Self-Sustaining Smoldering Combustion for NAPL Remediation: Laboratory Evaluation of Process Sensitivity to Key Parameters

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Ⓢ *Supporting Information*

ABSTRACT: Smoldering combustion has been introduced recently as a potential remediation strategy for soil contaminated by nonaqueous phase liquids (NAPLs). Published proof-of-concept experiments demonstrated that the process can be self-sustaining (i.e., requires energy input only to start the process) and achieve essentially complete remediation of the contaminated soil. Those initial experiments indicated that the process may be applicable across a broad range of NAPLs and soils. This work presents the results of a series of bench-scale experiments that examine in detail the sensitivity of the process to a range of key parameters, including contaminant concentration, water saturation, soil type, and air flow rates for two contaminants, coal tar and crude oil. Smoldering combustion was observed to be self-sustaining in the range 28,400 to 142,000 mg/kg for coal tar and in the range 31,200 to 104,000 mg/kg for crude oil, for the base case air flux. The process remained self-sustaining and achieved effective remediation across a range of initial water concentrations (0 to 177,000 mg/kg water) despite extended ignition times and decreased temperatures and velocities of the reaction front. The process also exhibited self-sustaining and effective remediation behavior across a range of fine to coarse sand grain sizes up to a threshold maximum value between 6 mm and 10 mm. Propagation velocity is observed to be highly dependent on air flux, and smoldering was observed to be self-sustaining down to an air Darcy flux of at least 0.5 cm/s for both contaminants. The extent of remediation in these cases was determined to be at least 99.5% and 99.9% for crude oil and coal tar, respectively. Moreover, no physical evidence of contamination was detected in the treatment zone for any case where a self-sustaining reaction was achieved. Lateral heat losses to the external environment were observed to significantly affect the smoldering process at the bench scale, suggesting that the field-scale lower bounds on concentration and air flux and upper bound on grain size were not achieved; larger scale experiments and field trials where lateral heat losses are much less significant are necessary to define these process limits for the purposes of field application. This work provides valuable design data for pilot field trials of both in situ and ex situ smoldering remediation applications.

■ INTRODUCTION

Nonaqueous phase liquids (NAPLs) are a class of organic compounds that are among the most frequently occurring subsurface contaminants throughout the industrialized world. Common NAPLs include petroleum hydrocarbons, polychlorinated biphenyls, chlorinated ethenes, creosote, and coal tar. Due to their physical and chemical properties, most of these contaminants represent a significant threat to the human health and the environment. Conventional remediation technologies such as pump and treat and soil vapor extraction have proven largely inefficient in addressing subsurface contamination present as NAPL. In particular, remediation of the most complex, long chain and/or less volatile NAPLs (e.g., coal tar, heavy petrochemicals) remains a significant challenge. Excavation and either disposal to hazardous waste landfill or incineration is the most common approach, entailing substantial cost and representing practices that score poorly in sustainability assessments.[1]

A recently introduced alternative approach is NAPL smoldering combustion.[2] At the basis of this concept is the observation that many common NAPLs are highly flammable and exhibit heats of combustion in excess of materials that are successfully burned in other industries (e.g., biomass energy, waste incineration).[3] However, since NAPLs in the environment occur as liquids embedded in a solid matrix, conventional incineration techniques (involving flaming combustion, a gas phase oxidation reaction) require a continuous supply of an external energy input. Smoldering combustion differs from these techniques in that it is the exothermic oxidation of a condensed (i.e., solid or liquid) phase occurring on the fuel's surface and is favored in heat transfer terms by the presence of a solid matrix in which the fuel is

