

## Research Paper

## Clays play a catalytic role in pyrolytic treatment of crude-oil contaminated soils that is enhanced by ion-exchanged transition metals



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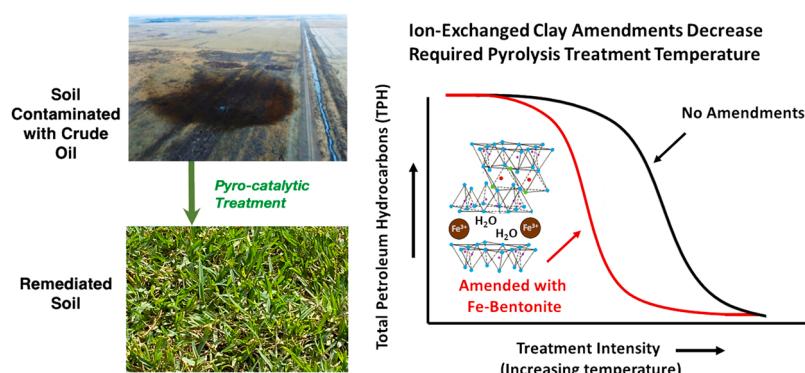
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## HIGHLIGHTS

- Pyrolytic treatment reliably removed TPH to remediate crude oil-contaminated soils.
- Metal-impregnated clay amendments (10 %wt) enabled treatment at lower temperatures.
- Pyrolysis degradation products appeared at lower temperatures in amended soils.
- Fe and Cu play a catalytic role, decreasing needed temperature & contact time.
- Fe-exchanged bentonite enhanced TPH removal more than Cu-exchanged bentonite.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Pyrolytic treatment of crude-oil contaminated soils offers great potential for rapid remediation without destroying soil fertility with lower energy requirements than incineration. Here, we show that clays impregnated with non-toxic transition metals (iron or copper) can be used as an amendment to decrease the required pyrolytic treatment temperature and time. Amending a weathered crude-oil contaminated soil with 10 % (by weight) of bentonite modified via ion-exchange with Fe or Cu, achieved 99 % removal of residual total petroleum hydrocarbons (TPH) at a pyrolysis temperature of 370 °C with 15-min contact time. Pyrolytic treatment of amended soils at the unprecedentedly low pyrolysis temperature of 300 °C resulted in 87 % TPH removal efficiency with Cu-bentonite and a 93 % with Fe-bentonite. We postulate that the transition metals catalyzed the pyrolysis reactions at lower onset temperatures. This hypothesis is supported by thermogravimetric analysis coupled with mass spectrometry, which revealed the release of hydrogen, methyl and propyl ion fragments (markers of pyrolytic degradation products of crude oil) at lower temperatures than those observed for unamended soil. Overall, this work shows proof of concept that metal-impregnated clays can

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enhance rapid pyro-catalytic treatment of crude-oil contaminated soils and encourages further work to understand the detailed reaction mechanisms and inform process design.

## 1. Introduction

Environmental pollution by petroleum hydrocarbons poses serious threats to public and ecosystem health. About 98 % of crude oil spills occur on land rather than in the ocean (Etkin, 2001; Duffy et al., 1980), and exposure to terrestrial spills can correlate to cancer, preterm births, neurocognitive deficits, and other public health concerns that can also span across generations due to genetic or birth defects (Song et al., 2019; Hussain et al., 2018). Amongst the constituents of crude oil, polycyclic aromatic hydrocarbons (PAHs) are of particular concern since they are probable carcinogens and persist in the environment due to their recalcitrance to microbial degradation (Hussain et al., 2018; Kang et al., 2020; Li et al., 2018).

Soils impacted by relatively high concentrations of petroleum hydrocarbons (e.g., > 100,000 mg/kg) are often remediated by thermal technologies that are fast and effective but have high energy demand, high costs, and destroy the soil fertility (O'Brien et al., 2018, 2017; Vidonish et al., 2016b; Stegemeier, 2001; Hinchee, 1992). Pyrolytic treatment of soils contaminated with crude oils is an alternative approach that may offer significant advantages over other thermal methods. It can efficiently remove total petroleum hydrocarbons (TPH) to meet regulatory standards (generally 1,000–10,000 mg/kg depending on type and location) and detoxify the soil by removing toxic pollutants like PAHs with much lower energy requirements than incineration (Kang et al., 2020; Li et al., 2018; O'Brien et al., 2018; Vidonish et al., 2016b; Michelsen and Boyce, 1993). In addition, pyrolytic treatment may preserve soil components responsible for water and nutrient retention since it can be carried out at lower temperatures than other methods (Song et al., 2019; Kang et al., 2020; Li et al., 2018; Vidonish et al., 2016b; Gao and Zygourakis, 2019; Plante et al., 2009). This restores (at least partially) the fertility of the soil, enhancing its value for ecosystem restoration and re-greening efforts.

Past research revealed potential tradeoffs between pyrolytic treatment efficiency and soil fertility restoration. These tradeoffs are governed by the treatment intensity that increases exponentially with increasing temperature and linearly with increasing reaction time (Song et al., 2019; Vidonish et al., 2016a; Kang et al., 2020; Gao et al., 2021). Increasing treatment intensity monotonically enhances contaminant removal and soil detoxification, but it results in a “bell-shaped” soil fertility curve (Song et al., 2019). While soil fertility initially increases with increasing treatment intensity, it may pass through a maximum and start decreasing as high temperatures and long treatment times cause significant soil degradation. These tradeoffs represent an opportunity for multi-objective process optimization to meet the requirements for effective pollutant removal and soil detoxification, lower the carbon footprint of remediation technologies and preserve soil fertility. Such optimization efforts would benefit from an improved understanding of how contaminated soil components (e.g., clays) affect the pyrolytic treatment through catalytic mechanisms that could decrease the pyrolysis temperature and, thus, the process energy requirements.

