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Treatment of Contaminated Soils by Batch Thermal Desorption

by

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## ABSTRACT

Low temperature thermal desorption is among the most promising and economic *ex situ* soil remediation alternatives. Experiments were performed on a novel bench scale thermal desorber, the Batch Thermal Reactor, which was developed as a prototype to commercial desorbers. A treatability study on five contaminated industrial samples was followed by a fundamental study of the thermal desorption process using three prepared samples contaminated with binary mixtures of selected polynuclear aromatic hydrocarbons.

For industrial samples, the effect of desorber residence time, temperature, and several pre-treatments on contaminant removal was investigated. Three of the five samples were successfully treated to legislated soil remediation limits. Using prepared samples, the effect of sample porosity, contaminant molecular weight, desorber residence time and temperature on thermal desorption was investigated. The results gathered were fitted to a generalized exponential desorption equation, and desorption rate curves were generated to provide a basis for scale-up to a commercial desorber.

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***Dedicated to my family:  
Rae, John and Dwayne***

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## NOMENCLATURE

a	amplitude parameter in exponential decay equation 6-1
A	anthracene
AC	activated carbon
b	rate of decay parameter in exponential decay equation 6-1
BM Ecos	Bromley Marr Ecos Inc.
BTR	batch thermal reactor
c	residual contaminant concentration
CCME	Canadian Council of Ministers of the Environment
EPA	United States Environmental Protection Agency
F	fluorene
GC	gas chromatography
n	shape of decay parameter in exponential decay equation 6-1
N	naphthalene
P	phenanthrene
PAH	polynuclear aromatic hydrocarbon
PCB	polychlorinated biphenyl
ppm	parts per million
SVOC	semi-volatile organic compound
t	time
TC	thermocouple
TCD	thermal conductivity detector
THC	total hydrocarbon contamination
THF	tetrahydrofuran
UST	underground storage tank
VOC	volatile organic compound

## CHAPTER ONE

### INTRODUCTION

---

The problem of effectively managing contaminated wastes is continually growing due to the implementation of ever stricter disposal regulations, the continued generation of contaminated waste streams, and the need to remediate contaminated sites. It is difficult to know the full extent of soil contamination around the world, because new sites are routinely located, and new sources of contamination are identified. Sites containing soil contaminated by petroleum products, chlorinated organics, creosote and heavy metals are common. Leaking underground storage tanks, abandoned flare pits and former industrial sites are often the culprits. The issue of long-term liability has forced many industries to deal with soil contaminated during spills and leaks, and to treat their contaminated materials rather than sending them to landfill, which has been the disposal method of choice for most of this century.

Legislation governing the treatment and disposal of contaminated waste and the remediation of contaminated land is still evolving. The trend, however, is toward increasingly stringent regulations and severe penalties against perpetrators. An enormous effort has been made in the past decade, by industry and entrepreneurs alike, to develop efficient methods to deal with hazardous waste streams and contaminated soil. Although the introduction and use of new remediation technologies has increased the number of treatment options for environmental engineers, only a few have gained widespread recognition for being both effective and economic processes.

Established treatment methods such as landfilling, incineration and stabilization still make up the bulk of soil and waste management operations. Innovative remediation technologies, however, such as soil vapour extraction, bioremediation and thermal desorption are rapidly growing in popularity as more data becomes available on the applicability and effectiveness of these technologies. The cost of soil remediation using innovative technologies tends to be lower than that associated with established methods. The potential for cheaper soil treatment alternatives has encouraged many companies to investigate the feasibility of using innovative technologies, and invest in new designs.

### **1.1 The Thermal Desorption Process**

Identified as a favorable alternative to incineration for dealing with soil contaminated by both volatile and semi-volatile organic compounds, thermal desorption has been rapidly gaining recognition for its versatility and cost effectiveness. Thermal separation or desorption is frequently selected because of the wide range of materials and contaminants it can effectively treat, and the relatively small size and mobility of commercial desorption systems. To date, there has been general public acceptance of the treatment approach, since it is considered a relatively safe technology, emitting little or no material into the atmosphere and is less energy intensive than incineration.

Incineration and desorption are both thermal treatments, however, thermal desorption is a significantly different process than incineration. While incineration, operating at temperatures around and above 1000°C, uses heat to actually destroy contaminants by combustion, thermal desorption uses heat to physically separate contaminants from the soil. Thermal desorption processes, typically operating at temperatures between 150°C and 500°C, heat the soil so that volatile and semi-volatile contaminants are vaporized and consequently separate from the soil. The vaporized contaminants are condensed and collected for further treatment and possible recovery.

Commercial units have demonstrated that thermal desorption is effective for separating organic compounds from refining wastes, coal tar wastes, and creosote from wood treatment wastes. Thermal desorption has also been successfully used to separate solvents, pesticides, PCBs, dioxins and fuel oil from contaminated soil (EPA, 1996; Hsieh *et al.*, 1994; Johnson, 1989).

A schematic diagram of a typical thermal desorption process is shown in Figure 1.1. Desorption systems consist of three main components: the pretreatment and materials handling system, the desorption unit, and the post-treatment systems which deal with vaporized contaminants and the remaining soil. Successfully remediated soil is typically redeposited onto the site, while desorbed contaminants are subjected to further treatment or disposal, and in some cases may be recycled (EPA, 1996).

## **1.2 Research Objectives**

This research addresses one of the more promising soil and solids remediation alternatives: low temperature thermal desorption. The opportunity to work on a novel bench scale thermal desorber was generously provided by Bromley Marr Ecos Inc. of Calgary, who developed the Batch Thermal Reactor (BTR) as a prototype to commercial thermal desorbers, and the fully assembled BTR was provided for this research. The purpose of the research program is to treat several contaminated samples using the desorber. In accordance with a contractual agreement with Bromley Marr Ecos, experiments were conducted on five contaminated industrial samples, obtained by the company, to determine the feasibility of treating these materials using the BTR. Additionally, experiments on three samples contaminated by polynuclear aromatic

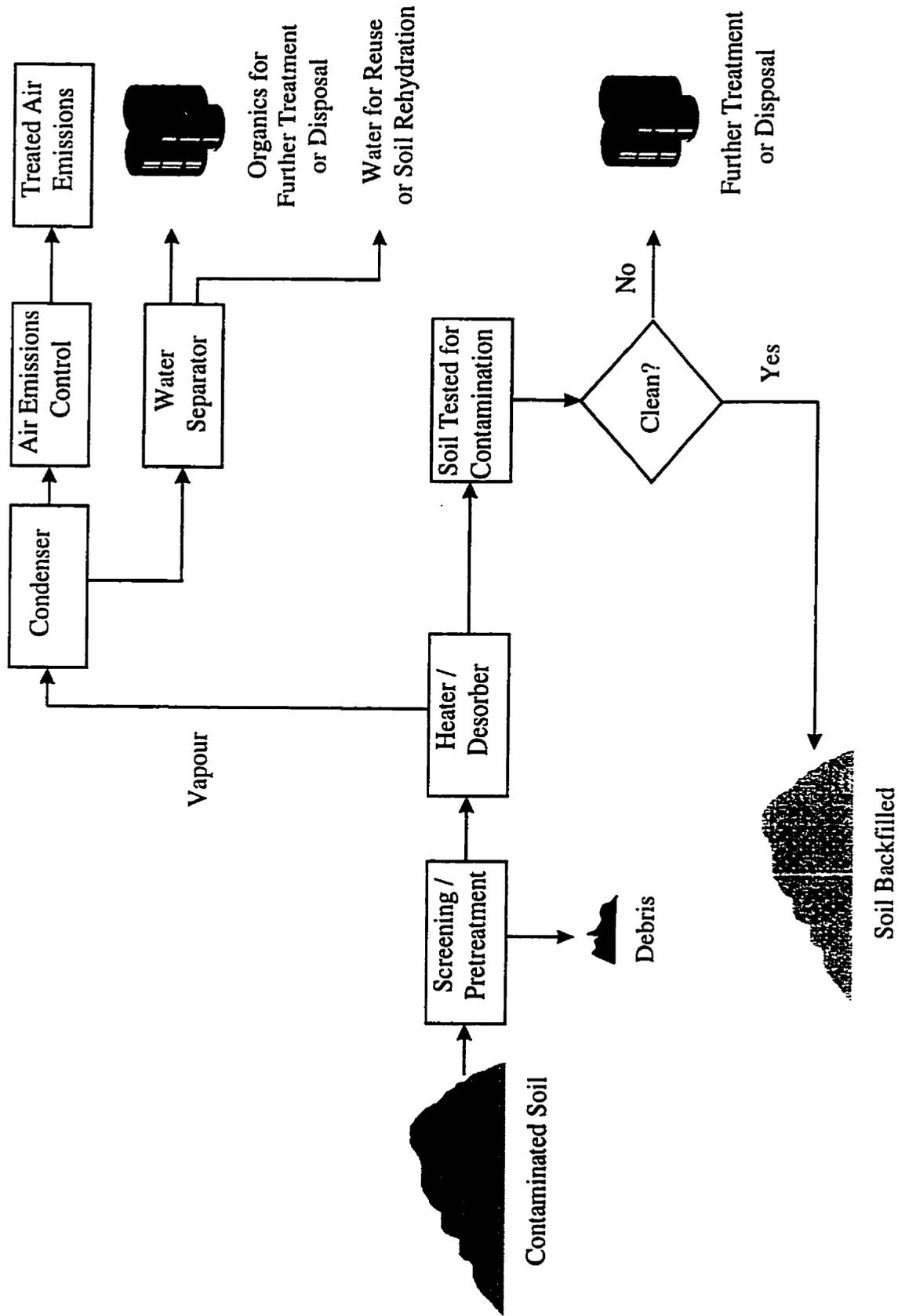


Figure 1-1: Thermal Desorption Process

hydrocarbons were conducted. Ultimately, Bromley Marr Ecos intends to develop a commercial scale thermal desorber loosely based on the Batch Thermal Reactor design. Thus, the three main objectives of this investigation are the following:

1. To investigate the feasibility of treating several industrial contaminated waste streams using the Batch Thermal Reactor, and get an idea of whether the samples could successfully be treated, using both pre-treatment methods and thermal desorption, to comply with Alberta Environment Tier 1 Criteria for Contaminated Soil Assessment and Remediation.
2. To determine, by several simple experiments, the effect of sample porosity, contaminant molecular weight, desorber residence time and desorber temperature on thermal desorption efficiency using samples artificially contaminated with polynuclear aromatic hydrocarbons.
3. To make use of the results gathered from both industrial samples and prepared samples to calculate contaminant desorption rates, a simple parameter that will give some idea of how the system might operate on a commercial scale.

## CHAPTER TWO

### LITERATURE REVIEW AND BACKGROUND

---

Over the past three decades there has been a growing appreciation, amongst the public, government and industry alike, of the need to protect and maintain the environment. Unfortunately, for most of this century little regard was given to proper waste disposal practices or to the maintenance of chemical and fuel storage facilities, both of which have left us with thousands of contaminated sites in North America and around the world.

The sources of soil contamination are wide ranging, and in the case of abandoned sites is often not recognized until contaminated groundwater or health effects, either human or environmental, are detected. The compounds of concern include heavy metals such as Pb, As and Hg, radioactive waste, explosive materials and organic compounds. Among these, hydrocarbon contamination, including volatile organic compounds, petroleum products, PCBs, pesticides and solvents, is by far the most common.

Manufacturing plants, petroleum refineries, fuel and chemical storage facilities, gas stations, and vehicle depots are all typical contamination sites (Long, 1993). At wood preserving sites, creosote and pentachlorophenol contamination is common (Mueller *et al.*, 1989), while at petroleum refineries, a mix of waste materials and chemicals is disposed of into flare pits. At some former gas plant sites, hydrocarbons contamination from pits, where a mixture of coke, coal tar, coal oil and aromatics were dumped, is

frequently detected in adjacent land or in the groundwater (Valenti, 1994). The largest source of hydrocarbon contamination, however, is leaking underground storage tanks (USTs). The problem is particularly serious, since USTs are located not only on industrial sites, but on urban residential land as well (Stokman *et al.*, 1997).

The United States Environmental Protection Agency, has identified some 36,000 abandoned waste sites, and assessments under the Superfund Program estimate that there are at least 320,000 storage tanks that require remediation in the United States (Mahoney, 1994). It is estimated that it will take several decades and cost more than \$500 billion to remediate Superfund sites, and these represent only a small fraction of the contaminated sites around the world (Mahoney, 1994). In Calgary alone, there have been dozens of leaking USTs discovered at former gas stations, although there are undoubtedly many more which have yet to be located (Nason, 1996). Clearly the magnitude of the problem is immense, but there are also many opportunities for engineers to develop new and more cost effective soil remediation technologies.

## **2.1 Soil Remediation Legislation**

Regulations governing the remediation of contaminated soil and the disposal of contaminated waste are still evolving to reflect new information on health and environmental risks, and the development of new remediation technologies. Although enforcement tends to be a provincial responsibility in Canada, and a state responsibility in the United States, there exists legislation at both the federal and provincial or state levels, since efforts have been made in both countries to develop national soil remediation criteria. It has been a challenge for many industries to stay up to date with the changing legislation.

In the United States, the Environmental Protection Agency (EPA) has supported the development of several remediation technologies and funded extensive research into the effects on human and ecological health of pollutant exposure. Federal initiatives including Superfund, the most aggressive and well funded soil remediation program in the world, the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), and the Resource Conservation and Recovery Act (RCRA) have made the United States one of the world leaders in soil assessment and remediation.

In Canada, Environment Canada is the federal government department responsible environmental quality. Although soil remediation legislation is provincially enforced, it is generally based on national guidelines called the “Canadian Council of Ministers of the Environment Interim Canadian Environmental Quality Criteria for Contaminated Sites” (CCME, 1994). The soil remediation guidelines in the document are based on intended land use, giving numerical contaminant concentration targets for remediation in terms of agricultural, residential/parkland and commercial/industrial land use applications.

In Alberta, a two-tier system for setting acceptable levels of residual contamination in remediated soil was developed by Alberta Environment, the provincial government department controlling waste disposal and soil remediation. Alberta Tier 1 Criteria for Contaminated Soil Assessment and Remediation are the guidelines most commonly applied in the province. Created by the Soil Protection Branch, Tier 1 Criteria list soil contaminant concentrations that are thought to pose insignificant risk to human health or to the environment under any land use scenario. In some circumstances, Tier 1 Criteria cannot reasonably be reached, and so the criteria become the basis for land use negotiations between the province and the site owner. Attainment of Tier 1 levels means that no further site monitoring is required, and the owner is no longer liable for the site. Most soil remediation technologies in Alberta are evaluated based on their ability to meet Tier 1 Criteria. Table 2-1 lists a few of the remediated soil hydrocarbon levels set out by the Alberta Tier 1 Criteria Contaminated Soil Assessment and Remediation guidelines.

Table 2-1: Alberta Tier 1 Criteria for Contaminated Soil Assessment and Remediation  
(Alberta Environment, 1994)

Classification	Compound	Concentration (ppm)
Monocyclic Aromatics	benzene	0.05
	chlorobenzene	0.05
	styrene	0.1
	toluene	1.0
Polycyclic Aromatics	Chlorinated PAH Total	0.1
	Non-Chlorinated PAH Individual	-
	anthracene	0.1
	naphthalene	0.1
	benzo anthracene	0.1
	chrysene	0.1
	fluoranthene	0.1
	fluorene	0.1
	phenanthrene	0.1
	pyrene	0.1
Non-Chlorinated PAH Total	1.0	
PCBs	PCB Total	0.5
Heterocyclics	dioxins	0.001
	furans	0.01
Phenolics	Chlorinated Phenolics Individual	-
	chlorophenols	0.05
	pentachlorophenol	0.05
	Non-Chlorinated Phenolics Total	0.1

Using Tier 2 remediation criteria, contaminated land is managed through the use of a site-specific risk assessment. In this case, the site owner or sponsor must gather and interpret sufficient information to assess the risk to both human and ecological health posed by the site. A CCME document entitled, “An Introduction to the Ecological Risk Assessment Framework for Contaminated Sites in Canada” (CCME, 1991) outlines how to obtain the necessary information for ‘ecological receptors’, although no similar document exists in Canada for human health evaluation. The Tier 2 option is seldom pursued due to the very complex nature of site specific risk assessments.

## **2.2 Soil Remediation Alternatives**

In the past, most industries practiced at best ‘passive remediation’, which relies on natural processes such as biodegradation, leaching, volatilization and photolysis (Newton, 1990) and at worst, dumping. Although passive remediation is still relied upon in some cases, the number and variety of soil remediation techniques has vastly increased. Treatment techniques are usually selected on the basis of the volume of material to be treated, the nature of the contaminants, the time available, and the level to which the site must be remediated.

Soil remediation technologies fall into two basic categories: *in situ* and *ex situ*. *In situ* methods manage contaminated material from the surface, and tend to be cheaper since the soil does not require excavation. Although they often require long periods of time to complete, *in situ* methods are preferred for large sites with low to moderate contaminant concentrations, or at sites where the contamination lies deep. Some of the common *in situ* remediation techniques include: air stripping, soil vapour extraction, bioremediation, soil flushing, chemical oxidation, leaching, solidification, stabilization and vitrification (Long, 1993; Newton, 1990).

*Ex situ* remediation methods require the excavation of contaminated material prior to treatment. Although cost varies a great deal for *ex situ* methods, in most cases *ex situ* is significantly more expensive than *in situ* treatment. *Ex situ* methods are often chosen at sites with relatively high contaminant concentrations, and have the advantage of treating contaminated soil relatively quickly. Long (1993) and Newton (1990) list landfilling, land treatment or farming, soil washing, asphalt incorporation and thermal treatment including incineration and thermal desorption among the common *ex situ* remediation techniques. These treatment techniques can be further divided into off-site and on-site processes. There has been a growing demand for on-site treatment of hazardous wastes, in order to avoid the high cost of transportation, and which has been met by the development of numerous mobile and transportable remediation systems (Johnson *et al.*, 1989).

Fiedler *et al.* (1996) have noted a distinct change in the type of remediation technologies selected at Superfund sites in the United States over the past decade. The trend is clearly toward the more extensive use of 'innovative' technologies, treatment methods that have been tested and used to treat contaminated materials, but still lack complete cost and performance data. Three innovative technologies, namely soil vapour extraction, bioremediation and thermal desorption are the most frequently chosen innovative treatment approaches. In 1984, these three technologies accounted for only 1% of the remediation technologies selected at Superfund sites, while by 1994 they had grown to 36% of the market (Fiedler *et al.*, 1996). It was also noted that use of two or more remediation technologies in a 'treatment train' is common. For instance, both bioremediation and thermal desorption are often followed by solidification and stabilization. Figure 2-1 summarizes the soil remediation technologies selected at Superfund sites in 1994.

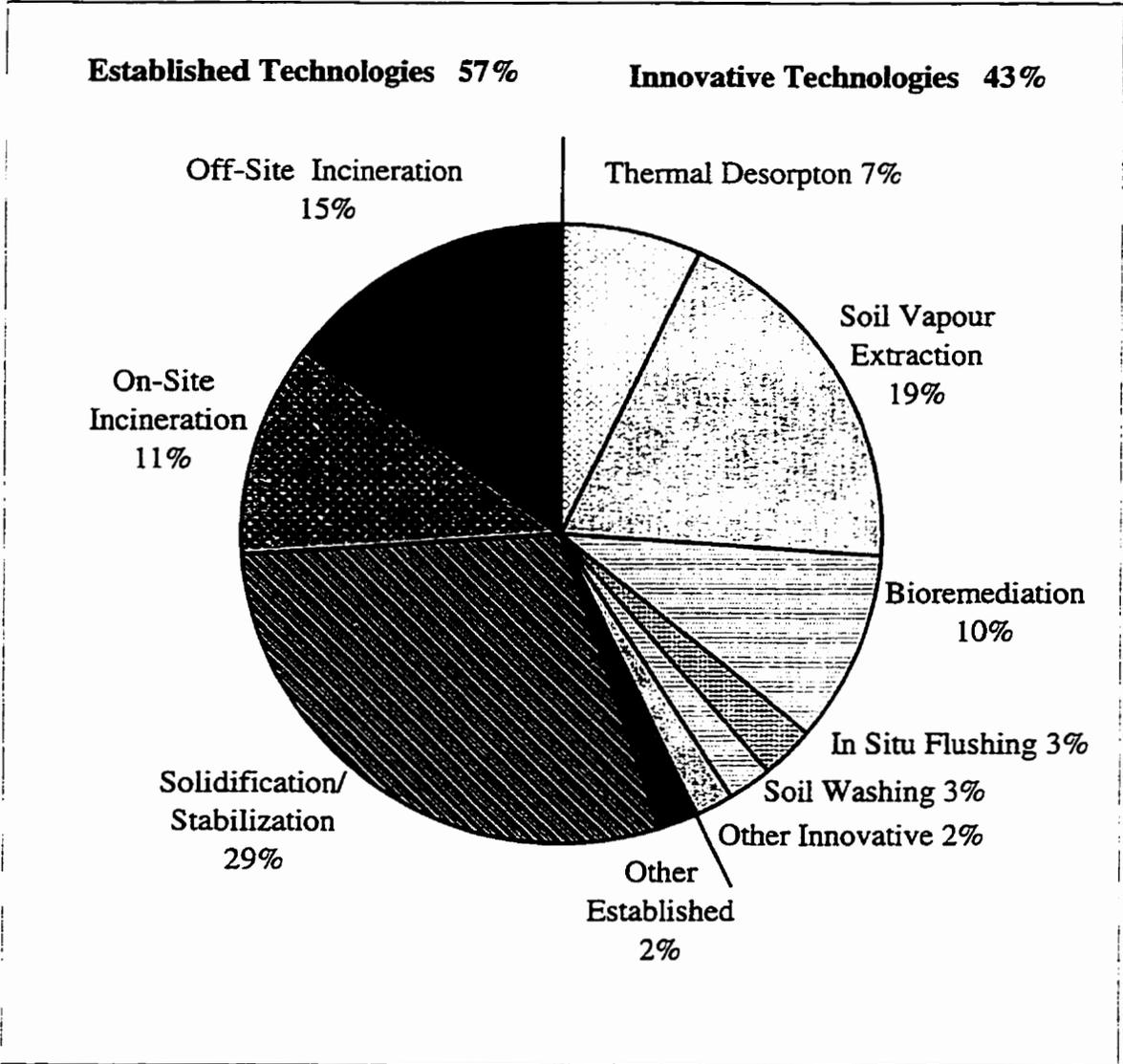


Figure 2-1: Soil Remediation Technologies Selected at Superfund Sites in 1994 (Fielder *et al.*, 1996)

### 2.3 Thermal Desorption and Desorption Systems

Thermal desorption is emerging as a preferred treatment technology for soils contaminated by volatile organic compounds, and has even been recommended for on-site treatment of mercury contaminated soil (Cha *et al.*, 1996). Widespread public concern over air emissions and the high cost of incineration have led waste remediation firms to develop methods, such as thermal desorption, for cleaning soil without incinerating it.

Thermal desorption is a separation process in which excavated contaminated soil is heated for relatively short times to thermally separate organic contaminants. As the soil is heated and agitated, water and contaminants volatilize, and are desorbed from the soil into a gaseous exhaust stream (EPA, 1996). The exhaust stream usually consists of an inert gas, such as nitrogen, to prevent oxidation of the vaporized material while in the desorber, or of combustion gases. Depending on the design of the system the vaporized contaminants are either condensed and recovered or are destroyed. In many cases, recovered hydrocarbons can be recycled. Thermal desorbers typically operate at temperatures between 150°C and 500°C, although some systems reach temperatures greater than 700°C (Troxler *et al.*, 1993).

All thermal desorption systems are based on the four basic thermal desorber configurations described by Troxler *et al.* (1993): rotary kiln, asphalt aggregate dryer, conveyor furnace and thermal screw. The heat required to volatilize contaminants from the soil can be provided either directly or indirectly to the systems. Directly heated desorbers rely on direct heat transfer from hot combustion gases, which also serve to sweep contaminants from the desorber. Indirectly heated desorbers are externally heated and rely on heat transfer through the vessel walls. Although less efficient in terms of heat transfer, there are several advantages to indirect heating. The first is that the volume of exhaust gas from the desorber may be a factor of 2 to 10 times less than that from a

directly heated system with similar processing capacity (Troxler *et al.*, 1993). Therefore, exhaust gas treatment systems can consist of relatively small and mobile unit operations. Soil with very high contaminant concentrations can only be treated by indirectly heated systems, since they can operate under inert or very low oxygen atmospheres preventing oxidation of desorbed organic compounds. Additionally, multiple temperature zones along the desorber are possible, and the rate of purge gas can be controlled (Fox *et al.*, 1991).