Table 1. Summary of One-Dimensional Smoldering NAPL Remediation Experiments

variable	experiment	contaminant	porous medium	concentration (mg/kg)	NAPL-occupied porosity	self-sustaining/remediated[b]
coal tar content	1	coal tar	coarse sand	14,200	5%	N
	2	coal tar	coarse sand	21,300	7.5%	N
	3	coal tar	coarse sand	28,400	10%	Y
	4	coal tar	coarse sand	71,000	25%	Y
	5	coal tar	coarse sand	99,400	35%	Y
	6	coal tar	coarse sand	142,000	50%	Y
crude oil content	7	crude oil	coarse sand	20,800	10%	N
	8	crude oil	coarse sand	31,200	15%	Y
	9	crude oil	coarse sand	52,000	25%	Y
	10	crude oil	coarse sand	72,800	35%	Y
	11	crude oil	coarse sand	104,000	50%	Y
water content	12	coal tar/water	coarse sand	71,000	25%/25%[c]	Y
	13	coal tar/water	coarse sand	71,000	25%/50%[c]	Y
	14	coal tar/water	coarse sand	71,000	25%/75%[c]	Y
mean grain size	15	coal tar	medium sand	67,000	25%	Y
	16	coal tar	6 mm gravel	90,000	"	Y
	17	coal tar	10 mm gravel	94,000	30%	N
air flux	18[a]	coal tar	coarse sand	71,000	25%	Y
	19[a]	crude oil	coarse sand	52,000	"	Y

[a] Air flux lowered to 0.53 cm/s soon after ignition. [b] The definition of remediated sand is given in the section 'Extent of remediation'. [c] The second number indicates water saturation.

embedded.[4] In this condition, the process can be self-sustaining; that is, it initiates with a short duration energy input and propagates through the fuel-embedded matrix without further input of externally supplied energy. Common examples, in which the solid matrix is itself combustible, include smoldering charcoal briquettes in a barbeque grill and smoldering foam cushions starting a house fire.[4] In the case of NAPL-smoldering, since the contaminant is the fuel being consumed by the propagating reaction, a certain degree of remediation is expected[2,5] while the inert matrix (i.e, soil) remains.

Proof-of-concept experiments at the bench (150 mm diameter column) scale conducted on coal tar were the first to demonstrate that smoldering combustion of a liquid contaminant can be initiated within an inert porous medium and that the process can become self-sustaining after the ignition source is removed.[5] Further, they demonstrated that the smoldering process self-terminates when all of the NAPL is destroyed or when the oxygen source is removed. Propagation rates of NAPL smoldering were similar to those observed in the smoldering of solids (e.g., polyurethane foam).[6,7]

Demonstrative experiments conducted at smaller (50 mm diameter beaker) scale also indicated that the process may be applicable across a broad range of NAPL and soil conditions.[2] Although insufficient to adequately quantify the process, these experiments showed that NAPL smoldering is applicable across a range of soil types and contaminants (including laboratory mixtures of dodecane, DCA/grease, TCE/oil, vegetable oil, crude oil, and mineral oil) as well as field-obtained samples of materials containing coal tar, oil drill cutting waste, and oil sands. Nearly total elimination of the contaminant mass was observed in the employed experimental conditions.[2]

A systematic evaluation of the sensitivity of NAPL smoldering to key process parameters has not been previously conducted. The one exception is that the effects of the rate of oxygen supply on the smoldering of coal tar and crude oil were explored previously[2] but at the smaller (beaker) scale. The velocity of the smoldering reaction

was observed to increase approximately linearly with increasing airflow; however, at high flow rates, declining peak temperatures suggested a cooling effect by the excess air.[2]

In this work the potential of NAPL smoldering as a remediation technology was evaluated and quantified in a systematic manner through a suite of bench-scale column experiments. The influence of a number of site-specific factors was investigated for both coal tar and crude oil to identify the parameter bounds within which the process is successful at this scale. Applications of NAPL smoldering as both an ex-situ technique and as an in situ approach (both above and below the water-table) are currently being investigated. The sensitivity of NAPL smoldering to key parameters is necessary information for advancing the design of pilot and full scale trials for both approaches.

■ EXPERIMENTAL METHODOLOGY

Parameters investigated in this study were contaminant type, contaminant concentration, water content and mean grain size, which are typical variables encountered in field scenarios (Table1). Most of the experiments were conducted under the operating conditions where oxygen through air injection was supplied in excess of the average stoichiometry requirements (for details of this analysis see ref 8), as this corresponds to conditions most likely to be found in future field applications. In addition, a reduced oxygen-supply experiment was run for each contaminant to evaluate the ability to initiate and sustain smoldering under low air supplies. Experiment 4 (coal tar saturation of 25% in coarse sand) was published previously[5] and is incorporated here as a base case for comparison.

