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Thermal Desorption Treatment of Contaminated Soils in a Novel Batch Thermal Reactor

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Low-temperature thermal desorption, in which thermal energy is used to vaporize and physically separate volatile and semivolatile organic contaminants from soil, is among the most promising and economic ex situ soil remediation alternatives. Experiments were performed using a bench-scale thermal desorber, the batch thermal reactor, which was developed as a prototype to commercial desorbers. A treatability study using four representative samples of industrial contaminated soil was followed by a fundamental study of the thermal desorption process using three controlled samples prepared by mixing a soil with binary mixtures of selected polynuclear aromatic hydrocarbons. For the industrial samples, the effect of desorber residence time, temperature, and several pretreatments on contaminant removal was investigated. Three of the five samples were successfully treated to the legislated soil remediation limits. Using the prepared samples, the effects of sample porosity, contaminant molar mass, desorber residence time, and temperature on thermal desorption were investigated. The experimental results were fitted to an exponential desorption equation, and the desorption rate curves were generated to provide a basis for scale-up.

Introduction

Thermal desorption is emerging as a preferred treatment technology for soils contaminated by volatile organic compounds (VOCs) because it is considered to be relatively safe, emitting little or no material into the atmosphere, and is less energy intensive than incineration.¹ While incineration, operating at temperatures above 1000 °C, uses heat to actually destroy contaminants by combustion, thermal desorption uses heat to physically separate contaminants from the soil. Depending on the design of the system, the vaporized contaminants either are condensed and recovered or are destroyed. In many cases, recovered hydrocarbons can be recycled.²

Commercial units have demonstrated that thermal desorption is effective for separating organic compounds from refining wastes and coal tar wastes, creosote from wood treatment wastes, and solvents, pesticides, polychlorinated biphenyls (PCBs), dioxins, and fuel oil from contaminated soils.^{3–5}

Using two bench-scale units to treat contaminated soils, Lighty et al.^{6–8} experimentally studied parameters such as the particle size, bed thickness, and effective diffusivity and found that the desorption rate is a strong function of soil type and most significantly of temperature. They also presented a mathematical model of the desorption behavior of contaminants from soil.

The thermal treatment of soil artificially contaminated by fuel oil was investigated by Bucalá et al.⁹ In studies applicable to several thermal treatment technologies, the effects of heating rate, final temperature,

and degree of contamination on contaminant removal were studied. Bucalá et al.¹⁰ also investigated how soil decomposition under thermal treatment affects desorption.

Interactions between binary mixtures of polynuclear aromatic hydrocarbons (PAHs) and the fulvic acid, humic acid, and inorganic fractions of soil were studied by Maguire et al.¹¹ and Laplante and Mehrotra.¹² PAHs were found to form miscible systems with the humic acid soil fraction, while no interaction between PAHs and other soil fractions was observed. Because of the formation of a miscible system, a temperature higher than the PAH boiling point was necessary to effect its removal by thermal desorption.

Keyes and Silcox¹³ investigated the nonisothermal desorption of toluene and *n*-dodecane from individual montmorillonite clay particles. Desorption rates, measured as a function of the heating rate, clay type, particle size, and purge gas flow rate, were obtained for several systems. Intraparticle diffusion was found to be the rate-controlling mechanism. Farrell and Reinhard^{14,15} published complementary papers on the desorption isotherms and desorption kinetics of chlorinated hydrocarbons from model solids and soils. The feasibility of thermally treating black tarry material containing pentachlorophenol and other hazardous compounds was investigated by Hsieh et al.⁴

Pilot-scale studies with a continuous, indirectly heated rotary kiln desorber were conducted by Fox et al.¹⁶ The effects of both the desorber temperature and residence time on the quality of treated soil were investigated. The unit successfully remediated three different types of soil contaminated by PCBs. Additional pilot-scale tests were performed on mixed waste-, dioxin-, and PAH-contaminated soils.

Rutberg and Baille¹⁷ found that a certain amount of thermal cracking of high molecular weight hydrocarbons

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occurred in the high-temperature desorber. They concluded that the removal of high molecular weight hydrocarbons occurs by a combination of volatilization and decomposition reactions.

Field demonstration results from four commercial thermal desorption processes were reported by de Percin.¹⁸ It was found that soils contaminated by VOCs, SVOCs, PCBs, and pesticides were successfully remediated by all four systems.

There are dozens of companies in North America that offer soil remediation by thermal desorption on a commercial basis, and a number of these technologies have been discussed in the literature.^{5,19–23}

The purpose of the current research program was to design an experimental batch, low-temperature thermal desorber and to test it by treating several representative industrially contaminated samples, with the aim of achieving remediation levels acceptable in accordance to local regulations (Alberta Tier 1 Criteria²⁴). Additionally, experiments on samples artificially contaminated with PAHs were aimed at investigating the effect of sample porosity, contaminant molecular weight, desorber residence time, and desorber temperature on thermal desorption efficiency. Another objective included the use of the results gathered from both industrial samples and prepared samples to calculate contaminant desorption rates in terms of a simple parameter that would guide the design, scale-up, and operation of the system on a commercial scale.