The rotary kiln dryer is the most common thermal desorber configuration, and exists as both fixed and mobile units (Troxler *et al.*, 1993). The unit can be heated either directly or indirectly, and usually consists of an inclined, cylindrical drum. A series of baffles inside the drum provide excellent mixing and heat transfer. Residence time in the desorber is controlled by the rotational speed and angle of inclination of the drum. Asphalt aggregate dryers, on the other hand, are always fixed installations. Asphalt plants use directly fired rotary dryers in the asphalt manufacturing process to dry aggregate such as sand or gravel before it is mixed with asphalt. These systems are occasionally used to treat petroleum contaminated soil by mixing the soil with aggregate and incorporating it into the asphalt. The third configuration, the conveyor furnace, is a directly heated, mobile thermal desorber that has not been particularly successful. A flexible metal belt is used to convey soil through the furnace. A series of burners fire into the chamber above the belt to heat the soil.

Mobile thermal screw desorber configurations are gaining popularity for dedicated soil remediation applications (Swanberg, 1993). Thermal screw systems are indirectly heated either by hot oil, process steam or electrically. Typically consisting of one to four screws or paddle augers which, in the case of multiple augers, can be arranged to increase residence time, or soil throughput. The augers convey, mix and heat the soil.

All four thermal desorber configurations follow the same basic treatment processing steps. These include pre-treatment, in which excavated soil is prepared, thermal desorption, and post-treatment, in which vaporized contaminants are managed. Figure 1-1 shows these treatment steps schematically.

The pre-treatment system usually begins with screening to remove foreign debris, rocks, and large lumps of dirt. The soil is then either crushed or sifted until the necessary particle size is reached, typically 1 to 2 inches for thermal screws and 4 to 5 inches for other types of desorbers (Troxler *et al.*, 1993). If the material has a very high moisture content or high concentration of organics, it may be blended with sand or lime to improve its handling characteristics (EPA, 1996).

Exhaust gases, consisting of volatilized contaminants, water, and combustion gases, in the case of indirectly heated desorbers, are swept from the desorber into the post-treatment system. Organic compounds are usually condensed and collected for further treatment or recycling, but may simply be sent to an afterburner. In many cases, multi-stage condensation units collect heavy hydrocarbons in primary condensers, while secondary condensers collect water and light hydrocarbons. This second liquid fraction is transferred to an oil/water separator to remove the oils. The water from the separator is usually cleaned by activated carbon before being sprayed on the processed soil to suppress dust formation. Non-condensable gases are passed through either a cyclone, baghouse or wet scrubber to remove particulates before being vented.

The cost associated with thermal desorption is still relatively high in comparison to treatment alternatives such as soil vapour venting or landfilling. However, when compared to other types of thermal treatment such as incineration or vitrification, thermal desorption is quite attractive. The principle advantage of thermal desorption over incineration is the moderate operating temperature. Not only is less heat required to separate the volatiles, but the bulk of the soil does not have to be heated to incineration

temperatures. In addition, little exhaust is vented into the atmosphere, the contaminants are separated and collected, rather than destroyed. Thermal desorption systems can, in some cases, be partially self-sustaining since certain non-chlorinated hydrocarbons extracted from contaminated soil, particularly at refinery sites, can be recycled as fuel to heat the desorber (Valenti, 1994).

## 2.4 Factors Affecting Thermal Desorption

There is a complicated array of factors to consider when determining the applicability and likely performance of thermal desorption systems. According to Troxler *et al.* (1993), these factors fall into three broad categories: equipment operating parameters, contaminant characteristics and soil characteristics.

In the category of equipment operating parameters, there are four primary factors affecting thermal desorption:

- Soil Temperature
- Treatment Time
- Exhaust Gas Type
- Heating Method

The key parameter is maximum soil temperature achieved in the desorber, which is a function of soil characteristics, including moisture content, heat capacity and particle size, and of desorber heat transfer and mixing characteristics. The treatment or residence time of soil in the desorber also affects the extent of soil decontamination. Desorber configuration, rotational speed of the conveying device and desorber incline all affect residence time, which is also a key parameter for determining treatment cost. The last two equipment operating parameters, exhaust gas type and heating method are closely linked. Desorber exhaust gas can be either oxidative or inert. For directly heated systems, in which heat is provided by combustion gases from a burner, the exhaust gas

will contain some oxygen which can lead to the oxidation of a certain amount of desorbed material. Indirectly heated systems, however, can be operated under inert or very low oxygen atmospheres which limit the oxidation of organic compounds. Additionally, the size of exhaust gas treatment systems is much smaller for indirectly heated in comparison to directly heated systems.

There are two contaminant characteristics that affect thermal desorption:

- Contaminant Vapour Pressure
- Contaminant Concentration

Contaminant vapour pressure influences the rate of contaminant desorption. Low molecular weight compounds will typically have high vapour pressures and thus will be desorbed faster than higher molecular weight compounds. The second characteristic is contaminant concentration, which is important mainly for safety reasons. In some desorber configurations, the lower explosion limit may be approached while treating highly contaminated materials. A system operated in a inert atmosphere can treat materials contaminated up to 50 wt% hydrocarbons, since there is little or no oxygen to support oxidation reactions.

There are five soil characteristics which affect the applicability and particularly the cost of thermal desorption systems:

- Bulk Density
- Moisture Content
- Plasticity
- Particle Size Distribution
- Humic Content

Soil bulk density affects the soil heat capacity and thus, the amount of energy required to heat the soil to treatment temperature. Similarly, the moisture content of the soil, which typically ranges from 5 to 30 wt%, will affect the amount of energy required to heat the soil. In addition to contributing to poor handling properties, soils with a high moisture

content may be above the plastic limit. The main difficulty associated with the plastic limit is that soils deform without shearing and separating. The soil can become molded into large particles that are difficult to heat, or coats the interior surfaces of the desorber, reducing both the reactor volume and hence the soil residence time and the desorber heat transfer efficiency. The particle size distribution of soils to be treated has an impact on desorber performance. Thermal desorbers usually cannot manage particles larger than 5 cm in diameter, thus pre-screening or crushing may be necessary. Additionally, fine particles such as silt can become entrained in the exhaust gas and exit the desorber without meeting residence time requirements, and so must be returned from the baghouse to the desorber. Finally, the naturally occurring organic matter or humic content of the soil can have a significant impact on thermal desorption. Maguire *et al.* (1995) showed that organic contaminants are more tightly sorbed to the humic material in the soil, making humic soils more difficult to treat.

## **2.5 Current Research in Thermal Desorption**

Research into thermal desorption over the past few years has been taking place in two distinct areas: fundamental studies and testing of bench, pilot and commercial scale desorbers. In addition, literature is available on commercial applications of mobile thermal desorption processes, however, these will be discussed in a subsequent separate section.

### **2.5.1 Fundamental Studies**

Lighty *et al.* (1989a, 1989b) report the experimental results of several studies on the desorption of contaminants from soil. Using two bench-scale units, a particle-characterization reactor and bed-characterization reactor, they studied parameters such as

particle size, bed thickness and effective diffusivity. It was found that desorption rate is a strong function of soil type, and most significantly of temperature. In a more recent paper, Lighty *et al.* (1990) present a mathematical model of the desorption behavior of soil in both the particle and bed-characterization reactors. The model, based on the assumption that equilibrium conditions exist between the local gas phase and adsorbed phase contaminant concentrations, correlated well to experimental data.

The thermal treatment of soil artificially contaminated by No. 2 fuel oil was investigated by Bucalá *et al.* (1994). In studies applicable to several thermal treatment technologies the effects of heating rate, final temperature and degree of contamination on contaminant removal were studied. Experiments were conducted at heating rates of 200 and 1000°C/s. At a heating rate of 1000°C/s, to a maximum temperature of 1033°C, all the fuel oil was removed in about 0.7 s regardless of initial contaminant concentration, while at a heating rate of 200°C/s, about 25 seconds was required to achieve the same result. In a second paper, Bucalá *et al.* (1996) investigated how soil decomposition under thermal treatment affects desorption. When soil was heated at a rate of 1000°C/s to 1033°C, a mass loss of 21 wt% due to volatilization was found. The major products evolved were CO<sub>2</sub>, CO and tars. A model consisting of first and second order reaction kinetics was developed to describe gaseous release rates and soil weight loss data.

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.* (1995). Using differential scanning calorimetry over a temperature range of 20-390°C, PAHs were found to form miscible systems with the humic acid soil fraction, while no interaction between PAHs and other soil fractions was observed. Due to the formation of a miscible system, a temperature higher than the PAH boiling point is necessary to effect its removal from the humic acid soil fraction by thermal desorption. A model was developed to predict differential scanning calorimeter results based on miscible and immiscible PAH-soil fraction systems.

Keyes and Silcox (1994) investigated the non-isothermal desorption of toluene and n-dodecane from individual montmorillonite clay particles. Desorption rates, measured as a function of 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. A comparison between the results obtained from a single-particle reactor and those from a pilot scale rotary kiln indicate that bed mass transfer resistances dominate in the rotary kiln.

Farrell and Reinhard published complementary papers on desorption isotherms (1994a) and desorption kinetics (1994b) of chlorinated hydrocarbons from model solids and soils. In the first paper, desorption isotherms were measured in order to investigate the mechanisms affecting isotherm shape. Four sorption mechanisms for hydrocarbon uptake from the vapour phase were examined: mineral surface adsorption, partitioning into natural organic matter, partitioning into surface-bound water, and adsorption into micropores. It was found that two mechanisms, mineral adsorption and organic matter partitioning, were responsible for the majority of the hydrocarbon uptake. In the second paper, Farrell and Reinhard investigated the mechanisms controlling desorption rates from soils and sediments by measuring trichloroethylene desorption kinetics. It was found that desorption proceeded according to two distinct time scales, all solids having both a fast and slowly released fraction. Intraparticle pores, or micropores, of molecular dimension are thought to be responsible for the slow release rates of sorbed contaminants.

### **2.5.2 Bench, Pilot and Commercial Scale Studies**

The feasibility of thermally treating black tarry material (BTM), which contains pentachlorophenol and other hazardous compounds, and prior to stabilization with gypsum, was investigated by Hsieh *et al.* (1994) using an unagitated bench scale thermal desorber. At a treatment temperature of 150°C, Hsieh *et al.* observed a significant

improvement in the handling and adhesive properties of the BTM, due to both desorption of volatile and semi-volatile organic compounds and certain polymerization reactions. After thermal treatment, the material was found to be suitable for stabilization, since the pentachlorophenol and other heavy compounds were encased in the hardened tarry material.

Pilot scale studies on a continuous, indirectly heated rotary kiln desorber were conducted by Fox *et al.* (1991). The effect of both desorber temperature and residence time on the quality of treated soil was investigated. The unit successfully remediated three different types of soil contaminated by PCBs in concentrations ranging from 250 ppm to 4%. Sandy soil was reduced from an initial PCB concentration of 4% to 52.3 ppm when treated in the unit at 377°C for 23 minutes, while at 450°C for 45 minutes the concentration was reduced to only 3.85 ppm. Soils with lower PCB concentrations were all reduced to below 2 ppm. Additional pilot scale tests were performed on mixed waste, dioxin and PAH contaminated soils. For the PAH contaminated soil in the pilot scale desorber, it was found that increasing desorber temperature, at a residence time of 9 minutes, resulted in increased PAH treatment efficiency. The PAH removal increased from 88% at 300°C, to 96.7% at 350°C and 99.1% at 400°C.

Ayen and Swanstrom (1992) reported results from pilot and full scale studies on the Chemical Waste Management Inc. X-Trax thermal desorption system. The X-Trax system is a sealed rotary kiln, externally heated by propane burners. A nitrogen sweep gas transports the volatilized compounds to the gas treatment train. Remarkably similar results were obtained from the pilot and full scale unit studies. Treatability studies on various refinery sludges revealed that all organics of concern, including compounds such as SVOCs, PCBs and PAHs were reduced to below best available technology levels, which are the Superfund equivalent of Alberta Tier 1 Criteria, at 425°C. In one study, the pilot scale desorber, operating at a feed rate of 145 kg/h, reduced the concentration of anthracene from 110 mg/kg to less than 28 mg/kg at 425°C. Furthermore, drying studies

on refinery sludges determined that dried filter cakes have a heating value suitable for use in alternative fuels programs.

Results of a thermal treatment study on PAH and cyanide contaminated sludge cakes were reported by Swanberg (1993). Using the MX-2500, an indirectly heated thermal screw desorber owned by Separation and Recovery Systems Inc., it was found that PAHs, including anthracene, pyrene and chrysene, were successfully desorbed to below EPA Land Disposal Regulations. The system was operated continuously at temperatures between 650 and 750°C, although no residence times were specified. When treating cyanide contaminated sludge from fluidized catalytic cracking units, even higher temperatures were required to promote cyanide dissociation reactions.

Rutberg and Baille (1996) found that a certain amount of thermal cracking of high molecular weight hydrocarbons was occurring in the Caswan Environmental Services Inc. (Calgary, Alberta) directly heated, high temperature desorber. The soil is dried in a low temperature desorber operating at 260°C prior to introduction into the high temperature desorber. Soil was treated at a rate of 9,525 kg/h, however neither operating temperatures nor residence times were specified. While treating soil contaminated with aged crude oil, very low molecular weight hydrocarbons, not present in the feedstock, were found in the desorber offgas. The authors conclude, that the removal of high molecular weight hydrocarbons occurs by a combination of volatilization and decomposition reactions.

Field demonstrations results from four commercial thermal desorption processes were reported by de Percin (1995). It was found that soils contaminated by VOCs, SVOCs, PCBs, and pesticides were successfully remediated by all four systems. Under certain operating conditions, de Percin found that products of incomplete combustion, such as dioxins and furans, can be formed. de Percin concludes, however, that formation of these products can easily be avoided by proper system control. Air emissions from the

desorption systems ranged from extremely low for indirectly heated systems to merely acceptable for directly heated systems.

## 2.6 Commercial Applications of Thermal Desorption

There are dozens of companies in North America that offer soil remediation by thermal desorption on a commercial basis. Annual surveys of contractors in the thermal treatment remediation industry reveal that both the number of contractors and the number of mobile or transportable thermal treatment systems in operation is rapidly on the rise (Fiedler *et al.*, 1996; Cudahy *et al.*, 1991).

Typically, mobile thermal desorbers, along with associated materials handling, gas and water treatment operations, are fixed to several flatbed trailers. In order to keep the cost of thermal treatment competitive with alternatives such as landfill, the cost of mobilization must be spread over as much soil as possible. In cases where the amount of waste material is less than 1000 metric tons, it is usually more economical to transport the contaminated material to off-site facilities. For larger sites, however, transportation of the thermal system to the site is preferable. There are several descriptions of mobile commercial desorbers available in the literature, particularly for removal of volatile and semi-volatile organic carbons, PCBs and mercury from soil.

Operated by Chemical Waste Management, the X-Trax thermal desorption system has been described in detail by several authors (Ayen *et al.*, 1991; Ayen *et al.*, 1992; Johnson *et al.*, 1989; Krukowski, 1992; Sudnick, 1993). X-Trax is a sealed rotary kiln, externally heated by propane burners. Operating at temperatures between 250°C and 450°C, with solids residence times varying from 60 to 300 minutes, the X-Trax system has been extensively used to treat refinery sludges. The recovered hydrocarbons, which have an increased heating value are used in an alternative fuels program. Capable of

treating 115 metric tons per day at a cost of \$250 - 350 per ton, economics favour feeds containing about 10% organics with a low moisture content, to reduce the cost associated with desorption of water.

Krukowski (1992) described the SoilTech Systems Inc. Anaerobic Thermal Process (ATP), which uses a two zone indirectly heated rotary kiln. Water and light hydrocarbons are vaporized in the preheat zone, while in the retort zone, at temperatures approaching 600°C, heavy hydrocarbons are vaporized. The ATP is operated in an oxygen starved environment to prevent oxidation of desorbed organics. The system has successfully been used to remediate clay and silt soils contaminated by PCBs.

The Purgo Soil Remediation Services mobile thermal desorber was described by McAdams (1994). This directly heated rotary kiln, operating at 340°C, is capable of treating 10 metric tons per hour. The desorber is followed by an afterburner at 760°C which both incinerates the waste material and heats the desorber.

An indirectly heated thermal screw desorber operated by Seaview Thermal Systems was described by both McAdams (1994) and Valenti (1994). The HT-6 desorber is an electrically heated system of augers which moves the soil through two treatment zones reaching a maximum treatment temperature of 1000°C. Operated under a nitrogen blanket, a slight negative pressure draws vaporized water and waste from the distillation chamber to be recycled as desorber fuel.

Another indirectly heated multiple screw conveyor is operated by Weston Services Inc. (Nielson *et al.*, 1989; Johnson *et al.*, 1989). The Low Temperature Thermal Treatment System or LT<sup>3</sup> is heated to 340°C by hot oil circulating both around the chamber and through the screw. Organics desorbed by the LT<sup>3</sup> are incinerated by an afterburner. The unit is capable of treating 9 metric tons per hour at a cost of \$220 to 275 per ton, based on 20% moisture and 10,000 ppm organics.

Finally, Separation and Recovery Systems' SAREX MX-2500 process, described by Swanberg (1993), is an electrically heated inclined screw. The screw gear arrangement allows both forward and reverse motion in increase soil residence time if necessary. The system typically operates under a nitrogen blanket, at temperatures between 650°C and 750°C. A slight negative pressure sweeps desorbed material into the condenser section where it is recovered and recycled. The SAREX system can process 90 metric tons of hydrocarbon contaminated soil per day. Several systems are currently treating petroleum contaminated soil to EPA Land Disposal Regulations at a number of refineries.

Many more new commercial applications of both established and innovative technologies are in the process of being developed. It is important to remember, however, that the success of soil remediation projects does not depend upon engineering and scientific criteria alone. As Eschenbach (1996) described, in the current political environment, not only must sound remediation results be demonstrated, but public acceptance of the treatment technology is required prior to its implementation.

## CHAPTER THREE

### EXPERIMENTAL

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Although two very distinct sets of thermal desorption experiments were performed as part of the work reported here, both employed the same experimental and analytical methods. First of all, this chapter provides a detailed description of the Batch Thermal Reactor. The experimental setup section is followed by sections describing the characteristics and preparation of contaminated sample materials used in this research. Sections on experimental and analytical methods round out the chapter.

#### 3.1 Description of Batch Thermal Reactor

The Batch Thermal Reactor or BTR is a bench scale, batch thermal desorber developed by Bromley Marr Ecos (BM Ecos) of Calgary to investigate the feasibility of treating several contaminated industrial samples by thermal desorption. The BTR was designed as a prototype to a commercial mobile low temperature thermal desorption unit that the company intends to build. The desorber, which had previously been constructed by BM Ecos, was kindly provided for this research. Although the BTR design does not fit precisely into any one of the four standard thermal desorber configurations discussed in section 2.3, it most closely resembles the thermal screw. Since the BTR is a batch desorber equipped with a helix-like auger, it is considered a novel variation on thermal screw units which usually operate continuously.

The BTR is an indirectly heated thermal desorber with an operating temperature range between 150°C and 600°C. Commercial indirectly heated desorbers described in the literature use an inert gas environment to prevent, or at least minimize, the oxidation of desorbed organics. In many cases, a slight negative pressure is used to draw both the sweep gas, typically nitrogen, and vaporized contaminants from the desorption chamber. Although there are many characteristics that distinguish one desorption system from another, the most significant feature of the BTR is that the unit is operated under vacuum. As with other indirectly heated desorbers, oxidation reactions are minimized, however, by operating under vacuum the need for an inert sweep gas is eliminated.

There are two main benefits realized by operating the BTR under vacuum. The first is that the gas stream exiting the BTR consists only of desorbed contaminants and water. Since both the water and organics are condensable, there should be virtually no air emissions from the BTR. Additionally, the volume of material to be processed by the condenser and exhaust gas treatment units is much smaller than for desorbers that rely on sweep gases, so that the size of these units can be minimized. The second benefit of operating under vacuum is boiling point depression. Thus, contaminants will desorb at a lower temperature in the BTR than they would at atmospheric pressure. Boiling point depression is significant, since the cost associated with maintaining vacuum on the desorber is relatively small in comparison with that required to heat it. Although the level of vacuum could have been considered as an operational variable, a single vacuum level was used to draw desorbed contaminants from the desorber, and other equipment operating parameters such as residence time and temperature were investigated.

### 3.1.1 Process Overview

A simplified schematic diagram of the BTR process appears in Figure 3-1. The BTR apparatus consists of three main elements, the desorber, the condenser system, and the data acquisition and temperature control system.

At the start of each experiment, the contaminated sample is fed into the BTR by gravity through a feed hopper. When the moisture content or degree of contamination prevented material from flowing freely through the hopper, the vacuum was used to pull the sample into the BTR. Once inside, the sample is mixed by the helix auger and rapidly heats to desorber temperature. Powered by a Reliance Electric  $\frac{1}{4}$  horsepower reversible motor, the auger rotates for 15 seconds in one direction and then reverses its direction. Upon completion of each of the tests, based on the desired residence time, the treated sample is dropped through the product discharge valve onto dry ice in a large metal pan. The dry ice effectively quenches any further desorption of hydrocarbons from the sample, and minimizes the oxidation of contaminants in the air.

Volatilized water and contaminants are drawn out of the BTR under vacuum of 0.45 atmospheres absolute through a single vapour exit line. The vapour then passes into a dual condenser system, consisting a primary trap, to capture the heavier compounds, and a secondary trap, to condense the water and lighter hydrocarbons.

Five thermocouples are located around the BTR. Two thermocouples are mounted along the outside surface of the desorber, with the thermocouples placed flush against the vessel to minimize conduction along the leads. These two thermocouples, one connected to the temperature controller and the other working as a reference, provide temperature control. A third thermocouple, inserted through the vapour exit line just

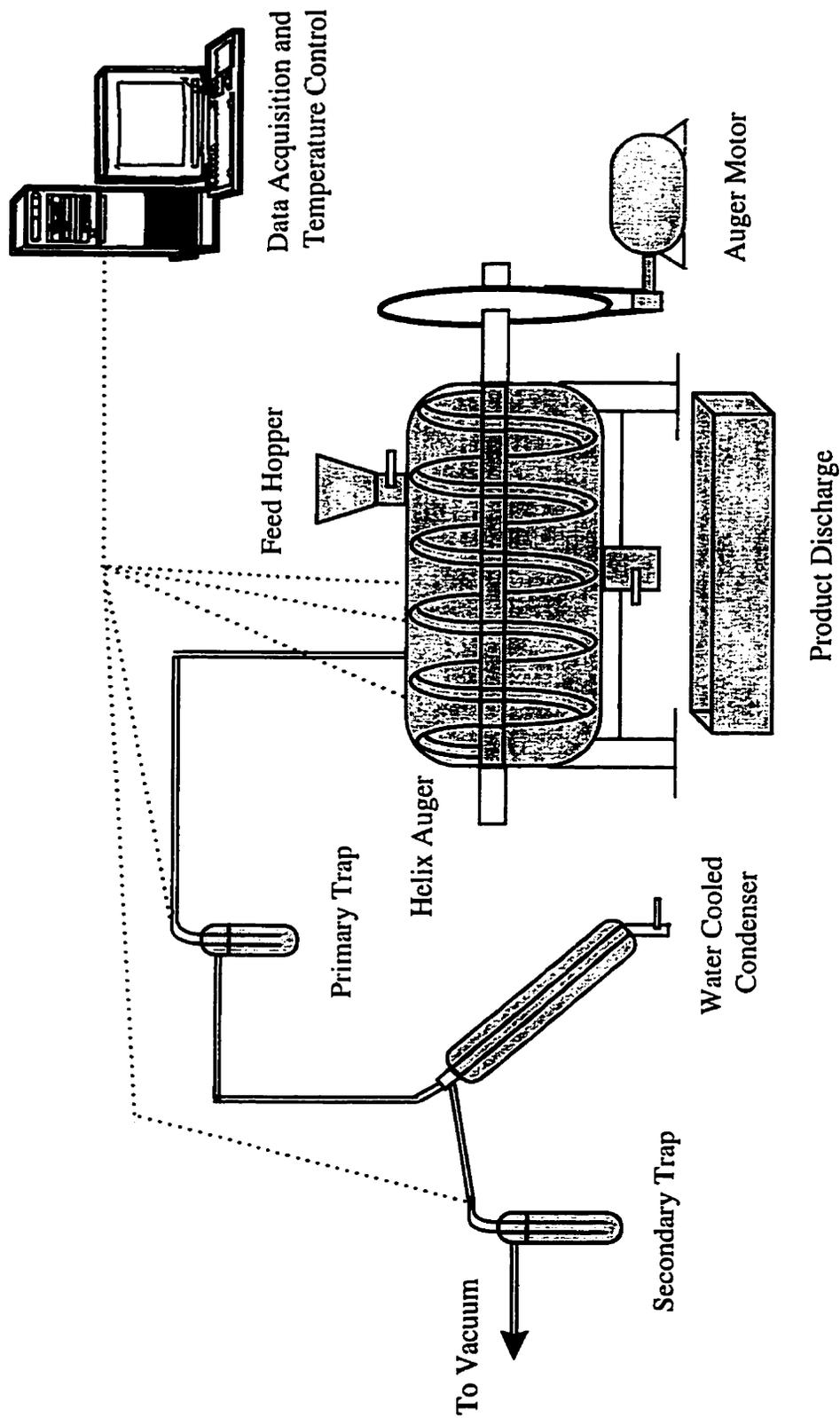


Figure 3-1: Schematic Diagram of Batch Thermal Desorption Process

inside the desorption chamber, monitors the internal desorber temperature. The fourth and fifth thermocouples are located at the inlets to the primary and secondary traps respectively. Output from the thermocouples was monitored and recorded by a Fluke Hydra Multichannel data logger linked to a 386 PC.