Forward smoldering combustion tests (upward propagation) were carried out in a quartz glass column 138 mm in diameter and 275 mm in height. Commercial grade fresh coal tar (Koppers, Scunthorpe, UK) and crude oil (Nynas, Dundee, UK) were

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employed as contaminants, with measured densities of 1200 and 880 kg/m^3, respectively. Four types of inert porous media (two sands and two gravels, described below) were employed. To prepare the contaminated material, NAPL and the selected porous medium were mixed in a mass ratio corresponding to the desired concentration. The batch was homogenized by mechanical mixing prior to packing in the apparatus. The high viscosity and cohesion of the material ensured no distinct layering or grain size separation occurred during emplacement of the 120 mm layer of contaminated material. This was underlain by an air diffuser supplied by an air compressor and an inconel-sheathed cable heater (Watlow Ltd., UK). Nine inconel-sheathed Type K thermocouples were inserted into the sand pack along the column central axis and spaced at 10 mm or 20 mm intervals above the cable heater (Figure S-1 in the Supporting Information). The thermocouples were connected to a data acquisition system (Multifunction Switch/Measure Unit 34980A, Agilent Technologies). More details on the experimental apparatus and methodology are available in refs 2 and 5.

At the start of each experiment, the contaminated material was heated until the threshold temperature of 400 °C was exceeded 2 cm above the igniter location. Then, air injection was initiated and maintained until the end of the experiment. Unless specified otherwise (i.e., except experiments 18 and 19), the air (Darcy) flux was maintained constant at 9.15 cm/s for all the experiments. The igniter was turned off when the temperature at thermocouple 1 (TC1, 2 cm above the igniter) began to decrease with time (i.e., postpeak), approximately 10 min after initiating the air flow. The maximum power used for these experiments was approximately 390 W. This ignition protocol was determined from a series of proof of concept experiments.[5]

The local velocity of the smoldering front is known from the time lapse of the front arrival (i.e., temperature peaks) at two consecutive thermocouples and the distance between them.[7] An average propagation velocity was computed for each experiment by performing a least-squares linear regression on the front distance versus time values; the average R^2 value for these regressions across all experiments was 0.987 (no R^2 less than 0.961). Pre- and post-treatment analysis of the samples was conducted for the two base-case experiments on coal tar (71,000 mg/kg, Experiment 4) and crude oil (52,000 mg/kg, Experiment 9). Accelerated solvent extraction (ASE) with a 50 mL mixture of dichloromethane and acetone was conducted on 20 g soil samples. The extract was analyzed for total extractable petroleum hydrocarbons (EPH) in the C_{10} to C_{40} range by a gas chromatograph equipped with flame ionization detector (Finnegan Focus GC, Thermo Electron Corporation, Hemel Hempstead, UK) and also for polycyclic aromatic hydrocarbons (PAHs) by gas chromatograph equipped with mass spectrometer (Thermo Quest Trace GC and Finnegan Trace MS, Thermo Electron Corporation, Hemel Hempstead, UK). The detection limit was 0.1 mg/kg for both EPH and PAH.

Experiments 1–6 and 7–11 examine the dependence of the smoldering process on NAPL concentration with a range of concentrations of coal tar (14,200 to 142,000 mg/kg) and crude oil (20,800 to 104,000 mg/kg), representing 5%-50% NAPL-occupied porosity, that are broadly representative of typical NAPL contents excavated from field sites.[9−11] These experiments employed commercially available quartz sand (Leighton Buzzard 8/16 sand, WBB Minerals, Sandbach, UK), characterized by a bulk density of 1700 kg/m^3, a mean grain size of 1.34 mm, and an average porosity of 40% when dry packed. This sand is indicated as "coarse sand" in Table 1.
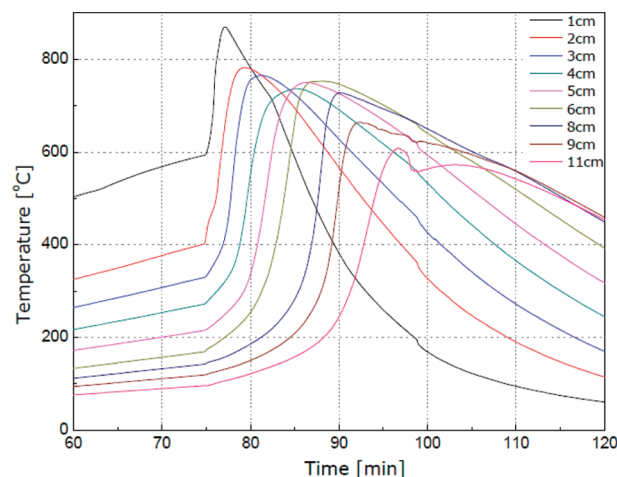

Figure 1. Temperature histories for coal tar in coarse sand at 28,400 mg/kg (Experiment 3 in Table 1). After ignition at $t = 75$ min, peak temperatures stabilize in the central portion of the column. Peak temperatures are observed to be less only in the top 2 cm of the contaminated sandpack due to boundary effects near the top free surface.

