural quality of thermally treated soils, however, are reactions associated with the release of significant amounts of CO₂. For our background soil 1, CO₂ release (trace of *m/z* = 44) begins around 300 °C and increases slowly in the 300–500 °C temperature range. As the temperature goes beyond 550 °C, the rate of CO₂ release increases sharply with a pronounced peak at about 650 °C. Since no other ions were detected in this temperature range, the CO₂ released is in all likelihood the product of carbonate decomposition. Thermogravimetric studies have shown that the various carbonate minerals decompose at different temperature ranges with siderite, magnesite, and calcite exhibiting sharp CO₂ peaks between 400 and 700 °C.⁴⁸ The literature data support our hypothesis that the CO₂ peak of Figure 1 is due to the decompositions of carbonates since soil 1 contains about 10% of carbonates (primarily calcite and dolomite or CaMg(CO₃)₂). We would expect, therefore, that heat treatment at temperatures exceeding 500 or 600 °C will have significant adverse effects on this soil, since the decomposition of carbonates may increase its pH to potentially caustic levels that hinder plant growth. The pyrolytic remediation process we have proposed, however, avoids this destructive decomposition of carbonates by keeping the processing temperature below 500 °C.

Pyrolytic Remediation of Contaminated Soils Involves Two Distinct Processes. Figures 2 and 3 present the evolved gas analysis data for contaminated soil 1. Since soil 1 contains only a few wt % of crude oil, the peaks of water and carbon dioxide again dominate the MS spectra as shown in Figure 2 (middle panel). After losing its moisture at around 100 °C, contaminated soil 1 releases water between 200 and 800 °C in a pattern similar to that we observed for the background soil (see Figure 1). Water loss is again due to dehydration and dehydroxylation of clay minerals.^{45,46}

Figure 2 (bottom panel) shows the intensities of three key ions that indicate the presence of hydrocarbon desorption and pyrolysis products in the exit gas stream: (a) the *m/z* = 29 ion corresponds to the *CH₂CH₃ fragment, one of the most prevalent products of alkane fragmentation; (b) the *m/z* = 15 or *CH₃ ion comes primarily from the fragmentation of methane; (c) the *m/z* = 2 fragment that indicates the presence of hydrogen. Note the different ion intensity scales used for the middle and bottom panels of Figure 2.

For temperatures between 150 and 350 °C, the ion intensities of Figure 2 (bottom panel) indicate that the exit gas stream contains alkanes but no hydrogen or methane. Hydrogen and methane appear only when the sample temperature is between 400 and 550 °C. Since methane is one of the main gaseous product of asphaltene pyrolysis³¹ and hydrogen is a key product of the initiation and propagation reactions of hydrocarbon pyrolysis,^{34,39} we can conclude that pyrolysis reactions take place when contaminated soil 1 is heated in the 400–550 °C range. Alkane fragments are also detected in the same temperature range since low molecular weight hydrocarbons (C₁–C₄) are also produced during the pyrolysis of asphaltenes.³¹ Figure 3 shows that fragments corresponding to unsaturated (olefins) or cyclic hydrocarbons are also observed between 400 and 500 °C but only in this

temperature range. This is another indication that pyrolysis reactions (like β-scission) take place when contaminated soil 1 is heated at temperatures between 400 and 500 °C in the absence of oxygen.^{34,39} On the other hand, the absence of pyrolysis products (like hydrogen or methane) in the 150–350 °C range strongly suggests that thermal desorption (evaporation) of lighter hydrocarbons is the dominant process occurring in this temperature range.