### **3.1.2 Batch Thermal Reactor**

Strictly speaking, the name Batch Thermal Reactor is a misnomer, since the unit is a thermal desorber rather than a reactor. However, this is the name that was selected by BM Ecos to market the process. A photograph of the BTR appears in Figure 3-2, while Figure 3-3 shows a more detailed schematic diagram of the desorber.

The BTR is electrically heated externally by a series of four ceramic band heaters fixed around the body of the vessel. Thus, heat transfer to the soil sample in the BTR occurs primarily by conduction through the vessel walls. The band heaters are rated to a maximum temperature of 750°C. However, the BTR was only operated in this project at temperatures between 150°C and 500°C, since the commercial unit would not likely be capable of operating above 500°C.

The helix auger was designed in an effort to achieve either plug flow or continually mixed conditions within the reactor. Plug flow conditions would exist with the auger acting as a screw, rotating in one direction only. In these experiments, with the auger rotating alternately in both directions, well mixed conditions exist within the desorber. A photo of the helix auger is shown in Figure 3-4. The auger consists of a single stainless steel blade, 1.5 mm thick, wound 5 times around and welded to a 2.54 cm diameter shaft. The overall diameter of the auger is 12.5 cm. The motor rotates the auger at a rate of 20 revolutions per minute for 15 seconds before reversing direction. Thus, 5 full revolutions are completed in each direction twice every minute.

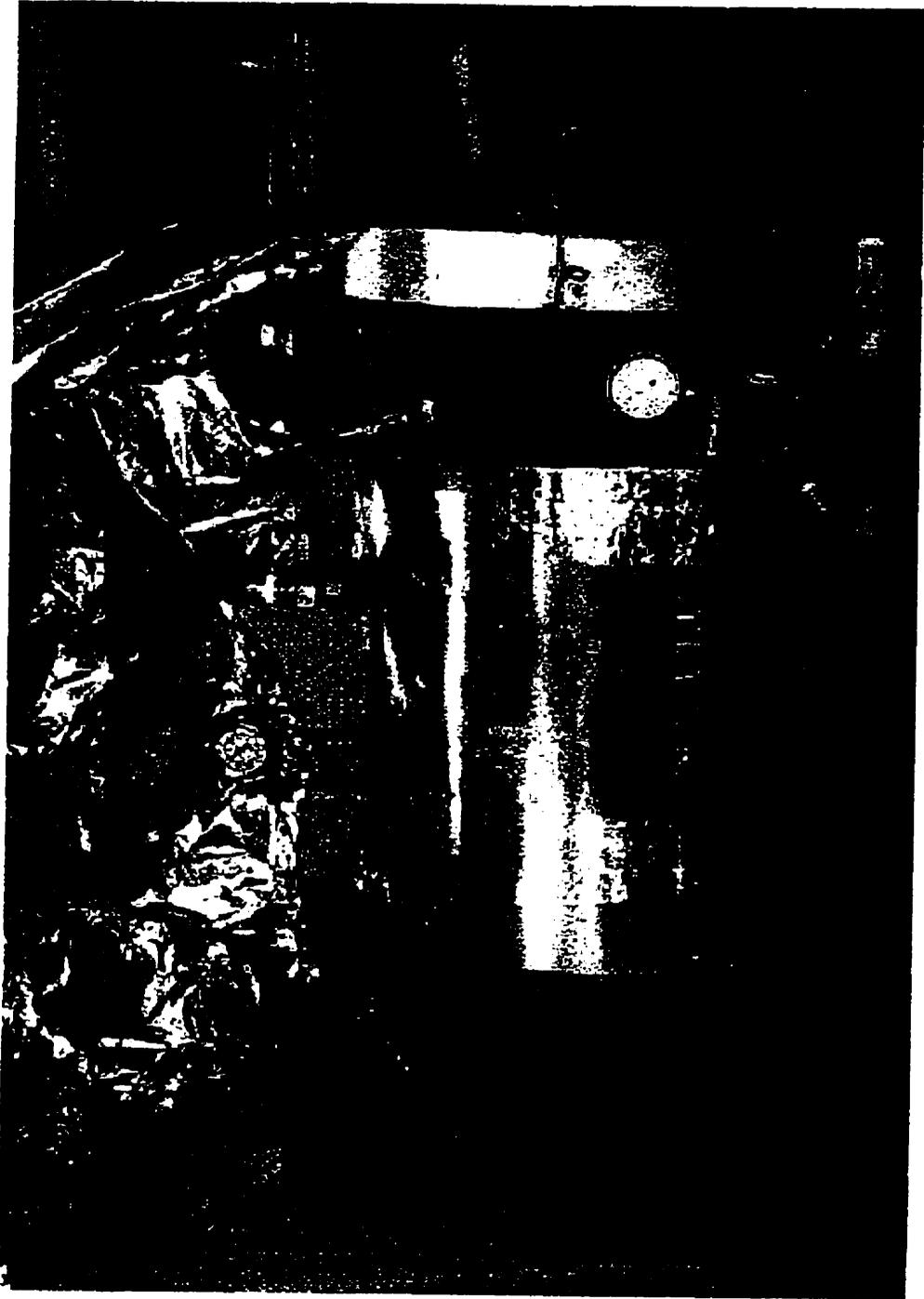


Figure 3-2: Photograph of Batch Thermal Reactor

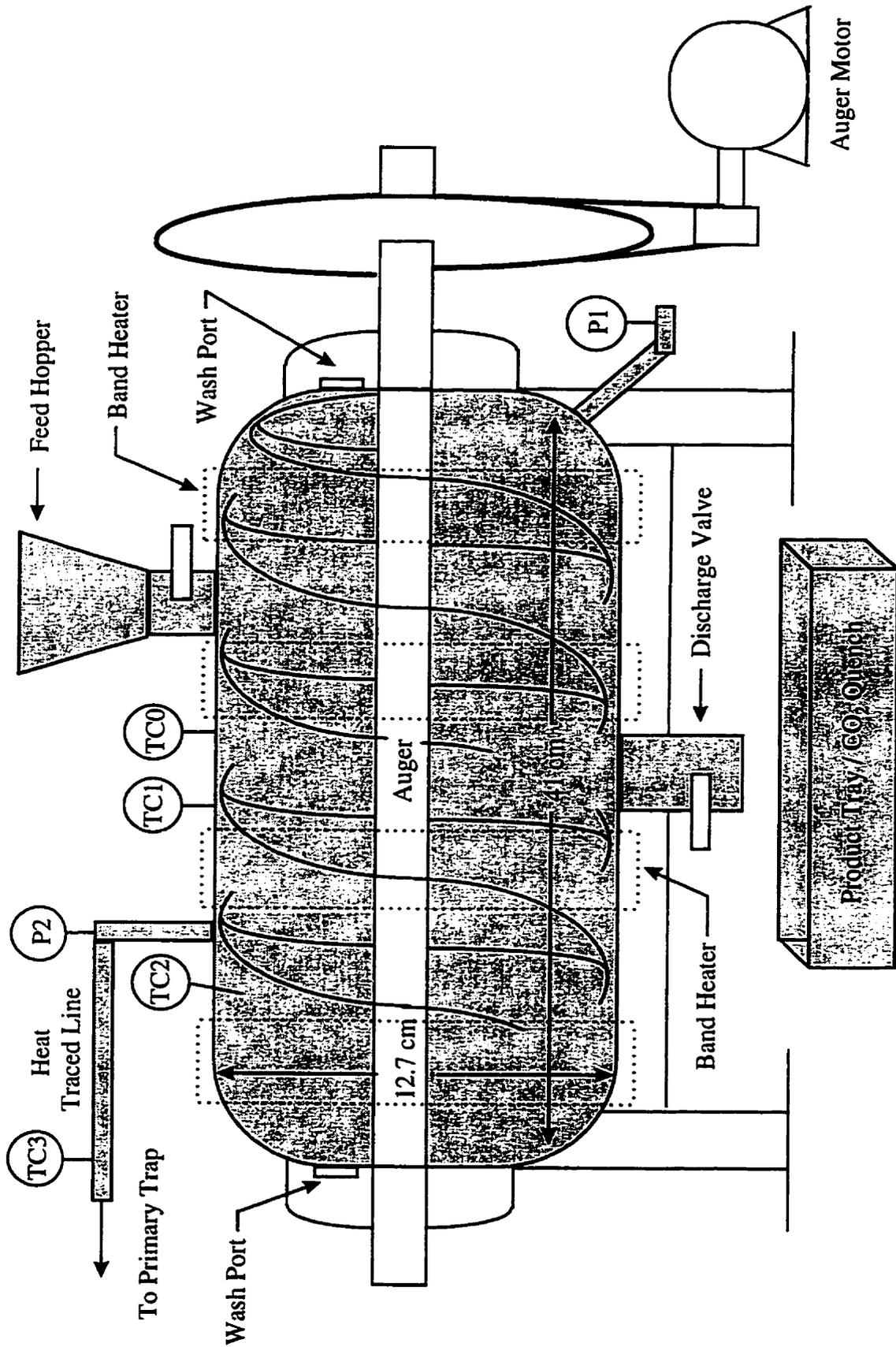


Figure 3-3: Schematic Diagram of Batch Thermal Reactor



Figure 3-4: Photograph of Helix Auger

Cast of carbon steel, the BTR has an internal volume of nearly 1.5 liters, although much smaller sample volumes were generally chosen in order to reduce the time required for the sample to reach temperature. The internal dimensions of the BTR desorption chamber, also provided in Figure 3-3, are 12.7 cm in diameter and 41 cm long. Both the feed and discharge valves are 2.54 cm in diameter, while the vapour exit line is ¼ inch stainless steel tubing. Although the BTR is capable of holding some pressure, it is intended to operate under vacuum, and so is equipped with a pressure relief valve in the event that the vapour exit line becomes blocked.

As shown in Figure 3-3, three thermocouples and two pressure gauges measure the conditions both inside and outside the BTR. Thermocouples 0 and 1 measure the desorption chamber exterior temperature, while thermocouple 2 measures the internal temperature. The pressure gauges, capable of reading both pressure and vacuum, measure vacuum both inside the desorption chamber and in the vapour exit line. 2.54 cm diameter wash ports are located at each end of the desorber.

### **3.1.3 Condenser System**

Under vacuum, desorbed water and organics are drawn out of the BTR and into the condenser system, which can be seen in Figure 3-1. Consisting of primary and secondary traps, compounds are condensed in one of the two traps based on their boiling points. It has been found commercially that multiple condensers can effectively separate high boiling point compounds such as creosote and PAHs from water and lighter compounds, and thereby reduce the cost of subsequent processing.

Certain modifications were made to the condenser system between the treatment of industrial and prepared samples. While treating the industrial samples, the condenser system consisted of a water-cooled, shell and tube primary condenser and a glass ice-

cooled vacuum trap. Cooling water passed on the shell side of the primary condenser, which had an outside diameter of 8 cm and was 61 cm long. The condenser was periodically emptied through a combination of two valves. The F configuration glass vacuum trap had a 34/40 ground glass joint, to which a 10.5 cm long, 4.5 cm diameter trap bottom was attached. ¼ inch stainless steel and brass tubing along with stainless steel and brass Swagelock fittings connected the primary condenser to the BTR. Lengths of flexible tubing connected the primary and secondary traps, and also the vacuum trap to a building vacuum tap.

For treatment of the prepared samples, the water-cooled condenser was replaced by a primary, quartz glass, ice-cooled vacuum trap. This modification was done in order to condense the PAHs desorbed off the prepared samples in one location with minimal losses to condensation in the tubing. The ¼ stainless steel tubing between the desorber exit and the primary trap was wrapped with a length of high temperature heating tape to keep the line temperature above the melting point of the PAHs and prevent the line from clogging with condensed material. The T configuration vacuum trap bottom had a 24/40 ground glass joint with Teflon sleeve to prevent sticking, and was 2.8 cm in diameter and 16 cm long. The trap was made out of blow quartz glass to resist cracking despite large temperature variation, and was equipped with Swagelock fittings which allowed it to be attached directly to the stainless steel lines. The secondary ice-cooled vacuum trap, described above, was connected to the primary trap by copper tubing and brass Swagelock fittings, and condensed any light fraction not captured by the primary trap.

### **3.2 Industrial Samples**

Five industrial samples were obtained by BM Ecos to investigate the feasibility of treating several typical waste types using the BTR. Rather than undertaking an extensive study on each sample, the company's goal was to get some basic ideas about the effects of

desorber temperature and residence time on remediation level. In addition, BM Ecos wanted to investigate the impact of certain sample pre-treatments, including lime addition and a physical process called aggregation, in which samples are dried using a modified rotary kiln. The aggregation process was designed to improve the handling characteristics of moist soils and to effectively blend additives or stabilizers into the soil. The pilot scale unit, operated at the BM Ecos facility in Redwater Alberta, produced pelletized solids of uniform size and moisture content.

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 pre-treatment additive (EPA, 1996), however, the energy required to heat the additional mass makes sand blending uneconomic in thermal desorption applications. Lime ( $\text{CaCO}_3$ ) is frequently selected as a soil amendment instead, since it does not increase the soil bulk density, and reduces stickiness of the contaminated soils. While lime has been found to react with sulphur and chlorine to form salts such as  $\text{CaSO}_4$  and  $\text{CaCl}_2$  during incineration, at desorption temperatures lime simply dehydrates the soil and stabilizes organic contaminants.

In the following five sections, a description of the sample characteristics, the type and degree of contamination and the pre-treatment done to prepare the samples is presented.

### **3.2.1 Domtar Flare Pit Sludge**

Flare pit material was obtained from a Domtar refinery site in Alberta. An analysis of the sample by Chemex Laboratories, revealed that the material was contaminated up to 20 wt% with hydrocarbons ranging from C8 to C60 with particularly

large quantities of xylene, toluene and C13 to C28 compounds. The sample also contained five heavy metals, barium, chromium, mercury, molybdenum and zinc, in concentrations well above Alberta Environment Tier 1 Criteria. The results of the Chemex analysis are provided in Appendix A.

The high degree of contamination, coupled with a moisture content of about 25%, made the untreated sludge very difficult to handle. A preliminary experiment failed, since the sludge adhered to the feed hopper and could neither be dropped, nor sucked under vacuum into the desorber. In order to improve the handling characteristics, the sludge was pre-treated at the BM Ecos Redwater facility. The sludge was rinsed once with water, and then blended with 3 wt% lime during aggregation. The resulting sludge pellets, about 8 mm in diameter, had a moisture content of about 10% and the hydrocarbon concentration had been reduced to 3.8 wt%. The handling characteristics of the sludge were vastly improved by aggregation. An additional pre-treatment of rehydrating some of the aggregated sludge with 10 wt% water was also done. Although this resulted in pellets with an overall moisture content slightly over 20%, it was thought that steam generated by desorbing water might promote the desorption of other contaminants

### **3.2.2 CanOxy Chlorinated Organic Soil**

Soil contaminated primarily by chlorinated organics was obtained from an undisclosed CanOxy Ltd. site in Canada. A soil analysis, commissioned by CanOxy, revealed several problem areas. The hydrocarbon concentration in the soil was 1.8%, apparently due to presence of several chlorophenols. The results of the analysis performed for CanOxy are available in Appendix A. Soxhlet extraction of the CanOxy soil performed in our lab found that the total hydrocarbon concentration was 1.7 wt%. A

high electrical conductivity, nearly twice the Tier 1 criteria value, was measured and the concentrations of two heavy metals, mercury and boron, were above the legislated limit.

The moisture content of the CanOxy soil was about 20 wt%. Although the moisture content was relatively high, under vacuum the soil could be sucked into the desorber. Thus, the soil was simply screened to remove rocks and other debris prior to treatment in the BTR.

### **3.2.3 Amoco Activated Carbon**

Spent activated carbon was obtained from the Amoco Canada Kaybob Plant. Unfortunately, no detailed analysis of the sample was done by a commercial lab. A basic analysis of the activated carbon, was done in our lab by Soxhlet extraction and gas chromatography. The hydrocarbon concentration of the Amoco sample was 9.8 wt%. Although several organic compounds, including toluene, xylene, phenol and some straight chain hydrocarbons, were recognized from the GC results, many others could not be identified. No pre-treatment or preparation was required for the sample, since it consisted of discreet, free-flowing particles.

### **3.2.4 PanCanadian Produced Sand**

Sand displaced during the drilling of oil wells was obtained from PanCanadian Petroleum Ltd. The produced sand was lightly contaminated with petroleum hydrocarbons and organic solvents used during the drilling process. An analysis performed by Chemex Laboratories found that the hydrocarbon concentration on the sand was 1.24 wt%, the majority of which consisted of C15 to C29 compounds. The results of the Chemex analysis are available in Appendix A.

The moisture content of the sand was about 20%, however, 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 pre-treatment, including various types of sample washes and lime addition in different concentrations, rather than on BTR variables. Table 3-1 summarizes the sand pre-treatments, all of which were done at the BM Ecos facility in Redwater. The hydrocarbon concentration found by Soxhlet extraction of the untreated sand was 1.01%, while that of the 30 minute cold water wash with 4% lime addition was 0.058%

Table 3-1: Produced Sand Pre-Treatments

Cold Water Rinse
Hot Water Rinse
Cold Rinse + 1.5% CaCO <sub>3</sub> Addition
Cold Rinse + 3.0% CaCO <sub>3</sub> Addition
Cold Rinse + 4.0% CaCO <sub>3</sub> Addition
30 minute Cold Water Wash
30 minute Cold Wash + 4% CaCO <sub>3</sub> Addition

### 3.2.5 Weyerhaeuser Dioxin/Furan Pulp Sludge

Contaminated pulp sludge was obtained from the Weyerhaeuser Kamloops Mill. Dioxins and furans produced during the pulping process were of primary concern, however, an analysis of the sample performed by Eco-Tech Laboratories in Kamloops BC, identified high levels of several metals including arsenic, cadmium, copper, lead and mercury. A copy of the analysis is provided in Appendix A. The total dioxin concentration was 3.75 µg/kg, more than three times the Alberta Environment limit. Octa and heptachlorodibenzodioxins made up the largest part of the dioxin contamination. The total furan concentration was 64.7 µg/kg, more than six times the limit.

The sludge sample received from Weyerhaeuser was nearly 90 wt% water, and contained large wood chips and sticks. Excess water was drained from the sludge, and it was sieved to remove debris. The remaining sample, which consisted primarily of fine wood fibers and a dark substance resembling soil was air dried in the fumehood for 48 hours. The moisture content of the resulting sludge was about 30 wt%. The addition of 10 wt% lime to the dried sludge was also considered as a pre-treatment.

### **3.3 Prepared Samples**

Three artificially contaminated samples were prepared using two model solids and binary mixtures of PAHs. These experiments were performed in order to investigate the effect of porosity, contaminant molecular weight, desorber residence time, and desorber temperature on desorption using controlled samples.

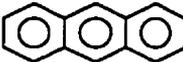
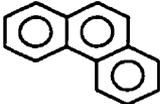
#### **3.3.1 Polynuclear Aromatic Hydrocarbons**

Polynuclear aromatic hydrocarbons (PAHs) are neutral, nonpolar organic molecules, consisting of two or more benzene rings arranged in a variety of configurations. These compounds are important environmentally since many demonstrate toxic and hazardous effects even in low concentrations, and several are recognized carcinogens. PAH contamination 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, representing a significant portion of PAHs typically found at creosote and petroleum contaminated sites, were selected to artificially contaminate both sand and activated carbon samples. Anthracene (97%), fluorene (98%),

naphthalene (99%) and phenanthrene (98%), were all purchased from Aldrich Chemical Company. Basic properties of the PAHs are listed in Table 3-2.

Table 3-2: Properties of Selected Polynuclear Aromatic Hydrocarbons

Polynuclear Aromatic Hydrocarbons				
	Anthracene	Fluorene	Naphthalene	Phenanthrene
Molecular Weight	178.23	166.22	128.17	178.23
Melting Point	217°C	114°C	80°C	100°C
Normal Boiling Point	340°C	298°C	218°C	340°C
Bubble Point at 0.5 atm	306°C	267°C	188°C	305°C
Chemical Formula	C <sub>14</sub> H <sub>10</sub>	C <sub>13</sub> H <sub>10</sub>	C <sub>10</sub> H <sub>8</sub>	C <sub>14</sub> H <sub>10</sub>
Chemical Structure				

### 3.3.2 Model Solids

Two model solids, sand and activated carbon, were selected in order to investigate the effect of material porosity on desorption.

#### Sand

Medium-coarse grain silica sand was chosen as the non-porous material for these experiments, in which contaminants are only sorbed onto the particle surface. Washed SIL-4 grade sand was obtained from Acklands Limited of Calgary. An analysis of the sand was performed by Core Laboratories of Calgary, the results of which are listed in Table 3-3.

Table 3-3: Sand Properties

Property	Value
exchange capacity (meq/100g)	0.24
mean particle diameter	363.6 $\mu\text{m}$
median particle diameter	368.6 $\mu\text{m}$
<u>Sieve Analysis</u>	<u>Weight Fraction</u>
very coarse sand: 1000 $\mu\text{m}$	0.002
coarse sand: 500 $\mu\text{m}$	0.153
medium sand: 250 $\mu\text{m}$	0.789
fine sand: 125 $\mu\text{m}$	0.054
very fine sand: 88.4 $\mu\text{m}$	0.001

### Activated Carbon

Activated carbon was selected as the porous material. In contrast to the sand, contaminants are easily sorbed into the pores within the carbon. Untreated activated charcoal was purchased from Sigma Canada. The properties, listed in Table 3-4, were provided by the manufacturer in a certificate of analysis.

Table 3-4: Activated Carbon Properties

Property	Value
minimum particle size	850 $\mu\text{m}$
maximum particle size	2.36 mm
moisture content	1.7%
residue on ignition	4.8%

### 3.3.3 Sample Preparation

The model solids were contaminated with two binary mixtures of PAHs. The combinations, naphthalene-phenanthrene and anthracene-fluorene, were chosen on the basis of the compound boiling points, so that the components would not desorb equally at a given temperature. Naphthalene and phenanthrene have normal boiling points of 218°C and 340°C and bubble points at 0.5 atm of 188°C and 305°C respectively, while anthracene and fluorene have normal boiling points of 340°C and 298°C and bubble points at 0.5 atm of 306°C and 267°C respectively. The effect of operating the desorber at 0.5 atm absolute vacuum instead of at atmospheric pressure reduced the boiling points of the PAHs by about 30°C. The sand was contaminated with both mixtures, while the activated carbon was only contaminated by the naphthalene-phenanthrene mixture.

In order to sorb and distribute the PAHs evenly over the surface and into the pores of the model solids, the contaminants were dissolved in a solvent, methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>). Methylene chloride is an appropriate solvent for this purpose, because it was found to have no significant interaction with either anthracene, fluorene or naphthalene (Maguire, 1994). It is reasonable to assume that methylene chloride has no interaction with phenanthrene either, since the chemical structure of phenanthrene is similar to that of anthracene. 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 a concentration of 5 wt%. The solvent was evaporated and recovered by vacuum distillation using a Brinkmann Rotavapour at 40°C. Similarly, a 50:50 weight mixture of anthracene and fluorene was also dissolved in methylene chloride, however, due to the low solubility of anthracene in the solvent, the sand was only contaminated to a concentration of 2 wt%.

After preparation, the samples were kept in sealed containers to minimize PAH losses by evaporation, and to ensure that the contaminants remained evenly distributed

over the samples. Each sample was assayed twice by Soxhlet extraction, once at the beginning of the experiments and again toward the end, to measure PAHs losses over the course of the experiments.

### **3.4 Experimental Method**

Both industrial and prepared samples were treated using essentially the same method. The procedure consisted of three stages, sample preparation, which was covered previously, BTR operation, and cleaning out the reactor to close the mass balance.

#### **3.4.1 Batch Thermal Reactor Operation**

BTR experiments began by heating the desorber under vacuum, 0.45 atmospheres absolute. Typically taking between 1 and 4 hours to reach the set point temperature, the time was used to check that exit lines were clear and that the BTR held vacuum. Once the desorber temperature stabilized, the auger was started and a known mass of sample, usually of volume between 600 mL and 1 L, was placed in the feed hopper. Once feed hopper valve was opened, it generally took about 5 seconds for prepared samples and about 1 minute for industrial samples to drop into the desorber.

Desorber temperatures were monitored and recorded, in part, so that the time required for a cold sample to reach temperature could be measured. This heat up time is particularly significant at short residence times, since it reduces the effective residence time of the sample at the desired temperature. It was found that samples generally reached temperature in less than 2 minutes, which suggests that the degree of desorption will only be slightly affected by heat up time. Figures 3-5 and 3-6 show typical time-temperature profiles.