The effect of varying initial water content of the contaminated soil was investigated in Experiments 12–14 at a fixed coal tar concentration of 71,000 mg/kg in coarse sand (25% NAPL-occupied porosity). Initial water contents of 0, 59,000, 118,000, and 177,000 mg/kg were employed, representing 0, 25, 50, and 75% water-occupied porosity, respectively (Table 1). In the 75% water/25% NAPL case, the initial air-filled porosity was approximately zero.

The influence of the mean grain size of the porous medium (from 0.75 mm to 10 mm) was studied in Experiments 15–17. In addition to the coarse sand, these experiments employed a medium sand (mean grain size of 0.75 mm, porosity of 38%, bulk density of 1700 kg/m^3, WBB Minerals, Sandbach, UK) and two types of gravel (B&Q, Eastleigh, UK). The 6 mm gravel had a bulk density of 1490 kg/m^3 and average porosity of 45%; the 10 mm gravel had a bulk density of 1580 kg/m^3 and average porosity of 41%.

Experiments 18 and 19 examined the ability of the reaction to be self-sustaining at significantly lower air flow rates. The experiments were conducted on coal tar and crude oil in coarse sand at concentrations of 71,000 and 52,000 mg/kg, respectively. The sample was ignited according to the standard procedure with an initial air flux of 6.3 cm/s. The air flux was lowered to the predetermined level after the reaction had propagated to approximately 4 cm from the igniter. To reduce heat losses at the perimeter to a level closer to that expected in field conditions, the column was insulated with a flexible electric heater (240 V, 1040 W, Omega Inc., USA) for these two experiments only. To ensure that the heater was not sustaining and/or driving the combustion, the heater was operated at variable power so as to maintain the temperature at the outer boundary at least 100 °C lower than the reaction temperature. This approach is common in combustion experiments near the limits of sustainability since it creates boundary conditions that may be considered more representative of field sites where distances to external boundaries are large relative to the reaction front size scale (e.g., refs 12 and 13).

RESULTS AND DISCUSSION

NAPL Concentration. Self-sustaining propagation of smoldering combustion was achieved for coal tar in the range 28,400 to 142,000 mg/kg and for crude oil in the range 31,200 to

104,000 mg/kg (Table 1). Successful self-sustaining propagation, identified by a sustained sequence of overlapping and consistent temperature peaks after the igniter was turned off[14] (e.g., Figure 1), was observed in 16 of the 19 experiments conducted (Table 1). At the scale of these experiments, and employing a fixed air flow rate and no thermal insulation at the boundaries, the lower limit for a self-sustaining reaction in coarse sand was between 21,300 and 28,400 mg/kg for coal tar and between 20,800 and 31,220 mg/kg for crude oil. At and below these lower bounds, ignition occurred but peak temperatures at successive locations exhibited a decreasing trend, indicating a progressive weakening of the reaction (Figure S-2 in the Supporting Information). With sufficient sandpack length, this behavior may lead to extinction before the reaction reached the end of the contaminated sample. At larger scales, it is expected that these bounds would be extended to lower concentrations due to the reduced heat losses from the reacting volume to the boundaries. Indeed, repeated experiments at the lower concentration experiments employing external insulation to reduce heat losses confirmed that improved performance is observed relative to the uninsulated experiments presented in Table 1. The insulated experiments exhibited a stronger reaction (i.e., lower rate of decay of the temperature peaks), bordering on self-sustainability at the lower limit of the stated bounds (i.e., 21,300 mg/kg for coal tar and 20,800 mg/kg for crude oil).