Experimental Section

Batch Thermal Reactor. The batch thermal reactor (BTR) consists of a 1.5-L electrically heated batch thermal desorber, equipped with a helixlike auger, which was capable of operating at temperatures in the range of 150–600 °C. Commercial indirectly heated desorbers described in the literature typically use an inert gas environment to prevent, or at least minimize, the oxidation of desorbed organics. The most significant feature of the BTR is that the unit operates under vacuum, thus realizing two main benefits. The first is that the gas stream exiting the BTR consists only of condensable desorbed contaminants and water; therefore, the volume of material to be processed by the condenser and exhaust gas treatment units is much smaller than that for desorbers that rely on sweep gases. The second benefit of operating under vacuum is the boiling point depression. Thus, contaminants will desorb at a lower temperature in the BTR than they would at atmospheric pressure. The BTR is equipped with a feed hopper and a solid product discharge port. The desorbed contaminants are withdrawn through a vapor exit line and separated using a primary trap followed by a water-cooled condenser and a secondary trap. The temperatures throughout the equipment are monitored using several thermocouples (three in the BTR and one in each of the traps) and recorded using a data acquisition system. Further details of the apparatus and experimental procedure are given by Smith.²⁵

At the start of each experiment, 600–1000 mL of a contaminated sample was fed into the BTR by gravity through a feed hopper. The sample was then mixed by the helix auger and allowed to heat to the desired preset temperature. To mix the sample, the auger, powered by an electric motor, rotated at 20 rpm for 15 s in one direction and then reversed its direction. It was found

that samples treated according to this methodology generally reached the set temperature in less than 2 min.²⁵

Upon completion of each test, i.e., upon reaching the desired residence time, the treated sample was dropped through the solid product discharge valve onto dry ice in a large metal pan. The dry ice effectively quenched any further desorption of hydrocarbons from the sample and minimized the oxidation of contaminants in the air.

Volatilized water and contaminants were drawn out of the BTR under a vacuum of 46 kPa (absolute) through a single vapor exit line. The vapor then passed into a dual-condenser system, consisting of a primary trap, to capture the heavier compounds, and a secondary trap, to condense the water and lighter hydrocarbons.

Two analytical methods, Soxhlet extraction and gas chromatography, were used to measure residual hydrocarbon concentrations and to determine the composition of PAHs desorbed off prepared samples. The residual hydrocarbon concentration of thermally treated samples was expressed as the weight percent of total hydrocarbon contamination (% THC).

Characteristic Industrial Samples. Four industrial samples were obtained to investigate the feasibility of treating several typical waste types using the BTR. Rather than undertaking an extensive study on each sample, the initial goal was to get a preliminary understanding of the effects of the desorber temperature and residence time on the remediation level. In addition, the impact of selected sample pretreatments was investigated, including lime (CaCO₃) addition and a physical aggregation process, in which very wet samples were dried using a rotary kiln. The aggregation process was designed to improve the handling characteristics of excessively moist soils and to effectively blend additives or stabilizers into the soil.

It is common in most types of soil remediation processes to blend very wet or highly contaminated soils with additives such as sand or lime to improve the handling characteristics of the soil and to stabilize contaminants. Sand is the most common soil pretreatment additive;³ however, the energy required to heat the additional mass compromises the economy of such processes. Alternatively, lime is frequently selected as a soil amendment, because it does not increase the soil bulk density and reduces the stickiness of the contaminated soils. While lime has been found to react with sulfur and chlorine to form salts such as CaSO₄ and CaCl₂ during incineration, at desorption temperatures lime simply dehydrates the soil and stabilizes organic contaminants.

The sample characteristics, the type and degree of contamination, and the pretreatment done to prepare the samples were as follows:

(1) Flare pit material (Domtar refinery, Alberta, Canada) contaminated up to 20 wt % with hydrocarbons ranging from C₃ to C₆₀ with particularly large quantities of xylene, toluene, and C₁₃–C₂₈ compounds. The sample also contained five heavy metals, namely, barium, chromium, mercury, molybdenum, and zinc. The high degree of contamination, coupled with a moisture content of about 25%, made the raw sludge extremely difficult to handle. Therefore, the sludge was pretreated by washing, partial drying, and blending with 3 wt % lime, resulting in sludge pellets, about 8 mm in diameter, with a moisture content of about 10%, while the hydrocarbon concentration reduced to 3.8 wt %. The

handling characteristics of the sludge were vastly improved by aggregation.

(2) Chlorinated soil (CanOxy Ltd., Canada) with a hydrocarbon concentration of 1.7%, due to presence of several chlorophenols, and a moisture content of about 20 wt %. A high electrical conductivity was measured, and the concentrations of two heavy metals, mercury and boron, were above the legislated limits.

(3) Spent activated carbon (Amoco Canada, Kaybob Plant, Alberta, Canada) with a hydrocarbon concentration of 9.8 wt %. Although several organic compounds, including toluene, xylene, phenol, and some straight-chain hydrocarbons, were recognized from the gas chromatography (GC) results, many others could not be identified. No pretreatment or preparation was required for the sample, because it consisted of discrete, free-flowing particles.

(4) Produced sand (PanCanadian Petroleum Ltd., Alberta, Canada) displaced during the drilling of oil wells, lightly contaminated with petroleum hydrocarbons and organic solvents (C_{15} – C_{29} compounds) used during the drilling process (1.24 wt %). The moisture content of the sand was about 20%, and the hydrocarbon contamination coupled with the moisture made the sand difficult to handle. The specific experimental program for this industrial sample focused on the impact of six kinds of pretreatment, including various types of sample washes with cold and hot water, and lime addition in different concentrations.²⁴

Artificially Prepared Samples. Three artificially contaminated samples were prepared using two model solids and binary mixtures of PAHs. Experiments were performed to investigate the effect of porosity, contaminant molecular weight, desorber residence time, and desorber temperature on desorption.

Two model solids, washed SIL-4 grade sand (Acklands Ltd., Calgary, Canada) and activated carbon (Sigma), were selected to investigate the effect of material porosity on desorption. The sand had a mean particle size of 364 μm , while the diameters of the activated carbon particles ranged between 850 μm and 2.36 mm, with a mean particle size of 1.58 mm.

The model solids were contaminated with two binary mixtures of PAHs. PAHs are neutral, nonpolar organic molecules, consisting of two or more benzene rings arranged in a variety of configurations. These compounds are typically toxic and hazardous even at low concentrations, and several are recognized to be carcinogens. PAH contamination of soils is particularly prevalent because it is associated with several common sources of soil contamination including gasoline, creosote, and solvents.

