Thermal Removal of Pyrene Contamination from Soil: Basic Studies and Environmental Health Implications

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Effects of temperature (400–1000°C) and rate of heating to 550°C (100, 1000, 5000°C/sec) on reduction of pyrene contamination in a Superfund-related soil and on yields of volatile products (tars, CO, CO2, methane, acetylene, ethylene) have been measured. Fifty (±3)-milligram thin layers (±150 µm) of 63- to 125-µm soil particles, neat (i.e., without exogenous chemicals), or pretreated with 4.75 wt% of pyrene, were heated for about 1 to 6 sec, under 3 psig (pounds per in.² gauge) of helium in a 12-liter sealed chamber. Pyrene removal, defined as the difference in weight loss of neat versus contaminated soil, was virtually immune to heating rate but increased strongly with increasing temperature, approaching 100% at about 530°C. However, for pyrene-polluted soil, excess soil weight loss and modified CO yields were observed above about 500°C for a 1000°C/sec heating rate. These observations suggest that soil chemical reactions with pyrene or pyrene decomposition products augment soil volatilization. Consequently at elevated temperatures, the difference in weight loss protocol may overestimate polycyclic aromatic hydrocarbon (PAH) removal from soil. Increasing heating rate caused yields of CO, CO2, and acetylene from pyrene-polluted soil to pass through maxima. Heating near or contaminated soil resulted in at least two gaseous products of particular environmental interest: acetylene, a precursor to PAH in thermal synthesis, and CO, a toxin to human hemoglobin. — Environ Health Perspect 106(Suppl 4):1097–1107 (1998). http://ehpnet1.niehs.nih.gov/docs/1998 Suppl 4/1097-1107/saito/abstract.html

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Introduction

Between 1982 and 1991, approximately 1200 U.S. sites had been placed on the National Priority List designating them as serious environmental threats, under what is now known as the Superfund program (1). Superfund and other sites (2) may contain hundreds or even thousands of tons of contaminated soil, so that soil cleanup and restoration have become prominent environmental issues. Thermal treatment is already an established technology for soil cleanup and is expected to be the basis for new above-ground and in situ decontamination processes. Thermal technologies are often selected to clean soils at Superfund sites (2) because they can provide high destruction and removal efficiencies (DREs) for diverse organic contaminants (3). Broadly based public acceptance is important to the selection, siting, and sustainable operation of virtually any environmental remediation technology. Experience with incineration, one of the most visible thermal methods for treating hazardous wastes—including polluted soils—shows that winning and sustaining stakeholder support can be challenging (4). Public opposition to incineration reflects concerns that process misbehavior will give rise to effluents or residues that could adversely affect human health (5), e.g., owing to inadequate destruction of the targeted waste or generation of toxic by-products (5,6). Better quantitative understanding of the behavior of soil and soil-contaminant mixtures during heating can improve the scientific and engineering foundations for design, operation, control, and monitoring of soil thermal cleanup technologies, and may identify totally new concepts for soil decontamination. Progress along these lines can in turn contribute to public confidence that soil thermal treatment technologies will economically meet prescribed clean-up goals in an environmentally sound manner.

From the behavior of other heterogeneous solids that release volatile materials on heating, e.g., coal and biomass, the thermal removal of organic substances from soil is expected to entail chemical reactions as well as inter- and intraphase transport of gaseous and liquid substances (Figure 1). Soil temperature–time history, particle size, bed depth, ambient atmosphere, and total pressure, as well as soil and contaminant properties, are therefore likely to impact decontamination efficiencies as well as the yields, identities, and generation rates of co-products. Environmental health-related questions include: a) How rapidly and efficiently are targeted contaminants removed from the soil or converted to benign products? b) Are the original contaminants transformed to hazardous substances, especially species more toxic or more resistant to destruction or decontamination? c) Do soil-contaminant interactions affect product yields and toxicity? d) How do soil type, contaminant type,
and individual operating conditions affect decontamination behavior?

Many studies contribute information responsive to these and related questions (7–32). Tognotti et al. (8) and Flytzanis-Stephanopoulos et al. (9) studied the dynamics of contaminant adsorption on and desorption from individual particles. Darvakis (10) found that rapid heating of a thin layer of clay particles at roughly 1000°C/sec gave weight losses consistent with essentially complete removal of pyrene contamination at temperatures above 600°C. McClennen et al. (11) detected benzene, toluene, ethylbenzene, styrene, benzaldehyde, benzofuran, and chlorostyrenes and chloroethylbenzenes among the vapor phase effluents of heating an ethylbenzene-contaminated soil bed in air. They ascribe the chlorinated products to reactions between organic effluents and chloride in the upper layers of the soil bed. Wu et al. (12,13) determined equilibrium and mass transfer parameters for contaminants in soil beds, e.g., gas–soil partition coefficients, heats of adsorption, axial dispersion coefficients, and intraparticle diffusion coefficients. Lighty et al. (14–22) provide data and mathematical models for soil decontamination with particular emphasis on bed configurations and operating conditions simulating various attributes of soil thermal treatment in rotary kilns. Linak et al. (23) and Wendt et al. (24) modeled the formation of "puffs" (short-lived surges of volatile substances) in terms of vapor release by fracture of solids during heating. Bucalá et al. (25) found that the efficiency of removing No. 2 fuel oil from a soil can be manipulated by adjustments, and to some extent tradeoffs, in temperature, heating rate, and treatment time, and that chemical reactions of the oil were in evidence at higher treatment temperatures (500°C). Essentially complete (approaching 100%) oil removal was indicated even at rather mild heating, i.e., to 300°C at 200°C/sec followed by about 25 sec further heating at that temperature. Bucalá et al. also report (26) a significant role for thermal decomposition of soil itself in generating volatile by-products including species of environmental health interest, e.g., CO (a toxin to human hemoglobin), acetylene (a polycyclic aromatic hydrocarbon [PAH] precursor in high temperature reactions, see below) and liquids of medium to low volatility (tars). Gilot et al. (27) found extensive removal (85–90%) of pyrene contamination from a clay soil by heating from room temperature to 200°C (5°C/min heating rate) or 300°C (50°C/min). They concluded that while evaporation could account for most (70% or more) of the pyrene release, other processes, e.g., desorption and possibly chemical reactions, are important in removing the last 5 to 10% (27).