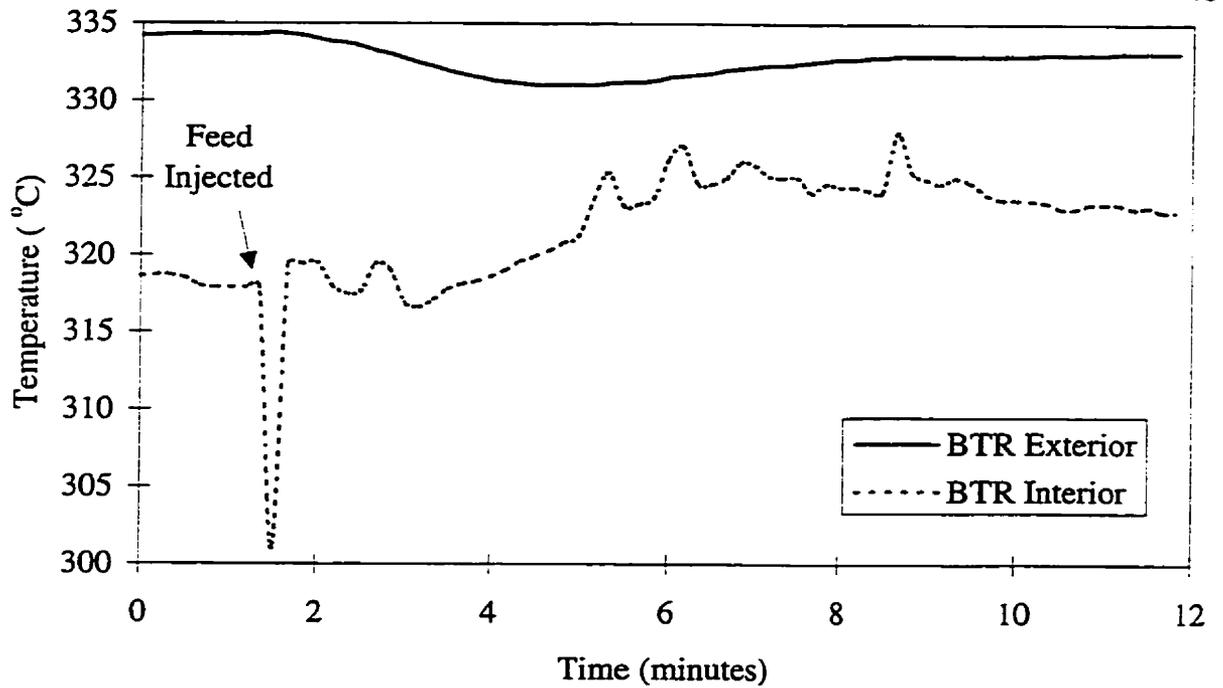


Figure 3-5: Time-Temperature Profile of Anthracene-Fluorene Contaminated Sand Treated at 320°C for 10 minutes

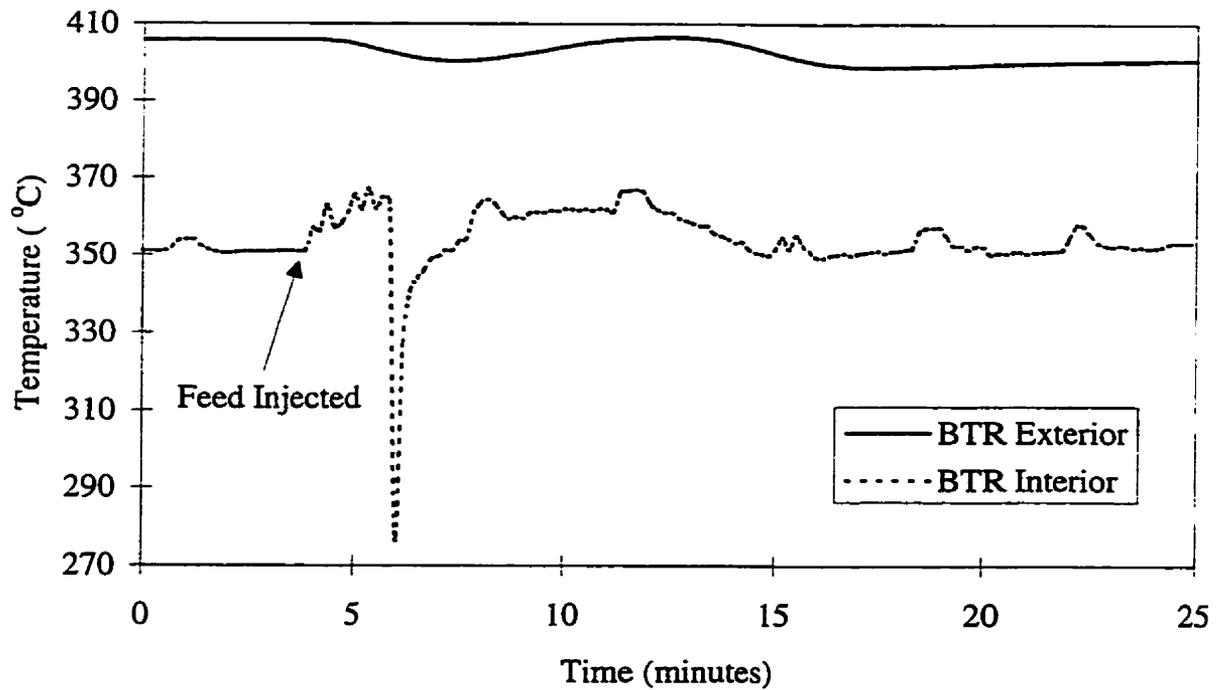


Figure 3-6: Time-Temperature Profile of Naphthalene-Phenanthrene Contaminated Sand Treated at 350°C for 20 minutes

The heat up time of aggregates or clumps of sample that might form in the BTR could not be measured directly, however, using Gurney-Lurie charts for spheres (Bennett and Myers, 1982) a rough estimate of the heat up time was calculated. It was assumed that the thermal conductivity,  $k$ , of the agglomerates was rather low,  $0.27 \text{ J/m-K}\cdot\text{s}$ , the heat capacity,  $c_p$ , of the soil was  $1840 \text{ J/kg-K}$ , and that the density,  $\rho$ , was  $1515 \text{ kg/m}^3$  (Incropera and DeWitt, 1990). In addition, it was assumed that conductive heat transfer was the only means by which the agglomerates were heated. It was calculated that the centre of agglomerates, 1 cm in diameter, reached the desorber temperature in about 3.5 minutes, while 14.5 minutes was required for the centre of 2 cm diameter agglomerates to reach desorber temperature. Clearly, aggregate size and the formation of clumps of sample have an impact on the heat up time of contaminated samples.

A gas flow meter was used to ensure that no combustion or pyrolysis of organics occurred in the desorber. Inserted into the vacuum line after the secondary trap, a GCA/Precision Scientific Wet Test Meter monitored the exhaust gas. Presumably, a spike in the gas flow would be observed after a sample was fed into the desorber if the contaminants were breaking down into lighter, non-condensable compounds such as  $\text{CO}_2$ . In all but one case, no increase in gas flow was observed.

The BTR pressure was recorded at 5 minute intervals using two gauges, one located on the outlet line just prior to the primary trap, and the other located in the body of the desorber, in order to detect exit line obstructions. The BTR was operated under a vacuum of 0.45 atmospheres absolute pressure off the building vacuum pump.

Once samples reached the desired residence time, the discharge valve was opened while the auger continued to rotate. Material was allowed to drop from the desorber onto dry ice for five minutes. Usually between 50 and 75% of the solid sample dropped from the desorber during this time, however, experiments in which the mass of sample collected was too small, or represented less than 50% of the solids fed to the desorber

were discarded. Although more material was washed from the BTR once the chamber had cooled, only sample collected during this five minute period was analyzed.

### **3.4.2 Mass Balance Closure**

The BTR was carefully cleaned between each experiment to close the mass balance around the process, as well as to prevent samples from being cross-contaminated. The cleaning procedure consisted of rinsing the reactor with water while the auger rotated. Wash ports at each end of the BTR accessed the space between the auger and the flanges, which was cleaned using a water jet. The heater and vacuum were then turned on to wash the chamber with boiling water and draw steam through the lines. If a line plug was detected by sluggish response to pressure changes, the lines were dismantled and cleaned with acetone and toluene. Material washed from the BTR was collected and air dried in the fumehood.

In order to close the mass balance, the mass of sample dropped onto dry ice was recorded along with the mass of all desorbed compounds, and the mass of material cleaned from the reactor. Unfortunately, the balances were not accurate enough to ascertain whether or not combustion products were being formed, so the gas flow measurements were relied upon. The total mass of products was compared to that of the single feed, and the mass balances were consistently closed within 95 and 100%, runs not closing to within 95% were discarded.

An additional mass balance around the hydrocarbon contaminants was determined for a few samples, however, the balance closed to only between 65 and 95% because line losses were in some cases quite significant. Although the mass balance around the contaminants was not very accurate, it did not affect the overall results, since the purpose of the experiments was to determine the residual hydrocarbon concentration on BTR

treated samples. The reproducibility of the results was demonstrated using prepared samples, in which the residual hydrocarbon concentration on samples from duplicate experiments varied less than 10%. Finally, inspection of the desorption chamber while the BTR was disassembled for maintenance revealed that neither solid sample nor hydrocarbons remained in the desorber, both were successfully removed from the desorber by the cleaning process.

### **3.5 Analytical Methods**

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.

#### **3.5.1 Soxhlet Extraction**

A mass of dried sample of between 30 and 90 g was placed in a 33x80 mm Whatman single thickness cellulose extraction thimble of known weight. The sample was refluxed in a Soxhlet extraction tube for 24 hours with an extraction solvent, tetrahydrofuran. Each sample was oven dried in a beaker at 50°C for 24 hours prior to Soxhlet extraction, to prevent moisture in the sample from skewing Soxhlet results. The organic extract was concentrated and the solvent was recovered using a Büchi RE121 Brinkmann Rotavapour at 75°C. The extracted organics were then re-dissolved in 25 mL of THF for analysis by gas chromatography.

Contaminant concentrations, expressed as weight percent total hydrocarbon contamination (%THC), are calculated by accurately determining the mass of

hydrocarbons stripped from the sample. The mass of stripped hydrocarbons is divided by the initial sample mass according to equation 3-1.

$$\% \text{ THC} = \frac{\text{mass contaminated sample} - \text{mass extracted sample}}{\text{mass contaminated sample}} * 100 \quad (3-1)$$

### 3.5.2 Gas Chromatography

A Hewlett Packard 5890 Series II Gas Chromatograph equipped with a thermal conductivity detector (TCD) was used to analyze the Soxhlet extraction solvent as well as condensed PAHs from the prepared samples. The column was a packed OV-101 on 10% Supelcoport from Supelco Canada, and the TCD output was sent to a Hewlett Packard 3396A Integrator.

In order to determine the composition of PAHs condensed in the primary trap during the prepared samples experiments, the desorbed material was dissolved in a known amount of methylene chloride. 2  $\mu\text{L}$  samples were injected into the GC. The oven temperature was ramped from 80°C to 300°C over 20 minutes, while the injection and detector port temperatures were 200°C and 250°C respectively. The helium carrier gas pressure was set at 20 psi, which corresponded to a flow rate of 60 mL/min. The relative amount of each PAH was determined by comparing peak areas.

## CHAPTER FOUR

### RESULTS AND DISCUSSION: INDUSTRIAL SAMPLES

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Experimental results from the five industrial samples obtained by BM Ecos are presented in this chapter. These industrial samples represent a wide range of types of contamination, and of typical contaminated material, from sands to soils to industrial waste products. The purpose of these experiments was to investigate the feasibility of treating the contaminated wastes using the BTR, and to determine whether Alberta Environment Tier 1 Criteria for Contaminated Soil Assessment and Remediation could successfully be reached using a combination of pre-treatment methods and thermal desorption.

The residual hydrocarbon concentration of thermally treated samples was determined by Soxhlet extraction, and is expressed as wt% total hydrocarbon contamination (%THC). Where appropriate, this data is presented in graphical form, the residual hydrocarbon concentration plotted as a function of desorber residence time at each temperature. In two cases, where several different pre-treatments were investigated, the data is presented only in tabular form. The thermal treatment results and the impact of pre-treatments for each sample are discussed in turn.

#### 4.1 Domtar Flare Pit Sludge

Seven experiments were performed using Domtar flare pit sludge, although results were obtained only from the last five. In the first two experiments, the excavated sludge was found to be so adhesive that it simply could not be fed into the desorber. Fortunately, the sludge was more manageable once it had been subjected to pre-treatment, which included a water rinse followed by aggregation, during which the sludge was blended with 3 wt% lime.

A summary of the results from both dried and re-hydrated aggregates is presented in Table 4-1, while the residual hydrocarbon concentration curve of dried aggregates treated at 400°C is shown in Figure 4-1. The highest degree of remediation achieved using dried aggregates was 1.33 %THC. This is more than thirteen times the Tier I Criteria, which for simplicity's sake is generally said to be 0.1 %THC, and is also shown graphically in Figure 4-1. The addition of 10 wt% water to re-hydrate the sludge aggregates was examined, since the steam generated by desorbing water is thought to promote desorption of other contaminants. Re-hydration increased contaminant removal by 13%, however, the hydrocarbon concentration of the treated sludge was still eight times the Tier I Criteria.

Analysis of the excavated flare pit sludge by Chemex Laboratories, showed a hydrocarbon concentration a little over 20 wt%. After pre-treatment, this concentration had dropped to 3.83 wt%. Apparently, the pre-treatment process had a larger impact on sludge remediation than did thermal desorption. About 80% of the hydrocarbons were removed during by washing and aggregation, while only an additional 15% were removed by desorption.

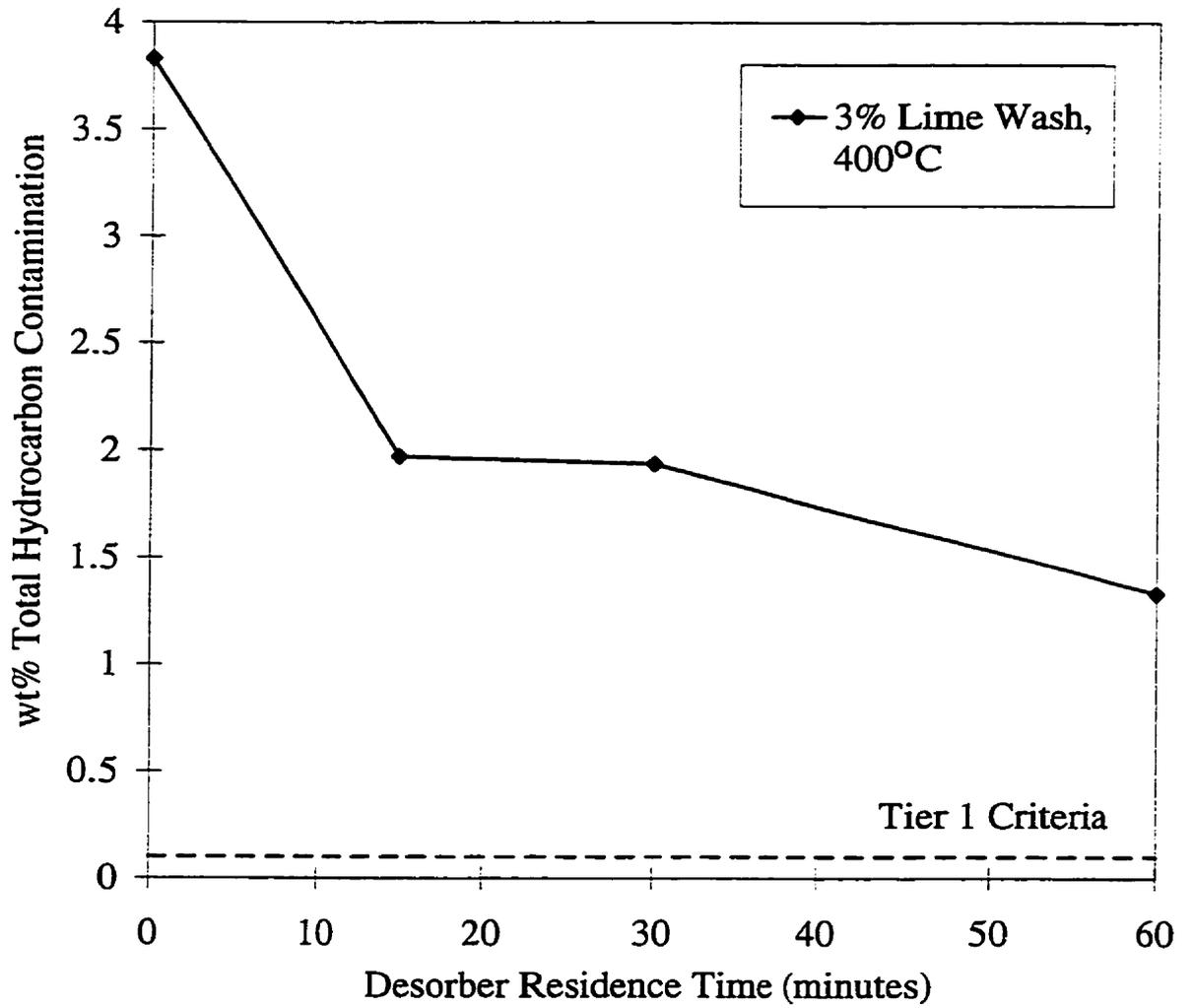


Figure 4-1: Domtar Flare Pit Sludge Residual Hydrocarbon Contamination

Table 4-1: Domtar Flare Pit Sludge Treatment Results

Sample Pre-Treatment	Temperature (°C)	Residence Time (minutes)	wt% THC
Untreated			3.83
3% CaCO <sub>3</sub> Addition	400	15	1.97
	400	30	1.94
	400	60	1.33
3% CaCO <sub>3</sub> and 10% Water Addition	400	30	1.44
	400	60	0.80

Soil washing with water is not frequently selected as a pre-treatment for soils with hydrocarbon contamination. In addition to the fact that hydrocarbons are not effectively removed using water, a water contamination problem is created once hydrocarbons have been washed from the soil. It would be preferable to avoid the use a water wash entirely. Ideally, the handling characteristics of the flare pit sludge could be sufficiently improved by aggregation and blending with lime alone, to be treated in the BTR.

Thermal desorption may not be the ideal treatment option for the Domtar flare pit sludge, since the contaminants included a significant number of hydrocarbons in the C30 to C60 range. Research has shown, that while volatile and semi-volatile organic compounds can be separated by thermal desorption, very heavy compounds are not effectively removed. An additional factor inhibiting desorption may have been the presence of humic material in the soil which sorbs contaminants closely and increase their effective boiling points. Based on the results from these experiments, it is unlikely that Tier 1 Criteria could be reached by desorption, even at slightly higher temperatures. Other treatment methods such as solvent washing or a combination of thermal desorption and stabilization, in which contaminant are immobilized by blending the soil with specialized additives, might be considered in order to successfully treat the sludge.

Analysis of the flare pit sludge also revealed high concentrations of several heavy metals including mercury. Thermal desorption is not effective for removing metals with the exception of mercury, which has a relatively high vapour pressure and so can be removed by thermal desorption. Thus another treatment technique would have to follow desorption in order to deal with the metal contamination. Although no mercury was observed in either of the condensers, it may have been desorbed by the BTR.

## 4.2 CanOxy Chlorinated Organic Soil

Despite the high moisture content of the CanOxy chlorinated organic soil, a preliminary BTR experiment established that the soil could easily be sucked into the desorber using vacuum. Since no soil pre-treatment was required, the experiments focused on the effects of desorber residence time and temperature. Table 4-2 summarizes the treatment results for the two temperatures and three residence times examined.

Table 4-2: CanOxy Chlorinated Organic Soil Treatment Results

Temperature (°C)	Residence Time (minutes)	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

At a desorber temperature of 400°C, remediation to Tier 1 Criteria for hydrocarbons was reached after 30 minutes. At 500°C, the hydrocarbon concentration had dropped to 0.028 %THF, one fifth of the Tier 1 Criteria, in just 15 minutes. Analysis

of the soil found that chlorophenols were the main source of contamination. These semi-volatile organic compounds have boiling points in the range of 200 to 300°C, and so were easily desorbed at 400 and 500°C. From the residual hydrocarbon concentration curves in Figure 4-2, it is apparent that the vast majority of contaminants on the soil are quite volatile and desorb rapidly. A small portion of the contaminants, however, continue 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, since there is very little difference between the concentrations at 30 and 60 minutes. If this is the case, a higher desorber temperature would be required to remediate beyond this level.

In Figure 4-2, there is some uncertainty associated with the desorption rates at both 400 and 500°C during the first 15 minutes. The straight lines joining the initial concentration at time zero to those at a residence time of 15 minutes could be considered a 'worst case scenario', in which the hydrocarbons desorb at the slowest possible rate. The hydrocarbon concentrations likely drop off in a curve, in which the rates of desorption are much faster during the first few minutes than that shown. Residual hydrocarbon concentrations were not examined at residence times shorter than 15 minutes, since the purpose of these experiments was to determine treatment conditions under which Tier 1 Criteria could be achieved. The remainder of the residual hydrocarbon contamination graph, between residence times of 15 and 60 minutes, is a more accurate representation of the desorption rate.

A high electrical conductivity of 5.4 meq/100g, more than twice the Tier 1 Criteria, was also detected in the CanOxy soil. Electrical conductivity measurement is a standard technique, high values usually indicate the presence of a high salt concentration. This secondary source of soil contamination cannot be managed by thermal desorption, however, since thermal desorption clearly managed the hydrocarbon contamination, a treatment train including desorption followed by soil washing might be considered.

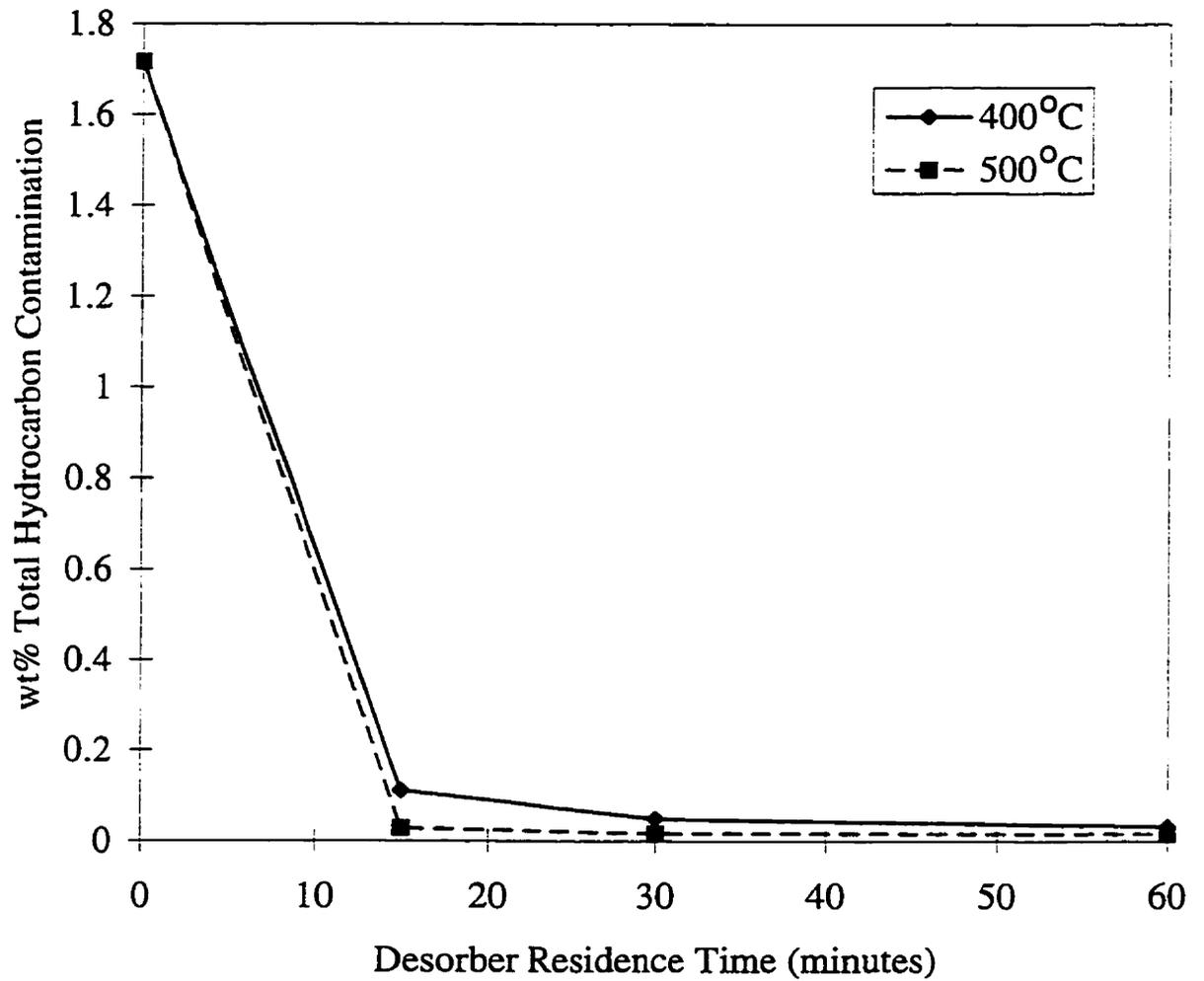


Figure 4-2: CanOxy Chlorinated Soil Residual Hydrocarbon Contamination

### 4.3 Amoco Activated Carbon

BM Ecos wanted to investigate the feasibility of using treated Amoco activated carbon as a soil amendment. 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 semi-volatile compounds such as xylene and phenol. A series of seven experiments at residence times of 15, 30 and 60 minutes, and temperatures of 400 and 500°C looked at the effect of these two parameters on level of remediation.