Four PAHs with varied boiling points were selected as representative of PAHs typically found at creosote and petroleum contaminated sites: anthracene, fluorene, naphthalene and phenanthrene (Aldrich Chemical Co., Milwaukee, WI). Two combinations, i.e., naphthalene–phenanthrene and anthracene–fluorene, were chosen on the basis of their boiling points, so that the components would not desorb similarly at a given temperature. Naphthalene and phenanthrene have normal boiling points of 218 and 340 °C and bubble points at 46 kPa of 188 and 305 °C, respectively. Anthracene and fluorene have normal boiling points of 340 and 298 °C and bubble points at 46 kPa of 306 and 267 °C, respectively. Therefore, the effect of operating the desorber at 46 kPa absolute vacuum instead of at

atmospheric pressure decreased the boiling points of the PAHs by approximately 30 °C in both cases.

Equal weights of naphthalene and phenanthrene were dissolved in an excess of methylene chloride in order to contaminate both sand and activated carbon samples to concentrations between 3 and 5 wt %. The solvent was evaporated and recovered by vacuum distillation at 40 °C. Similarly, a 50:50 weight mixture of anthracene and fluorene was also dissolved in methylene chloride; however, because of the low solubility of anthracene in the solvent, the sand was only contaminated to a concentration of 2 wt %. The sand was contaminated with both mixtures, while the activated carbon was only contaminated with the naphthalene–phenanthrene mixture.

This series of simple experiments on two solids contaminated by 50:50 binary mixtures of PAHs illustrated the effect of four factors on thermal desorption: two equipment operating parameters (desorber residence time and temperature), one contaminant characteristic (PAH molecular weight), and one sample characteristic (porosity). In contrast to the experiments with industrial samples described earlier, in which the object was to study BTR effectiveness for treating typical industrial samples to reach acceptable limits, the experiments on prepared samples were designed to gain insight into the thermal desorption process.

To study the effect of temperature on desorption, three desorber temperatures were chosen on the basis of the PAH boiling points. In both cases, one temperature was selected below the boiling points of both compounds, another temperature between the two boiling points, and the third temperature above both. For sand contaminated by fluorene and anthracene, desorber temperatures of 250, 320, and 350 °C were selected. Desorber temperatures of 150, 250, and 350 °C were used for sand and activated carbon contaminated by naphthalene and phenanthrene.

Desorber residence times of 10, 20, 40, and 60 min were used for all experiments. The effective time spent at each temperature is reduced by the sample heatup time, the impact of which is most significant in experiments with very short residence times. To reduce the time to reach the temperature, relatively small amounts of sample were used: prepared sand samples of approximately 250 g and prepared activated carbon samples of 125 g.

The mass of desorbed PAHs collected in the primary trap was measured at the end of each experiment, to measure the desorption efficiency as a function of temperature and residence time and to close the mass balance.²⁴ The composition of PAHs desorbed from samples treated for 60 min at each temperature was determined by GC. This analysis, coupled with gas-flow measurements, verified that the PAHs were not cracking or otherwise reacting in the BTR. Residual hydrocarbon concentrations were determined by Soxhlet extraction.

Results and Discussion

Industrial Samples. (a) Domtar Flare Pit Sludge. Five experiments were performed using Domtar flare pit sludge, pretreated with 3 wt % lime sludge. The material was treated at 400 °C, and the highest degree of remediation achieved was to a residual level of 1.33% THC. This is more than 13 times the desired target of 0.1% THC (Alberta Tier 1 Criteria²⁴). Analysis of the

Table 1. CanOxy Chlorinated Organic Soil Treatment Results

temp (°C)	residence time (min)	wt % THC
untreated		1.716
400	15	0.111
400	30	0.049
400	60	0.031
500	15	0.028
500	30	0.016
500	60	0.015

untreated flare pit sludge showed a hydrocarbon concentration of around 20 wt %, and after pretreatment, this concentration had dropped to 3.83 wt %. Apparently, the pretreatment process had a larger impact on sludge remediation than the thermal desorption step. About 80% of the hydrocarbons was removed during drying and aggregation, while only an additional 15% was removed by desorption.

Thermal desorption was proven not to be the ideal treatment option for the Domtar flare pit sludge, because the contaminants included a significant number of very heavy hydrocarbons in the C₃₀–C₆₀ range, for which thermal desorption is not effective. An additional factor inhibiting desorption may have been the presence of humic material in the soil which bounds the contaminants tightly.

(b) CanOxy Chlorinated Organic Soil. Despite the high moisture content of the CanOxy chlorinated organic soil, the soil did not require any pretreatment to improve handling. Therefore, the experiments focused on the effects of desorber residence time and temperature. Table 1 summarizes the treatment results for the two temperatures and three residence times examined.

At a desorber temperature of 400 °C, the target remediation (Alberta Tier 1 Criteria²⁴) for hydrocarbons was reached in just over 15 min. At 500 °C, the hydrocarbon concentration had dropped to 0.028% THC, one-fifth of the Tier 1 Criteria, within the first 15 min. Analysis of the soil revealed that chlorophenols were the main contaminants. These semivolatile organic compounds have boiling points in the range of 200–300 °C and were easily desorbed at 400 and 500 °C. Small portions of the contaminants, however, continued to desorb at a much slower rate. These compounds may have higher boiling points or may be tightly sorbed to humic material in the soil. At 500 °C, the residual hydrocarbon concentration appears to be approaching its minimum value, because there is very little difference between the concentrations at 30 and 60 min. If this is the case, a higher desorber temperature would be required to remediate beyond this level.

(c) Amoco Activated Carbon. Soxhlet extraction followed by an analysis of the extracted organics revealed that the vast majority of the hydrocarbon contamination was quite light, including volatile compounds such as toluene and straight-chain hydrocarbons and semivolatile compounds such as xylene and phenol. A series of seven experiments at residence times of 15, 30, and 60 min and temperatures of 400 and 500 °C examined the effect of these two parameters on the level of remediation.