PAHs are an important class of soil contaminants. Many PAHs are mutagenic, carcinogenic, or both. They are encountered at numerous hazardous waste sites, notably those with wood preservatives, coal and pine tars, and sludges (28). Simonich and Hites (29) report that PAHs may be carried into soil by the debris of plants on which PAH collected. Most PAH are of high molecular weight and low volatility, and many PAHs are strongly resistant to biochemical breakdown. Thus, they are relatively difficult to remove from soil, and clean-up methods based on intense heating, e.g., incineration (4), are appealing. To better understand soil thermal decontamination, this article describes effects of temperature and heating rate on removal of exogenous pyrene from a Superfund-related soil, and on the yields of volatile co-products. The temperatures and heating rates studied are pertinent to the thermal desorption or devolatilization stages of some of the current and emerging thermal technologies for above-ground and \textit{in situ} remediation, i.e., to the initial heating of the soil as well as continued heating, in nonoxidizing atmospheres. Effects of oxygen during or after release of volatile substances are not addressed; our focus is on soil pyrolysis, not combustion of soil or soil-derived volatile substances. No one soil or individual PAH
compound can comprehensively represent all PAH-polluted soils. However, pyrene has a molecular weight, volatility, and thermochemical reactivity relevant to mid-boiling range PAH. Pyrene is not mutagenic to bacterial cells or human cells in vitro and is negative in carcinogenicity assays. However, pyrene has been found in complex organic mixtures at hazardous waste sites, e.g., heavy oils, sludges, tars. These substances are of environmental health interest because of their potential for occupational or public exposure and prior findings of toxicologic activity in these or related mixtures.

**Materials and Methods**

The soil was a U.S. Environmental Protection Agency (U.S. EPA) synthetic soil matrix prepared elsewhere to reflect attributes of soils at Superfund sites (30). Its makeup was guided by extensive review of 86 records of decision (RODs), and an independent study of the composition of soils in the eastern United States. The following components in the indicated weight percentages were blended to formulate this soil matrix (31,32): sand (31%), no. 9 gravel (6%), silt (28%), topsoil (20%), and clay (15%) (montmorillonite [5%] and kaolinite [10%]). This material has been analyzed by other workers (31,32) and found to be free of anthropogenic organic contamination. This soil matrix has been used in other studies of decontamination (25,26,32).

To reduce intraparticle temperature and concentration gradients during rapid heating, we prepared a 63- to 125-μm fraction by sieving. Chemical analysis found 0.39 wt% organic carbon, 3.96 wt% carbonate carbon, 0.76 wt% hydrogen, and approximately 1 wt% moisture (after conditioning with a drying agent). X-ray fluorescence (26) detected Ca, Ti, Fe, Cu, Sr, Zr, Zn, Ni, Al, and Si, and small quantities of S and Cl, and X-ray diffraction (26) identified the minerals quartz [SiO2], calcite [CaCO3], kaolinite [Al2Si2O5(OH)4], dolomite [CaMg(CO3)2], ankerite [CaMgFe3CO33], and minnesotaite [CaZn(CO3)2].

To obtain the desired 4.75 wt% pyrene contamination level thus obtained was checked by extracting a known weight of contaminated soil with methylene chloride. The weight of the residue upon evaporating the extract solution in a preweighed aluminum pan was taken as the weight of pyrene contaminant on the soil, and revealed a contamination within 2% (relative) of that targeted, i.e., 4.75 ± 0.10 wt%.

This level of exogenous pyrene was used to facilitate gravimetric measurements of decontamination efficiencies (below) and quantitation of by-product yields. It is within the higher range of contamination by organic substances at Superfund sites (30) and pertinent to the appreciable pollution concentrations encountered during rapid response to spills of hazardous substances. Further details on the contamination procedures are provided by Saito (33).

The soil heating apparatus is an adaptation of electrical screen heater reactors used to study pyrolysis of coal (34,35) and cellulose (36,37), where solid fuels are heated within a folded stainless steel screen. Here the screen is replaced (25,26,33) by a 0.001-in. thick 302 stainless steel foil relieved with an internal diameter × 0.11-in. deep cylindrical well to hold the soil (Figure 2). The soil was heated by heat transfer from the foil. The foil was heated ohmically, using manually variable transformers and power relays actuated by automatic timers, to provide electrical current of the necessary magnitude and duration. Thereby, shallow soil beds (i.e., ≤150 μm) can be subjected to independent variations in heating rate (100–600°C/sec), temperature (300–1100°C), and time at final temperature (0–30 sec), under inert or reactive gaseous atmospheres. The hot foil and sample cool by conduction, natural convection and radiation, at initial rates that vary between 400 and 600°C/sec, depending on peak temperature (25).

Soil temperature–time histories are measured throughout each experiment using a rapid response (0.0005-in. thick film) type K thermocouple placed beneath the hot stage and read by a digitizing recorder. Heat transfer calculations imply that the thermocouple closely tracks the bulk mean temperature of the soil particles (e.g., conservatively to within about 10°C at a nominal heating rate of 1000°C/sec). Figure 3 is a schematic of the temperature–time histories used in soils and related studies (25,26,37), and defines heat-up time, (total) heating time, and peak temperature. To buffer the ambient gaseous atmosphere during heating, facilitate product collection, and quench volatile substances, soil is heated within a 9-in. diameter × 12-in. high cylindrical Pyrex chamber, sealed at each end with aluminum flanges (Figure 2). The heater foil is connected to two electrodes mounted to, but electrically insulated from, the top aluminum flange, which can be raised and lowered to introduce soil samples and recover condensed phase products.