Clays, which are common soil constituents, are composed of regular layers of anionic compounds in geometrical arrangements interspersed with cations and water molecules. The bentonite used in this study, for example, is composed of two sheets of silicon dioxide in a tetrahedral arrangement sandwiching a sheet of aluminum oxide in an octahedral arrangement (Rupert, 1973). Bentonite is negatively charged due to isomorphic substitutions of  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  in the tetrahedral layer and  $\text{Mg}^{2+}$  for  $\text{Al}^{3+}$  in the octahedral layer. This negative charge is balanced by the presence of exchangeable cations (e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ) in the interlayer region. These cations allow bentonite to easily adsorb contaminants, and can be easily exchanged with other metal cations, either

via ion exchange or naturally (Bananezhad et al., 2019; Ma et al., 2013; Neumann and Gessner, 2002). The presence of these naturally occurring or exchanged cations gives clays like bentonite affinity to aromatic hydrocarbons (that account for 17–50 %wt of the crude oil (Speight, 2017)) and catalyze transformations. A fundamental process underlying these interactions is the formation of a pi-cation system, wherein an electron-rich aromatic compound (including PAHs and other aromatics) donates an electron to a cation within the clay structure (Rupert, 1973). This pi-cation interaction can promote adsorption of aromatic compounds (Karaca et al., 2016; Lu and Zhu, 2012; Liang et al., 2016; Qu et al., 2008; Zhang et al., 2015, 2011) and subsequent transformations such as the formation of environmentally-persistent free radicals (EPFRs) (Jia et al., 2018), which are oxygenated species such as anthraquinone (Jia et al., 2014; Ni et al., 2021), or oligomerization reactions leading to higher molecular weight aromatic products (Karimi-Lotfabad et al., 1996). The rate and extent of these transformations depend on several interrelated factors, including the structure of the aromatic compounds, soil composition (Lu and Zhu, 2012; Liang et al., 2016; Qu et al., 2008; Zhang et al., 2015; Jia et al., 2014), the amount of soil organic matter (SOM) (Lu and Zhu, 2012; Zhang et al., 2011), humidity (Jia et al., 2014; Ni et al., 2021), soil pH (Zhang et al., 2011), and soil water content (Jia et al., 2014; Karimi-Lotfabad et al., 1996). Such transformations of aromatic hydrocarbons to oxygenated derivatives may also proceed under anaerobic conditions (Jia et al., 2014).

These reactions are known to be catalyzed by transition metals (Cu(II), Fe(III), Pb(II)) that can be present in clays from geogenic sources or as co-contaminants. The catalytic activity of a metal cation depends on the structure of aromatic molecules (Liang et al., 2016; Qu et al., 2008; Jia et al., 2018, 2014), the ionization potential of the metal (Liang et al., 2016; Jia et al., 2018, 2014), the polarizability of the metal (Zhang et al., 2011), and on how easily the aromatic contaminants can access the metal inserted into the clay structure (Zhang et al., 2011; Jia et al., 2018, 2014; Ni et al., 2021). Previous studies have shown that amending petroleum-contaminated soils with materials like  $\text{Fe}_2\text{O}_3$ ,  $\text{K}_2\text{CO}_3$  or red mud can enhance TPH removal via pyrolytic treatment (Liu et al., 2020, 2021a, 2021b). For example, Liu and coworkers showed that pyrolysis experiments carried out at 400 °C for 30 min achieved 70 % removal of TPH from unamended soils and up to 95 % removal when red mud was added to the petroleum-contaminated soil (Liu et al., 2021b). However, the significance of catalytic reactions and the enhancement mechanisms in thermal remediation of contaminated soils has not been fully addressed in the literature.

This study investigates the possible catalytic enhancement by natural and metal-impregnated clays during pyrolytic treatment of soils contaminated with crude oil. Our working hypothesis is that transition metal cations (e.g. Fe(III), Cu(II)) or interlayer cations in natural clays (e.g. Na(I), Al(III)) accelerate the cascade of reactions that begin with pi-cation interactions of aromatic molecules on the surface of clays (Liang et al., 2016; Qu et al., 2008; Zhang et al., 2015; Jia et al., 2018, 2014) and end with the conversion of aromatic constituents to char via radical polymerization reactions (Gao and Zygourakis, 2019; Vidonish et al., 2018; Gray and McCaffrey, 2002; Savage, 2000; LaMarca et al., 1993; Van Speybroeck et al., 2003; Savage et al., 1985; Yasar et al., 2001). The main objective here is to determine whether the use of natural or ion-exchanged clays as amendments to contaminated soils can improve the effectiveness of pyrolytic treatment by lowering the required temperature or contact time. As previously shown (Song et al., 2019), lower pyrolysis temperatures and shorter treatment times decrease the energy requirements and, thus, the total cost of pyrolytic treatment while also minimizing irreversible loss of soil fertility and resulting in a more sustainable process with a smaller carbon footprint.

## 2. Materials and methods

### 2.1. Materials

We used pure bentonite (Sigma Aldrich) to amend the contaminated soil and prepare metal-impregnated amendments. A contaminated soil prepared for our earlier work (Song et al., 2019) was also used for this study. The background soil was a kaolinitic, sandy, clay loam (approximately 25 % clay content) from the B horizon in Hearne, TX. After the clean soil was dried, homogenized, and sieved to remove large particles, it was blended with a heavy crude oil (Doba-blend, API 21°, Chevron, Houston, TX). The contaminated soil was stored in closed containers under air for the past four years. The total petroleum hydrocarbon (TPH) content of the contaminated soil was determined again before the start of this study by measuring the hydrocarbons extractable with S316 solvent using an InfraCal 2 TRANS-SP instrument (Spectro Scientific, Chelmsford, MA) according to the ASTM D7066–04 method. The TPH content of the weathered contaminated soil was 13,000 mg/kg.

### 2.2. Ion exchange procedure

Bentonite was modified by liquid phase ion exchange (LPIE) technique to obtain Fe-bentonite and Cu-bentonite. To create the Fe(III)-exchanged bentonite, 18.75 g of bentonite and 7.18 g of iron(III) nitrate (nonahydrate, > 98 %, Sigma Aldrich) were added to 300 mL of deionized water. After stirring the mixture at 300 rpm and room temperature for 24 h, the material was filtered and dried at 105 °C for 24 h. The metal-exchanged bentonite was then ground using a mortar and pestle, and sieved (mesh N° 60, < 250 µm). Cu(II)-exchanged bentonite was prepared using the same procedure as Fe(III)-exchanged bentonite. The only difference was the replacement of 7.18 g of Fe(III) nitrate with 11.25 g of Cu(II) nitrate (hemi(pentahydrate), > 98 %, Sigma Aldrich) added to the deionized water. The bentonite used for control experiments was obtained by adding deionized water without the metal ion precursor to the parent bentonite and submitting it to the same drying treatment as the ion-exchanged bentonite. The metal content of the parent bentonite, Fe-bentonite, Cu-bentonite and soil samples were determined by ICP according to ASTM Method E1979–16.