The treatment results presented in Table 2 show that Alberta Tier 1 Criteria²⁴ were successfully met only at the most stringent conditions of 500 °C for 60 min. Like the CanOxy soil, the majority of contaminants were desorbed during the first few minutes.

There are two plausible explanations for the rapid change in the desorption rates and the slow removal of

Table 2. Amoco Activated Carbon Treatment Results

temp (°C)	residence time (min)	wt % THC
untreated		9.8
400	15	0.532
400	30	0.380
400	60	0.260
500	15	0.302
500	30	0.177
500	60	0.106

Table 3. Produced Sand Treatment Results

sample pretreatment	temp (°C)	residence time (min)	wt % THC
untreated			1.01
untreated 30-min wash + 4% CaCO ₃			0.058
cold water rinse	400	30	0.189
	400	60	0.147
	500	30	0.071
hot water rinse	400	30	0.122
	400	60	0.071
cold rinse + 1.5% CaCO ₃	400	30	0.23
	400	60	0.107
cold rinse + 3.0% CaCO ₃	400	30	0.152
	400	60	0.106
cold rinse + 4.0% CaCO ₃	400	15	0.292
	400	30	0.093
	400	60	0.058
30-min cold water wash	400	30	0.021
30-min cold wash + 4% CaCO ₃	400	15	0.027
	400	30	0.015
	400	60	0.021

some residual contaminants. One possibility is that the sample contains a few heavy hydrocarbons, which desorb at a slower rate, while the other is that the desorption rate is heavily affected by intraparticle diffusion and pore sorption. In all likelihood, the slow desorption rate resulted from a combination of the two factors. In contrast to sorption to humic substances, as in the CanOxy soil, longer residence times would result in further desorption from the activated carbon, because the hydrocarbons diffuse through the particle rather than form a miscible mixture.

(d) PanCanadian Produced Sand. More than 25 experiments were performed using pretreated PanCanadian produced sand. Preliminary experiments demonstrated that the sand required pretreatment to improve its handling characteristics. For this set of experiments, the main objective was to investigate the effect of several sample pretreatments, including water rinses, water washes with agitation, and the addition of lime in three concentrations. The BTR variables of temperature and residence time were not well examined in this case, because multiple experiments were performed at the same conditions with different samples.

A summary of the treatment results, including the pretreatment method, residence time, and temperature, for all six pretreated samples is presented in Table 3. The sand was successfully remediated to Alberta Tier 1 Criteria,²⁴ 0.1% THC, in more than half of the experiments. Both the rinse temperature and the lime blending had an impact on the level of remediation. For instance, switching from a cold to a hot water rinse resulted in an overall contaminant removal increase of 7%. Meanwhile, the addition of 4 wt % lime resulted in a 2-fold decrease in the hydrocarbon residual concentration over simple cold water rinsing.

Agitation also had a significant impact on the level of remediation achieved. Among the pretreatments examined, the cold water washes with agitation pro-

duced treated sand with the lowest residual hydrocarbon concentrations. Sand that was washed and blended with 4% lime even met Alberta Tier 1 Criteria²⁴ prior to treatment in the BTR. Although a small reduction in hydrocarbons was seen after thermal treatment, the wash with agitation managed to remove nearly 95% of the hydrocarbons from the untreated sand, reducing the concentration from 1.01% THC to 0.058% THC. However, it is important to consider that the water washes and rinses created a secondary water contamination problem, and there is no indication that they promoted desorption of the remaining contaminants. An analysis of the sand showed that contamination was limited to hydrocarbons in the C₁₅–C₂₉ range.

Temperature was also found to have a notable effect on remediation of the produced sand. The single experiment performed at 500 °C on cold water rinsed sand showed that the hydrocarbon concentration was reduced to half that of the same sample treated at 400 °C. The impact of the desorber temperature and residence time may be at least as important as the sample pretreatment method. Perhaps a viable pretreatment option, avoiding the use of a water wash and the associated water contamination problem, might be simply aggregation and blending of the sand with lime or some other suitable additive.

Prepared Samples. A total of 14 experiments were performed on each sample, one at each desorber temperature and residence time combination, and two random duplicates. The residual hydrocarbon concentration on the duplicates was found to vary within 10% in each case, demonstrating a satisfactory reproducibility of the experimental results.

(a) Naphthalene–Phenanthrene-Contaminated Sand. Medium-coarse grain sand ($d_p = 364 \mu\text{m}$) was chosen to represent a nonporous contaminated material, in which contaminants are not tightly bound but rather are physically attached to the particle surface. Thus, PAHs were expected to be easily desorbed from the sand.

As mentioned previously, a 50:50 naphthalene–phenanthrene mixture was dissolved in methylene chloride in order to contaminate the sand to 3.1 wt %. Soxhlet extraction followed by GC analysis showed that the sand was contaminated by approximately equal amounts of both PAHs.