The transition to self-sustaining propagation occurred in a similar concentration range for both coal tar and crude oil (Figure 2). For coal tar, the transition to self-sustaining behavior corresponded to a temperature of approximately 700 °C and a front velocity of approximately 4.5 cm/min; the corresponding values for crude oil are 550 °C and 4.5 cm/min. 95% confidence intervals on the front velocity varied from 5% (at 10% coal tar saturation) to 26% (at 50% coal tar saturation) with an average of 13% across all of the experiments, and the 95% confidence interval on peak temperature varied from 2% to 10% with an average of 6%; experiment-specific uncertainty values are plotted in Figure 2. Five repeats of the base case experiment found variations of maximum temperature and propagation velocity (represented by 95% confidence intervals) respectively of 7% and 13%. Uncertainty on NAPL concentration was 1%.

For coal tar, both maximum temperature and average velocity of the front increased as the NAPL concentration increased until approximately 75,000 mg/kg (Figure 2). For concentrations less than 75,000 mg/kg, the propagation rate was likely limited by the rate of fuel consumption in the reaction front (i.e., fuel consumption kinetics) or the energy losses from the reaction front. In other words, in this regime, increasing fuel concentration increases the heat release rate such that the smoldering front accelerates despite having to consume more fuel in order to advance. As the NAPL concentration increased beyond 75,000 mg/kg, the rate of reaction in the combustion front likely became high enough to consume all the incoming oxygen releasing heat at the maximum rate; oxygen-limited conditions at the reaction front are consistent with the observed velocity decreases with further increased concentrations.

Smoldering temperatures depend on the reaction rate and thermophysical properties of the reacting medium (i.e., heat capacity and thermal conductivity),[15] which in turn depend on both soil type and NAPL content. NAPL has a significantly higher heat capacity than air. Thus, the observed reduction in peak temperatures at high NAPL concentrations (e.g., above 100,000 mg/kg) is likely the consequence of an increase in sensible energy via heating the contaminated porous medium in
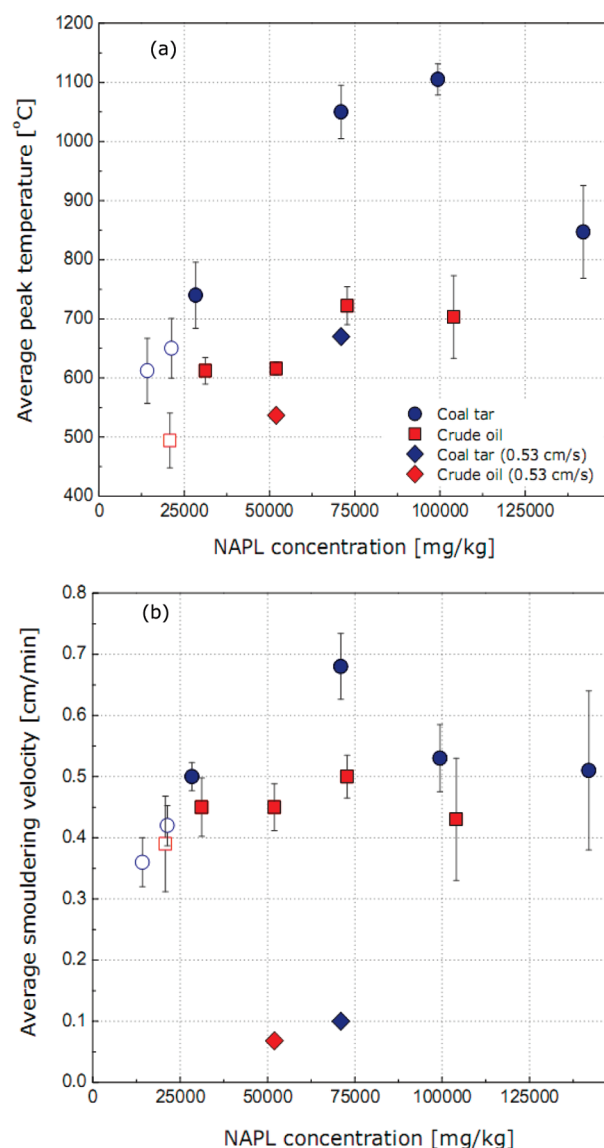

Figure 2. (a) Average peak temperature and (b) average smoldering velocity as a function of NAPL concentration in coarse sand. Empty symbols indicate not self-sustaining combustion. Diamonds refer to experiments conducted at low air flux (Experiments 18 and 19 in Table 1). 95% confidence intervals on the mean for each experiment are plotted, expressing variability in the local values.

an oxygen-limited regime (see details in the Supporting Information).