Evolved gas analysis for contaminated soil 2 revealed a similar pattern to that of contaminated soil 1 for water loss (Figure 4, middle panel). However, soil 2 exhibited a much smaller peak for CO₂ release around 650 °C and significant CO₂ release above 700 °C. This is because soil 2 contains only 3% total carb-

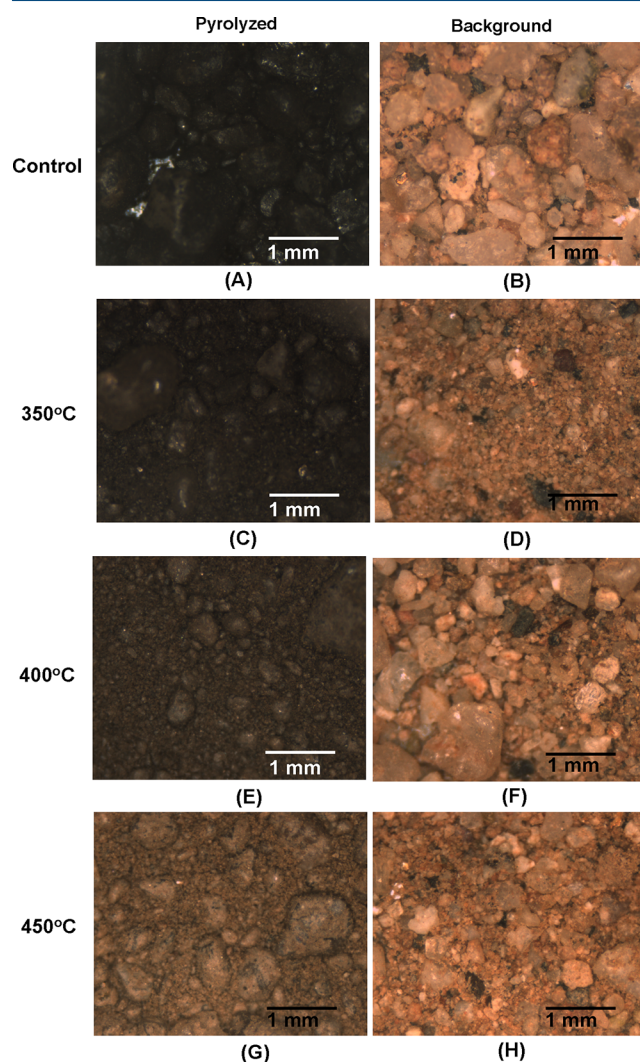


Figure 5. Left column: Optical images of contaminated soil 1 after pyrolytic treatment and partial combustion. Image A shows pyrolyzed soil 1 that has not been subjected to partial combustion (control), while images C, E, and G show samples of pyrolyzed soil 1 after partial combustion at 350, 400, and 450 °C, respectively. As the combustion temperature increases, the color of the pyrolyzed soil gets progressively closer to that of the background soil (see images on right column). These observations support the theory that pyrolyzed soils are covered with a film of combustible “char” that is removed through combustion at progressively increasing temperatures. Right column: Image B shows a sample of the uncontaminated or background soil 1 (control), while images D, F, and H show samples of background soil 1 after partial combustion at 350, 400, and 450 °C, respectively. The visual appearance of background soil remains practically unchanged after combustion.

onates (vs 10% for soil 1) with different proportions of calcite and dolomite. The bottom panel of Figure 4 presents the ion intensities of fragments that indicate the presence of hydrocarbons and pyrolysis products in the purge stream. The patterns are very similar to those observed with contaminated soil 1. Pyrolysis products (methane and hydrogen) appear only in the 400–500 °C temperature range, while only alkanes (and no H₂ or CH₄) are detected between 150 and 350 °C.

Figures 2–4 and MS spectra obtained from additional experiments with the two contaminated soils support our original

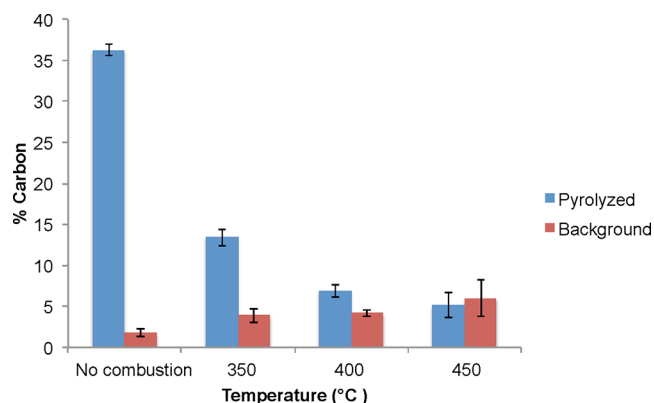


Figure 6. Percentage of carbon found on the surface of soil particles partially combusted at different temperatures. The controls are pyrolytically treated contaminated soil and uncontaminated (background) soil. Both controls have not been subjected to partial combustion. The percentage of carbon was calculated using the areas of the C peaks and the corresponding sensitivity factor of the orbital and pass energy. This plot supports the optical microscopy findings showing that a layer of carbonaceous char covers the pyrolyzed soil particles. Subsequent combustion of this char removes the char film producing a soil with similar surface carbon content as background soils.