The treatment results presented in Table 4-3 show that only at the most stringent conditions, 500°C for 60 minutes, were Tier 1 Criteria met. The residual hydrocarbon concentration curves are shown in Figure 4-3. Like the CanOxy soil, the majority of contaminants were desorbed during the first few minutes. This is consistent with the preponderance of relatively low boiling point compounds on the sample, however, after the bulk of the material has desorbed, hydrocarbons desorption progressed at a much slower rate. Again, there is uncertainty associated with the shape of the desorption rates in the first 15 minutes, and the contaminants likely desorb at a faster rate than that shown.

Table 4-3: Amoco Activated Carbon Treatment Results

Temperature (°C)	Residence Time (minutes)	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

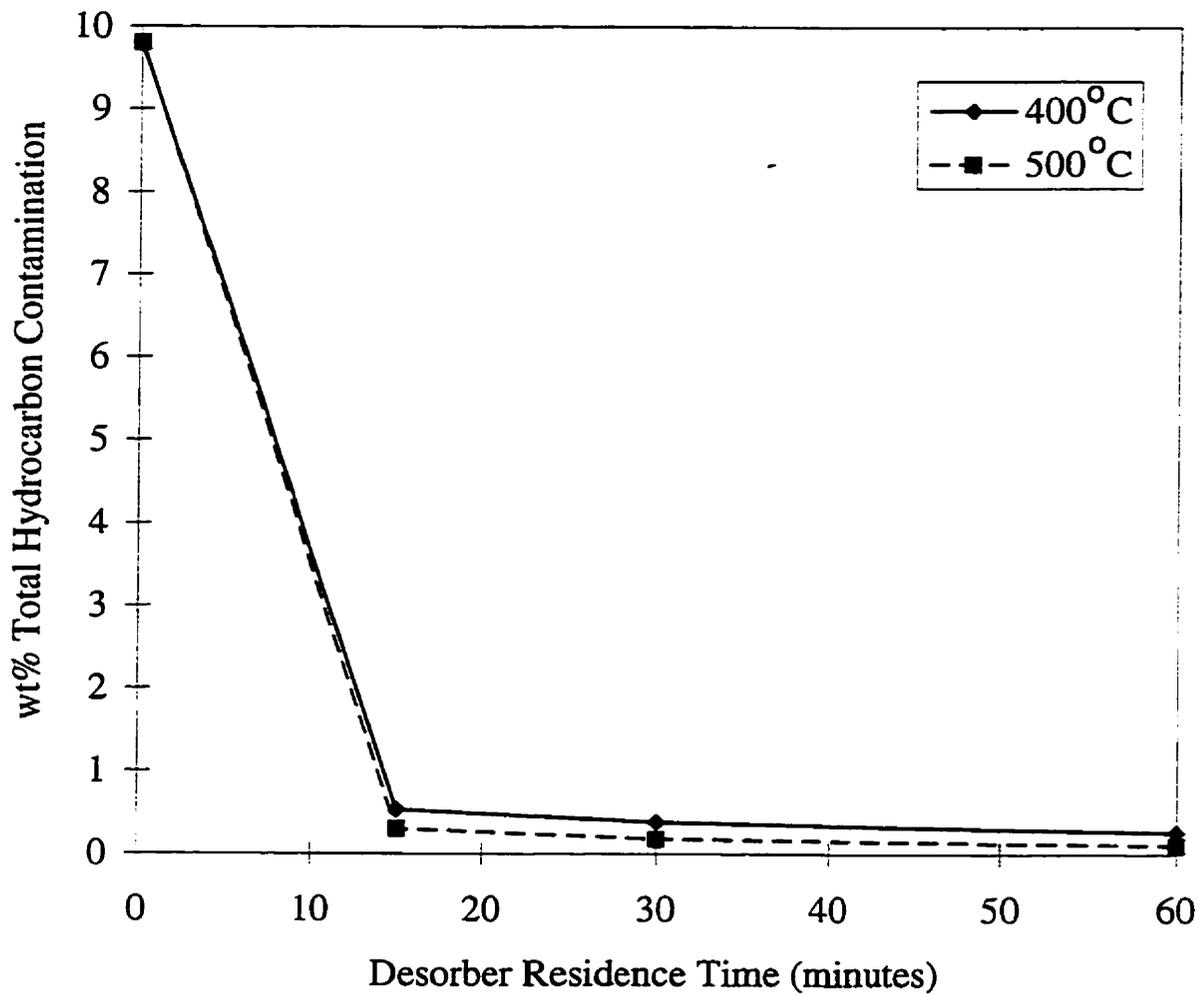


Figure 4-3: Amoco Activated Carbon Residual Hydrocarbon Contamination

There are a couple of plausible explanations for the rapid change in desorption rates, and the contaminants that are slowly removed. One possibility is that the sample contains a few heavy hydrocarbons, which desorb at a slower rate, while another is that the desorption rate is 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 time would result in further desorption from the activated carbon, since the hydrocarbons diffuse through the particle rather than form a miscible mixture.

According to these results, BTR treated Amoco activated carbon would be suitable for use as a soil amendment. The sample would also have to be checked for other types of contamination, however, particularly heavy metals.

#### **4.4 PanCanadian Produced Sand**

More than 25 experiments were performed using pre-treated PanCanadian produced sand. Preliminary experiments demonstrated that the sand required pre-treatment to improve its handling characteristics. For this set of experiments, BM Ecos was most concerned with the effect of several sample pre-treatments, including water rinses, water washes with agitation, and the addition of lime ( $\text{CaCO}_3$ ) in three concentrations. BTR variables of temperature and residence time were not well examined in this case, since multiple experiments were performed at the same conditions with different samples.

A summary of the treatment results, including pre-treatment method, residence time and temperature, for all six pre-treated samples is presented in Table 4-4. The sand was successfully remediated to Tier 1 Criteria, 0.1 %THC, in more than half of the experiments. Rinse temperature and lime blending both had an impact on the level of

Table 4-4: Produced Sand Treatment Results

Sample Pre-Treatment	Temperature (°C)	Residence Time (minutes)	wt% THC
Untreated			1.01
Untreated 30 minute Wash + 4% CaCO <sub>3</sub>			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 <sub>3</sub>	400	30	0.23
	400	60	0.107
Cold Rinse + 3.0% CaCO <sub>3</sub>	400	30	0.152
	400	60	0.106
Cold Rinse + 4.0% CaCO <sub>3</sub>	400	15	0.292
	400	30	0.093
	400	60	0.058
30 minute Cold Water Wash	400	30	0.021
30 minute Cold Wash + 4% CaCO <sub>3</sub>	400	15	0.027
	400	30	0.015
	400	60	0.021

remediation. For instance, the switch from cold to hot water rinse resulted in an overall contaminant removal increase of 7 %THC. Meanwhile, the decision to add 4 wt% lime resulted in a twofold decrease in the hydrocarbon concentration over simple cold water rinsing.

Agitation also had a significant impact on the level remediation achieved. Among the pre-treatments examined, the cold water washes with agitation produced treated sand with the lowest residual hydrocarbon concentrations. Sand that was washed and blended with 4% lime even met Tier 1 Criteria 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.

Pre-treatment was deemed necessary, however, 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 found that contamination was limited to hydrocarbons in the C15 to C29 range. These compounds are easily managed by thermal desorption, particularly since the sand is a non-porous, non-organic material so that neither pore diffusion, nor sorption to humic material is a factor. Unfortunately, no experiments were performed on untreated sand samples to see if Tier 1 Criteria could be met by desorption alone.

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 one half that of the same sample treated at 400°C. The impact of desorber temperature and residence time may be at least as important as the sample pre-treatment method. Perhaps a viable pre-treatment 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.

#### **4.5 Weyerhaeuser Dioxin/Furan Pulp Sludge**

Several attempts were made to treat the Weyerhaeuser dioxin/furan pulp sludge. In all of four experiments performed at 400°C, the screened and dried pulp sludge ignited upon introduction into the desorber. Although thermal desorption of some contaminants appears to have occurred along with the removal of all moisture, even the addition of 10 wt% lime did nothing to prevent the sludge from burning. The production of a large quantity of non-condensable gas was measured by the wet test meter. A significant portion of the gas was likely CO<sub>2</sub>, resulting from the combustion of wood fibers, however, combustion sources may well have included some of the sludge's organic contaminants. In addition, dark smoke was visible passing through the glass vacuum trap. The production of smoke and gas stopped after about 30 seconds in each case, probably as all oxygen was consumed. When the product discharge valve was opened, however, the pulp re-ignited inside the desorber and dropped onto the dry ice in flames. The 'treated' sludge was nothing but ash.

From these experiments, it is apparent that pulp fibers are simply too flammable to be treated using the BTR. Not only does a small amount of oxygen enter the desorber with the sample, but on discharge it must come in contact with the air. Perhaps another thermal desorption process, one using an inert gas blanket, would be able to treat extremely flammable samples such as pulp sludge.

## 4.6 Summary

Determining the feasibility of treating the five industrial samples using the BTR was the primary concern of this set of experiments. A method was devised to treat four of the five samples. The fifth sample, Weyerhaeuser dioxin/furan pulp sludge, was found to be unsuitable for treatment using the BTR, since the pulp fibers ignited in the desorber.

The treatment goal for each of the four remaining samples, which included two soil, one sand and one activated carbon, was to find a method by which Alberta Tier 1 Criteria could be achieved. Three samples including CanOxy chlorinated organic soil, Amoco activated carbon, and PanCanadian produced sand were successfully remediated to Tier 1 Criteria. Both the CanOxy soil and Amoco activated carbon were treated by desorption alone, while experiments on the produced sand focused on the effects several pre-treatments. The Domtar flare pit sludge proved much more difficult to remediate. Given that the lowest hydrocarbon concentration achieved was still eight times the Tier 1 Criteria, other treatment methods such as stabilization might be considered.

Both the Domtar flare pit sludge and the PanCanadian produced sand required pre-treatment prior to thermal desorption in order to feed the samples into the desorber. In both cases, a preliminary water wash removed a significant portion of the hydrocarbon contamination. Although these pre-treatments improved the handling characteristics of both samples, other pre-treatment methods such as aggregation and lime blending should be considered in order to avoid the generation of hydrocarbon contaminated water.

## CHAPTER FIVE

### RESULTS AND DISCUSSION: PREPARED SAMPLES

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The results of BTR experiments performed on prepared PAH contaminated samples are presented in this chapter. The experimental method, along with the results from each of the three samples is discussed. This series of simple experiments on two solids contaminated by 50:50 binary mixtures of PAHs illustrates 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, are examined. In contrast to the set of experiments described in Chapter 4, in which the object was to study BTR effectiveness for treating several typical industrial samples to Alberta Tier 1 Criteria, the experiments on prepared samples were designed to investigate the fundamentals of the thermal desorption process.

#### 5.1 Experimental Program

Details on the preparation of the samples are discussed in Chapter 3. Essentially the same method was used to treat both the sand and activated carbon samples, although different desorber temperatures were chosen for each of the two mixtures of PAHs.

In order to get an idea of the effect of temperature on desorption, three desorber temperatures were chosen on the basis of the PAHs 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, whose normal boiling points are 298 and 340°C and bubble points at 0.5 atm are 267 and 306°C respectively, 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, with normal boiling points of 218 and 340°C and bubble points at 0.5 atm of 188 and 305°C respectively.

Desorber residence times of 10, 20, 40 and 60 minutes were used throughout the experiments. The effective time spent at each temperature is reduced by sample heat up time, the impact of which is most significant in experiments with very short residence times. In order to reduce the time to reach temperature, relatively small amounts of sample were used. Prepared sand samples of approximately 250 g, and prepared activated carbon samples of 125 g, since the density of activated carbon is much lower than that of sand, were used.

Since there was little water associated with either of the samples, they dropped easily into the desorber in less than 5 seconds. Desorbed contaminants were drawn out of the BTR through the heat traced exit line and into the primary trap where they were condensed. The exit line was maintained at temperatures above the melting points of the PAHs to prevent them from condensing in the line, 150°C for naphthalene-phenanthrene contaminated samples, and 250°C for anthracene-fluorene contaminated samples. Glass wool blocked the trap exit to keep condensed PAHs, usually fine crystals, from being drawn out of the trap.

The mass of desorbed PAHs collected in the primary trap was measured at the end of each experiment, both to measure the desorption efficiency as a function of temperature and residence time, and to close the mass balance. The composition of PAHs

desorbed from samples treated for 60 minutes 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.

A total of fourteen 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 less than 10% in each case, clearly demonstrating the reproducibility of the experimental results. The mass of desorbed PAHs condensed in the primary trap, however, varied as much as 50%, although the relative amounts of PAHs appeared to be unaffected. For each sample, the residual PAH concentrations at all three desorber temperatures are plotted on a single figure as a function of residence time.

## **5.2 Naphthalene-Phenanthrene Contaminated Sand**

Medium-coarse grain sand ( $d_p = 369 \mu\text{m}$ ) was chosen to represent a non-porous contaminated material, in which contaminants are not tightly bound, but rather are physically attached to the particle surface. Thus, PAHs would be easily desorbed from the sand.

The naphthalene-phenanthrene mixture was dissolved in methylene chloride in order to contaminate the sand to 5 wt%, and to distribute the PAHs evenly over the surface of the grains of sand. Although the PAHs were successfully sorbed to the surface of the sand, a portion of the material crystallized onto every other available surface. Despite repeated efforts to promote sorption to the sand alone, the maximum PAH concentration achieved, which may represent complete coverage of the sand surface, was 3.1 wt%. Soxhlet extraction followed by GC analysis showed that the sand was

contaminated by approximately equal amounts of both PAHs. While the sand was kept in a sealed container, the PAH concentration dropped from 3.14 wt% to 3.08 wt% over the course of the experiments. An intermediate value of 3.1 wt% has been used as the initial concentration.

Figure 5-1 shows the residual PAH concentration plotted as a function of residence time at the three desorber temperatures, 150, 250 and 350°C. Although most visible in the 150°C curve, all three curves show that the effect of increasing 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 desorber temperature, was to significantly reduce 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, since PAHs were condensed in the primary trap, however, at each temperature the mass of PAHs captured did not account entirely for the drop in 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 desorber temperatures investigated. Occasionally while cleaning out the BTR between runs, small lumps of PAHs would be 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 were removed in the first 10 minutes. After 60 minutes, the residual PAH concentration had dropped to 0.57 %THC. Analysis by GC on a weight basis showed that naphthalene represented 98% of the PAHs condensed in the primary trap, which demonstrates that the lighter hydrocarbon was more easily desorbed. The effect of

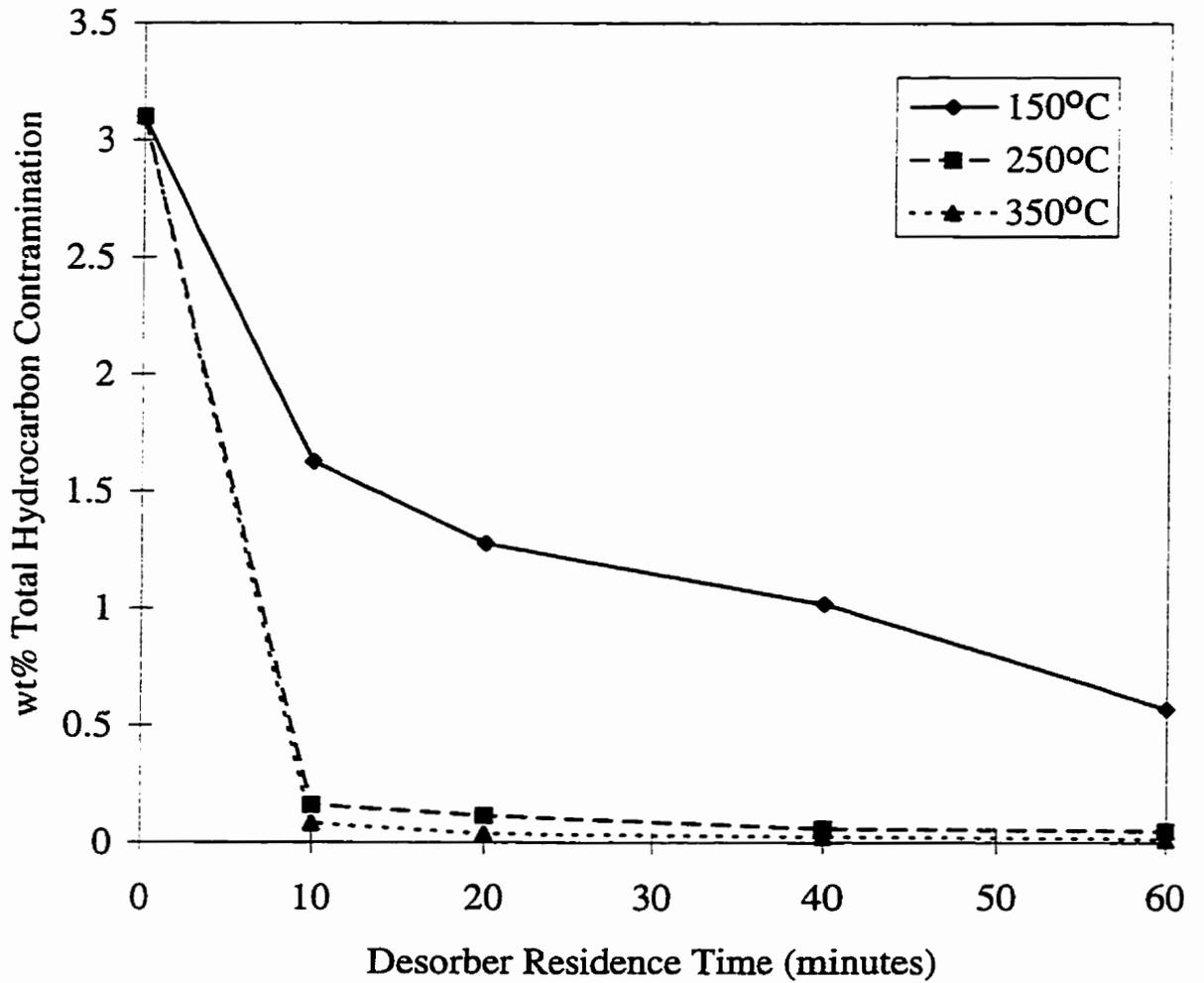


Figure 5-1: Naphthalene-Phenanthrene Contaminated Sand  
Residual Hydrocarbon Contamination

contaminant loss due to melting was striking at both 250 and 350°C, and resulted in extremely low residual PAH concentrations after only 10 minutes. 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.

There some uncertainty in Figure 5-1 associated with the shape of the 250 and 350°C residual PAH concentration curves during the first 10 minutes. The straight line joining the PAH concentration at time zero to that at a residence time of 10 minutes, represents the slowest case of contaminant removal. The PAHs are likely removed at a much faster rate, which would be depicted by a curved profile during these first few minutes. The data gathered is inadequate to define the curve in this region, however, since it is difficult to get reliable data for residence times shorter than 10 minutes. The impact of sample heat up time is particularly significant at such short residence times, and the actual sample temperature may be below the desired desorption temperature for a large portion of the residence time, leading to inaccurate results.

The results of these experiments confirm that both increasing desorber residence time and temperature reduce the residual PAH concentration. It was also found that the contaminants were not tightly sorbed to the surface of the non-porous sand particles, since the PAHs both desorbed off the surface and were 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.

### **5.3 Anthracene-Fluorene Contaminated Sand**

Sand was also contaminated with a binary mixture of anthracene and fluorene. Due to low solubility of anthracene in methylene chloride, a PAH concentration of 2 wt%

was used. Unlike the naphthalene-phenanthrene sand, no problem with losses of PAHs due to crystallization onto other surfaces was found. Virtually all of the PAHs sorbed to the surface of the sand, resulting in a concentration of 1.99 wt%. A second Soxhlet extraction revealed that the PAH concentration had not dropped at all over the course of these experiments.

Residual PAH concentration curves are shown in Figure 5-2 as a function of 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, and so liquefy at all desorber temperatures chosen. Since the contaminants are not tightly sorbed to the sand surface, the PAHs melted and drained off the sand. As before, small lumps of PAHs encased in sand were occasionally washed from the BTR. Artificially low residual PAH concentrations were particularly notable at both 320 and 350°C, not only because of the extremely rapid PAH loss, but because the mass of PAHs condensed in the primary trap was much lower than that lost in the desorber. As with the naphthalene-phenanthrene sand residual PAH concentration curves, there is uncertainty in the desorption rate within the first 10 minutes, particularly for the 320 and 350°C curves. The actual rate is likely much faster than that shown in Figure 5-2, which could be considered a 'worst case scenario' for PAH removal.

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,

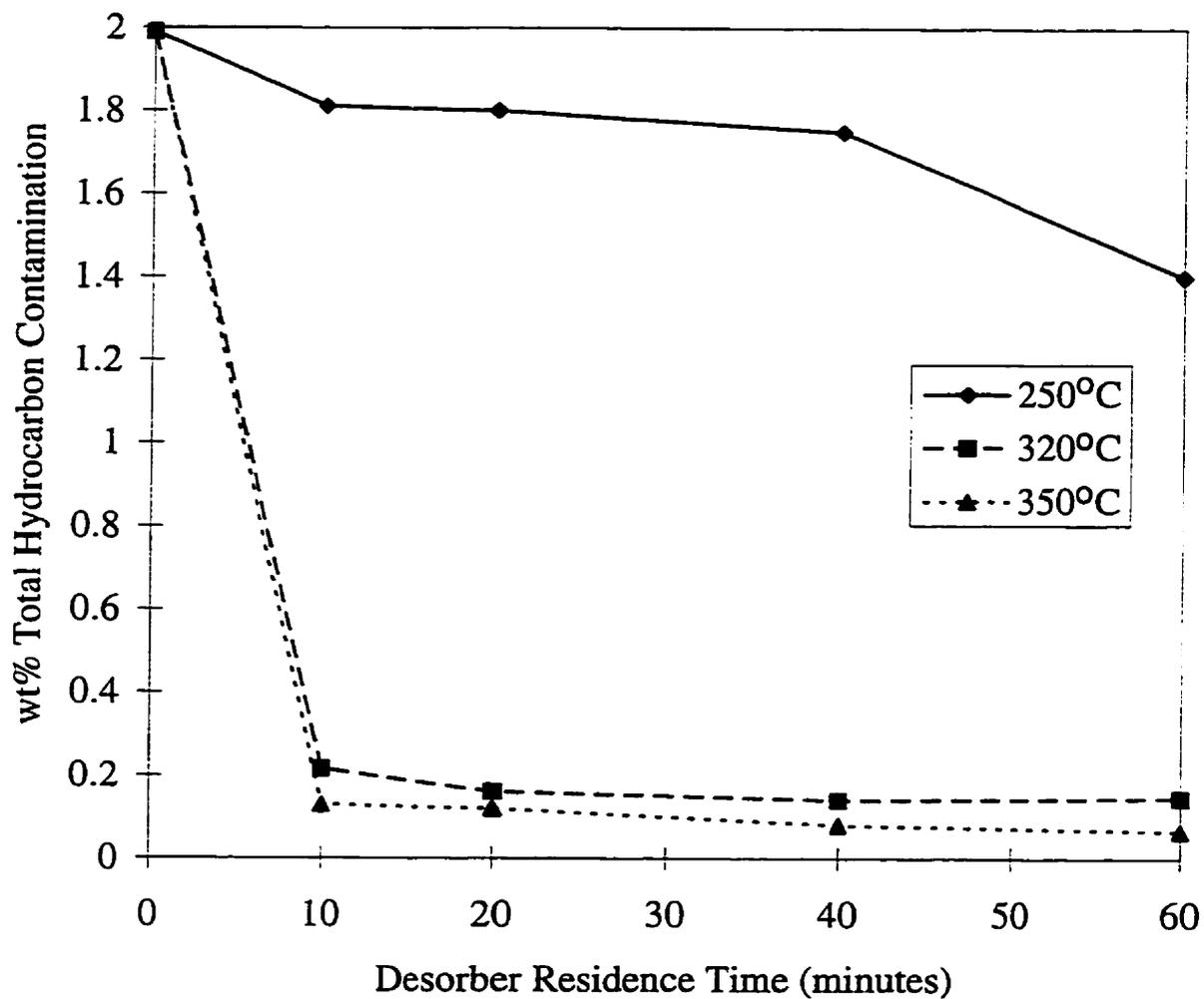


Figure 5-2: Anthracene-Fluorene Contaminated Sand  
Residual Hydrocarbon Contamination

the PAH concentration dropped to 0.22 %THC in the first 10 minutes, and for the next 50 minutes continued to fall at a much slower rate. 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, the PAH concentration falling to 0.13 %THC in the first 10 minutes.