Figure 1 shows the residual PAH concentration as a function of the residence time at the three desorber temperatures of 150, 250, and 350 °C. Although most visible in the 150 °C curve, all three curves show that the effect of increasing the desorber residence time is a reduction in the residual PAH concentration. As expected, longer residence times allowed more PAHs to desorb. The effect of increasing the desorber temperature was to significantly decrease the residual PAH concentrations. Evidence suggests, however, that two PAH removal mechanisms were responsible for the low concentrations of naphthalene and phenanthrene remaining on the sand after treatment, particularly at 250 and 350 °C. Certainly desorption was an important mechanism, because PAHs were condensed in the primary trap; however, at each temperature the mass of PAHs captured did not account entirely for the drop in the contaminant concentration. The second mechanism for PAH removal was melting. Naphthalene and phenanthrene have melting points of 80 and 100 °C, respectively, which means that they both melt at the

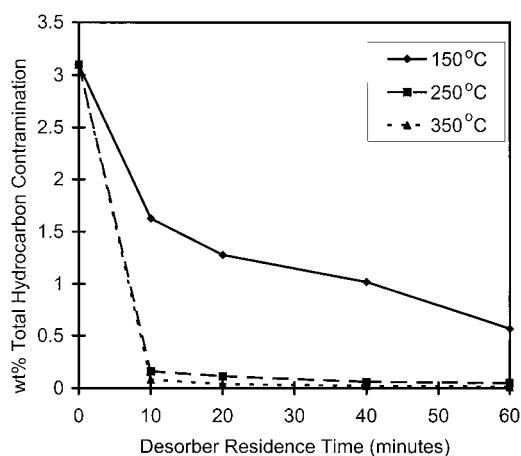


Figure 1. Residual hydrocarbon contamination for treated naphthalene–phenanthrene-contaminated sand at different temperatures and treatment times.

desorber temperatures investigated. Occasionally, while cleaning out the BTR between runs, small lumps of PAHs were found encased in sand. Thus, one fraction of the PAHs desorbed by vaporization while another would liquefy and drain off the sand, resulting in very low residual PAH concentrations.

At 150 °C, above the melting points of both naphthalene and phenanthrene, nearly 50% of the PAHs was removed in the first 10 min. After 60 min, the residual PAH concentration dropped to 0.57% THC. GC analysis showed that naphthalene represented 98 wt % of the PAHs condensed in the primary trap, which demonstrates that the lighter hydrocarbon was more easily desorbed. The effect of contaminant loss due to melting was significant at both 250 and 350 °C and resulted in extremely low residual PAH concentrations after only 10 min. At both temperatures, the PAH concentration dropped rapidly in the first few minutes and then continued to fall at a much reduced rate. At 250 °C, 89% of the PAHs condensed was naphthalene, while at 350 °C, it represented only 67% of the naphthalene–phenanthrene mixture.

The results of these experiments confirm that increasing both the desorber residence time and temperature decreases the residual PAH concentration. It was also found that the contaminants were not tightly sorbed to the surface of the nonporous sand particles, because the PAHs desorbed off the surface and melted, draining off the sand to form small lumps. Melting of both naphthalene and phenanthrene led to artificially low PAH concentrations, particularly at 250 and 350 °C.

(b) Anthracene–Fluorene-Contaminated Sand. Sand was also contaminated with a binary mixture of anthracene and fluorene. Because of the low solubility of anthracene in methylene chloride, a PAH concentration of 2 wt % was used.

The residual PAH concentration curves are shown in Figure 2 as a function of the residence time for desorber temperatures of 250, 320, and 350 °C. The trends of all three profiles are qualitatively similar to those for naphthalene–phenanthrene sand. Lower PAH concentrations resulted when either the desorber residence time or temperature was increased. As with the naphthalene–phenanthrene sand, melting of PAHs played a role in these experiments. Anthracene and fluorene melt at 217 and 114 °C, respectively; hence, they would

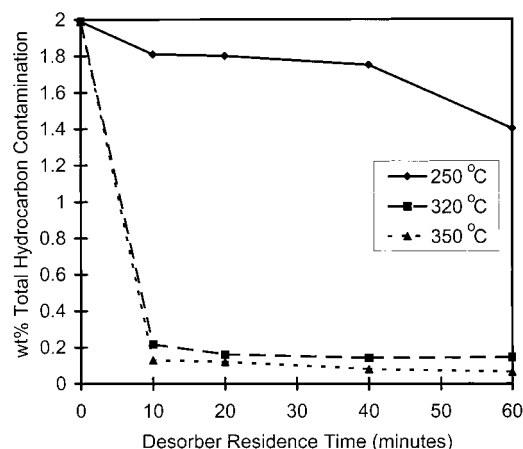


Figure 2. Residual hydrocarbon contamination for treated anthracene-fluorene-contaminated sand at different temperatures and treatment times.

exist as liquids at all desorber temperatures chosen. Because the contaminants are not tightly sorbed to the sand surface, the PAHs melted and drained off the sand, and small lumps of PAHs encased in sand were occasionally washed from the BTR.

At the lowest desorber temperature, 250 °C, the PAHs desorbed at a fairly slow and steady rate, and it was found that the mass of PAHs condensed in the primary trap corresponded to that lost by the sand in the desorber. Despite the fact that 250 °C is above the melting points of both anthracene and fluorene, this match suggests that only desorption occurred. Analysis on a weight basis of the PAHs in the primary trap showed that fluorene, the lighter compound, made up 95% of the condensed material. At 320 °C the PAH concentration dropped to 0.22% THC in the first 10 min and continued to fall at a much slower rate for the next 50 min. Fluorene represented 83% of the condensed anthracene-fluorene mixture at 320 °C, while at 350 °C, 62% of the PAHs was fluorene. The effect of melting losses was most pronounced at 350 °C, with the PAH concentration falling to 0.13% THC in the first 10 min.

(c) Naphthalene-Phenanthrene-Contaminated Activated Carbon. The results from the naphthalene-phenanthrene-contaminated activated carbon experiments are significantly different from those found using PAH-contaminated sand. Activated carbon was chosen to represent a porous contaminated material, in which the contaminants are not only sorbed to the surface of the particles but also sorbed in pores within the particles.

The naphthalene-phenanthrene mixture was dissolved in methylene chloride which allowed the PAHs to penetrate into the pores of the activated carbon particles, resulting in a 5% contamination.