hypothesis² that pyrolytic soil remediation occurs in two steps. Desorption of the lighter hydrocarbons is the dominant process for temperatures between 150 and 350 °C. Pyrolytic reactions dominate in the 400–500 °C range releasing pyrolysis products (like hydrogen, methane, or olefins) and leading to the formation of a carbonaceous solid material (char) that remains in the treated soil.

XPS Analysis Reveals That Pyrolyzed Soil Particles Are Covered by a Coke Film. We previously showed that pyrolyzed soils contain higher amounts of carbon than background, uncontaminated soils.² Furthermore, we presented H/C ratios measured with elemental analysis showing that the residual char left in pyrolyzed soils had a composition in the range of petroleum coke.

Figure 5 presents digital optical microscopy images of (i) pyrolyzed soil 1 (panel A), (ii) samples of pyrolyzed soil 1 that were heated for 1 h in the presence of air at 350, 400, and 450 °C (panels B, C, and D, respectively), (iii) background uncontaminated soil 1 (panel E), and (iv) samples of background soil 1 that were heated for 1 h in the presence of air at 350, 400, and 450 °C (panels F, G, and H, respectively). The pyrolyzed soil (panel A) has a shiny appearance and much darker color than background soil (panel E). As the pyrolyzed soil is oxidized in air at progressively higher temperatures from 350 to 450 °C (panels B, C, and D), its color gets closer and closer to that of uncontaminated (background) soil treated under the same conditions (panels F, G, and H). These observations suggest that pyrolysis covers the treated soil particles with a layer of “coke-like” char, which burned away upon exposure to air at gradually higher temperatures. Pyrolyzed soil particles that were not oxidized (Figure 5A) should be coated with the thickest layer of carbonaceous material (char). Below this layer, we should find the inorganic soil constituents: quartz (SiO₂), K-spar (KAlSi₃O₈), clays like illite/mica (usually represented by the formula