Volatile materials are collected by purging the reactor gas through a filter and...
two series-connected traps (Figure 4), respectively, designed to collect tars, condensables (benzene to naphthalene), and light gases (CO, CO₂, C₁–C₂ hydrocarbons). The tar filter is a 1-μm pore size teflon filter paper within a stainless steel casing. The condensables trap is a 6-mm OD Pyrex tube containing 1.5 in. each of 3% OV-17 on GasChrom Q (80/100 mesh; Alltech, Deerfield, IL) and Porapak Q (50/80 mesh; Supelco, Bellefonte, PA) gas chromatographic packings. The light gas trap consists of 15 in. of Porapak Q within a 1/4 in. OD stainless steel tubing. To guard against gaseous impurities entering the reactor during a run, the reactor ambient gas (helium) is passed through a prefilter consisting of 15 in. of Porapak QS (50/80 mesh) within a 3/8-in. OD stainless steel tube. The helium prefilter and light gas trap are immersed in Dewar flasks of liquid nitrogen (boiling point [bp] 77°K) during the experiment. A funnel constructed from heavy-duty aluminum foil was attached to the tar filter inlet to help direct the flow of volatiles into the traps. The inner surfaces of the top and bottom flanges of the reactor were covered with aluminum foil to collect tar condensate.

Typical steps in a run were to form the soil containment well in the foil, load the soil sample into the reactor, flush and pressurize the reactor with inert gas, heat the soil, and purge the reactor to recover volatile products. The foil, prior to forming the well, was heated to a peak temperature above 900°C under about 3 psig of unfiltered helium to remove organics from the foil surface. The well was formed by pressing the foil between two pipe fittings. A known weight of soil (50 ± 3 mg) was spread into approximately a monolayer in the well before mounting the foil between the electrodes. The top and bottom reactor liners, the tar filter, the tar filter funnel, and the condensables trap were preweighed and then connected to, or mounted within, the reactor. The reactor was then closed and flushed seven times with prefiltered helium. In a flush, the reactor is pressurized to 7 psig and then evacuated to ~30 in Hg with a mechanical vacuum pump. Liquid nitrogen was then added to the Dewar flask surrounding the light gas trap, and a helium flow of 0.5 l/min (at ambient conditions) was then established with the reactor pressurized slightly above atmospheric pressure (3 psig) to prevent in-leakage of air by pressure driven flow.

Each soil sample was heated through a preselected temperature–time history. The helium flow was continued for 2 hr after cooldown, to collect volatile products (the cumulative helium purge amounted to about five reactor volumes). The light gas trap was then removed from the reactor system and set aside for analysis. The foil and heat-treated soil, as well as the other traps, the liners, and the funnel, were then removed from the reactor and weighed. Tar is operationally defined, and gravimetrically determined, as the material collected on the tar filter and funnel, the top and bottom aluminum liners, and on the inside reactor wall, the last estimated by wiping the surface with preweighed glass filters. The light gas trap was connected to a Hewlett-Packard 5890A Series II gas chromatograph (Hewlett-Packard, Andover, MA) and heated in a separate oven at 100°C for 1 hr before carrier gas was flown through the trap to transfer its gases onto the head of the gas chromatography column. Light gas analysis was performed on a 6-ft 80/100 mesh Carbosphere packed column (Alltech).

**Results**

**Effects of Temperature**

Effects of temperature on total weight loss, tar and light gas yields (Figures 5–11) were studied by heating neat or contaminated soil from room temperature to peak temperatures (Figure 3) between 350 and 1050°C, at a nominal rate of 1000°C/sec. There was no further heating after attaining the peak temperature, i.e., cooling was allowed to begin immediately. The laboratory data are corrected to and plotted on a basis of 50 mg of contaminant-free soil, i.e., for contaminated soil runs the corrected initial mass of specimen is 52.49 mg to account for the 2.49 mg of pyrene contaminant. For the present experiments it is very difficult to replicate experimental temperature–time histories and peak temperatures with sufficiently high precision to create data sets for computing conventional means and standard deviations at one specific peak temperature. To provide some indication of the uncertainty in yields of various products, standard deviations of the mean (see error bars in Figures 5–11) were therefore calculated for groups of yield data measured for particular ranges of peak temperatures. The resulting standard deviations were then assigned to each of the points in that group. A more narrow band of peak temperatures was selected when the data exhibited stronger sensitivity to temperature.

Assuming no interaction between the pyrene and the soil and negligible experimental errors, the difference in the weight loss curves (Figure 5) for contaminated and neat soil should give the weight of pyrene removed from the soil. Based on these assumptions, Figure 12 indicates that the extent of pyrene removal increases with increasing temperature and approaches completion at about 530°C. However, Figure 12 further implies the clearly impossible result that pyrene removal exceeds 100% at temperatures above about 530°C. A plausible explanation for this artificially elevated level of decontamination, is that pyrene or its reaction products augment soil volatilization when treatment temperatures exceed a certain value, which according to Figure 12 is about 500°C. This hypothesis is supported by the following observations. With increasing temperature, tar yields from contaminated soil, which should include volatilized pyrene, in
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Figure 5. Weight loss data for neat (○) and 4.75 wt% pyrene-contaminated soil (●) as affected by peak temperature (nominal heating rate = 1000°C/sec, zero holding time). Curves are free drawn trend lines.

Figure 6. Yield of tars volatilized from neat (○) and 4.75 wt% pyrene-contaminated soil (●) as affected by peak temperature (nominal heating rate = 1000°C/sec, zero holding time). Curves are free drawn trend lines.

Figure 7. Carbon monoxide yields from neat (○) and 4.75 wt% pyrene-contaminated soil (●) as affected by peak temperature (nominal heating rate = 1000°C/sec, zero holding time). Curves are free drawn trend lines. Reprinted from Saito et al. (7) with permission of John Wiley & Sons, Inc.