Figure 3 shows the residual PAH concentrations at desorber temperatures of 150, 250, and 350 °C. Although the profiles show decreasing PAH concentration with increasing desorber residence time and temperature, the curves corresponding to the activated carbon differ significantly from those corresponding to the sand. Not only does the PAH concentration at each temperature drop slowly and steadily over the 60 min, but the 250 °C concentration profile falls evenly between the other two, rather than following closely the 350 °C profile, as it did in the case of contaminated sand (Figure 1). The differences between the residual hydro-

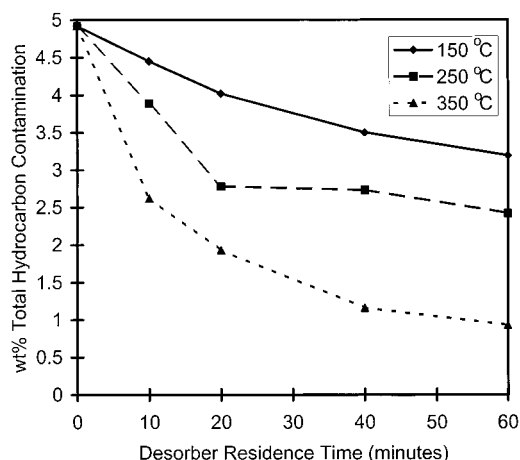


Figure 3. Residual hydrocarbon contamination for treated naphthalene-phenanthrene-contaminated activated carbon at different temperatures and treatment times.

carbon concentration profiles for activated carbon and sand are explained by the fact that no melting of PAHs was observed off the activated carbon, even at the highest temperature. Although the PAHs likely melted at desorber temperatures, the liquid apparently was retained within the pores.

At all of the desorber temperatures, desorption was the main mechanism of PAH removal from the activated carbon. At 150 °C, naphthalene represented over 99 wt % of the desorbed PAHs captured in the primary condenser, and only a trace of phenanthrene was detected. At 250 °C, between the boiling points of the compounds, naphthalene still accounted for 94%. Finally, at 350 °C, naphthalene had dropped to only 76% of the PAHs condensed in the primary trap.

Desorption Rate Curves and Scale-Up. The desorption rate curves for three of the four industrial samples and all of the prepared samples were studied to investigate the physical significance of the desorption rate parameters and their temperature dependence. Based on the remediation results obtained, distinct desorption rate profiles expressed in terms of contaminant concentration could be generated for each sample at the temperatures investigated, for samples treated at a minimum of three residence times.

All of the residual hydrocarbon concentration versus desorber residence time curves were exponential in nature. The data were fit using nonlinear least-squares regression to an exponential decay equation of the form

$$\text{total residual contamination} = c = a \exp(-bt^n) \quad (1)$$

where parameter a represents the initial contaminant concentration and parameter b represents the rate of decay of the function. The temperature dependence of parameter b is a measure of the temperature dependence of the rate of desorption for a given sample. Finally, n represents the shape of the decay curve. Parameter n affects the shape in three possible ways: if $n = 1$, then the decay is purely exponential, if n is greater than 1, then the decay is faster than exponential, and if n is less than 1, the decay is slower than exponential.

To determine the desorption rate, eq 1 can be expressed in a logarithmic form:

$$\ln c = \ln a - bt^n \quad (2)$$

Table 4. Summary of Desorption Parameters for Industrial Samples

sample/temperature	param	param value	
Domtar flare pit sludge with 3 wt % lime 400 °C	<i>a</i>	3.83	
	<i>b</i>	0.24 ± 0.07	
	<i>n</i>	0.34 ± 0.08	
CanOxy chlorinated organic soil 400 °C	<i>a</i>	1.72	
	<i>b</i>	1.19 ± 0.11	
	<i>n</i>	0.31 ± 0.03	
	500 °C	<i>b</i>	3.08 ± 0.22
		<i>n</i>	0.11 ± 0.02
		<i>a</i>	9.80
Amoco activated carbon 400 °C	<i>b</i>	1.90 ± 0.001	
	<i>n</i>	0.16 ± 0.0002	
	500 °C	<i>b</i>	2.06 ± 0.03
		<i>n</i>	0.19 ± 0.004

which can be differentiated to yield the desorption rate, $-dc/dt$, in terms of the residence time, t :

$$-dc/dt = cbnt^{n-1} \quad (3)$$

To convert the desorption rate in eq 3 from an expression in terms of both contaminant concentration and residence time to one which is a function of only the contaminant concentration, a substitution is made for t . Rearranging eq 2, we get an expression for t in terms of concentration:

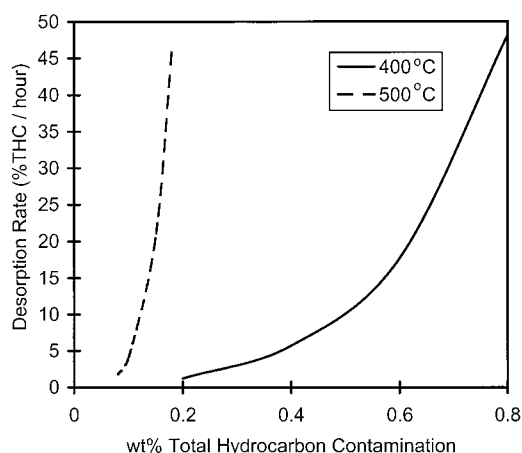
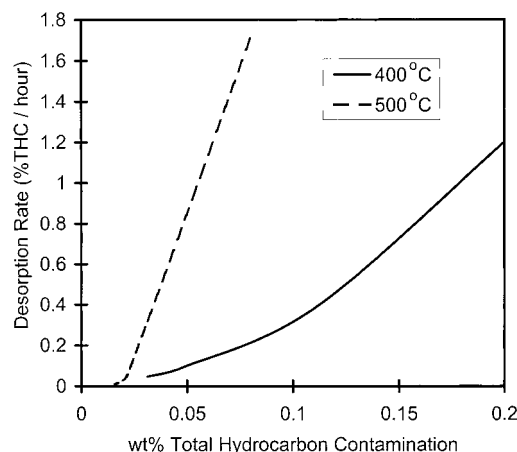
$$t = \left(-\frac{1}{b} \ln \frac{c}{a} \right)^{1/n} \quad (4)$$