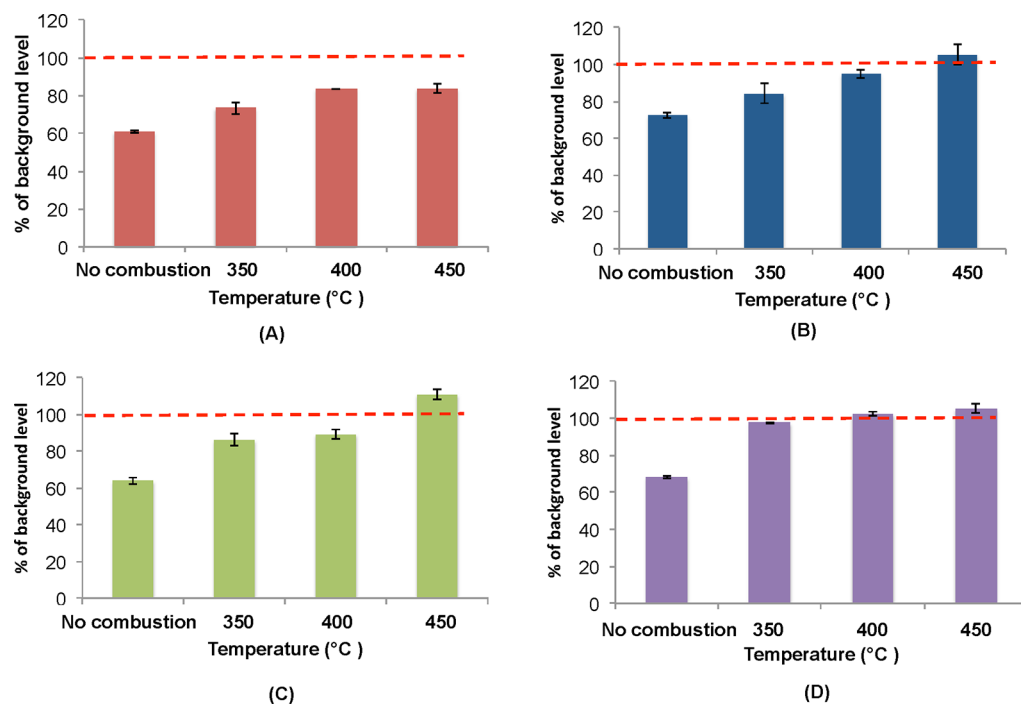


Figure 7. Percentage of (a) silicon, (b) aluminum, (c) calcium, and (d) oxygen on the surface of partially combusted pyrolyzed soils. 100% represents the amount of each element found in uncontaminated background soil. In conjunction with the results of Figure 6, the increase of these elements to background levels following combustion shows that the carbon film found on the surface of pyrolyzed soils is progressively removed as the temperature increases.