In the case of crude oil, above the threshold concentration for a self-sustaining reaction, propagation velocity remained essentially constant, and the increase in peak temperature is significantly less than that observed for coal tar in the same range of concentrations (approximately 16% vs 57%, respectively) (Figure 2). For crude oil, the increase in reaction rate may be balanced by the increase in fuel concentration such that oxygen-limited conditions were not reached. The overall modest increase in the burning temperature is qualitatively consistent with this observation and suggests that the increase in energy generated is balanced by the increase in volumetric heat capacity associated with increased NAPL content.

Initial Water Content. In all experiments with nonzero water content, ignition was successful, and, after turning off the igniter,
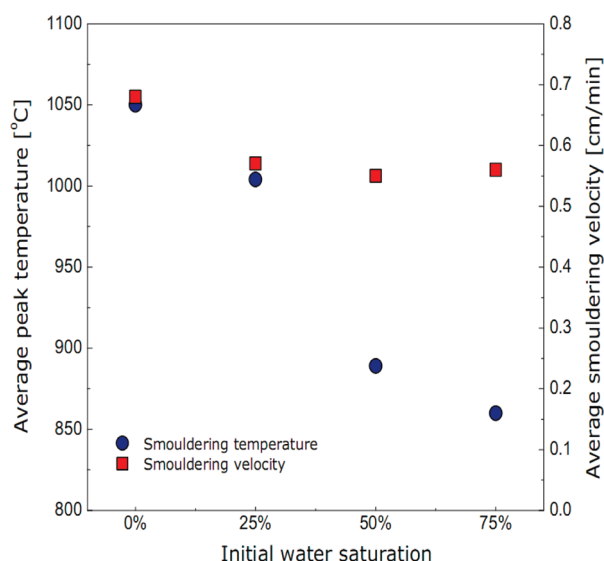
Figure 3. Average peak temperature (circles) and average self-sustaining smoldering front velocity (squares, right vertical axis) as a function of initial water saturation. Initial coal tar concentration was constant at 71,000 mg/kg.

Figure 4. Average peak temperature (circles) and average propagation velocity (squares, right vertical axis) as a function of mean grain size. Coal tar NAPL concentration is reported on the top horizontal axis for ease of comparison with Figure 2. Empty symbols indicate not self-sustaining combustion.

the front was observed to propagate in a self-sustaining manner until all the coal tar was destroyed. An increase in the time necessary to achieve ignition was observed with increasing water content (from 60 to 120 min in the 0% and 75% water-occupied porosity cases, respectively), which is expected due to the time lag associated with evaporating and displacing the water during preheating of the ignition zone. The fraction of the length of contaminated sandpack containing moisture at the time of ignition (as evidenced by temperatures at or below 100 °C) increased with increasing initial water concentration, from about 33% cm at 59,000 mg/kg water (Expt 12) to 50% at 177,000 mg/kg water (Expt 14). It is observed that the region influenced by the heater is highly localized around the ignition point due to the insulating properties of the porous medium. These results are consistent with previous observations that the igniter has a short duration influence over a limited volume of material.[2] Thus, in all cases examined, the NAPL smoldering combustion reaction generated enough power (i.e., rate of energy release) to maintain self-sustaining propagation and vaporize the water ahead of the front as it advanced.

As the water content increases, water increasingly acts as a heat sink, absorbing energy from the reaction. If the ratio of NAPL to water content decreases below a threshold for a given soil and NAPL type, self-sustaining propagation is expected to not be possible; however, for the NAPL content employed here (25% of porosity) this threshold was exceeded for all conditions and remediation success was independent of water content. In these experiments, reduced peak temperatures were observed but the self-sustaining smoldering front velocity was not significantly affected (Figure 3).