The same qualitative results were obtained from both sand samples. The PAHs, anthracene and fluorene in this case, are not tightly bound to the surface of the sand grains, and so both desorb and melt off the sand. While increasing residence time and desorber temperature were found to reduce the residual PAH concentration, melting losses led to artificially low PAH concentrations on the sand, particularly at higher temperatures.

#### **5.4 Naphthalene-Phenanthrene Contaminated Activated Carbon**

The results from the naphthalene-phenanthrene contaminated activated carbon experiments are extremely 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 and sorb into the pores of the activated carbon particles. Although the activated carbon was contaminated to 5 wt% as the naphthalene-phenanthrene sand had been, there was no problem with PAH crystallization on other surfaces. A Soxhlet extraction of the contaminated activated carbon confirmed that virtually all of the PAHs were sorbed onto the activated carbon. Results from two Soxhlet

extractions both showed that the PAH concentration was 4.92 wt%, and thus very little of the PAHs were lost over the course of the experiments.

Figure 5-3 shows the residual PAH concentrations at desorber temperatures of 150, 250 and 350°C. As expected, the profiles show decreasing PAH concentration with increasing desorber residence time and temperature. What is interesting about the figure, however, is that the profiles corresponding to the activated carbon differ so much from those corresponding to the sand. Not only does the PAH concentration at each temperature drop slowly and steadily over the 60 minutes, the 250°C concentration profile falls evenly between the other two, rather than following the 350°C profile as it did in the case of contaminated sand. The differences between the residual hydrocarbon 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 remained in the pores, rather than draining away. It should also be noted, that unlike the contaminated sand samples, there is little uncertainty in the initial desorption data. The residual PAH concentration curve is well defined by the data gathered.

At all of the desorber temperatures, the mass of desorbed PAHs condensed in the primary trap, while typically a bit smaller, was quite close to the mass lost by the activated carbon sample. Thus, desorption was the main mechanism of PAH removal from the activated carbon. At 150°C, naphthalene represented over 99 wt% of the desorbed PAHs, since 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.

These results demonstrate that sample porosity has a limiting effect on the removal of PAH contaminants, if only in that the pores hold melted compounds on the sample. Since desorption was the only mechanism for PAH removal from the activated

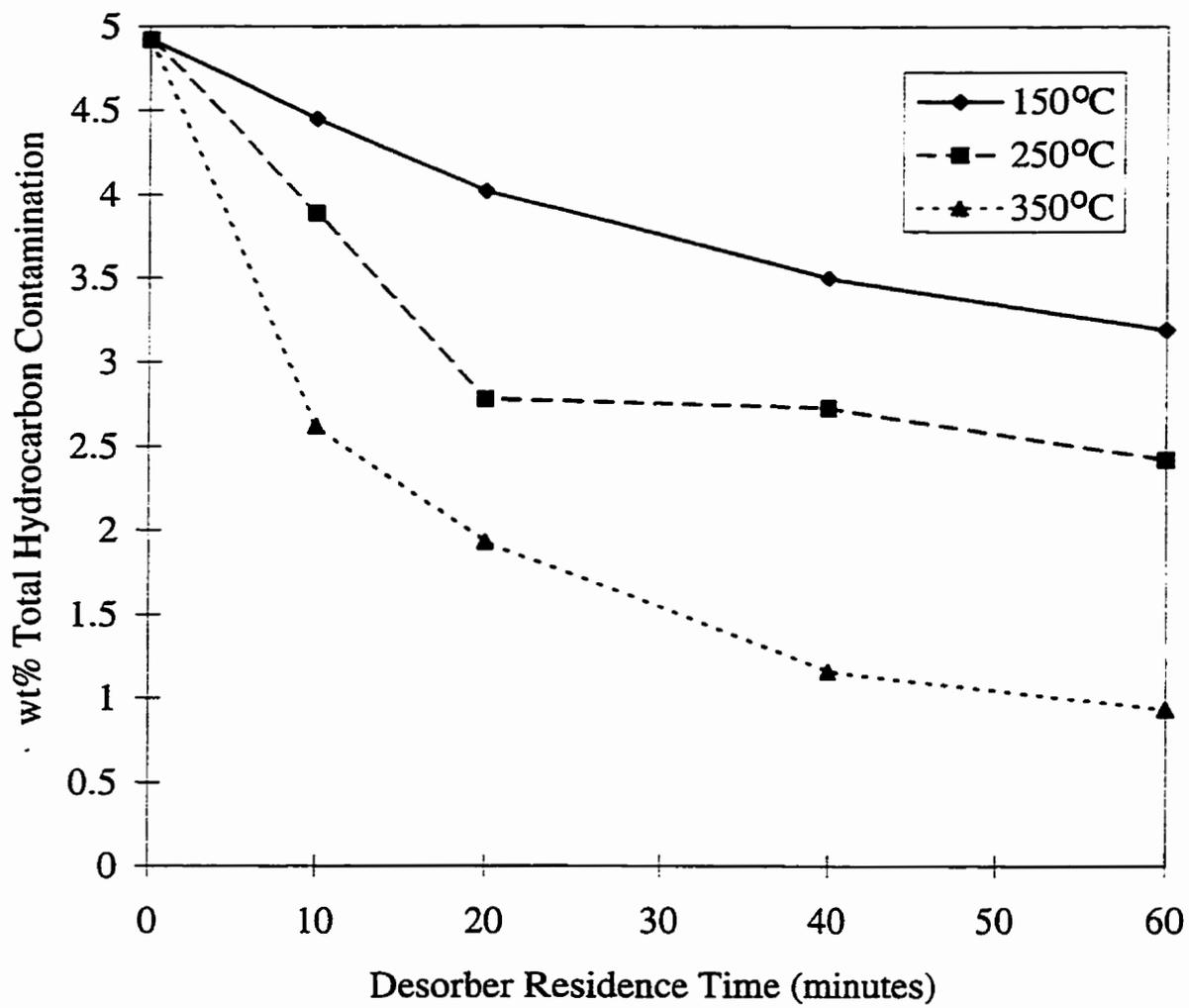


Figure 5-3: Naphthalene-Phenanthrene Contaminated Activated Carbon  
Residual Hydrocarbon Contamination

carbon, the effects of increasing temperature and residence time on desorption are plainly seen by comparing the residual concentration profiles. Diffusion of the naphthalene and phenanthrene through the activated carbon pores to surface prior to desorption likely played a role in reducing the desorption rate, however, the magnitude of the effect cannot be quantified based on these results. Thus, the overall rate of desorption is either a combination of both the desorption and diffusion rates, or is limited by one of the two rates.

Presumably, the effect of temperature is more predictable in the case of non-porous solids than it is in the case of porous solids, since desorption is a function of temperature, whereas diffusion is function of both temperature and pore characteristics. One would expect that the effect of temperature on non-porous solids, in which diffusion is not a factor, could be more easily predicted, and that the desorption rate at 250°C would fall approximately between the rates at 150 and 350°C. The effect of temperature on the combination of desorption and diffusion in porous solids is not likely to be linear, since the desorption rate will be affected by temperature in a different manner than will the diffusion rate. Thus, it is important to recognize that the effect of temperature on the apparent rate of desorption can be quite unpredictable, particularly from porous solids in which the rate of diffusion plays a role, or from soils with humic content, in which PAHs form miscible mixtures with the soil fraction.

## **5.5 Summary**

Using three prepared samples, the effects of contaminant molecular weight, desorber residence time, desorber temperature and sample porosity on desorption have been investigated. The impact of contaminant molecular weight was investigated using binary mixtures of PAHs with different molecular weights, and thus different boiling

points. In all cases, the lighter molecular weight compound desorbed first, and so represented the majority of the PAH mixture condensed in the primary trap.

The effect of increasing residence time varied in magnitude between the sand and activated carbon samples. While residual PAH concentrations dropped with increasing residence time throughout all the experiments, sand samples run at high temperatures did not show much increased desorption, because the vast majority of PAHs were removed during the first few minutes. The effect of residence time was more pronounced in the activated carbon sample, as the residual PAH concentration dropped slowly with increasing residence time.

The three temperatures chosen in each case, below, between and above the PAH boiling points, showed that increasing desorber temperature increased PAH removal. Increasing temperature affected more than the desorption phenomenon, however, as PAHs melted and drained off the sand at higher temperatures. The effect of temperature on desorption is easily seen in the activated carbon sample, where the three temperature curves are clearly separated. To maximize desorption, the desorber would ideally be operated above the boiling points of the contaminants.

Finally, sample porosity had a very pronounced impact on contaminant removal. Pore sorption in the activated carbon prevented melted PAHs from draining off the sample as they had off the non-porous sand. It was found that the PAHs were removed from the activated carbon by desorption alone. Since desorption was preceded by diffusion within the pores in the activated carbon, the rate of desorption off the non-porous material was faster than the rate off the porous material.

## CHAPTER SIX

### DESORPTION RATE CURVES AND SCALE-UP

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The BTR was developed as a bench-scale model of a mobile commercial thermal desorber that BM Ecos intends to build for onsite treatment of contaminated wastes. Scale-up from the BTR directly to the commercial unit was initially considered, however, a pilot plant desorber will be needed since proposed designs for the proposed commercial scale unit differ from the BTR in a couple of fundamental ways. Although the commercial designs include a desorber operated under vacuum, very similar to the BTR, a pre-heat desorber, where water and other light compounds will be removed, is incorporated. The most significant proposed design change however, is that the auger design would allow the desorber to operate either batch-wise or continuously. Clearly a pilot-scale unit is needed in order to ensure that remediation goals could still be achieved using one of the new designs.

A simple parameter, desorption rate, was chosen in order to get an idea of how the BTR might operate on a larger scale. For very common desorber configurations, such as rotary kiln, generalized scale-up correlations are available. Since the BTR design is quite unique, the results of such correlations would be of little use. Desorber scale-up is, in most other cases, based either on geometric similarity or on mass and heat transfer rates coupled with data on gas flow rates and desorption rates. While scale-up based on geometric similarity is relatively straight forward, the results would be unpredictable, given that the geometry of the commercial unit will not be the same at that of the BTR, so

mixing and heat transfer characteristics might be quite different. The last approach, based on mass and heat transfer rates, requires certain modifications in order to be applicable to the BTR. Since the BTR is operated under vacuum, there isn't gas flow in the conventional sense, the flow consisting only of desorbed contaminants. Therefore, the mass transfer rate is actually a desorption rate. In order to provide a simple basis for desorber scale-up, desorption rate curves were generated from residual hydrocarbon concentration data.

This chapter looks at the desorption rate curves for three of the five industrial samples, and all of the prepared samples. The physical significance of desorption rate parameters and the temperature dependence of the desorption rate are also examined. Finally, the scale-up of the BTR to a proposed commercial scale desorber is discussed.

## 6.1 Mathematical Foundation

The following mathematical analysis was used to generate desorption rate profiles in terms of contaminant concentration. Based on the remediation results presented in Chapters 4 and 5, distinct desorption rate profiles could be generated for each sample at the temperatures investigated. Although four or more contaminant concentration data points at different residence times provide a more statistically significant fitted equation, a minimum of three points is required. Thus, contaminant desorption rate profiles were determined only for samples treated at a minimum of three residence times.

The residual hydrocarbon concentration versus desorber residence time curves were all exponential. The data was fit using non-linear least squares regression to an exponential decay equation of the form:

$$\text{Total Residual Contamination} = c = a \exp(-bt^n) \quad (6-1)$$

using Sigma Plot, a mathematics and statistics software package.

In equation 6-1, parameters  $a$ ,  $b$  and  $n$  all have meaning. Parameter  $a$  represents the amplitude of the function, or in this case, the initial contaminant concentration. Parameter  $b$  represents the rate of decay of the function. This parameter has particular physical importance for desorption, since the rate of decay or contaminant removal rate is affected by temperature. 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. 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 decay the faster than exponential, and, if  $n$  is less than 1, the decay is slower than exponential. The effect of parameter  $n$  can be seen in Figure 6-1, in which residual hydrocarbon contamination is plotted on a semi-log graph as a function of residence for each of the three cases of values for parameter  $n$ .

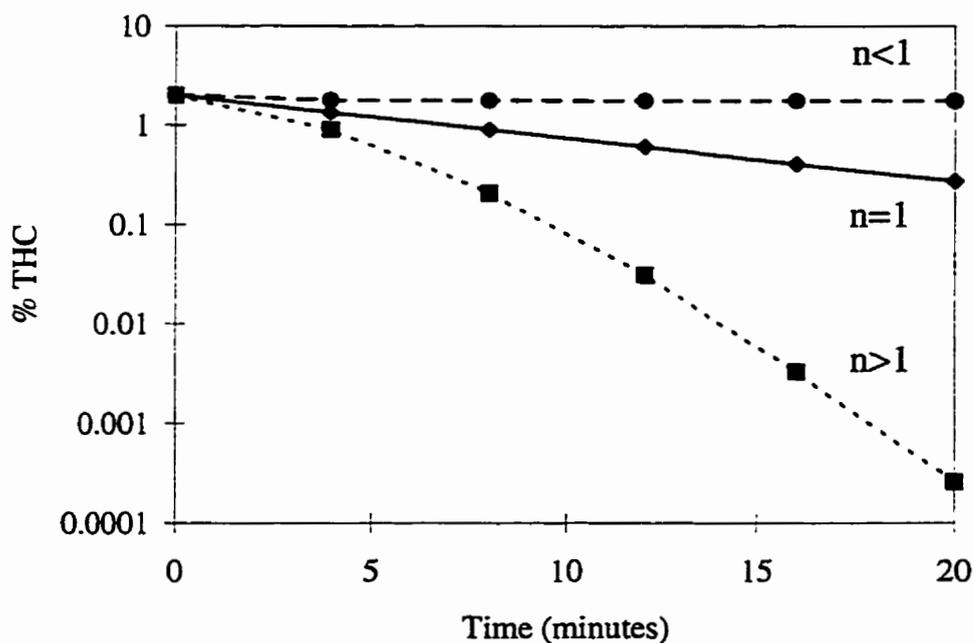


Figure 6-1: Effect of Parameter  $n$  on the Shape of Desorption Curves

In order to determine the desorption rate, equation 6-1 is differentiated from the logarithmic form:

$$\ln c = \ln a - bt^n \quad (6-2)$$

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

$$-\frac{dc}{dt} = cbnt^{n-1} \quad (6-3)$$

To convert the desorption rate in equation 6-3 from an expression in terms of both contaminant concentration and residence time, to one which is a function only of contaminant concentration, a substitution is made for  $t$ . Re-arranging equation 6-2 we get an expression for  $t$  in terms of concentration:

$$t = \left( -\frac{1}{b} \ln \frac{c}{a} \right)^{\frac{1}{n}} \quad (6-4)$$

An expression for the desorption rate in terms of contaminant concentration is obtained by substituting equation 6-4 into the desorption rate equation, 6-3:

$$\text{Desorption Rate} = -\frac{dc}{dt} = bnc \left[ -\frac{1}{b} \ln \frac{c}{a} \right]^{\frac{n-1}{n}} \quad (6-5)$$

The desorption rate from equation 6-5, plotted as a function of contaminant concentration, gives the instantaneous desorption rate at any given concentration. Perhaps a more valuable tool is the generalized exponential decay equation 6-2, which is applicable to any type of desorption system. Given the experimentally evaluated parameters  $b$  and  $n$ , one can use equation 6-2 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 Alberta Tier 1 Criteria. It should be noted, that although the temperature dependence of parameter  $b$  is discussed in detail, both parameters  $b$  and  $n$  are functions of desorber temperature. Due to 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.

## 6.2 Industrial Samples

Desorption rate curves were generated for three of the five industrial samples based on the residual hydrocarbon concentration results presented in Chapter 4. Although many experiments were performed using PanCanadian produced sand, the experiments focused on the effect of pre-treatment, and so didn't cover the necessary three residence times at a single temperature. Sufficient data existed to generate desorption rate curves for Domtar flare pit sludge, CanOxy chlorinated organic soil, and Amoco activated carbon.

The fit of the data generated by the exponential decay equation to the experimental data from the CanOxy chlorinated organic soil treated at 400°C is shown in Figure 6-2. As was discussed in Chapter 4, there is uncertainty associated with the desorption rate during the first 15 minutes. The hydrocarbon concentration likely decreases at a faster rate than is indicated by the straight line joining the initial concentration to the residual concentration after 15 minutes. The data generated by the fitted exponential decay equation show a much faster rate of desorption during the first few minutes, which quickly drops off in a curve, rather than linearly. A similar relationship between the experimental data and the fitted data was found for the Amoco activated carbon, and for the CanOxy soil treated at 500°C. Figure 6-3 shows a comparison of the data generated by the exponential decay equation to the experimental data from the Domtar flare pit sludge treated at 400°C.

The desorption rate curve for Domtar flare pit sludge, washed and blended with 3% lime, and treated at 400°C is shown in Figure 6-4 for relatively high hydrocarbon concentrations, and Figure 6-5 is a magnification of Figure 6-4 at relatively low hydrocarbon concentrations. Although a second pre-treatment, which included re-hydration of the sludge aggregates with 10 wt% water, was investigated, the residual

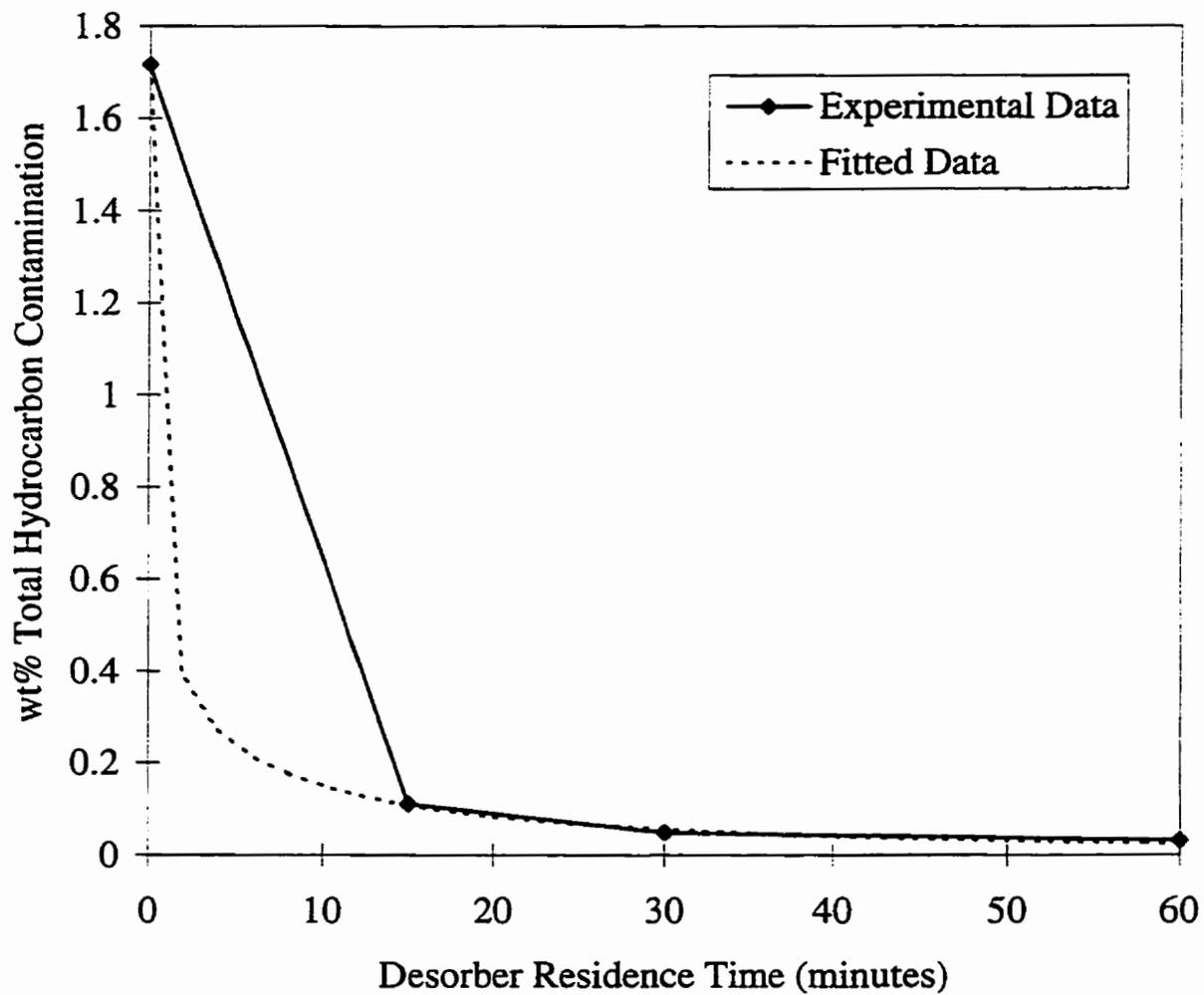


Figure 6-2: Comparison of Experimental and Fitted Data for CanOxy Chlorinated Organic Soil Treated at 400°C

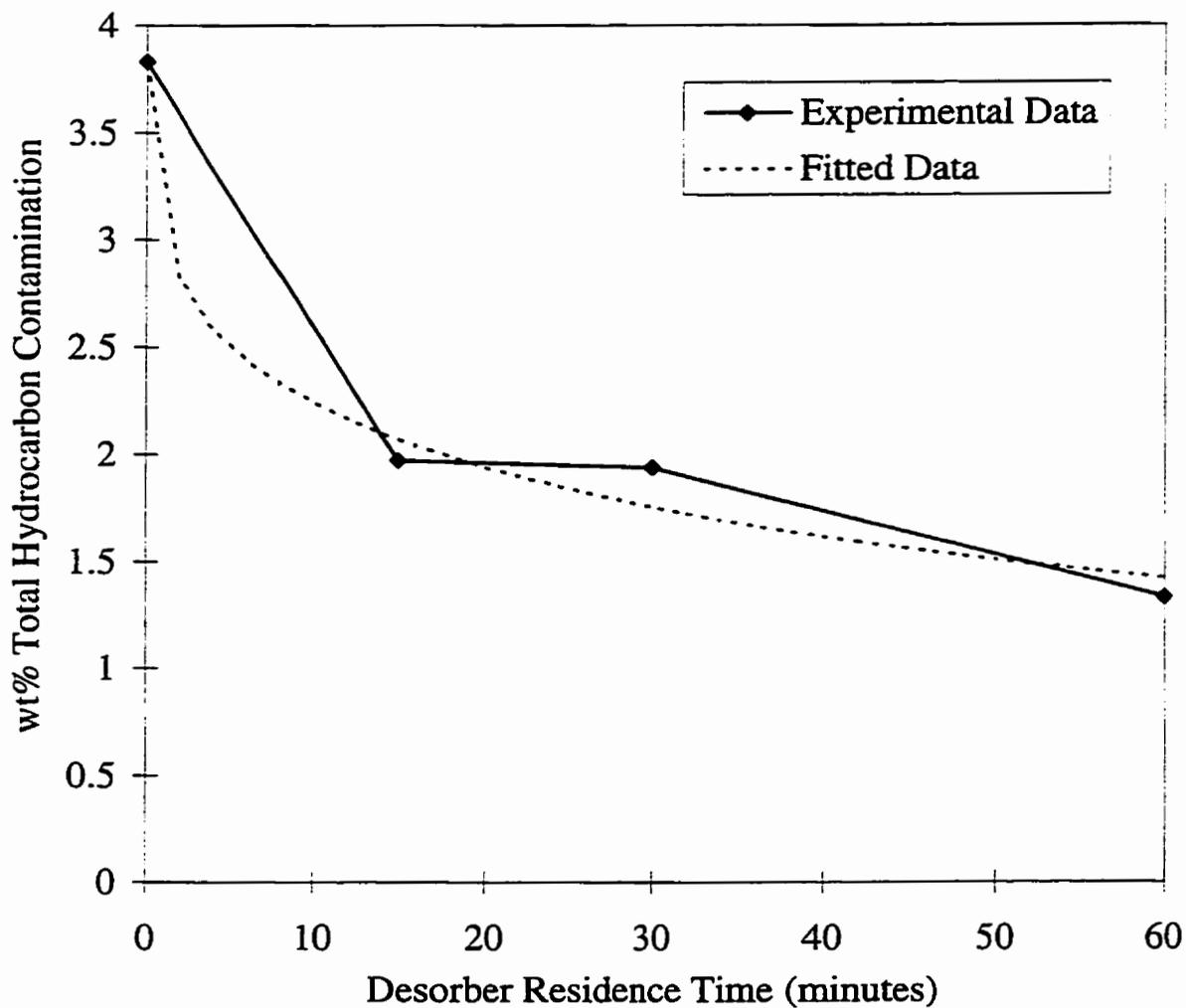


Figure 6-3: Comparison of Experimental and Fitted Data for 3% Lime Wash  
Domtar Flare Pit Sludge Treated at 400°C