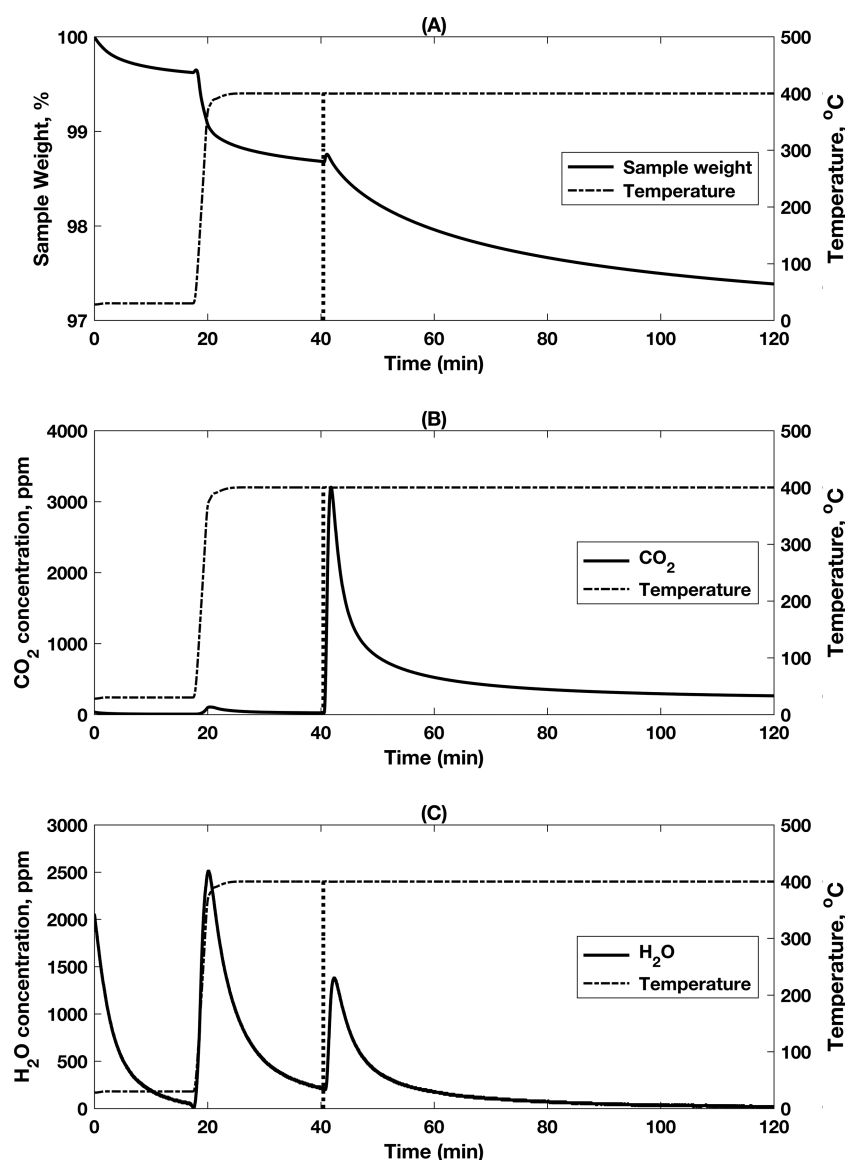


Figure 8. Plot showing (A) sample weight loss, (B) outlet CO₂ concentration, and (C) H₂O concentration observed as a sample of pyrolyzed soil 1 undergoes partial combustion at 400 °C. The dotted vertical line at 40 min denotes the introduction of air into the TGA furnace. Clearly, the introduction of air triggers the combustion of the char layer covering the surface of pyrolyzed soil particles.

$K_{0.65}Al_{2.0}[Al_{0.65}Si_{3.35}O_{10}](OH)_2$, and carbonates (dolomite $CaMg(CO_3)_2$ and calcite $CaCO_3$).

To corroborate this hypothesis, we used XPS to measure the chemical composition of the surface of uncontaminated, pyrolyzed, and oxidized soil particles. XPS analysis of the pyrolyzed particles (sample of Figure 5A) revealed that carbon was the dominant chemical component of their top surface layer and that this concentration was much higher than that of the surface of uncontaminated soil (leftmost pair of bars of Figure 6). The carbon of uncontaminated soil was from its 10% carbonate content. In addition to C, the top surface layer of pyrolyzed soil particles had smaller amounts of Si, Al, Ca, and O, which clearly came from the various inorganic soil minerals. These amounts, however, were only about 60% of the Si, Al, Ca, and O that XPS detected on the surface of the uncontaminated soil (see leftmost bars of Figure 7A–D). Taken together, these observations lead to the conclusion that the char film coating the pyrolyzed particles either (a) was thinner than the maximum depth reached by the XPS rays (usually 5–10 nm) or (b) has nonuniform

thickness allowing the X-rays to hit inorganic soil minerals in certain parts of the scanned area.

When we analyzed the samples of pyrolyzed soils exposed to oxygen at 350, 400, and 450 °C (panels C, E, and G, respectively, of Figure 5), XPS detected decreasing amounts of C with increasing reaction temperature until the surface C concentrations reached levels equal to those observed for uncontaminated soil (Figure 6). This is a clear indication that the char film thickness decreased as the carbonaceous material gradually burned away. And as the thickness of the char layer decreased, XPS detected more and more electrons coming from Si, Al, Ca, or O and fewer electrons coming from C. Figure 7 shows exactly these trends. The surface concentrations of Si, Al, Ca, and O gradually increased with oxidation temperature to approach the levels XPS detected for the uncontaminated soil particle.

Evolved Gas Analysis Confirms the Presence of Char in Treated Soils. Figure 8 presents thermogravimetry and evolved gas analysis results from a partial combustion experiment of contaminated soil 1 that was treated at 420 °C with our

pyrolysis process. The sample weight loss (about 1.3%) detected during the initial purge and heating periods (Figure 8A) is primarily due to the loss of moisture that results in a sharp peak in the outlet H₂O concentration at about 18 min when the sample temperature starts to rise rapidly (Figure 8C). The H₂O concentration decreases rapidly as the sample reaches its final reaction temperature of 400 °C. We should note, however, that dehydration of the clay components of soil 1 at temperatures above 200 °C may also contribute to weight loss and release of water as shown in Figures 1 and 10. By contrast, very low CO₂ concentrations are detected during the first 40 min of the experiment (Figure 8B). Calibration experiments have established that