Figure 8. Carbon dioxide yields from neat (○) and 4.75 wt% pyrene-contaminated soil (●) as affected by peak temperature (nominal heating rate = 1000°C/sec, zero holding time). Curves are free drawn trend lines.

Figure 9. Methane yields from neat (○) and 4.75 wt% pyrene-contaminated soil (●) as affected by peak temperature (nominal heating rate = 1000°C/sec, zero holding time). Curves are free drawn trend lines.

Figure 10. Acetylene yields from neat (○) and 4.75 wt% pyrene-contaminated soil (●) as affected by peak temperature (nominal heating rate = 1000°C/sec, zero holding time). Curves are free drawn trend lines.
addition to exhibiting the expectable overall increase (Figure 6), also showed color changes suggestive of pyrene chemical reactions: white (the color of pyrene) below 500°C, yellow-tinged pink between 500 and 750°C, and brown above 750°C. Unfortunately, detailed chemical analyses of these tars are not available to test for pyrene transformations to PAH or other products. Further, CO yields from contaminated soil exceed those from neat soil beginning at temperatures of 500°C or perhaps lower (Figure 7). Because pyrene contains no oxygen, the oxygen in this extra CO must have come from the soil, unless there were impurities like air or water in the immediate neighborhood of the heating appliance. This seems unlikely given that the reactor chamber was extensively purged prior to each run and that soil heating was conducted at super-atmospheric pressure (3 psig).

For neat and contaminated soils, tars (Figure 6), CO (Figure 7), carbon dioxide (Figure 8), methane (Figure 9), acetylene (Figure 10), and ethylene (Figure 11) each show an overall trend of increasing yields with rising temperature. Compared to neat soil, contaminated soil evolves somewhat more CO from about 450 to 800°C, and appreciably more above 800°C (Figure 7). Yields of the other four gases exhibit little or no distinct difference between neat and contaminated soil. Ethane and condensables (benzene to naphthalene) yields are not shown. Condensables were insignificant, and ethane yields were small and too scattered to reveal clear trends with temperature or the presence of contaminant.

**Effects of Heating Rate**

Heating rate effects were investigated by heating neat or contaminated soil from room temperature to about 550°C at nominal rates of 100, 1000, or 5000°C/sec, and then allowing cooling to begin immediately. Error bars in the yield data (Figures 13–19) are standard deviations calculated separately for neat and contaminated soil from duplicate experiments performed at each heating rate. The laboratory data are corrected to and plotted on a basis of 50 mg of contaminant-free soil.

Weight loss (Figure 13) from neat or contaminated soil shows little change with increasing heating rate from 100 to 1000°C/sec, but decreases when heating rate is increased to 5000°C/sec. No clear effect of heating rate on the implied pyrene removal calculated from the difference in the two curves in Figure 13 was discerned. Tar yields from neat soil show no effect of heating rate (Figure 14). Tar production from contaminated soil increases slightly when heating rate is increased from 100 to 1000°C/sec, but shows little or no change when heating rate is increased from 1000 to 5000°C/sec (Figure 14). Tar yields from the contaminated soil runs were white with a very slight pink hue for the 100 and 5000°C/sec heating rates, but yellowish pink for the 1000°C/sec runs. Changes in tar color suggest chemical reac tion(s) of the pyrene, but detailed chemical analyses of these tars are not available to test this hypothesis. No significant amounts of condensables (benzene to naphthalene) were collected in any of the runs.

Carbon monoxide yields (Figure 15) show little or no effect of heating rate for neat soil, but for contaminated soil exhibited an apparent maximum at 1000°C/sec. For neat and contaminated soil, acetylene, carbon dioxide, methane, and ethylene yields (Figures 16–19, respectively) indicate an apparent maximum at or near 1000°C/sec, although the data scatter equivocate this interpretation for methane and ethylene, and for CO₂ from neat soil. Figure 15 to 19 suggest little or no differences in the CO, acetylene, CO₂, methane, and ethylene yields from neat vs contaminated soil at 100 and 5000°C/sec. For contaminated soil at 1000°C/sec, clearly higher yields of CO (Figure 15) and acetylene (Figure 16) are seen, as are slightly higher CO₂ yields (Figure 17) and possibly higher ethylene yields (Figure 19).

**Discussion**

**Effects of Temperature**

Assuming that the difference in weight loss method of determining the extent of decontamination is valid, Figure 12 indicates that for heating at 1000°C/sec, about 3/4 of the pyrene can be released by heating the soil to a peak temperature equal to the boiling point of pyrene (404°C), and that virtually complete pyrene removal occurs by heating to a peak temperature of 530°C. Given the rapid heat-up and initial cool-down rates of 1000°C/sec and 400 to 600°C/sec, respectively, the implied overall rates of decontamination are fast i.e., heat-up plus cooling require only a few (<5) seconds (Figure 3). With similar apparatus and procedures Darivakis (10) deduced that about 7 wt% pyrene contamination
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Figure 13. Weight loss data for neat (○) and 4.75 wt% pyrene-contaminated soil (●) as affected by heating rate (nominal peak temperature = 550°C, zero holding time). Curves are free drawn trend lines. Reprinted from Saito et al. (7) with permission of John Wiley & Sons, Inc.

Figure 14. Mass of tars volatilized from neat (○) and 4.75 wt% pyrene-contaminated soil (●) as affected by heating rate (nominal peak temperature = 550°C, zero holding time). Curves are free drawn trend lines.

Figure 15. Carbon monoxide yields from neat (○) and 4.75 wt% pyrene-contaminated soil (●) as affected by heating rate (nominal peak temperature = 550°C, zero holding time). Curves are free drawn trend lines. Reprinted from Saito et al. (7) with permission of John Wiley & Sons, Inc.

Figure 16. Acetylene yields from neat (○) and 4.75 wt% pyrene-contaminated soil (●) as affected by heating rate (nominal peak temperature = 550°C, zero holding time). Curves are free drawn trend lines. Reprinted from Saito et al. (7) with permission of John Wiley & Sons, Inc.