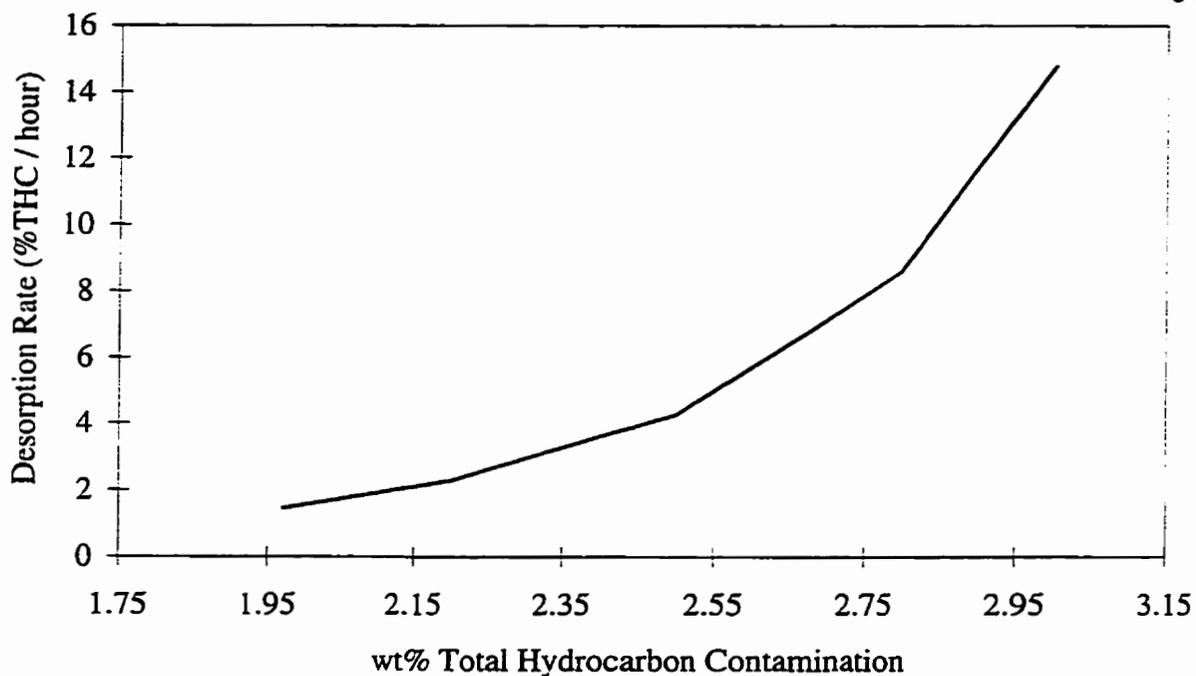


Figure 6-4: Domtar Flare Pit Sludge Desorption Rate Curve for High Hydrocarbon Concentrations

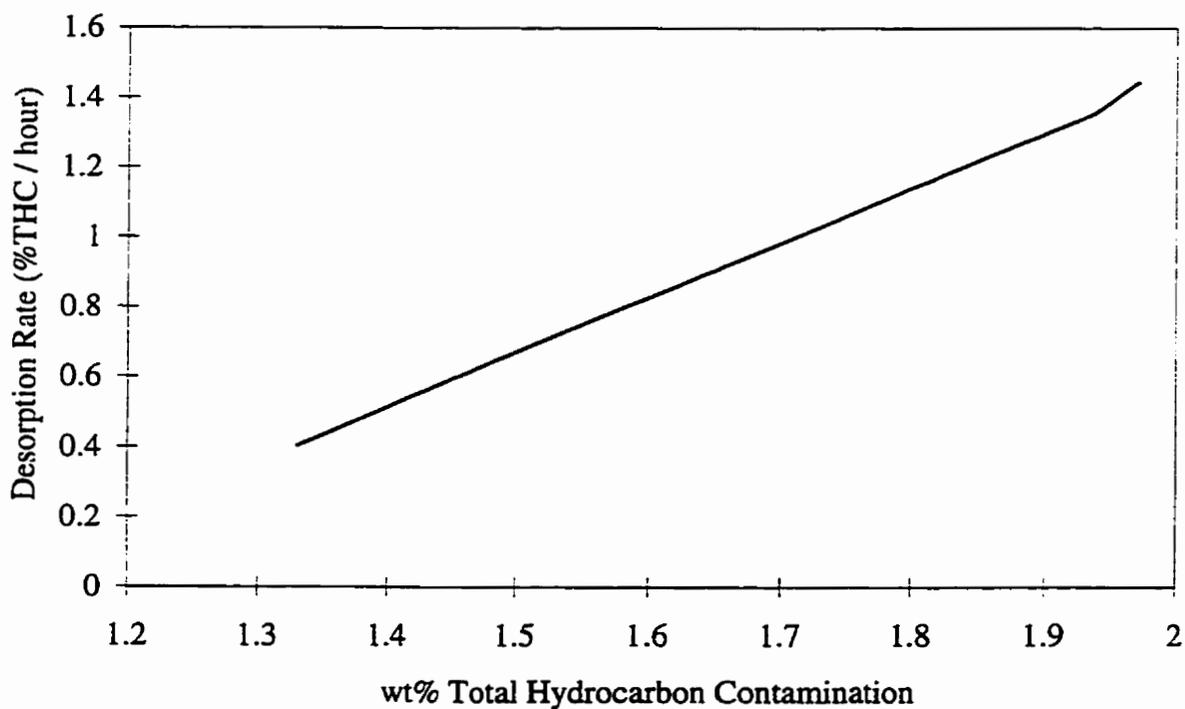


Figure 6-5: Domtar Flare Pit Sludge Desorption Rate Curve for Low Hydrocarbon Concentrations

hydrocarbon concentration at only two residence times was determined. The hydrocarbon concentration after pre-treatment was 3.83 %THC, and the highest degree of remediation achieved for plain aggregates was only 1.33 %THC. The exponential decay equation parameters,  $a$ ,  $b$  and  $n$ , fitted to the data were 3.83, 0.24 and 0.34 respectively. In Figure 6-4, the desorption rate for high hydrocarbon concentrations, the rate is seen to fall relatively slowly with decreasing hydrocarbon concentration. Figure 6-5 for low hydrocarbon concentrations shows, however, that even at 1 %THC, the desorption rate had fallen well below a useful range. If one extrapolates this desorption rate curve to Tier 1 Criteria of 0.1 %THC, the desorption rate falls to 0.002 %THC/hour. Clearly, the time required to treat the flare pit material by thermal desorption is prohibitive.

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 curves for high hydrocarbon concentrations are shown in Figure 6-6, while the curves for low concentrations, around Alberta Tier 1 Criteria, are shown in Figure 6-7. The value of the exponential decay parameter,  $a$ , was the same at both temperatures, 1.72. At 400°C,  $b$  was 1.19 and  $n$  was 0.31, while at 500°C,  $b$  was 3.08 and  $n$  was 0.11. The desorption rates were initially extremely high, since a large quantity of light hydrocarbons were removed rapidly in the first few minutes. At 500°C the residual concentration fell to one fifth of the Tier 1 criteria in the first 15 minutes. 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. At 400°C, Tier 1 Criteria was reached at a desorption rate of 0.4 %THC/hour, while at 500°C the desorption rate was still 4 %THC/hour. 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 would likely be achieved.

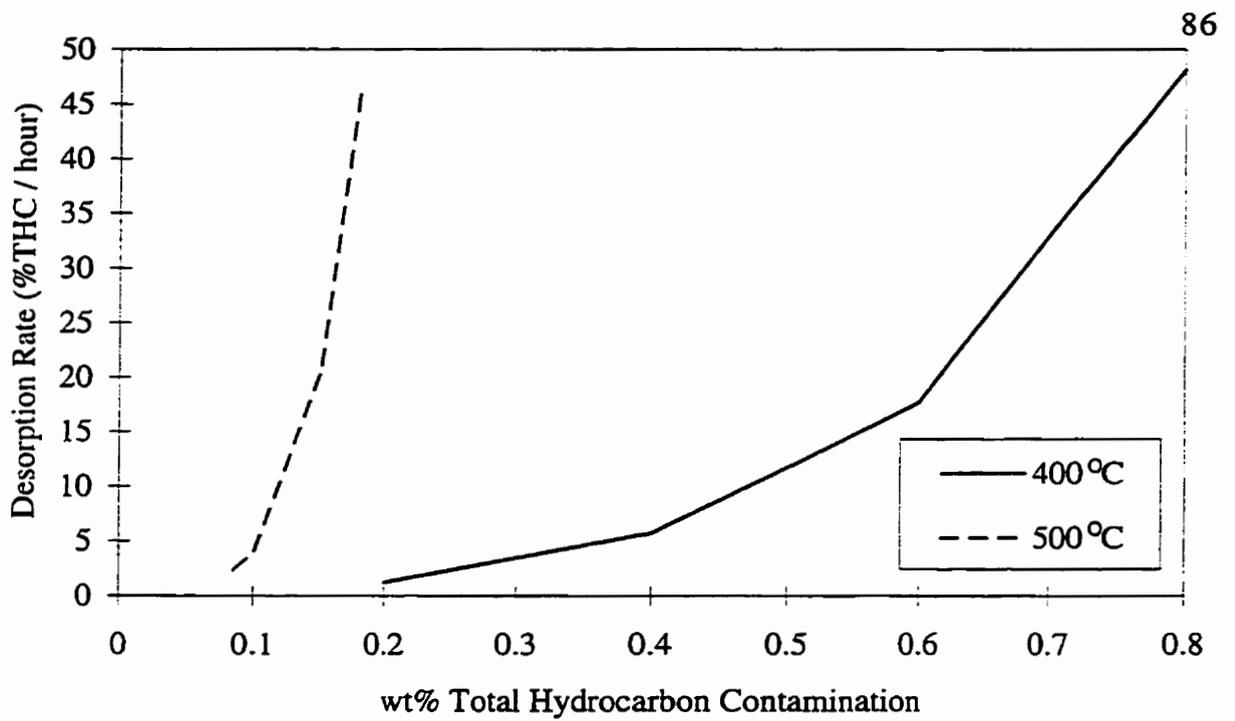


Figure 6-6: CanOxy Chlorinated Organic Soil Desorption Rate Curves for High Hydrocarbon Concentrations

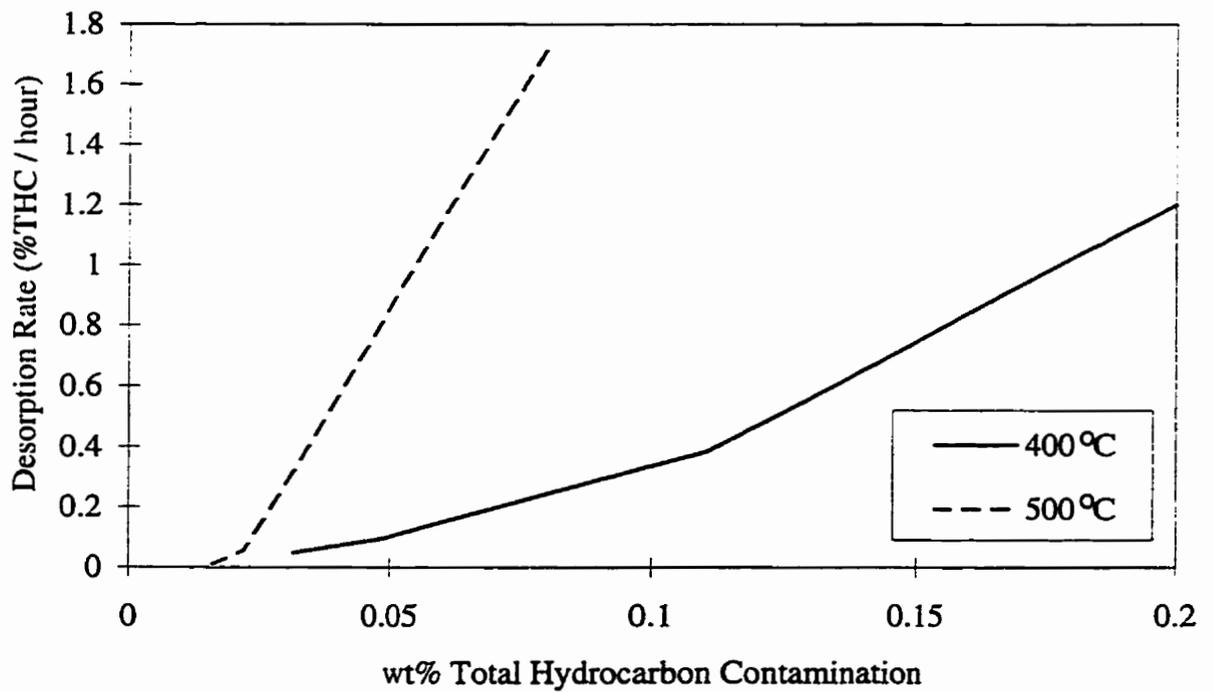


Figure 6-7: CanOxy Chlorinated Organic Soil Desorption Rate Curves for Low Hydrocarbon Concentrations

Desorption rate curves for the Amoco activated carbon at 400 and 500°C are shown in Figures 6-8 and 6-9. The sample was highly contaminated with several volatile organic compounds, the majority of which were removed in the first few minutes. Due to the magnitude of contaminant desorption between the initial concentration and that after 15 minutes, the  $R^2$  value of the fitted desorption curve was only 0.94. For the other two industrial samples,  $R^2$  was 0.98. The exponential decay equation parameter  $a$ , was 9.8 at both temperatures. The values of  $b$  and  $n$  were 1.90 and 0.16 at 400°C, and at 500°C were 2.06 and 0.19. Figure 6-8 shows that the desorption rates were still extremely high at contaminant concentrations one sixth of the initial value. In Figure 6-9, the desorption rate curves for low hydrocarbon concentrations, the rates become quite slow despite the fact that contaminants are still present on the sample. This could either be due to pore sorption, or a small concentration of heavy compounds. Although Tier 1 Criteria were met at 500°C and 60 minutes, the desorption rate fell slightly below 0.1 %THC/hour. If the 400°C curve is extrapolated to 0.1 %THC the rate falls to 0.017 %THC/hour. The impact of temperature on the activated carbon desorption rate curves, although not as great as on the CanOxy soil in which the difference was more than an order of magnitude, was to increase the desorption rate at a given hydrocarbon concentration.

The values for parameters  $a$ ,  $b$ , and  $n$  in the exponential decay equations fitted to the data gathered from the contaminated industrial samples are summarized in Table 6-1. In addition to parameter values, the coefficient of variation for each is included in the table. The coefficient of variation, which is defined as:

$$\text{Coefficient of Variation} = \frac{\text{Standard Error} * 100}{\text{Value of Parameter}} \quad (6-6)$$

provides an indication of the uncertainty associated with the given parameter.

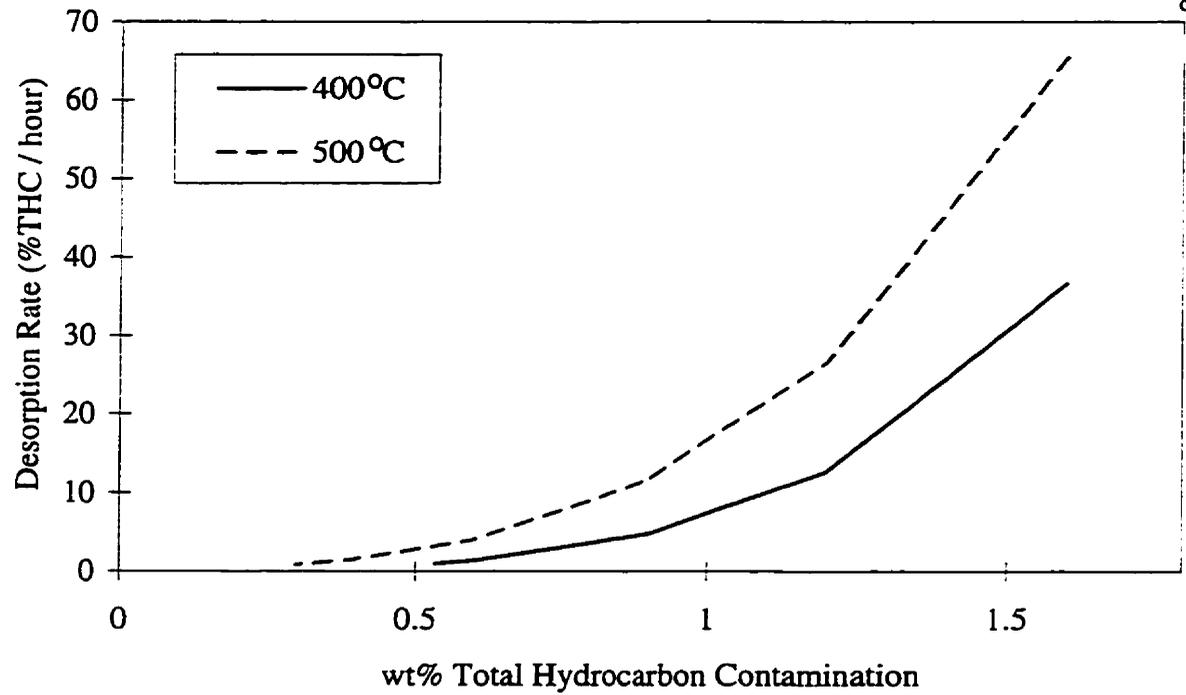


Figure 6-8: Amoco Activated Carbon Desorption Rate Curves for High Hydrocarbon Concentrations

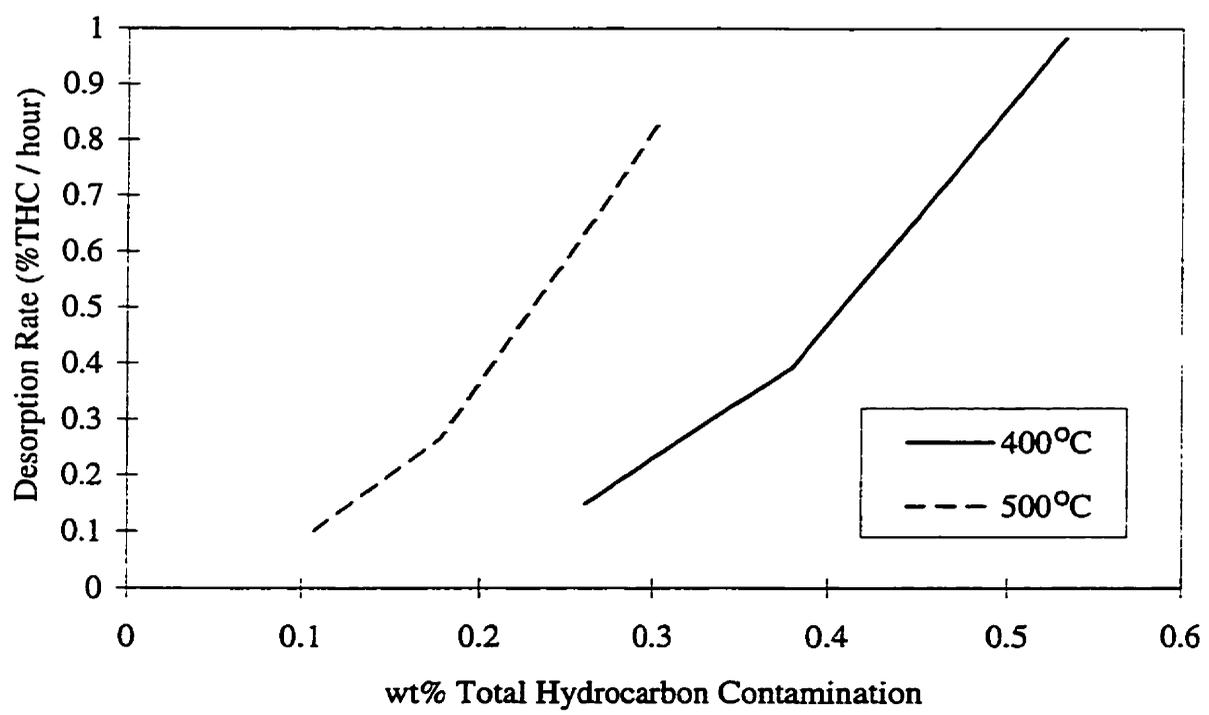


Figure 6-9: Amoco Activated Carbon Desorption Rate Curves for Low Hydrocarbon Concentrations

Table 6-1: Summary of Desorption Parameters for Industrial Samples

Sample	Parameter	Parameter Value	Coefficient of Variation (%CV)
Domtar Flare Pit Sludge 3 wt% Lime Addition 400°C	a	3.83	5.94
	b	0.24	63.0
	n	0.34	51.0
CanOxy Chlorinated Organic Soil 400°C	a	1.72	0.59
	b	1.19	18.9
	n	0.31	20.1
CanOxy Chlorinated Organic Soil 500°C	a	1.72	0.22
	b	3.08	14.8
	n	0.11	41.9
Amoco Activated Carbon 400°C	a	9.80	0.05
	b	1.90	0.13
	n	0.16	0.26
Amoco Activated Carbon 500°C	a	9.80	0.06
	b	2.06	2.96
	n	0.19	4.90

### 6.3 Prepared Samples

For each of the prepared samples, desorption rate curves were generated from residual hydrocarbon concentration results presented in Chapter 5. The desorption rate curves for the prepared samples are more statistically significant than those for the industrial samples, since a fourth residence time point was taken for each. The  $R^2$  value of fitted equations was 0.99 in each case.

A comparison of the experimental data to that generated by the exponential decay equation is shown in Figure 6-10 for the naphthalene-phenanthrene contaminated sand at 150 and 250°C. As was discussed in Chapter 5, there is uncertainty in the desorption rate within the first 10 minutes at desorber temperatures of 250 and 350°C. It is likely that the PAH concentration actually dropped at a much faster rate than that described by the straight line connecting the initial concentration to the concentration at a residence time

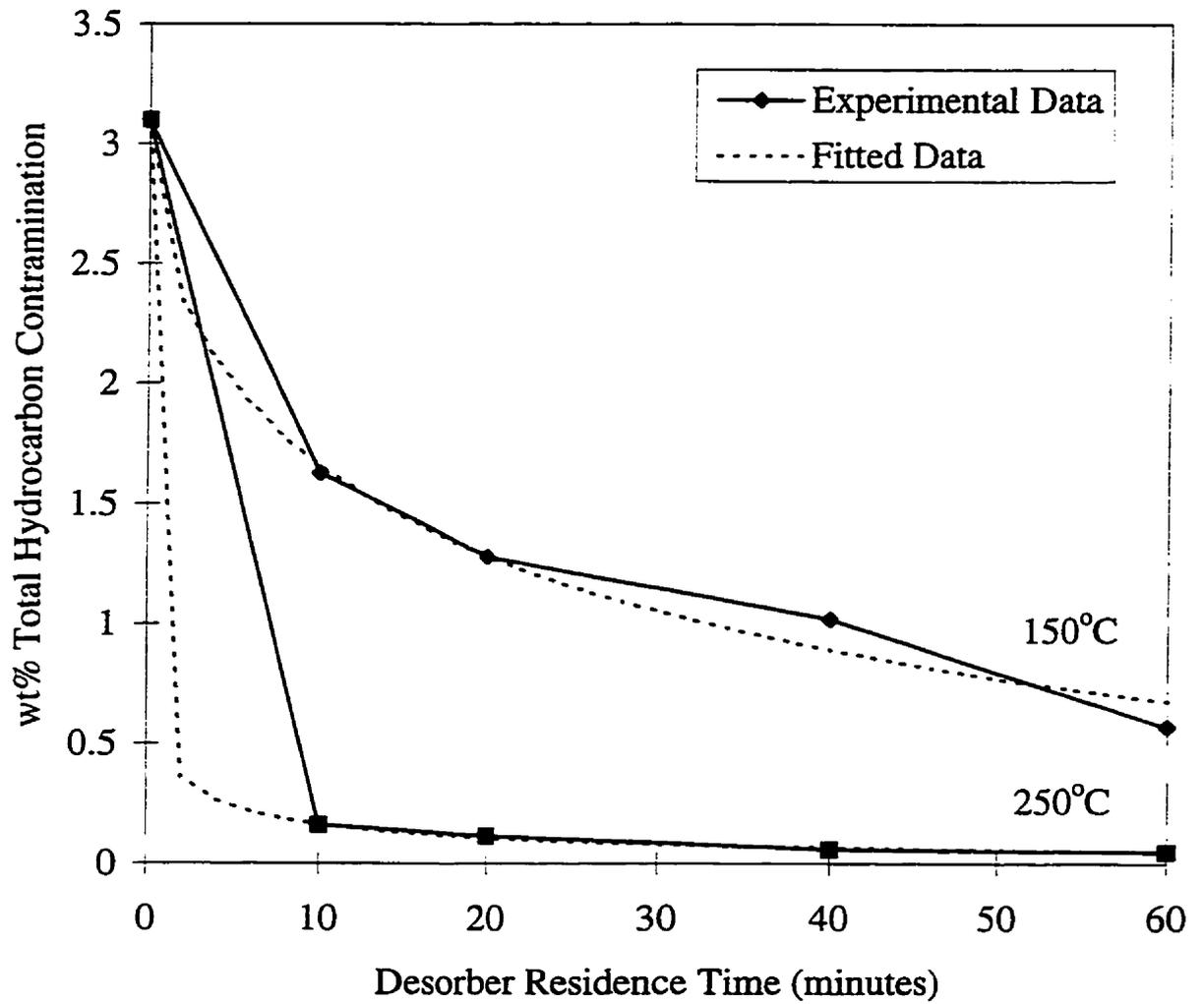


Figure 6-10: Comparison of Experimental and Fitted Data for Naphthalene-Phenanthrene Contaminated Sand at 150 and 250°C

of 10 minutes. The curve in the data generated by the fitted equation over the first 10 minutes is probably a better description of the actual desorption rate. Comparable results were seen for the anthracene-fluorene contaminated sand. Figure 6-11 shows a comparison of the fitted and experimental data at all three desorber temperatures of the naphthalene-phenanthrene contaminated activated carbon.