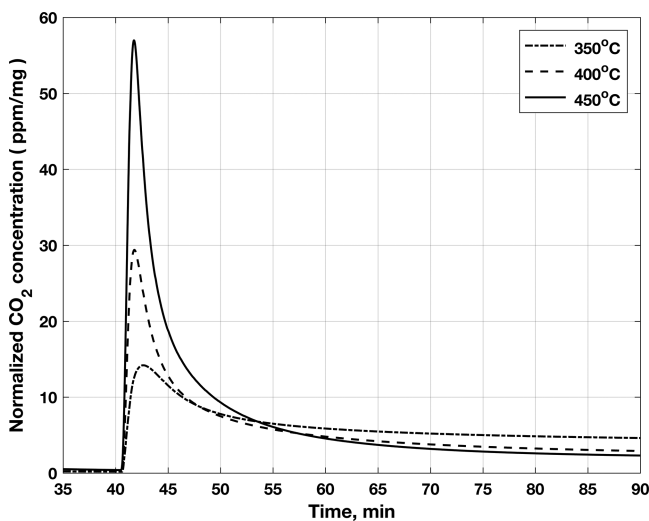


Figure 9. Normalized outlet CO₂ concentrations measured by partially combusting samples of pyrolyzed soil 1 at three different temperatures. Concentrations are normalized with respect to the weight of each sample. As expected for a chemical reaction, the peak outlet CO₂ concentration is strongly affected by the combustion temperature.

the CO₂ detected during the last part of this stage is due to the impurities of the air.

At about 40 min after the start of the experiment, the furnace gas was switched from nitrogen to air. This gas switch is indicated in all panels of Figure 8 by a vertical dotted line. Almost immediately after the gas change, the CO₂ concentration jumps from less than 20 ppm to more than 3,200 ppm (Figure 8B). This large increase is clearly caused by a combustion reaction. The char covering the soil particles is slowly reacting with oxygen to form carbon dioxide and water. The H₂O concentration also exhibits a sharp peak that is slightly shifted by a few minutes due to the slower response of the NDIR analyzer to changes in the moisture content of the gas.

The outlet CO₂ concentration is strongly affected by the reaction temperature and its initial value approximately doubles for every 50 °C temperature increment (Figure 9), another indication that a chemical reaction (combustion) is taking place with activation energy of about 50 kJ/mol.

EGA Analysis Suggests That Pyrolysis Is Less Destructive than Incineration. To better understand the impacts of thermal treatment, we carried out additional TG–MS runs with pyrolyzed (420 °C, nitrogen) and incinerated (650 °C, air) soils.² Since pyrolytic treatment had almost completely removed their total petroleum hydrocarbon (TPH) content, pyrolyzed soils released negligible amounts of hydrocarbons or pyrolysis products and smaller amounts of water due to dehydration of clay minerals in the background soil.

The MS spectra of pyrolyzed soils still showed a strong CO₂ peak suggesting that pyrolysis at 420 °C prevented significant decomposition of carbonate minerals while still removing TPH. This is clearly seen from Figure 10 that shows the TG, DTG, and EGA curves for a sample of pyrolyzed soil 1 and a comparison with Figures 1 and 2.

However, the MS spectra of incinerated soils showed a drastic reduction in the amount of CO₂ released in the 550–650 °C range and, consequently, a much smaller overall weight loss.