Mean Grain Size. In all cases studied except one (10 mm gravel), a successful self-sustaining front propagated the length of the column. Both coarse and medium sand presented the most favorable conditions for smoldering propagation (i.e., maximum peak temperature and maximum average velocity) (Figure 4). The similarity in values from coarse to medium sand suggests a balance between the expected increase in the smoldering reac-
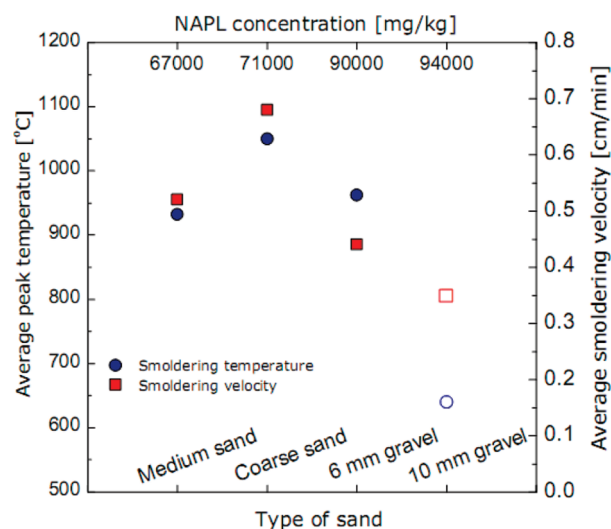
tion rate due to decreased pore size (i.e., increased fuel surface area per unit volume) and the decreased NAPL concentration (associated with equal NAPL-occupied porosity, see Table 1). In 6 mm gravel, smoldering of coal tar was self-sustaining but the average peak temperature was 100 °C lower than that observed in the coarse sand (Figure 4). Furthermore, the combustion front velocity was 36% lower than in coarse sand, and this decrease was greater than would be expected based on the increase in NAPL concentration alone. For 10 mm gravel, the decrease in smoldering front velocity was 50%, and the average peak temperature exhibited a 40% decrease. The temperature histories for the 10 mm gravel experiment as well as the visible contamination remaining in the excavated gravel pack suggest that the reaction was not self-sustaining in this medium at this scale. As the grain size increases, not only does reaction surface area per unit volume decrease, but the sensible energy per unit volume requirements increase and the porous medium may not have sufficient time to equilibrate with the temperature of the gas phase.[17] Thus, the porous medium ahead of the smoldering front is preheated to a lower temperature, effectively increasing its role as a heat sink. This effect may become sufficient to progressively diminish the reaction intensity with the distance from the igniter. The threshold between 6 and 10 mm grain size may be scale dependent, and this limitation may be less apparent at larger experimental scales or in situ, where field soils have a distribution of grain sizes and boundary heat loss effects are less significant.

Reduced Air Flux. Results for both coal tar and crude oil revealed that the reaction is self-sustaining at least down to an air flux of 0.5 cm/s (Figure 2). Reducing the air flux by 95% (9.5 to 0.53 cm/s) caused the average peak temperature to decrease for coal tar by 36% (from 1050 to 670 °C) and for crude oil by 13% (616 to 537 °C). The air flux reduction caused the velocity of the front to decrease by 85% (from 0.68 to 0.10 cm/min) for coal tar and by 85% (0.45 to 0.068 cm/min) for crude oil (Figure 2). The decreased smoldering temperatures are consistent with the values observed for the low NAPL concentration cases, yet remain in the self-sustaining region. Combining the results from this research with those from a previous study[2] underscores the

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dominant influence of air flux on smoldering propagation velocity (Figure S-3). This relationship is expected since smoldering propagation is typically an oxygen-limited process.[16,18]

These experiments demonstrate the ability of NAPL smoldering to be operated at greatly reduced air delivery rates than reported previously. Further work is exploring in detail the influence of air flux on smoldering NAPL remediation at larger experimental scales, where heat loss effects are much less significant.

Extent of Remediation. Detailed chemical analysis on spatially continuous subsamples was carried out for the two base-case experiments on coal tar (71,000 mg/kg, Experiment 4) and crude oil (52,000 mg/kg, Experiment 9). Prior to the experiment, the coal tar sand pack exhibited EPH of approximately 38,000 mg/kg and PAH content of approximately 9500 mg/kg. The difference between the EPH value and the total initial concentration is a consequence of the analysis methodology, which provides a measure of the extractable hydrocarbons in the range C_{10} to C_{40}. Numerous analyses (via both internal and external laboratories) on created samples of coal tar and crude oil in sand reveal that EPH reports a concentration value that is typically approximately one-third to one-half of that known to be present in fresh samples (results not shown).

The concentrations of EPH and PAH in the treated coal tar sand are below the detection limit in the majority of the samples and never exceed 1.5 mg/kg, which represents a concentration reduction of more than 99.9999% at all locations (Table S-1 in the Supporting Information). For crude oil, pretreatment analysis revealed concentrations of EPH and PAH of approximately 18,000 and 90 mg/kg, respectively. After the experiment the concentrations were reduced more than 99.5% in all locations (average EPH reduced from 18,000 to 38 mg/kg, Table S-1) excluding the top two centimeters where boundary effects (heat losses to the free surface) were significant.