### 2.3. Evolved gas analysis (EGA) of soil samples with TG-MS

To detect the release of hydrocarbons and hydrogen occurring during pyrolysis, we also carried out TG–MS experiments using a TGA (Q500, TA Instruments, New Castle, DE) equipped with an evolved gas analysis (EGA) furnace and connected to a quadrupole mass spectrometer (Discovery, TA Instruments, New Castle, DE) with a heated capillary transfer line. The mass spectrometer was operated in electron impact ionization mode with 70 eV electron energy. All TG–MS experiments were carried out using high-purity nitrogen purge gas with a flow rate of 100 mL/min to simulate the pyrolysis atmosphere of an actual reactor. The samples were heated at 10 °C/min to a final temperature of 900 °C. The TG–MS experiments utilized a heating rate of 10 °C/min, a rate significantly faster than the 1 °C/min used in all other TGA experiments, to enhance the volatile release rates and improve the signal-to-noise ratio. To further improve the signal-to-noise ratio, we used the selected ion monitoring technique 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 several ion fragments were recorded together with the sample weight and temperature. The monitored ions included hydrogen ( $m/z = 2$ ),  $\text{CH}_3^+$  \* or methyl fragment ( $m/z = 15$ ),  $\text{C}_3\text{H}_7^+$  \* or propyl fragment ( $m/z = 43$ ), water ( $m/z = 18$ ) and carbon dioxide ( $m/z = 44$ ), which are key markers identifying the onset, type and duration of various transformations involving soil minerals or hydrocarbons. Each ion intensity curve was normalized by the 'dry' sample weight recorded at 120 °C. Ion intensities were then corrected using a standard baseline determined from a comparison of each sample

measurement. EGA with online mass spectrometry is a very sensitive method for detecting pyrolysis products in the TGA off-gas. However, only a fraction of the gaseous stream exiting the TGA enters our mass spectrometer transfer line through its capillary front end. Moreover, high molecular weight hydrocarbons may condense in the coupling connecting the transfer line of our mass spec to the TGA. For these reasons, the collected TG–MS data were only used to identify the temperature ranges in which hydrocarbon desorption and pyrolysis take place. No quantitative analysis was done with TG–MS data.

### 2.4. Pyrolytic treatment of contaminated samples in a tube furnace

Pyrolysis was performed in a stainless-steel fixed-bed reactor heated by a split-hinge tube furnace (Thermo Scientific Lindberg/Blue M) under continuous  $\text{N}_2$  flow (1 L/min). The reactor tube was 24" long. Contaminated soil was packed in the center 8" of the reactor tube, while two 8"-long layers made of borosilicate beads (4 mm in diameter) filled the entrance and exit sections of the reactor to smooth the gas flow and ensure uniform exposure of the soil sample to the purge stream. A thermocouple located at the middle of the outer surface of the reactor tube was used to control the pyrolysis temperature (Fig. 1). A second thermocouple located at the same point was used to continuously record the pyrolysis temperature, while a third thermocouple was placed near an end of the furnace heated zone to measure the temperature variations. A ceramic shield was placed between the furnace heating elements and the reactor tube to prevent exposing the thermocouples to the red-hot heating elements of the furnace. Without the shield, radiation heat transfer between the red-hot heating elements and the thermocouple would be significant due to the large temperature difference and cause large errors in the temperature measurement.

The pyrolysis experiments were carried out at 370 °C or 300 °C for 15 min before the sample was allowed to cool down under continuous  $\text{N}_2$  flow (1 L/min). The TPH concentration of treated soils was determined by measuring the solvent-extractable hydrocarbons using an InfraCal 2 TRANS-SP instrument (Spectro Scientific, Chelmsford, MA) according to the ASTM D7066–04 method.

### 2.5. Data analysis

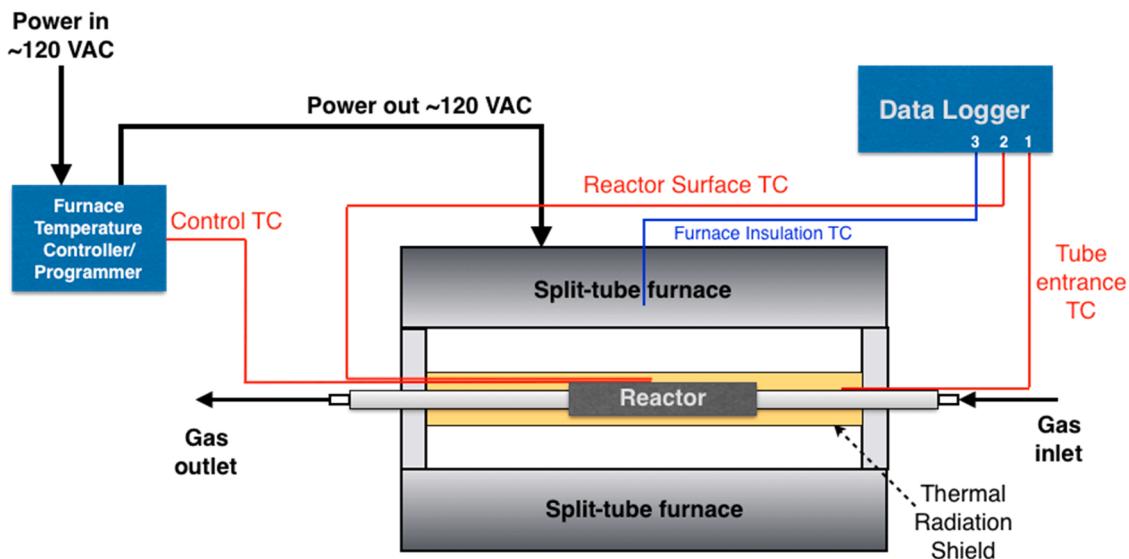
All TG-MS and pyrolysis experiments were run in triplicates. Three samples from each of the three pyrolysis experiments performed at 300 and 370 °C were analyzed for residual TPH and means with standard errors were calculated. Statistical significance tests were done using Student's t-test.

## 3. Results and discussion

### 3.1. Clays and transition metals greatly enhanced TPH removal

Pyrolysis experiments with amended and non-amended contaminated soil were carried out at 370 and 300 °C. Amended soils contained 10 %wt of one of the following clays: bentonite, Fe-modified bentonite or Cu-modified bentonite. The elemental analysis of all pyrolyzed samples, as measured by ICP, is shown in Table 1. A comparison of the metal content of the pure and modified bentonites reveals that the exchangeable alkali and alkali earth cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) present in the interlayer region of the pure bentonite were replaced (as expected) by iron and copper cations in the modified Fe-bentonite and Cu-bentonite (Bananezhad et al., 2019).