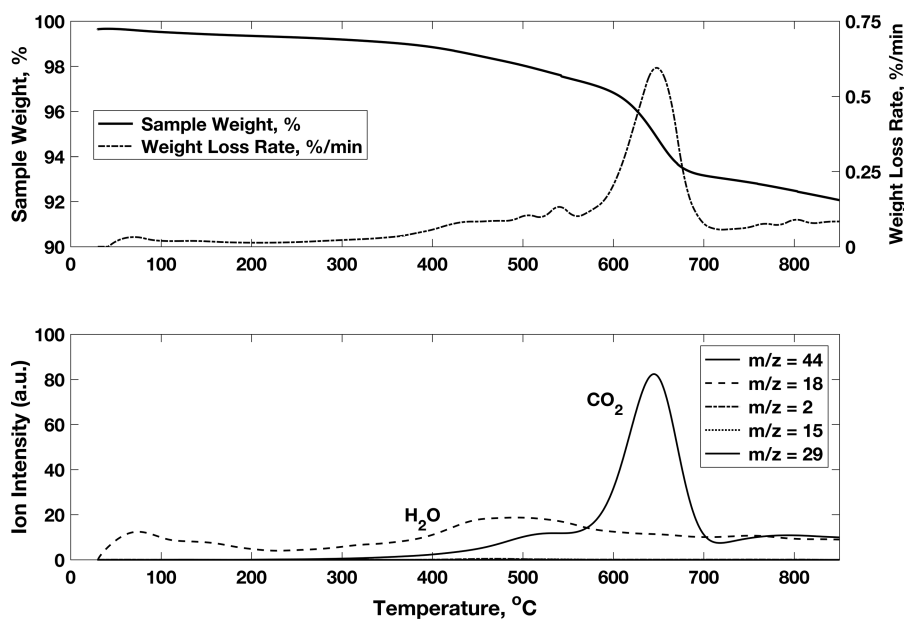


Figure 10. TG–MS analysis of pyrolyzed soil 1. The presence of a strong CO₂ peak shows that the carbonate minerals were not decomposed during the pyrolytic remediation of the contaminated soil. Also, negligible amounts of hydrocarbon fragments or hydrogen were detected for all runs with pyrolyzed (treated) soil 1. Top panel: Thermogravimetry (TG) and differential thermogravimetry (DTG) curves showing the weight loss and weight loss rate vs temperature. Bottom panel: Evolved gas analysis (EGA) curves showing ion intensities vs temperature of selected fragments: $m/z = 44$ for CO₂, $m/z = 18$ for H₂O, $m/z = 2$ for H₂, $m/z = 15$ for CH₃, and $m/z = 29$ for C₂H₅.

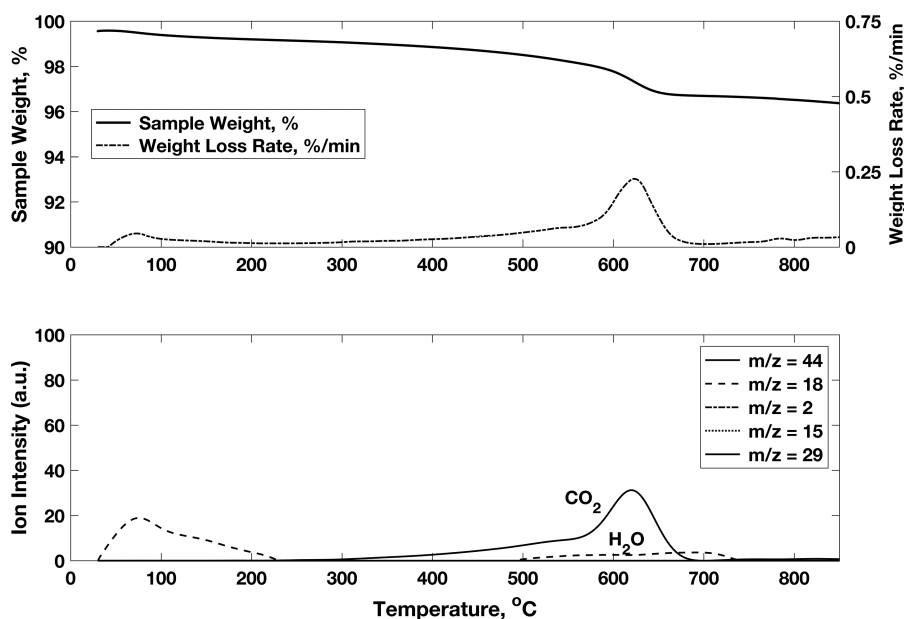


Figure 11. TG–MS analysis of soil 1 incinerated in air at 650 °C for 3 h. Notably, significantly less CO₂ was released from incinerated soil 1 than from either pyrolyzed (treated) soil 1 or contaminated soil 1, a strong indication that carbonates underwent some decomposition during the incineration process. Top panel: Thermogravimetry (TG) and differential thermogravimetry (DTG) curves showing the weight loss and weight loss rate vs temperature. Bottom panel: Evolved gas analysis (EGA) curves showing ion intensities vs temperature of selected fragments: $m/z = 44$ for CO₂, $m/z = 18$ for H₂O, $m/z = 2$ for H₂, $m/z = 15$ for CH₃, and $m/z = 29$ for C₂H₅.