Figure 17. Carbon dioxide yields from neat (○) and 4.75 wt% pyrene-contaminated soil (●) as affected by heating rate (nominal peak temperature = 550°C, zero holding time). Curves are free drawn trend lines.

Figure 18. Methane yields from neat (○) and 4.75 wt% pyrene-contaminated soil (●) as affected by heating rate (nominal peak temperature = 550°C, zero holding time). Curves are free drawn trend lines.
Figure 13. Ethylene yields from neat (○) and 4.75 wt% pyrene-contaminated soil (●) as affected by heating rate (nominal peak temperature = 550°C, zero holding time). Curves are free drawn trend lines.

was removed from a clay soil heated to about 600°C at 1000°C/sec. Figure 12 shows that when heating at 1000°C/sec, decontamination efficiencies deduced from the difference in weight loss of neat and pyrene-polluted soil exceed 100% above a certain temperature. Consequently, the difference in weight loss protocol must be viewed as unreliable above a certain temperature at which soil-contaminant chemical reactions begin to affect the weight loss behavior of neat soil. The value of this temperature will in general depend upon heating rate, soil type, and type of contaminant. Thus, Bucalà et al. (25) found that when heating samples of this same soil matrix contaminated with No. 2 fuel oil, the weight difference method was valid up to about 700°C. This conclusion was based on their findings of comparable yields of methylene chloride extractables from cooled residues of soil heated to temperatures that gave high extents of oil removal, and from cooled residues of uncontaminated soil. Figure 12 suggests that for pyrene removal from this soil matrix, the weight difference protocol is suspect above about 530°C. However, this temperature is only an estimate because Figure 12 is deduced from the two curves in Figure 5, each of which reflects significant uncertainty in experimental weight loss data. Likewise the 750°C denoted by Figure 12 as the temperature for which the excess weight loss begins a plateau, is only approximate.

To elaborate, a breakdown in the difference in weight loss method can be rationalized if pyrene or its reaction products augment neat soil volatilization by converting soil-bound oxygen to CO. Soil-contaminant chemical reactions, i.e., between organic volatile substances and chloride in the upper layers of a soil bed were proposed by McClennen et al. (17) to explain the appearance of chlorostyrenes and chloroethylbenzenes in volatiles from heating ethylbenzene-contaminated soil in air. Between about 450 to 500°C and 750°C, the present CO yields are slightly larger for contaminated versus neat soil (Figure 7) and thus could account for some of the excess weight loss imputed from Figure 12. At about 950°C, the excess CO from pyrene-treated soil (Figure 7) could account for about two-thirds of the imputed excess weight loss of soil (Figure 12). However, 950°C is much higher than the 750°C indicated by Figure 12 as the temperature above which excess weight loss ceases. The uncertainty in Figure 12, and the absence of material balances connecting starting materials to products preclude quantitative evaluation of plausible as well as more speculative explanations for observed differences between the behavior of neat and contaminated soil heated under similar conditions. Literature on the pyrolysis of pyrene and other aromatic hydrocarbons gives guidance on chemical reactions that may impact the yields, compositions, and toxicologic activity of tars and other products from thermal decontamination of PAH-polluted soils. Pyrolysis of aromatic compounds in the presence of CaO at 400 to 800°C produces solid carbon (38,39). If these or other carbon-forming reactions occur before the PAH exits the soil, i.e., if the relevant chemistry is fast compared to pyrene mass transfer from the soil, solid carbon will deposit on the soil, leading to lower weight loss than if all the contaminants had escaped the soil as volatile substances. This could in turn lead to an error in the difference in weight loss method opposite in sign to that implied by Figure 12, i.e., an underestimation of the extent to which a volatilizable contaminant has been affected by thermal treatment of the soil. PAH may also undergo thermal conversion to other PAH. In low temperature (450°C), long soak time (4 hr) pyrolysis studies, Sharkey et al. (40) found gaseous and condensed phase products suggestive of pyrene condensation to biphenylenes, i.e., dihydropyrene and diphenylenes. Mukherjee et al. (41) identified various PAHs, e.g., cyclopenta[cd]pyrene (CPEP), cyclopenta[bj]acephenanthrylene (CPAP), benzo[ghi]fluoranthene, biphenylenes, and triphenylenes, in tars from short residence time (-0.75 sec) pyrolysis at temperatures of 940 to 1210°C. CPEP is mutagenic to bacterial cells (42) and human cells (43) in vitro. If pyrene undergoes analogous reactions when heated in the presence of soil, toxicologically active by-products may arise. Further, if there are catalytic effects of soil minerals, unwanted reactions may occur at lower temperatures. The tars in Figure 6 were not bioassayed or subjected to detailed chemical analysis, so we lack crucial information to test for the generation of adverse by-products.

Effects of Heating Rate

Effects of heating rate on soil decontamination are more complex than those of peak temperature. Assuming the difference in weight loss method is valid, Figure 13 suggests that there is little effect of heating rate on pyrene removal at a peak temperature of 550°C, when heating rate was reduced from 5000 to 1000°C/sec or further to 1000 to 100°C/sec (Figure 13). However, at somewhat lower temperatures and considerably lower heating rates, Gilot et al. (27) found that a 10-fold reduction in heating rate, i.e., from 50 to 5°C/min, lowered the temperature to achieve 85% pyrene removal from a clay soil, from 275 to 200°C. Further mathematical modeling of heating rate and temperature effects on soil thermal decontamination, for broad ranges of these two variables, would shed further light on these observations. Differences in soil type, heating apparatus, and soil bed configuration may also be important, i.e., Gilot et al. (27) heated a shallow bed of soil in a thermogravimetric analyzer.