We carried out the first set of pyrolysis experiments at 370 °C, the lowest temperature used in our earlier study (Song et al., 2019). The reactor temperature was ramped up to 370 °C as fast as the furnace would allow and held there for 15 min before cutting off the furnace power to allow the reactor to cool down. A typical temperature profile for our pyrolysis reactor is shown in the supplementary material (Fig. S1).



**Fig. 1.** Schematic showing the reactor system used for pyrolytic remediation of oil-contaminated soils, the location of the thermocouples (TC) used for controlling and monitoring the reaction temperature, the split-tube furnace, and the ceramic tube that surrounds the reactor assembly and acts as a thermal radiation shield.

**Table 1**  
Metal content in bentonite and soil samples (all values are reported in %wt).

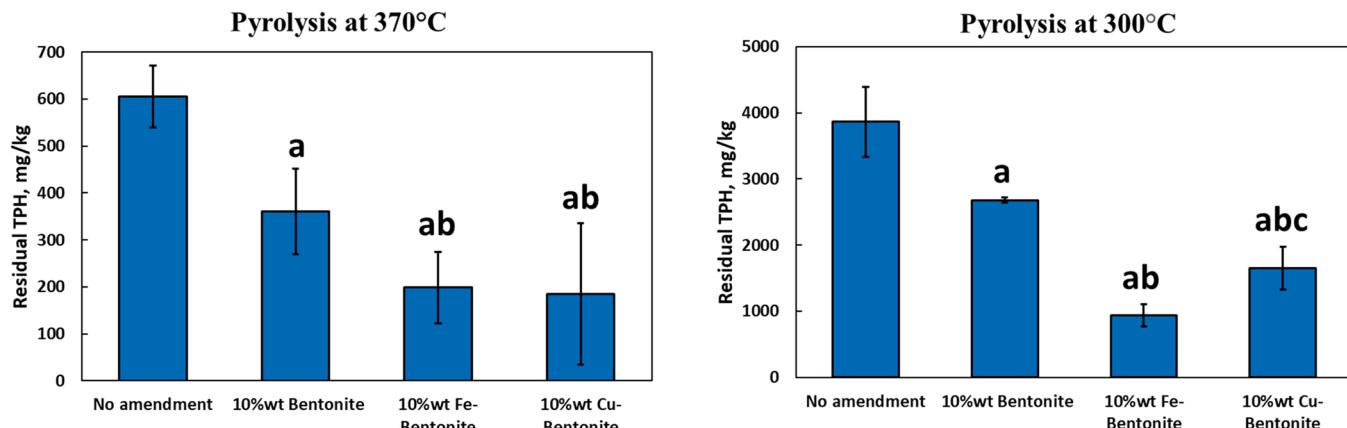
	Fe	Si	Al	Cu	Mg	Na	Ca
Bentonite	2.69	26.80	8.46	< 0.01	1.23	1.53	0.59
Fe-bentonite	4.29	26.60	5.46	< 0.01	0.63	0.26	0.08
Cu-bentonite	2.37	25.07	6.17	2.69	0.77	0.23	0.12
Background soil (clean)	1.30	22.09	0.74	0.012	0.08	0.64	0.29
Crude-oil contaminated soil	1.21	23.52	0.53	0.010	0.09	0.66	0.34

The results obtained are shown in Fig. 2 and Table 2. Pyrolyzing the unamended contaminated soil lowered its TPH from 13,000 mg/kg to 606 mg/kg (> 95 % removal efficiency). The addition of 10 % by weight of pure bentonite to the contaminated soil lowered the residual TPH to 361 mg/kg, for a better than 40 % improvement over the removal level achieved for the unamended contaminated soil (Fig. 2a). This statistically significant decrease in residual TPH (Fig. 2a) exceeded the drop we would expect from “diluting” the contaminated soil by adding 10 %wt of pure bentonite and strongly suggests that the bentonite may speed up

the pyrolysis reactions leading to the formation of char from the heavy petroleum hydrocarbons (Vidonish et al., 2016a, 2018; Gao and Zygourakis, 2019).

Amending the contaminated soil with 10 %wt of Fe-bentonite (i.e., bentonite with ion-exchanged Fe) further decreased the residual TPH of treated soil to 198 mg/kg for a 67 % improvement over the removal level observed with unamended soil. As also shown in Fig. 2a, the differences in the post-pyrolysis TPH levels between unamended and amended samples are statistically significant at the 95 % level. The addition of 10 %wt of Cu-bentonite to the contaminated soil reduced the TPH of treated soil to about the same level observed with the Fe-bentonite amendment, but the variability was higher for this amendment (Fig. 2a).

While pyrolytic treatment at 370 °C was very efficient in removing TPH, a close inspection of the data showed that the relative TPH measurement uncertainties (expressed by the error bars of Fig. 2) were a significant fraction of the actual TPH measurements. For the soil amended with Cu-bentonite, for example, the TPH uncertainty was about 80 % for the actual measurement. Such high uncertainties could mask subtle differences in the relative effectiveness of the treatment conditions (e.g., pyrolysis temperature) and amendments (e.g., Fe-



**Fig. 2.** TPH removal is significantly enhanced by the addition of natural bentonite and (to a greater extent) bentonite with ion-exchanged Fe or Cu. For this crude-oil contaminated soil, TPH was consistently removed below the common 10,000 mg/kg regulatory threshold at both 370 °C (left panel) and –unprecedentedly– 300 °C (right panel). The letters indicate statistically significant differences ( $p < 0.05$ ) in the residual TPH of samples compared to (a) the contaminated soil treated without any amendments, (b) contaminated soil amended with 10 %wt natural bentonite, (c) contaminated amended with 10 %wt iron-exchanged bentonite.

**Table 2**

Residual TPH for pyrolysis experiments at 300 °C and at 370 °C with unamended contaminated soil, contaminated soil with 10 %wt bentonite, contaminated soil with 10 %wt Fe-bentonite and contaminated soil with 10 %wt Cu-bentonite.