Figure 11 presents TG, DTG, and EGA curves for a sample of incinerated soil 1. The drastic differences in the size of CO₂ peaks and the overall weight losses shown in Figures 10 and 11 suggest that incineration at 650 °C caused significant decomposition of the carbonate minerals.

We postulate that the loss of buffering capacity caused by carbonate destruction has negative effects on soil fertility, mainly by contributing to an increase of the pH of treated soils. This finding is supported by the results presented in our earlier work,² in which we reported that soils incinerated at 650 °C reached caustic pH levels and exhibited poor overall plant growth.² When contaminated soil 1 was incinerated, its pH increased from 7.7 to 11.9, while the corresponding pH increase for soil 2 was about 15–20% smaller. Our TG–MS measurements support the hypothesis that the observed pH increases were at least partially due to carbonate decomposition. The larger the difference between the amounts of CO₂ released from background and pyrolyzed or incinerated soils, the higher was the differential increase in the pH of treated soils. We should note that even though we can mitigate pH increases by adding lime to treated soils, carbonate decomposition reactions are endothermic and will increase the total energy costs of pyrolysis.

There are, however, additional factors that can trigger soil pH changes during thermal treatment. The decomposition of soil organic matter (SOM) may destroy organic acids and increase the soil pH.¹⁹ Since SOM can be replaced after treatment, this may not be a serious problem for fertility restoration. However, high temperatures can also trigger clay dehydration (see, for example, the water release curves in Figures 1 and 2). Dehydration can lead to clay collapse, soil texture changes and the formation of base oxides via a mechanism involving the displacement of H⁺ and their replacement by alkali cations.^{45,49} As a result, high treatment temperatures can lower the pH of soils containing large amounts of clays and little SOM.⁴⁹ However, the same investigators showed that even small amounts of magnesium carbonate (3.7 wt %) can trigger significant pH increases when

a topsoil with low SOM and very high clay content is heated to 500 °C.⁴⁹ This is consistent with the results of our study.

We conclude that multiple processes (e.g., SOM decomposition, clay dehydration, carbonate decomposition) interact to determine the magnitude of soil pH changes during thermal treatment. Still, it is advisable to avoid, if possible, high heat treatment temperatures that might lead to irreversible clay dehydration and/or carbonate decomposition. In addition to potential soil damage, these endothermic processes will increase the energy costs.

CONCLUDING REMARKS

Soil pyrolysis shows promise as a relatively benign thermal treatment technology for the remediation and vegetative reuse of soils contaminated with heavy petroleum hydrocarbons. This paper addresses key knowledge gaps concerning the fundamental mechanisms occurring during pyrolysis and the spatial distribution and of residual char in pyrolyzed soils.

We found that pyrolytic soil remediation occurs in two steps. The lighter hydrocarbons desorb (evaporate) when the temperature is between 150 and 350 °C. Pyrolysis reactions dominate in the 400–500 °C range releasing hydrogen and more hydrocarbons (methane, higher alkanes, and olefins) and leading to the formation of a residual carbonaceous material (char) that coats the soil particles. The process is complete at temperatures below 500 °C and is effective in reducing the TPH content of contaminated soils to levels well below the regulatory requirements.

Another important finding is that thermal soil remediation processes should try to avoid exposing the soil to high temperatures (greater than 550 °C in our case) to avoid decomposition of carbonates. This and similar findings from the literature^{25,49} emphasize the importance of carefully designing remediation projects to strike a balance between achieving sufficient contaminant reduction and avoiding high temperatures that can lead to severe deterioration of soil function or

unnecessarily high energy costs. The toolbox of analytical techniques used in this study (EGA, TG–MS, TGA) combined with the new mechanistic pyrolysis model can provide rapid evaluation of key properties of any soil–oil system and guide the optimal selection of processing conditions for field applications.

By improving fundamental understanding of pyrolytic treatment, this paper may facilitate regulatory acceptance of this novel technology and ultimately enable deploying a thermal remediation technology that offers the potential for cost-effective contaminated soil reuse and ecosystem recovery.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.iecr.7b04651](https://doi.org/10.1021/acs.iecr.7b04651).

Table S1 listing clay mineralogy analysis results and Table S2 listing carbon content and soil parameters (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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