The higher maximum temperatures observed in the coal tar experiments and more significant boundary effects observed in the crude oil experiments suggest that smoldering of coal tar is a more exothermic reaction, releasing a higher net energy at the smoldering front and thus a slightly higher degree of remediation than smoldering of crude oil (because a more exothermic reaction will result in higher peak temperatures and therefore in a longer time available for the reaction to reach completion). These differences may be inherent to the various properties of the two contaminants, such as fluid density and the range of reaction temperatures and boiling points exhibited by the broad spectrum of compounds each contains. At a larger experimental scale (reduced heat losses) or with a different initial composition of hydrocarbons (more energetic smoldering front), energy losses at the front may be reduced. Thus, remediation efficiency of the process (i.e., amount of NAPL destruction per unit of externally provided energy) is expected to increase as the scale of application increases via (i) more complete local reactions producing cleaner soil, and/or (ii) reduced preheating time to reach ignition, and (iii) less ignition, events to remediate a given volume of NAPL-contaminated soil.

The contaminated sandpack was remediated effectively in every experiment that exhibited self-sustaining smoldering (i.e., all except Experiments 1, 2, 7, and 17). 'Remediated' here means no visible evidence of contamination in the treatment zone, which was confirmed as very low to nondetect EPH and PAH concentrations (Table S-1). The treatment zone is taken as the contaminated sandpack greater than 2 cm from the external boundaries of the apparatus. The entire set of experiments suggests that when combustion was self-sustaining, the extent of remediation was thorough. Visible traces of contamination remained only in the cases where the reaction was not self-sustaining at this scale (i.e., when the NAPL content was too low or the grain size was too large).

This work has explored a range of site-specific parameters where NAPL smoldering remediation may be applied. Smoldering velocity was demonstrated to be a strong function of air flux and also to vary with NAPL concentration, NAPL type, and soil grain size. Minimum threshold concentrations at this scale were established on the order of 20,000 mg/kg for coal tar and crude oil; this represents soil exhibiting at least residual NAPL (i.e., disconnected blobs and ganglia). In addition, the ability for self-sustaining smoldering to be maintained despite a drastic reduction in air delivery rate was established. It is noted that these threshold values are expected to depend on the scale of the experiment[16] as well as on the soil and NAPL type; indeed, self-sustaining smoldering of field soil exhibiting an order of magnitude lower concentration has been recently demonstrated at a larger experimental scale (~1 m), and lower concentrations are expected to be possible depending on the energy content of the contaminant. Even for these synthetic contaminated soils, it is expected that the minimum NAPL content will decrease, maximum grain size will increase and relative air delivery requirements will decrease with increased scale of investigation, due to improved efficiency through reduced heat loss effects.

For this reason, while all of the self-sustaining results can be extrapolated to field performance, large scale experiments and field pilot trials are necessary to establish practical lower air flux and concentration limits of the process. The results suggest that NAPL destruction is essentially complete when the process is self-sustaining. The results further suggest that the presence of significant amounts of water may not be a barrier to applying NAPL smoldering ex situ to wet soils or in situ within the capillary fringe or below the water table; however, for the latter it is suspected that a necessary condition would be that the rate of groundwater inflow toward the reaction front be less than the rate of propagation of the front (and the boiling front that precedes it). Water migration relative to smoldering and its relationship to combustion byproducts being detected in groundwater have been explored at large scales in underground coal gasification trials (e.g., refs 19 and 20). These and related questions (e.g., associated with heterogeneity of NAPL source zones and subsurface permeability) are being explored with two-dimensional laboratory experiments and pilot field trials.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Figures S1-S3, Table S1, and text. This material is available free of charge via the Internet at http://pubs.acs.org.

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(Canada). Smouldering combustion of liquids as a remediation concept is pending patent approval (UK Application 0525193.9 and PCT Application PCT/GB2006/004591, priority date December 2005). The patent is owned by University of Edinburgh and employed by University of Western Ontario under license. SiREM/Geosyntec holds an exclusive license to commercialize the STAR (Self-sustaining Treatment for Active Remediation) technology.

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