Temperature	Sample	Avg. Residual TPH (mg/kg)	% Difference Res. TPH (compared to sample with no amendments)	% TPH Removal
300 °C	Contaminated soil (no amendments)	3863 ± 529	N/A	70.4
	Contaminated soil + 10 %wt bentonite	2680 ± 39	- 30.6	79.5
	Contaminated soil + 10 %wt Fe-bentonite	937 ± 166	- 75.7	92.8
	Contaminated soil + 10 %wt Cu-bentonite	1652 ± 327	- 57.2	87.4
370 °C	Contaminated soil (no amendments)	606 ± 66	N/A	95.4
	Contaminated soil + 10 %wt bentonite	361 ± 91	- 40.5	97.2
	Contaminated soil + 10 %wt Fe-bentonite	198 ± 77	- 67.3	98.5
	Contaminated soil + 10 %wt Cu-bentonite	185 ± 151	- 69.5	98.6

bentonite vs. Cu-bentonite), an issue that was also resolved with our second set of experiments at a lower temperature with higher residual TPH levels.

Since our primary objective was to lower the energy requirements of pyrolytic soil remediation, we carried out a second set of pyrolysis experiments at 300 °C to determine whether the use of amendments could help us achieve high TPH removal rates at temperatures well below those reported until now in the literature. The ability to effectively remediate contaminated soil at 300 °C would also help us minimize or even eliminate the irreversible damage to soil fertility that occurs at higher temperatures (Song et al., 2019). Pyrolyzing the non-amended contaminated soil at 300 °C decreased its TPH from 13,000 mg/kg to 3,863 mg/kg for a slightly over 70 % removal efficiency. The addition of 10 %wt pure bentonite further reduced the residual TPH to 2,780 mg/kg for an almost 80 % removal efficiency. Again, the observed TPH removal was higher than what we would expect from the “dilution” effect of pure bentonite addition. The effect of Fe-bentonite was even stronger, reducing the residual TPH to 937 mg/kg for an almost 93 % total removal. However, the addition of 10 %wt Cu-bentonite to the contaminated soil resulted in a slightly lower total TPH removal of about 87 %.

The 300 °C data also resolved the question raised earlier about the relative effectiveness of the Fe-bentonite vs. the Cu-bentonite. The relative uncertainties of residual TPH measurements for the 300 °C samples are much lower than those for the 370 °C samples (e.g., less than 20 % for the Cu-bentonite samples), a fact that allows us to discern the much stronger effect of the Fe-bentonite amendment compared to Cu-bentonite one, a difference that is statistically significant at the 95 % level (Fig. 2).

Note that high TPH removal efficiencies were obtained even at an unprecedentedly low temperature of 300 °C, which is much lower than those previously reported in recent studies that pyrolyzed amended petroleum-contaminated soils at temperatures 400 °C or higher to achieve TPH removal efficiencies over 70 % (Liu et al., 2020, 2021a, 2021b). Typical regulatory requirements for TPH removal vary between

1,000 and 10,000 mg/kg, which can easily be achieved at lower temperatures than previously considered (and possibly lower contact times) by amending the contaminated soils with clays or clays containing transition metals like Fe or Cu.

### 3.2. Pyrolysis markers reveal the potential catalytic role of clays and especially metal-impregnated clays

The significant enhancement of TPH removal efficiencies by the tested amendments (Table 2) strongly suggest that clays and, in particular, clays impregnated with Fe or Cu have a strong catalytic effect on pyrolytic soil remediation. These observations also suggest that different metal ions may act differently under pyrolysis treatment.

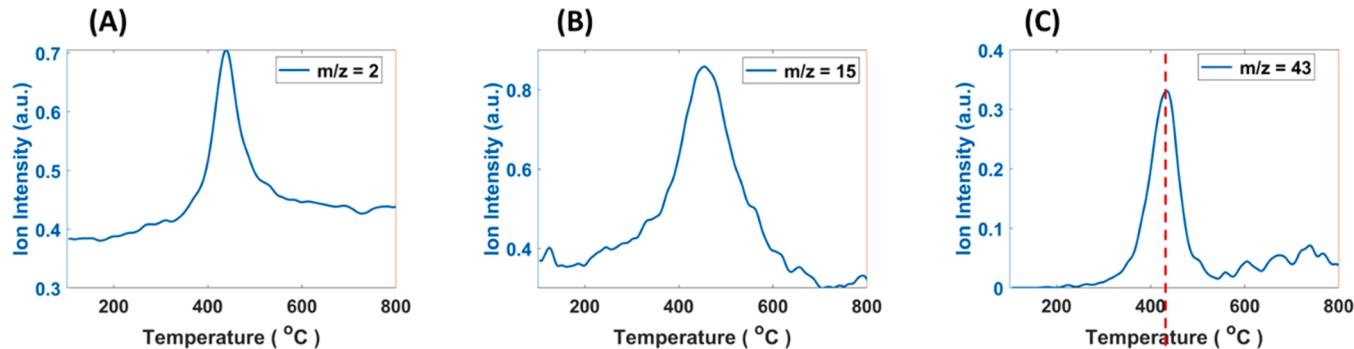
To gain better insights into the mechanism of our process, we used evolved gas analysis with online mass spectroscopy (TG-MS) to study the treatment of (a) unamended contaminated soil and (b) contaminated soil amended with 10 %wt bentonite, 10 %wt Fe-Bentonite and 10 %wt Cu-bentonite. TG-MS runs were carried out under an inert N<sub>2</sub> atmosphere to mimic pyrolytic conditions. As we have demonstrated earlier (Song et al., 2019; Vidonish et al., 2018), TG-MS continuously monitors the effluent gas of pyrolyzing samples to identify the presence of specific gaseous “markers” that identify the onset, type and duration of various transformations involving soil minerals or hydrocarbons. For example, the onset of pyrolysis reactions is characterized by a strong release of two specific ion fragments: H<sub>2</sub> with *m/z* = 2 and CH<sub>3</sub><sup>\*</sup> with *m/z* = 15 that indicates the release of methane (Vidonish et al., 2018). While these fragments may be detected in other phases of pyrolytic treatment, they are most pronounced during pyrolysis (Vidonish et al., 2018; Savage et al., 1985). If soil amendments such as bentonite, Fe-bentonite, or Cu-bentonite are effective catalysts for pyrolytic reactions, one would observe a shift in the evolution of key pyrolysis products species towards lower temperatures due to the catalytic effect of these amendments.