For neat soil, the present study detected little or no effect of changing heating rate from 100 to 5000°C/sec on yields of tars and CO (Figures 14, 15), but indicated maxima in the yields of CO (Figure 15),
acetylene (Figure 16), CO₂ (Figure 17), and methane (Figure 18), from contaminated soil, and of acetylene and possibly CO₂ and methane from neat soil (Figures 16–18). These trends cannot be explained in terms of a simple mechanistic picture, valid for a single first-order kinetic model, that increasing heating rate allows less time for product formation, e.g., by evaporation or chemical reaction. More complex kinetic networks, e.g., sequential reactions, are suggested. Saito (33) found that for uncontaminated soil, a kinetic model based on two chemical reactions in series would predict a maximum in acetylene yields with increasing heating rate, but that the detailed fit to experimental data was strongly sensitive to temperature [discussed also by Saito et al. (7)].

Concordance: Environmental Health Implications

Broadly based public acceptance is needed to site and operate most environmental remediation technologies. This requires stakeholder confidence that the process will provide desired cleanup efficiencies at reasonable economic costs, without adverse environmental health impacts, e.g., impacts owing to toxic effluents or residues. Better understanding of engineering and environmental health related issues is important in building and maintaining this confidence. This and other studies, e.g., (7–32), for soil thermal treatment contribute to this understanding.

The present research addressed effects of temperature and heating rate on removal of a medium volatility PAH contaminant, i.e., pyrene, from a U.S. EPA synthetic soil matrix prepared to reflect attributes of soils at Superfund sites. Based upon the differences in experimentally determined weight losses of uncontaminated and contaminated soil (Figure 5), it was concluded that a high initial level of pyrene contamination, i.e., 4.75 wt%, can be substantially reduced by heating a thin bed (<150 µm) of 63- to 125-µm soil particles to 530°C at 1000°C/sec (Figure 12). More generally the rates and extents of soil decontamination will be influenced by soil type, contaminant volatility and chemical reactivity, bed depth, and heating conditions, e.g., (7–27).

For the present experimental conditions, thermal treatment of pyrene-contaminated soil generates numerous volatile by-products in yields that depend on temperature (Figures 6–11) and in some cases heating rate (Figures 14–19). Thermal reactions of neat soil [discussed also by Bucală et al. (26)] can be a significant or dominant source of many of these volatiles, especially at some heating rates (Figures 8–11, 15–19). In the present study, two gaseous volatile substances of environmental health concern emitted by heating both neat and pyrene-contaminated soil are acetylene (Figures 10, 16), a known precursor to PAH formation at higher temperatures (44), and CO (Figures 7, 15), which poisons humans by chemically deactivating the oxygen-carrying capacity of blood hemoglobin (45). The tarlike liquid products from heating pyrene-polluted soil at 1000°C/sec (Figures 6, 14) are also of environmental health interest in light of documented observations on pyrene pyrolysis products (41), and present observations indicating pyrene chemical reactions above approximately 500°C, i.e., augmented soil volatilization (Figure 12), increased CO release (Figure 7), and distinct color changes in the product tars, i.e., from white (presumably pyrene) to yellow-pink at 500°C, and from pink to brown at 750°C. Mukherjee et al. (41) found that pyrolysis of pyrene vapor at 940 to 1210°C for approximately 0.75 sec generated several PAHs including CPEP, a yellow-orange bacterial cell (42) and human cell (43) mutagen, similar in molecular weight to pyrene (226 vs 202). Detailed chemical analyses and toxicologic assays are not available for the present tars. Consequently the question of whether heating of pyrene-polluted soil according to the current procedures generates genotoxic tars requires further research. Nevertheless, it is prudent to consider the possibility that bioactive organic volatile substances may be generated when heating PAH-contaminated soils. Practical scale thermal technologies can be designed to decontaminate or destroy these and other undesired volatile substances, e.g., by oxidation within the primary thermal treatment chamber or in downstream after-burners or other effluent cleaning equipment. On-line monitors are useful in detecting unacceptable toxicant concentrations and in actuating appropriate clean-up measures.

Above a certain temperature, the measured weight loss of contaminated soil exceeded the sum of the corresponding weight loss of neat soil plus the initial weight of the pyrene pollutant (Figure 12). The exact temperature at which this behavior begins is uncertain, because Figure 12 is constructed from the difference in two curves which show significant data scatter (Figure 5). For heating the present soil at 1000°C/sec, 500°C is a rough estimate for this temperature. The cause of this excess weight loss is believed to be augmented volatilization of the soil, owing to chemical reactions of the pyrene or its decomposition with the soil. An important environmental health consequence is that decontamination efficiencies computed from the difference in weight loss of contaminated versus neat soil may be seriously overestimated, especially at higher treatment temperatures or when rapid heating rates reduce the time available for contaminants to escape the soil before they or their reaction products can react chemically with the soil. Thus it is wise to test for this effect and another potential source of error in the difference in weight loss method, i.e., conversion of contaminant to solid carbon deposits on the soil, which would lead to an underestimate of the amount of pollutant affected by the treatment protocol. A plausible approach is to close material balances by measuring the yield of all products from treating a known weight of soil and contaminant. This procedure should include testing of solid residues of soil thermal treatment for residual contamination, e.g., by solvent extraction. However, such measures may not be feasible in larger scale systems that integrate several treatment operations, or even in some research equipment.

Conclusions

This article focuses on how temperature increase and heating rate each affect volatile substance yields and reduction of pyrene contamination, during rapid heating of thin layers of soil particles in the absence of oxygen. The experiments employed heating protocols that are relevant in practice and provided information for estimating the identities and fluxes of (partially) cleaned soil (i.e., solid residue), and of soil- and contaminant-derived volatiles that in full-scale processes would in general be further treated by oxidation or other clean-up methods. Thus, this study is pertinent to the thermal desorption and/or pyrolysis stages of soil thermal treatment, but does not address effects of heating soil in contact with oxygen or of exposing newly released volatile substances to oxygen. Some or all of the present findings may be extrapolated, at least qualitatively, to other PAH similar in volatility, chemical structure, and thermochemical reactivity to pyrene, but this must be assessed by further research.