An expression for the desorption rate in terms of the contaminant concentration is obtained by substituting eq 4 into eq 3, yielding

$$\text{desorption rate} = -\frac{dc}{dt} = bnc \left[-\frac{1}{b} \ln \frac{c}{a} \right]^{(n-1)/n} \quad (5)$$

The desorption rate from eq 5, plotted as a function of the contaminant concentration, gives the instantaneous desorption rate at any given concentration. Perhaps a more valuable tool is the generalized exponential decay equation (1), which is applicable to any type of desorption system. Given the experimentally evaluated parameters b and n , one can use eq 1 to identify the residual hydrocarbon concentration c , for any initial contaminant concentration a , at any time t . Using this generalized equation, it is possible to either extrapolate or interpolate the desorption data in order to identify the treatment time required to meet specific targeted levels of remediation. It should be noted that, although the temperature dependence of parameter b is discussed in detail, both parameters b and n are functions of the desorber temperature. Because of the limited number of data points, n is probably the least accurate parameter, especially when attempting to describe the initial desorption rate at high contaminant concentrations. The low values of parameter n may suggest the presence of significant mass-transfer resistances.

Industrial Samples. Desorption rate curves were generated for three of the four industrial samples based on the residual hydrocarbon concentration results presented earlier. Although many experiments were performed using PanCanadian produced sand, the experiments focused on the effect of pretreatment and so did not cover the necessary three residence times at a single temperature. Sufficient data existed to generate

**Figure 4.** CanOxy chlorinated organic soil desorption rate curves for high hydrocarbon concentrations.**Figure 5.** CanOxy chlorinated organic soil desorption rate curves for low hydrocarbon concentrations.

desorption rate curves for Domtar flare pit sludge, CanOxy chlorinated organic soil, and Amoco activated carbon. The regressed parameters are presented in Table 4.

As a characteristic example, the desorption rate curve for the CanOxy chlorinated organic soil at high hydrocarbon concentrations is shown in Figure 4, while the curve for low concentrations (around the target remediation limits) is illustrated in Figure 5.

In the case of the Domtar flare pit sludge, the desorption rate is seen to fall with decreasing hydrocarbon concentration to very low levels, such that thermal desorption does not appear to be an acceptable remediation technology to reach Alberta Tier 1 Criteria²³ of 0.1% THC.

The CanOxy chlorinated organic soil, with an initial hydrocarbon concentration of 1.72% THC, was treated at temperatures of 400 and 500 °C. The desorption rate at 500 °C was uniformly greater than that at 400 °C for the same hydrocarbon concentration, although at very low concentrations the two rates approach. Tier 1 criteria can be easily reached within reasonable residence times at both temperatures, and given that the rates were still quite high despite low hydrocarbon concentrations, even lower residual contaminant concentrations could be achieved by thermal desorption. Alternatively, using a lower desorber temperature, Tier 1 criteria could likely be achieved.

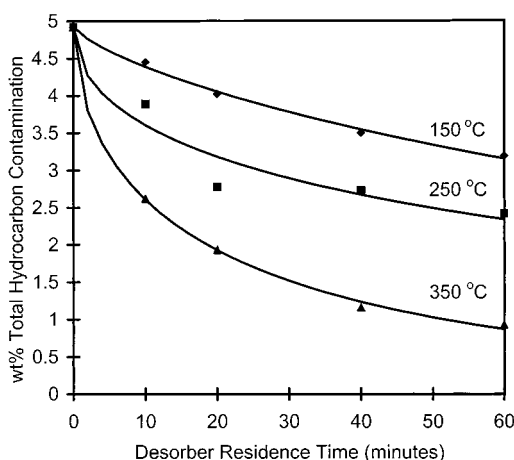


Figure 6. Representation of experimental data by eq 1 for naphthalene-phenanthrene-contaminated activated carbon.

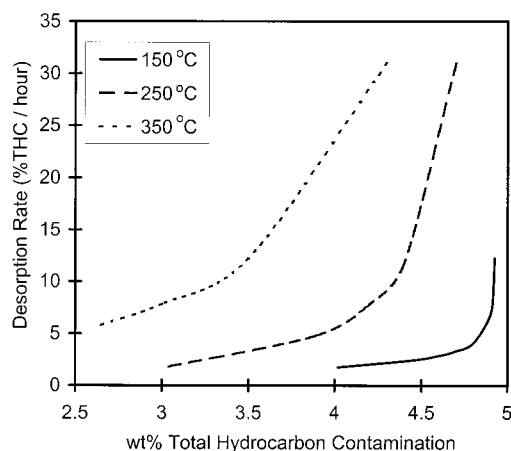


Figure 7. Naphthalene-phenanthrene-contaminated activated carbon desorption rate curves for high hydrocarbon concentrations.

Desorption rate curves for the Amoco activated carbon at 400 and 500 °C show similar trends. However, the desorption rate for low hydrocarbon concentrations becomes quite slow, despite the fact that contaminants are still present on the sample, likely because of pore sorption.

Prepared Samples. For each of the prepared samples, desorption rate curves were generated from residual hydrocarbon concentration results.

Figure 6 shows a comparison of the fitted and experimental data at all three desorber temperatures of the naphthalene-phenanthrene-contaminated activated carbon. Figures 7 and 8 show the corresponding set of desorption rate curves.

The study of the desorption curves as functions of temperature allowed one to identify the relative influence of other remediation phenomena, in addition to desorption.