The TG-MS results presented in Fig. 3A, B and C for pyrolytic treatment of the unamended contaminated soil agree well with the results from our earlier study (Vidonish et al., 2018). Pyrolytic treatment of soils contaminated with petroleum crudes proceeds in two stages. When the unamended contaminated soil is heated above 100 °C, the more volatile contaminants desorb first. TG-MS detects the release of these lighter hydrocarbons by monitoring the fragment ions produced as the volatiles are ionized in the mass spectrometer. The most abundant fragments for petroleum-contaminated soils were CH<sub>3</sub><sup>\*</sup>, C<sub>2</sub>H<sub>5</sub><sup>\*</sup> and C<sub>3</sub>H<sub>7</sub><sup>\*</sup> with mass-to-charge ratios *m/z* = 15, *m/z* = 29 and *m/z* = 43 respectively (Vidonish et al., 2018). Since our TG-MS experiments use N<sub>2</sub> to simulate the pyrolysis conditions in an actual reactor, the signal from the C<sub>2</sub>H<sub>5</sub><sup>\*</sup> fragment with *m/z* = 29 overlaps with the signal from <sup>14</sup>N-<sup>15</sup>N which also has *m/z* = 29. Since the <sup>15</sup>N isotope is stable and has natural abundance between 0.3 % and 0.4 %, the ion intensity of the nitrogen isotope emits a strong overlapping signal that hinders consistent detection of the ethyl ion fragment. Ion fragments from olefins and light aromatics are also detected during this stage, but their signals are weaker and noisy even though we always use the selective ion monitoring technique to improve the signal-to-noise ratio of TG-MS measurements.

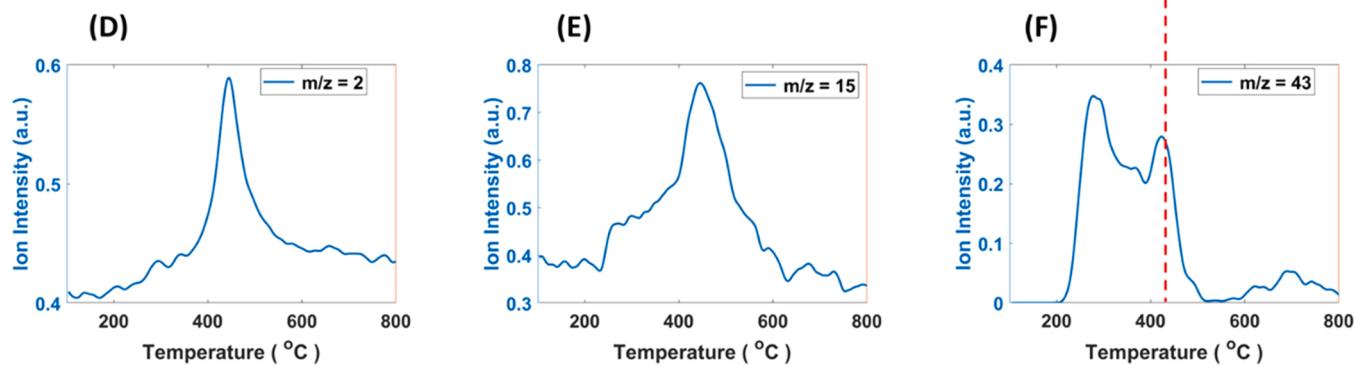
As temperatures increase above 350 °C for unamended contaminated soils, heavier hydrocarbons (including aromatics and PAHs) undergo pyrolytic reactions that release hydrogen and C<sub>1</sub>-C<sub>4</sub> hydrocarbons and ultimately form a carbonaceous material (coke) that is nontoxic and refractory to further chemical reactions (Gray and McCaffrey, 2002; Savage, 2000; LaMarca et al., 1993; Van Speybroeck et al., 2003; Savage et al., 1985; Yasar et al., 2001; Banerjee et al., 1986). Coke formation proceeds via a cascade of reactions that include radical formation via hydrogen abstraction or C-C bond breaking, and propagation via β-scission or cyclization (Van Speybroeck et al., 2003, 2007; Wauters and Marin, 2002). PAHs play a big role in this process via the formation of aryl radicals (Van Speybroeck et al., 2007).

The distinctive fingerprints of pyrolysis reactions are the very

## No Amendments



## 10%wt Bentonite



**Fig. 3.** Intensities of key ion fragments from TG-MS pyrolysis runs with (a) unamended contaminated soil (Top Row) and (b) contaminated soil with 10 %wt pure bentonite (Bottom Row). The addition of pure bentonite enhances the release of methyl and propyl fragments before the onset of pyrolysis reactions but does not qualitatively change the release pattern of hydrogen, which is the key marker of pyrolysis. **Top Row- Unamended Soil:** Ion intensities vs temperature for hydrogen ( $m/z = 2$ , Panel A), methyl fragment ( $m/z = 15$ , Panel B), and propyl fragment ( $m/z = 43$ , Panel C). **Bottom Row- Soil Amended with 10 %wt bentonite:** Ion intensities vs temperature for hydrogen ( $m/z = 2$ , Panel A), methyl fragment ( $m/z = 15$ , Panel B), and propyl fragment ( $m/z = 43$ , Panel C).

pronounced peaks of hydrogen ( $m/z = 2$ ) and methane (uniquely identified by the  $\text{CH}_3^+$  fragment with  $m/z = 15$ ) that appear as the temperature of the pyrolyzing sample is ramped from about 350–600 °C at 10 °C/min (Fig. 3A and B). A sharp peak of the propyl cation fragment ( $m/z = 43$ ) is also detected in the pyrolysis range (Fig. 3C), which is again consistent with the release of  $\text{C}_3\text{-C}_4$  hydrocarbons in this temperature range. At temperatures lower than the onset of pyrolysis, smaller amounts of hydrocarbon fragments are detected and appear as “shoulders” to the left of the pyrolysis peaks (Fig. 3B and C).