The present work provides further support for the picture that temperature strongly affects the yields and apparent release rates of volatilizable organic...
contaminants and other volatiles during soil thermal treatment. Changing heating rate from 1000 to 100 or 5000°C/sec little affected the apparent pyrene removal efficiency at a peak temperature of 550°C, but gave reduced yields of CO and acetylene, and possibly CO₂ and methane from contaminated soil. Based upon the differences in experimentally determined weight losses of uncontaminated and contaminated soil, we concluded that a high initial level of pyrene contamination, i.e., 4.75 wt%, can be substantially and rapidly reduced by heating a thin bed (<150 µm) of 63- to 125-µm soil particles to rather modest temperatures, e.g., to about 530°C at 1000°C/sec.

Chemical reactivities of pyrene with soil or its decomposition products are indicated at about 500°C and have environmental health consequences, i.e., increased yields of CO and apparently augmented volatilization of soil. More specifically, above about 530°C (1000°C/sec), CO yields from pyrene-treated soil (Figure 7) were significantly higher than those from heating neat soil (CO is a potent toxin to the oxygen carrying capability of human blood hemoglobin). Color changes in the tars from pyrene-polluted soil i.e., from white (presumably pyrene) to yellow-pink at 500°C, and from pink to brown at 750°C are also ascribed to pyrene chemical reactions. This interpretation is environmentally intriguing in light of literature (41) showing that pyrolysis of pyrene vapor at 940 to 1210°C produces several PAH including the bacterial cell (42) and human cell (43) mutagen, cyclopenta[cd]pyrene (CPEP), which is yellow-orange in color. Detailed chemical analyses and toxicologic assays are not available for the present tars. Consequently the question of whether heating pyrene-polluted soil under the current conditions generates genotoxic-by-products requires further research. Nevertheless there is merit in remaining alert to the possibility that toxico logically active compounds may occur among the volatile products of heating PAH-contaminated soils. Practical scale soil thermal treatment technologies can incorporate countermeasures, e.g., one or more stages of oxidation, and possibly other downstream cleaning methods to destroy or capture organic toxics that survive soil pyrolysis. Pathologic reactions of PAH may occur at unexpectedly low temperatures owing to catalysis or other promotional effects of soil inorganic matter.

An environmental health consequence of pyrene-enhanced volatilization of soil is that computations based on the difference in weight loss of contaminated vs neat soil, may seriously overestimate the extent of soil cleanup. Thus soil decontamination efficiencies should be measured or checked by closing material balances, i.e., by quantifying all products yields including testing residues of treated soil for residual contamination.

REFERENCES AND NOTES

1. U.S. EPA. Superfund: Focusing on the Nation at Large—1991. Publ 9200.5-701A. Document PB919-212-02. Washington: U.S. Environmental Protection Agency. 1991.

2. Cudahy J, Troxler WL. Thermal treatment remediation industry contractor survey. J Air Waste Manage Assoc 42(6):844 (1992).

3. Daley PS. Cleaning up sites with on-site process plants. Environ Sci Technol 25(8):912–916 (1991).

4. Long GM. Clean up hydrocarbon contamination effectively. Chem Eng Prog 89(5):58–67 (1993).

5. Linak WP, Kilgroo JD, McSorley JA, Wendt JOL, Dunn JE. On the occurrence of transient pits in a rotary kiln incinerator simulator. I: Prototype solid plastic wastes. J Air Pollut Control Assoc 37(1):54–65 (1987).

6. Seeker WR, Koshland CP. Combustion-by-product formation: an overview. Combust Sci Technol 74:i–viii (1990).

7. Saito HH, Howard JB, Peters WA, Bucála V. Soil thermal decontamination: fundamentals. In: The Encyclopedia of Environmental Analysis and Remediation. Vol 7 (Meyers RA, ed). New York: John Wiley & Sons, 1998:4554–4589.

8. Tognotti, L, Flynatzni-Stephanopoulos MF, Sarofim AF, Kopsinis H, Stoukides M. Study of adsorption-desorption of contaminants on single soil particles using the electrodynamic thermogravimeteric analyzer. Environ Sci Technol 25(1):104–109 (1991).

9. Flynatzni-Stephanopoulos MF, Sarofim AF, Tognotti, L, Kopsinis H, Stoukides M. Incineration of contaminated soils in an electrodynamic balance. In: Emerging Technologies in Hazardous Waste Management. II: American Chemical Society Symposium Series 468 (Tedder DW, Pohland FG, eds). Washington: American Chemical Society, 1991:29–49.

10. Darivaks GS. Unpublished data.

11. McClenen WH, Arnold NS, Roberts KA, Meuzelaar HLC, Lighty JS, Lingren EG. Fast, repetitive GC/MS analysis of thermally desorbed polycyclic aromatic hydrocarbons (PAHs) from contaminated soils. Combust Sci Technol 74(1–6):397–3490 (1990).

12. Wu YG, Dong J, Bozzelli JW. Mass transfer of hazardous organic compounds in soil matrices: experiment and model. Comb Sci Technol 85:151–163 (1991).

13. Wu YG, Bozzelli JW. Thermal adsorption-desorption of C₆H₆ and C₆H₅Cl on soil matrices by gas chromatography. Hazard Waste & Hazard Mater 11(1):227 (1994).

14. Lighty JS, Eddings, EG, Lingren ER, Xiao D, Winter RM, McClenen WH. Rate limiting processes in the rotary-kiln incineration of contaminated solids. Combust Sci Tech 74:31–49 (1990).

15. Lighty JS, Pershing DW, Cundy VA, Linz DG. Characterization of thermal desorption phenomena for the cleanup of contaminated soil. Nucl Waste Manage 8(1):225–237 (1988).

16. Lighty JS, Silcox GD, Pershing DW, Cundy VA, Linz DG. Fundamental experiments on thermal desorption of contaminants from soils. Environ Prog 8(1):57–61 (1989).