For example, the desorption rate curves for naphthalene-phenanthrene-contaminated sand at all three desorber temperatures (not shown here) demonstrated the difference in rates between the 150 °C case, where contaminants were removed primarily by desorption, and the 250 and 350 °C cases, in which a portion of the PAHs were removed by melting (Smith²⁵). The desorption rate curves for anthracene-fluorene-contaminated sand show very similar trends (Smith²⁵). Overall, the effect of increasing temperature is best exhibited by the

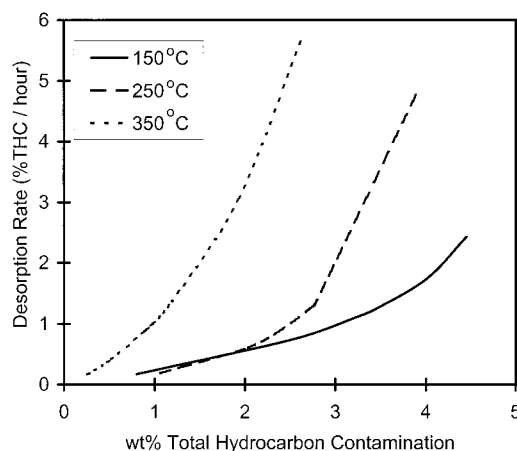


Figure 8. Naphthalene-phenanthrene-contaminated activated carbon desorption rate curves for low hydrocarbon concentrations.

Table 5. Summary of Desorption Parameters for Prepared Samples

sample/temperature	param	param value
naphthalene-phenanthrene-contaminated sand	<i>a</i>	3.10
150 °C	<i>b</i>	0.20 ± 0.03
	<i>n</i>	0.50 ± 0.04
250 °C	<i>b</i>	1.87 ± 0.04
	<i>n</i>	0.20 ± 0.01
350 °C	<i>b</i>	2.12 ± 0.07
	<i>n</i>	0.24 ± 0.01
anthracene-fluorene-contaminated sand	<i>a</i>	1.99
250 °C	<i>b</i>	0.13 ± 0.006
	<i>n</i>	0.26 ± 0.04
320 °C	<i>b</i>	1.80 ± 0.08
	<i>n</i>	0.10 ± 0.015
350 °C	<i>b</i>	2.03 ± 0.08
	<i>n</i>	0.12 ± 0.015
naphthalene-phenanthrene activated carbon	<i>a</i>	4.93
150 °C	<i>b</i>	0.03 ± 0.004
	<i>n</i>	0.75 ± 0.03
250 °C	<i>b</i>	0.10 ± 0.015
	<i>n</i>	0.48 ± 0.07
350 °C	<i>b</i>	0.18 ± 0.01
	<i>n</i>	0.56 ± 0.015

activated carbon, because PAHs were removed by desorption alone at all temperatures (Figures 7 and 8).

The values of parameters *a*, *b*, and *n* in the exponential decay equations fitted to the data gathered from the prepared samples are summarized in Table 5.

In the exponential decay equations fitted to residual hydrocarbon concentration data, parameter *b* represents the rate of decay of the function, which is a function of desorber temperature. Thus, the temperature dependence of parameter *b* is a measure of the temperature dependence of the rate of contaminant desorption from a given sample.

Figure 9 shows parameter *b* as a function of the desorber temperature for all three prepared samples. To show the relationship between the contaminant boiling point and changes in parameter *b*, the PAH bubble points at 0.5 atm, the operating pressure of the BTR, are included. Both of the prepared sand samples show a very significant increase in the value of *b* from the lowest temperature to the two higher temperatures.

The third prepared sample, naphthalene-phenanthrene activated carbon, shows a linear relationship between *b* and temperature. Although parameter *b* has

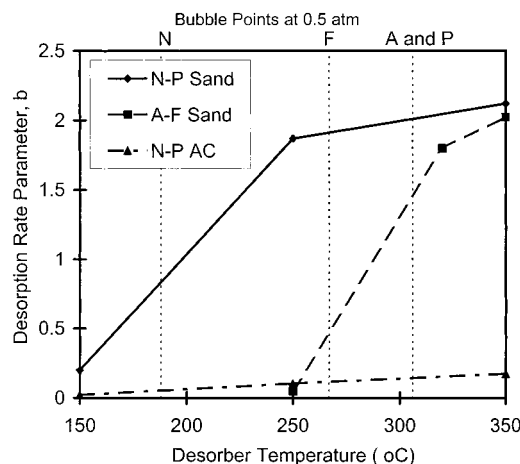


Figure 9. Temperature dependence of parameter b for prepared samples.

about the same value for all three prepared samples at the lowest temperature, in comparison to the two contaminated sand samples in which melting of PAHs accounted for some contaminant removal, the activated carbon showed only a very small increase of b with temperature.

Conclusions

A treatability study on four contaminated industrial samples was followed by a fundamental study of the thermal desorption process using three prepared samples contaminated with binary mixtures of PAHs.

Results from the samples, both industrial and prepared, show that reduced residual hydrocarbon concentrations occur when either the sample residence time is increased or the treatment temperature is increased.

Similar trends are observed when the desorption of contaminants from industrial samples is compared to that from prepared samples. The Domtar flare pit sludge shows a slow desorption rate curve similar to the prepared activated carbon. Both the CanOxy soil and the Amoco activated carbon showed desorption rates similar to those of the prepared sand samples. Although no melting was observed from the industrial samples, desorption of light contaminants of these samples was akin to the removal rate due to melting.

Desorption rate curves were generated from the data gathered for both the industrial and prepared samples based on an exponential decay equation fitted to the experimental data. The correlation proposed would be useful for other desorption systems. Although this study has provided an improved understanding of, and data for, the thermal desorption process, issues related to the agglomeration and attrition of solids in the reactor need to be studied further, preferably by using a larger scale unit.

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Nomenclature

a = initial contaminant concentration, wt %
 b = remediation decay parameter
 c = total residual contamination, wt %
 d_p = mean particle diameter, m
 n = decay constant (eq 1)
 t = time, h
 PAH = polynuclear aromatic hydrocarbons
 THC = total hydrocarbon content, wt %

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