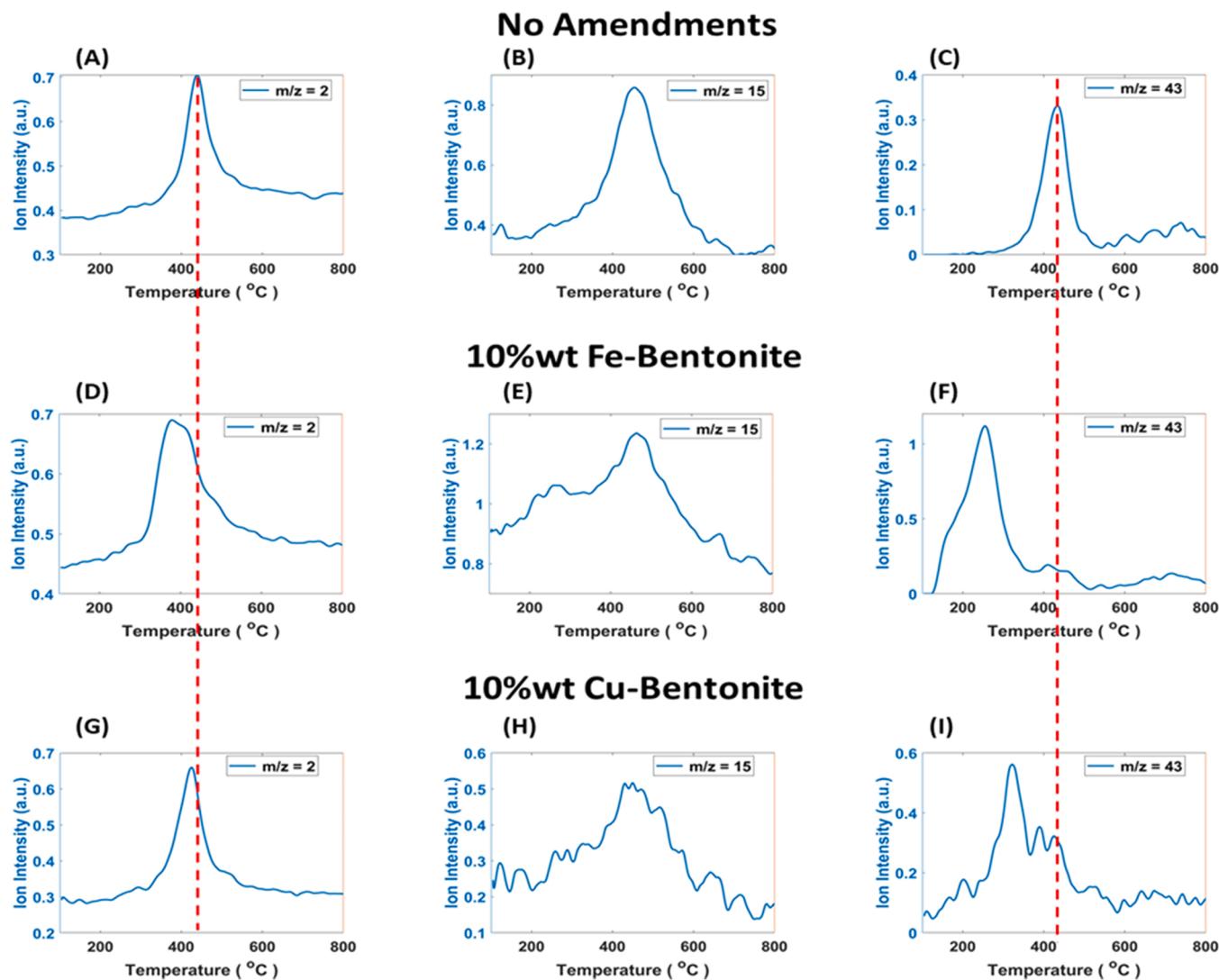
The addition of 10 %wt of pure bentonite to the contaminated soil enhanced the release of methyl and propyl fragments before the onset of pyrolysis reactions (Fig. 3E and F). The methyl peak for the amended soil has a very pronounced shoulder at temperatures lower than 400 °C (Fig. 3E), while the propyl release pattern was now bimodal with one peak at about 300 °C and a second lower peak at about 450 °C that is in the pyrolysis temperature range of unamended soil (Fig. 3F). The addition of pure bentonite, however, did not qualitatively change the release pattern of hydrogen, which is the key marker of pyrolysis (Fig. 3D).

Pyrolysis of contaminated soil with 10 %wt Fe-bentonite had a pronounced effect on the release patterns of the pyrolysis markers. To emphasize the differences, Fig. 4 plots again the ion intensities of three key markers observed for (a) the pyrolysis of unamended contaminated soil (Fig. 4A, B, C) and (b) the pyrolysis of contaminated soil amended with Fe-bentonite. A comparison of Fig. 4A and D shows a shift of the hydrogen peak to a significantly lower temperature (by ~75 °C) than the one observed when we pyrolyzed contaminated soil without

amendments. In addition, much more methane than before was detected in the temperature range between 250 and 350 °C (Figs. 4B and 4E), while the ion intensity pattern of the  $\text{C}_3\text{H}_7^+$  fragment ( $m/z = 43$ ) completely changed with the dominant peak now centered at about 250 °C (Fig. 4C and F). All these are clear indications that the presence of the ion-exchanged Fe sites in the Fe-bentonite amendment has enhanced the catalytic effect of pure bentonite and significantly lowered the onset temperature for pyrolysis reactions.

Pyrolysis of contaminated soil with 10 %wt Cu-bentonite had a less pronounced effect on the release patterns of the pyrolysis markers. The hydrogen peak shifted to a slightly lower temperature than we observed for the pyrolysis of contaminated soil without amendments (Fig. 4A and G). We also detected significantly more  $\text{CH}_3^+$  fragments in the temperature range between 250 and 350 °C (Figs. 4B and 4H) and a marked shift in the ion intensity pattern of the  $\text{C}_3\text{H}_7^+$  fragment (Fig. 4C and I). Even though the limitations of TG-MS preclude a quantitative comparison, the intensity patterns of the three key markers shown in Fig. 4 clearly indicate that (a) both Fe-bentonite and Cu-bentonite have significant catalytic effects that result in lowering the onset temperature of pyrolysis reactions; and (b) the catalytic effects of Fe sites appear to be significantly stronger than those of Cu sites. These conclusions are consistent with the TPH removal results reported in the previous section (Fig. 2) and explain the better than 90 % TPH removal at a temperature of 300 °C observed when the contaminated soil was amended with 10 % wt Fe-bentonite (Table 2).