17. Lighty JS, Silcox GD, Pershing DW, Cundy VA, Linz DG. Fundamentals for the thermal remediation of contaminated soils. Particle and bed desorption models. Envir Sci Technol 24:750–757 (1990).

18. Larsen FS, Silcox GD, Keyes BR. The development of a thermal treatment assessment procedure for soils contaminated with hydrocarbons. Combust Sci Technol 101(1–9):443–459 (1994).

19. Keyes BR, Silcox GD. Fundamental study of the thermal desorption of toluene from montmorillonite clay particles. Environ Sci Technol 28(5):840–849 (1994).

20. Owens WD, Silcox GD, Lighty JS, Deng XX, Pershing DW, Cundy VA, Leger CB, Jakway AL. Thermal analysis of rotary kiln incineration: comparison of theory and experiment. Combust Flame 86(1–2):101–114 (1991).

21. Owens WD, Silcox GD, Lighty JS, Deng XX, Pershing DW, Cundy VA, Leger CB, Jakway AL. The desorption of toluene from a montmorillonite clay adsorbent in a rotary kiln environment. J Air Waste Manage Assoc 42(5):681–690 (1992).

22. Silcox GD, Larsen FS, Owens WD, Choroszy-Marshall M. Kinetics of hydrocarbon and pesticide removal from clay soils during thermal treatment in a pilot-scale rotary kiln. Waste Manage 15(5/6):339–349 (1995).
23. Linak WP, McSorley J A, Wendt JOL, Dunn JE. On the occurrence of transient puffs in a rotary kiln incinerator simulator. II: Contained liquid wastes on sorbent. J Air Pollut Control Assoc 37(8): 934–942 (1987).

24. Wendt JOL, Linak WP. Mechanisms governing transients from the batch incineration of liquid wastes in rotary kilns. Combust Sci Technol 61:169–185 (1988).

25. Bucala V, Saito H, Howard JB, Peters WA. Thermal treatment of fuel oil-contaminated soils under rapid heating conditions. Environ Sci Technol 28(11):1801–1807 (1994).

26. Bucala V, Saito H, Howard JB, Peters WA. Products compositions and release rates from intense thermal treatment of soil. Ind Eng Chem Res 35:2725–2734 (1996).

27. Gilot P, Howard JB, Peters WA. Evaporation phenomena during thermal decontamination of soils. Environ Sci Technol 31(2):461–466 (1997).

28. U.S. EPA. Innovative treatment technologies: semi-annual status report. Rpt EPA/540/2-91/001, no 2. Washington:U.S. Environmental Protection Agency, 1991.

29. Simonich SL, Hites RA. Importance of vegetation in removing polycyclic aromatic hydrocarbons from the atmosphere. Nature 370:49–51 (1994).

30. Frederick RM. Personal communication, 1993.

31. U.S. EPA. Development and Use of EPA Synthetic Soil Matrix (SSM/SARM). Edison, NJ:U.S. Environmental Protection Agency, 1989.

32. Esposito P, Hessling J, Locke BB, Taylor M, Szabo M, Thurnau R, Rogers C, Traver R, Barth E. Results of treatment evaluations of a contaminated synthetic soil. J Air Pollut Control Assoc 39(3):294–304 (1989).

33. Saito HH. Effects of temperature and heating rate on off-gas composition and pyrene removal from an artificially-contaminated soil. PhD Thesis. Cambridge, MA:MIT, 1995.

34. Suuberg EM. Rapid pyrolysis and hydropyrolysis of coal. ScD Thesis. Cambridge, MA:MIT, 1977.

35. Suuberg EM, Peters WA, Howard JB. Product composition and kinetics of lignite pyrolysis. Ind Eng Chem Process Design Develop 17:37–46 (1978).

36. Hajaligol MR. Rapid pyrolysis of cellulose. PhD Thesis. Cambridge, MA:MIT, 1980.

37. Hajaligol MR, Howard JB, Longwell JP, Peters WA. Product compositions and kinetics for rapid pyrolysis of cellulose. Ind Eng Chem Process Design Develop 21:457–465 (1982).

38. Ellig DL, Lai CK, Mead DW, Longwell JP, Peters WA. Pyrolysis of volatile aromatic hydrocarbons and n-heptane over calcium oxide and quartz. Ind Eng Chem Process Design Develop 24:1080–1087 (1985).

39. Lai C-KS. Thermal reactions of aromatic hydrocarbons and mesityl oxide over calcium oxide. ScD Thesis. Cambridge, MA:MIT, 1986.

40. Sharkey AG Jr., Shultz JL, Friedel RA. Mass spectra of pyrolysis products of several aromatic structures identified in coal extracts. Carbon 4:365–374 (1966).

41. Mukherjee J, Sarofim AF, Longwell JP. Polycyclic aromatic hydrocarbons from the high temperature pyrolysis of pyrene. Comb Flame 96:191–200 (1994).

42. IARC. IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans. Vol 32: Polynuclear Aromatic Compounds. Part 1: Chemical, Environmental and Experimental Data. Lyon:International Agency for Research on Cancer, 1983.

43. Lalley AL, Longwell JP, Marr JA, Monchamp PA, Plummer EF, Thilly WG, Mulder PPY, Boere BB, Cornelisse J, Lugtenburg J. Bacterial and human cell mutagenicity study of some C25H10 cyclopenta-fused polycyclic aromatic hydrocarbons associated with fossil fuels combustion. Environ Health Perspect 110(2):146–153 (1993).

44. Lam FW, Longwell JP, Howard JB. The effect of ethylene and benzene addition on the formation of polycyclic aromatic hydrocarbons and soot in a jet-stirred/plug-flow combustor. In: Proceedings Twenty-Third Symposium (International) on Combustion. Pittsburgh, Pennsylvania: The Combustion Institute, 1991:1477–1484.

45. National Research Council. Prudent Practices for Handling Hazardous Chemicals in Laboratories. Washington:National Academy Press, 1981;92–93.