In addition to lowering the onset temperature of pyrolysis, a detailed analysis of the thermogravimetric data for the amended crude-oil



**Fig. 4.** Intensities of key ion fragments from TG-MS pyrolysis runs with (a) unamended contaminated soil (Top Row), (b) contaminated soil with 10 %wt Fe-bentonite (Middle Row) and (c) contaminated soil with 10 %wt Cu-bentonite (Bottom Row). The addition of Fe-bentonite shifted the hydrogen peak to a lower temperature and increased the intensity of methyl and propyl fragments at temperatures between 250 and 350 °C. Cu-bentonite amendment had similar but less pronounced effects. The TG-MS intensities for the unamended contaminated soil of Fig. 3 are also shown here (Top Row) for easy benchmarking. **Top Row- Unamended Soil:** Ion intensities vs temperature for hydrogen ( $m/z = 2$ , Panel A), methyl fragment ( $m/z = 15$ , Panel B), and propyl fragment ( $m/z = 43$ , Panel C). **Middle Row- Soil Amended with 10 %wt Fe-bentonite:** Ion intensities vs temperature for hydrogen ( $m/z = 2$ , Panel D), methyl fragment ( $m/z = 15$ , Panel E), and propyl fragment ( $m/z = 43$ , Panel F). **Bottom Row- Soil Amended with 10 %wt Cu-bentonite:** Ion intensities vs temperature for hydrogen ( $m/z = 2$ , Panel D), methyl fragment ( $m/z = 15$ , Panel E), and propyl fragment ( $m/z = 43$ , Panel F).

contaminated soils samples (Fig. S2) revealed that the Fe-bentonite amendment promoted the catalytic conversion of heavy hydrocarbons to char. The weight loss of contaminated soil pyrolyzed with 10 %wt Fe-bentonite in the 300–550 °C temperature range was significantly lower ( $p < 0.05$ ) than that observed when pyrolyzed with 10 %wt pure bentonite (Fig. S3). Apparently, heavy hydrocarbons were preferentially converted to char rather than to gaseous products in the presence of Fe sites. This is very similar to the behavior observed by Liu and coworkers who studied the pyrolysis of a weathered petroleum contaminated soil amended with 5 %wt  $\text{Fe}_2\text{O}_3$  (Liu et al., 2022). When we pyrolyzed our contaminated soil with 10 %wt Cu-bentonite, however, the weight loss for the 300–550 °C pyrolysis range was similar or even slightly higher than that observed for pyrolysis with 10 % pure bentonite (Fig S3). The hydrogen release patterns for the pure bentonite and Cu-bentonite amendments are almost identical (Fig. 4). Only the methyl and propyl fragment patterns differ, an indication that Cu sites may catalyze different reactions.

These results also suggest that pyrolytic treatment of petroleum-contaminated soils in the presence of amendments like natural clays or metal-containing clays can decrease the treatment temperature to levels well below those previously considered by our group and other investigators (Song et al., 2019; Li et al., 2018; Liu et al., 2020, 2021a, 2021b).

Even though it is not possible at this stage to propose a definitive catalytic mechanism, it is reasonable to postulate (as illustrated in the TOC graph) that the interaction that underlays sorption to clays and most catalytic mechanisms in clays (particularly those containing metal active sites) is that between the electron-rich  $\pi$ -system of aromatic and PAH molecules and positively-charged ions (e.g. metals) (Qu et al., 2008; Jia et al., 2014). In some catalytic interactions, the  $\pi$ -system donates an electron, creating a free radical PAH that is easily attacked by reactive species in soil, leading to their decay into quinones or other derivatives (Jia et al., 2018). During pyrolytic treatment of contaminated soil, similar catalytic interactions may trigger the formation of

highly reactive free radicals that accelerate the conversion of PAHs and heavy aromatic hydrocarbons to char that has a polynuclear aromatic character and very little hydrogen (Vidonish et al., 2016b; Van Speybroeck et al., 2003; Savage et al., 1985; Yasar et al., 2001; Wen and Cain, 1984; Yan et al., 2015).

#### 4. Conclusion

This work offers proof-of-concept of the benefits of using natural clays and clays impregnated with non-toxic transition metals as a practical amendment to catalytically enhance pyrolytic treatment of weathered crude-oil contaminated soils. Addition of either 10 %wt ion-exchanged Fe-bentonite or 10 %wt ion-exchanged Cu-bentonite to crude-oil contaminated soil reduced the residual TPH by 99 % at a pyrolysis temperature of 370 °C with only a 15-min contact time. Substantial TPH removal of 87 % for Cu-bentonite and 93 % for Fe-bentonite was also observed at a pyrolysis temperature of 300 °C that is much lower than those previously reported. Pyrolysis with transition metal additives achieved residual TPH concentrations well below regulatory threshold for soils (1,000–10,000 mg/kg) at both treatment temperatures. Using a low-end treatment temperature that reduces the energy requirement to meet treatment objectives is conducive to remediation technology decarbonization, while lower contact times at a given temperature may result in higher throughput capacity.

The catalytic effect of Fe and Cu sites in the bentonite that was modified via ion-exchange was inferred by the release of hydrogen, methyl and propyl fragments (which are indicators of pyrolytic degradation of crude oil) at lower temperatures than those observed for unamended contaminated soil. While metal-impregnated clays may be a practical low-cost additive to significantly improve pyrolytic treatment of crude oil contaminated soils, further mechanistic studies are needed to inform process design. To determine the feasibility of this promising pyro-catalytic soil remediation approach, techno-economic analyses must be carried out to evaluate tradeoffs of increasing treated soil volume though modified clay amendments versus decreasing energy requirements and contact time.

#### Environmental implication

Terrestrial oil spills significantly outnumber marine spills every year, and rapid, reliable and cost-effective remediation is needed to protect public and environmental health. Pyrolysis rapidly remediates contaminated soil and restores soil fertility using less energy than other thermal treatment processes. Here, we show that clays impregnated with non-toxic transition metals can be used as an amendment to decrease the required pyrolysis temperature and contact time. Addition of iron and copper ion-exchanged clays to contaminated soil reduced residual TPH below regulatory thresholds at unprecedentedly low pyrolysis temperatures, which reduces energy requirements and costs with a smaller carbon footprint.

#### Associated Content

**Supporting Information** includes a table with properties of the petroleum crude used to prepare our PCS; a plot with the temperature vs. time history of a typical pyrolysis run; a plot with the average TG and DTG curves obtained by pyrolyzing unamended PCS, PCS amended with 10 %wt of bentonite, PCS amended with 10 %wt Fe-bentonite, and PCS amended with 10 %wt Cu-bentonite; a plot with weight loss percentages in three temperature ranges obtained by pyrolyzing PCS with three different amendments: 10 %wt pure bentonite, 10 %wt Fe-bentonite, and 10 %wt Cu-bentonite.

#### CRediT authorship contribution statement

**Sara B. Denison:** Conceptualization, Methodology, Investigation,

Validation, Visualization, Formal analysis, Writing – original draft. **Priscilla Dias Da Silva:** Conceptualization, Methodology, Investigation, Validation, Visualization, Formal analysis, Writing – original draft. **Caroline P. Koester:** Visualization, Investigation. **Pedro J.J. Alvarez:** Supervision, Writing – review & editing. **Kyriacos Zygourakis:** Conceptualization, Methodology, Investigation, Software, Supervision, Writing – review & editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2022.129295.

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