The desorption rate curves for the prepared samples, along with the temperature dependence of the rate of decay of the function parameter  $b$ , are discussed in the following sections.

### 6.3.1 Desorption Rate Curves

The desorption rate curves for naphthalene-phenanthrene contaminated sand at all three desorber temperatures are presented Figures 6-12 and 6-13. The curves clearly show 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 rather than by desorption. Although not as steep as the 350°C desorption curve, the 250°C shows the same extremely fast rate of desorption even at very low hydrocarbon concentrations. Since 250°C lies between the PAH boiling points, had desorption been the only method of contaminant removal, one would expect the 250°C curve to lie evenly between the other two temperatures, rather than follow the 350°C curve. Unlike the other two curves, the desorption rate curve at 150°C falls off rather slowly, and is likely the only one of the three to actually represent the desorption rate rather than a 'removal rate'. The exponential decay parameters  $a$ ,  $b$ , and  $n$  were 3.1, 0.20 and 0.50 respectively at 150°C, 3.1, 1.87 and 0.20 at 250°C and at 350°C were 3.1, 2.12 and 0.24.

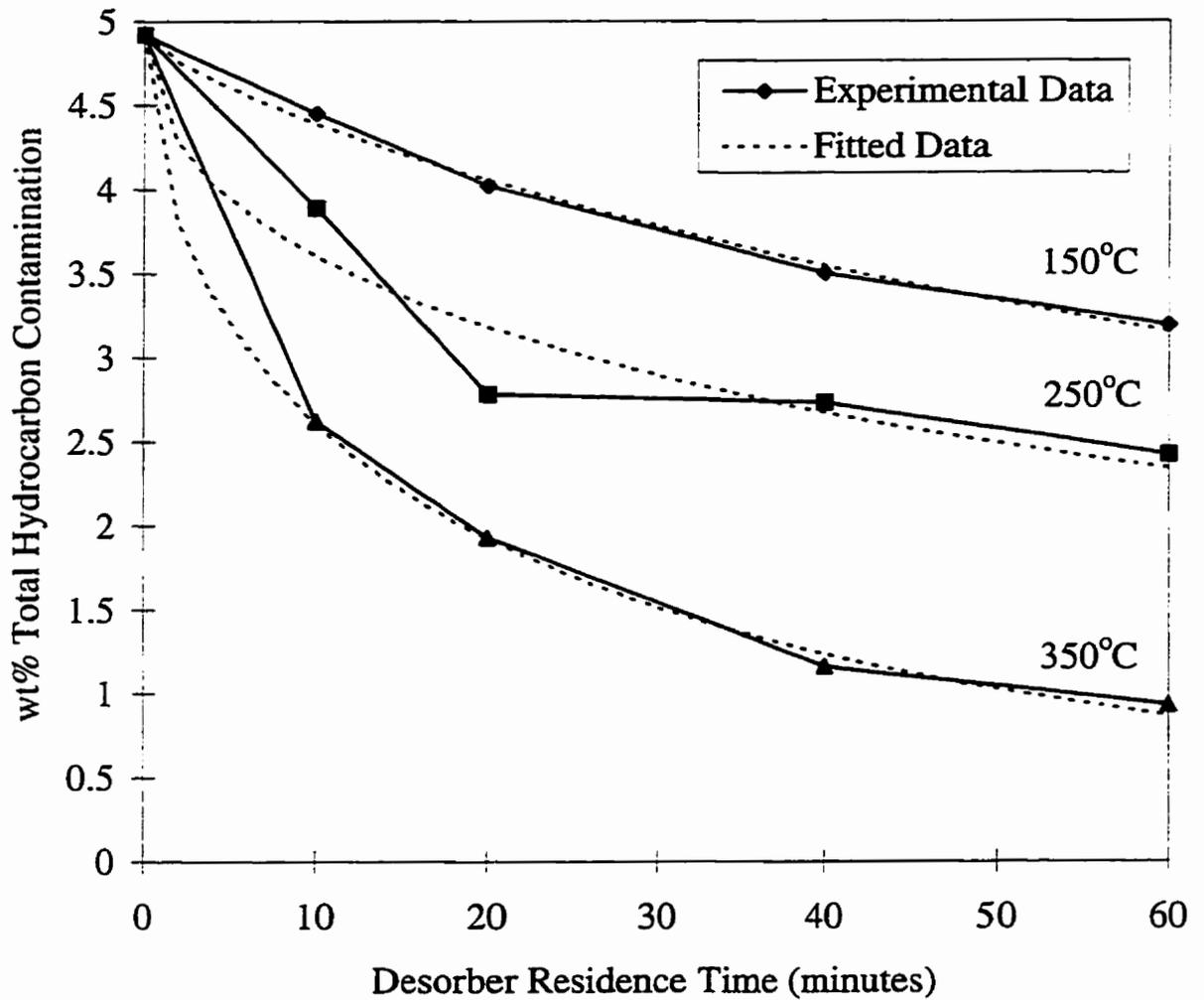


Figure 6-11: Comparison of Experimental and Fitted Data for Naphthalene-Phenanthrene Contaminated Activated Carbon

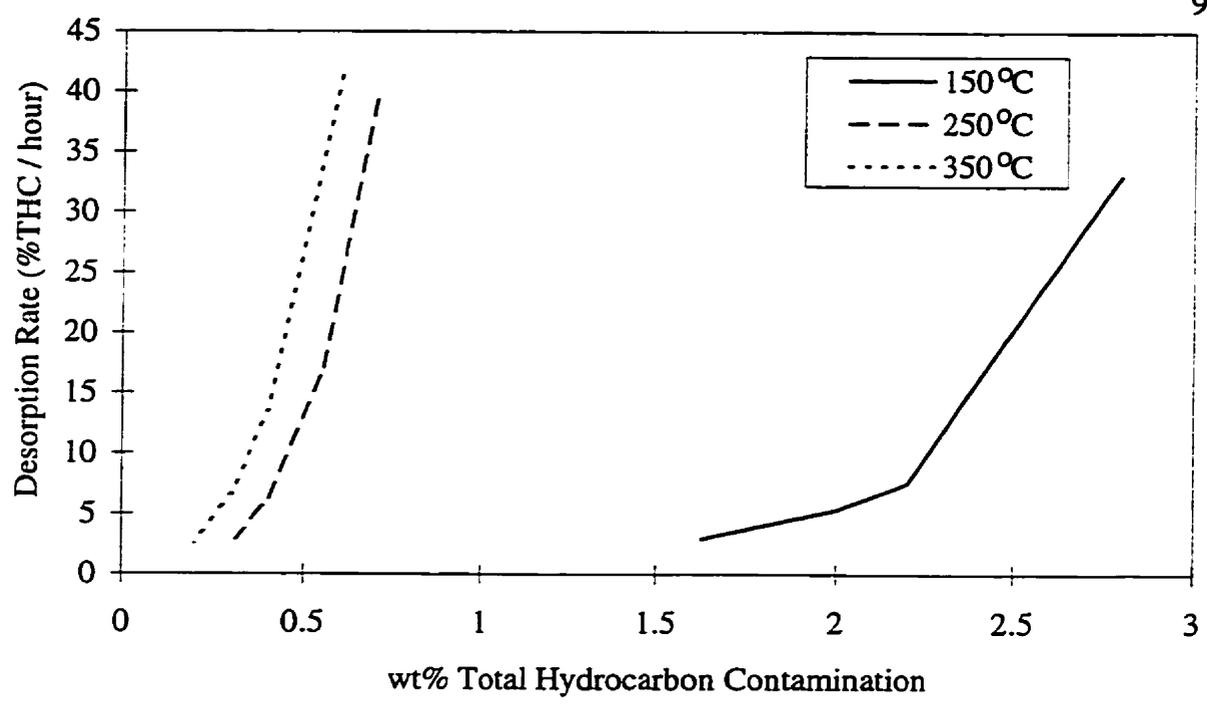


Figure 6-12: Naphthalene-Phenanthrene Contaminated Sand Desorption Rate Curves for High Hydrocarbon Concentrations

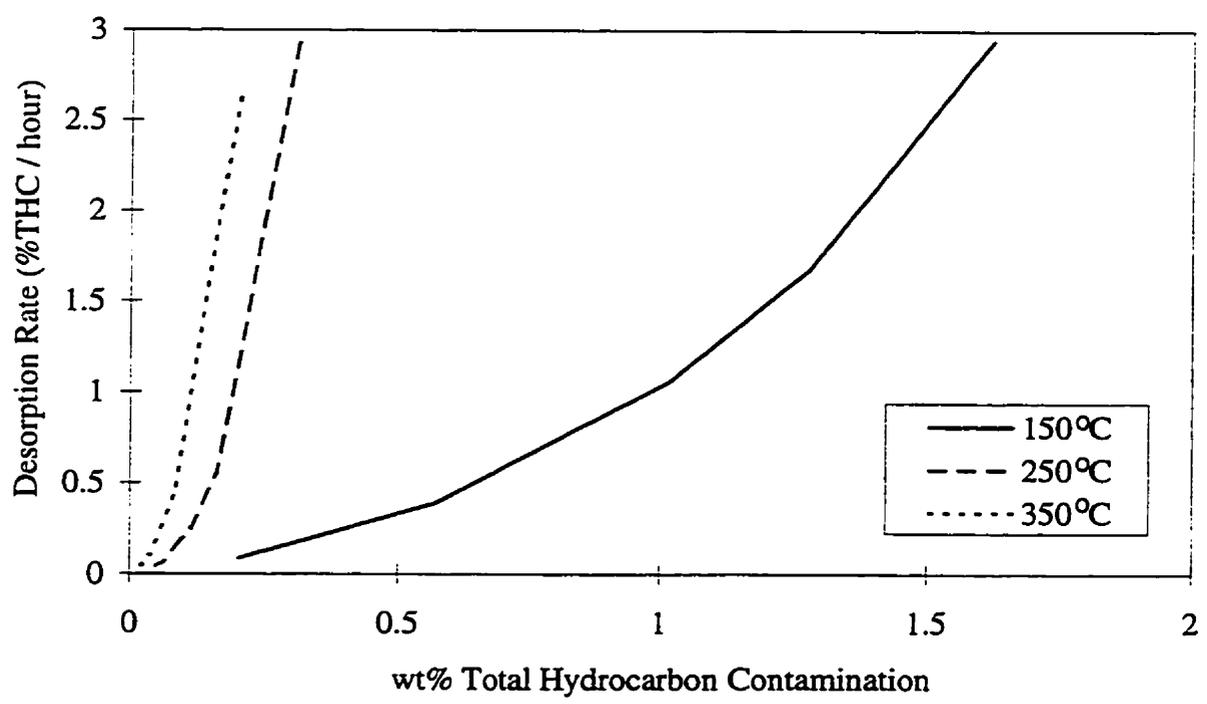


Figure 6-13: Naphthalene-Phenanthrene Contaminated Sand Desorption Rate Curves for Low Hydrocarbon Concentrations

The desorption rate curves for anthracene-fluorene contaminated sand presented in Figures 6-14 and 6-15 show very similar trends to those discussed above for naphthalene-phenanthrene sand. The exponential decay equation parameters  $a$ ,  $b$  and  $n$  were 1.99, 0.13 and 0.26 respectively at 250°C, at 320°C they were 1.99, 1.80, and 0.10, and at 350°C were 1.99, 2.03 and 0.12. The higher temperature curves, in this case 320 and 350°C, show virtually the same behaviour with extremely fast desorption rates even at very low PAH concentrations. The desorption rate curve for 250°C, however, drops off at a slow and steady rate, since the primary mechanism of PAH removal was desorption. Figure 6-15 shows only the desorption curves for 320 and 350°C below 0.5 %THC. Despite the low PAH concentration, the both rates were both around 70 %THC/hour, while the 250°C removal rate fell to only 0.15 %THC/hour at 0.5 %THC. Once again, the lowest temperature curve is probably the only genuine desorption rate curve.

The set of desorption rate curves for naphthalene-phenanthrene contaminated activated carbon is presented in Figures 6-16 and 6-17. Among the prepared samples, the effect of increasing temperature is best exhibited by the activated carbon, since PAHs were removed by desorption alone at all temperatures. The exponential decay parameters,  $a$ ,  $b$  and  $n$ , at 150°C were 4.93, 0.03 and 0.75 respectively, while at 250°C were 4.93, 0.10 and 0.48 and at 350°C were 4.93, 0.18 and 0.56. In Figure 6-16, it can be seen that the desorption rate at 150°C quickly drops off to 1 %THC/hour. Since the temperature is below the boiling points of both contaminants, they are desorbed quite slowly. As expected, the 250°C curve lies roughly mid-way between the 150 and 350°C curves. It should be noted, however, that the 150 and 250°C curves cross at about 1.5 wt%. Although this is not likely to happen in reality, it points out that the desorption rate curves may not be very accurate when extrapolated far beyond available data. Finally, the desorption rate curve for 350°C, above the boiling points of both PAH contaminants, drops much more slowly than those at the lower temperatures, the rate remaining relatively high even at low hydrocarbon concentrations.

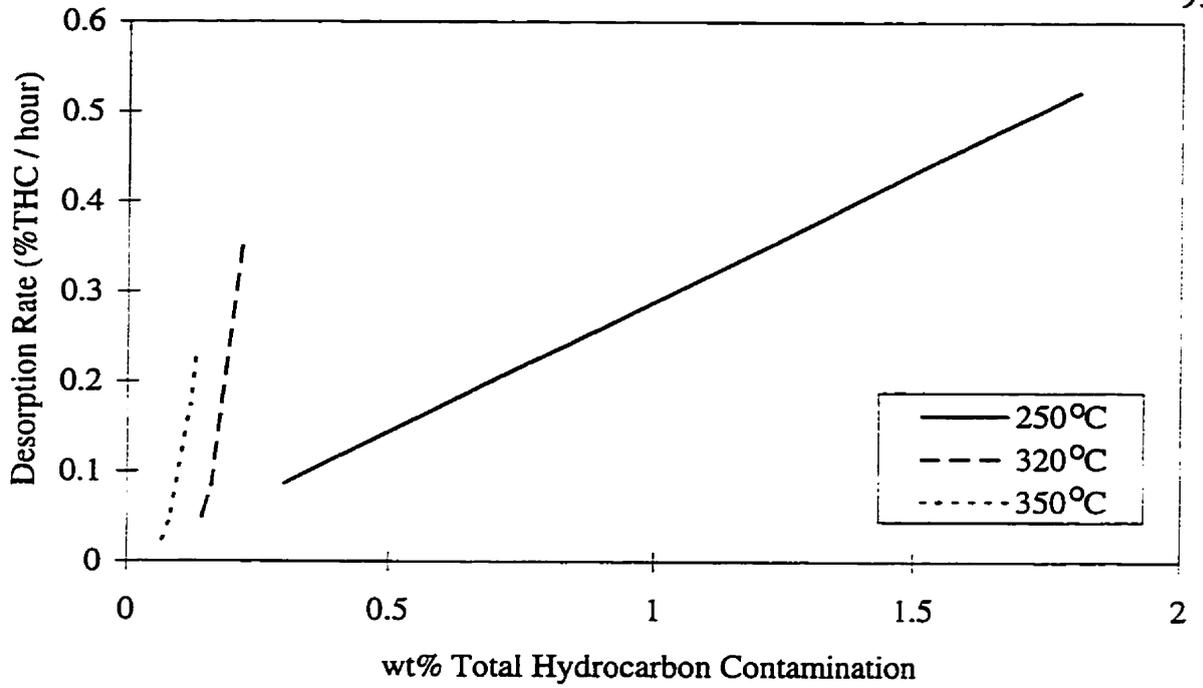


Figure 6-14: Anthracene-Fluorene Contaminated Sand Desorption Rate Curves

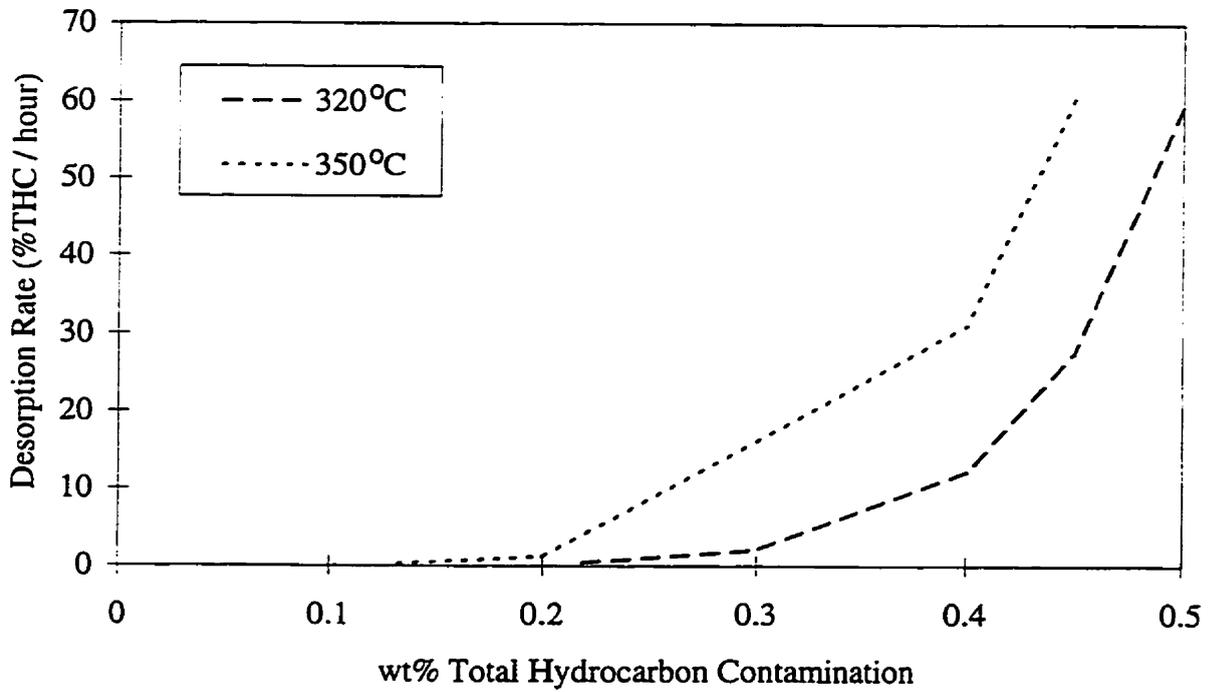


Figure 6-15: Anthracene-Fluorene Contaminated Sand Desorption Rate Curves for 320 and 350°C

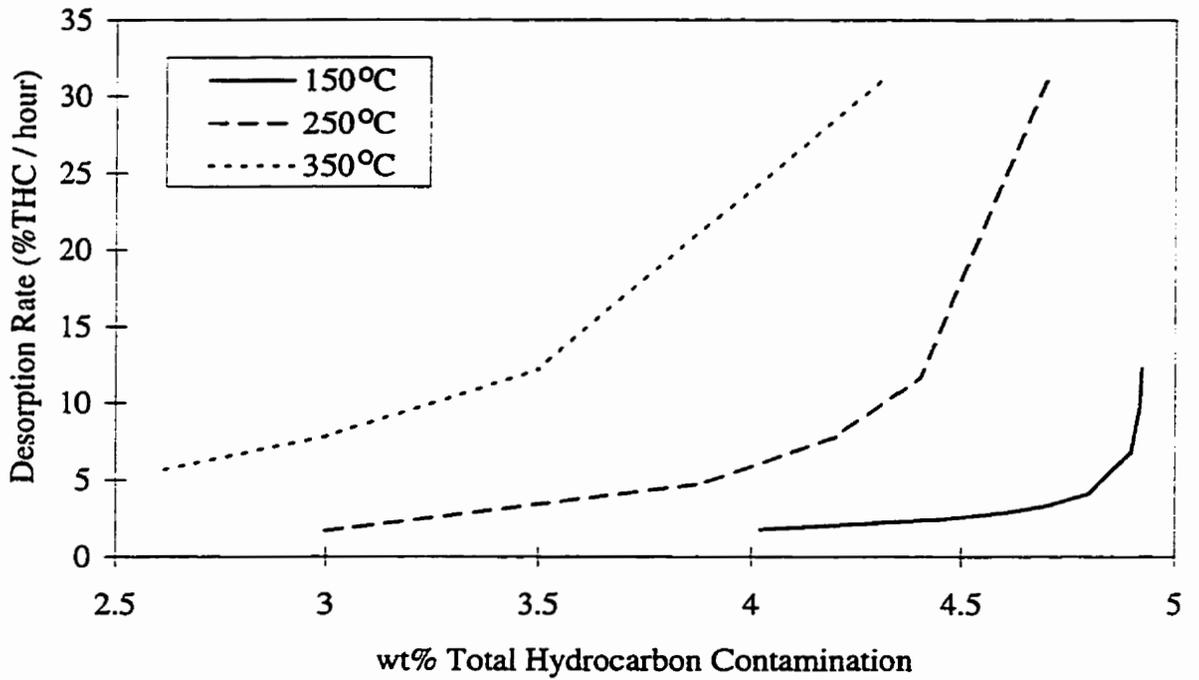


Figure 6-16: Naphthalene-Phenanthrene Contaminated Activated Carbon Desorption Rate Curves for High Hydrocarbon Concentrations

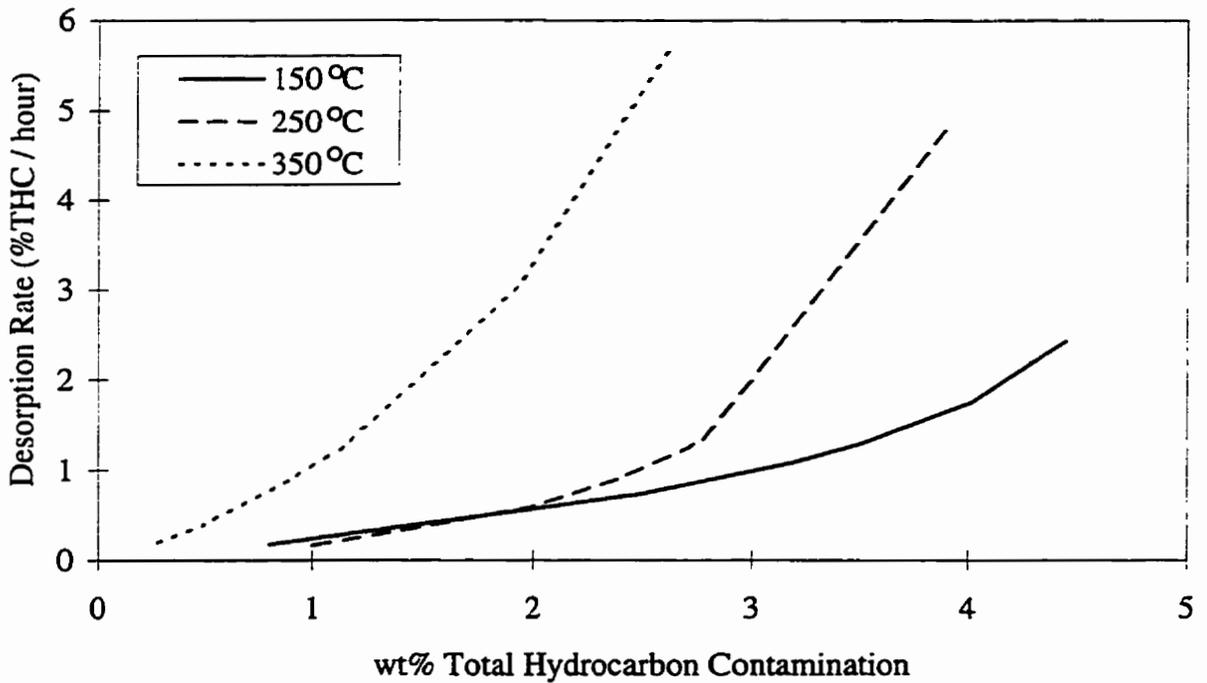


Figure 6-17: Naphthalene-Phenanthrene Contaminated Activated Carbon Desorption Rate Curves for Low Hydrocarbon Concentrations

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 6-2. The coefficient of variation for each of the parameters is also included in the table.

Table 6-2: Summary of Desorption Parameters for Prepared Samples

Sample	Parameter	Parameter Value	Coefficient of Variation (%CV)
Naphthalene-Phenanthrene Contaminated Sand 150°C	a	3.10	3.84
	b	0.20	29.7
	n	0.50	17.3
Naphthalene-Phenanthrene Contaminated Sand 250°C	a	3.10	0.23
	b	1.87	4.90
	n	0.20	8.59
Naphthalene-Phenanthrene Contaminated Sand 350°C	a	3.10	0.16
	b	2.12	7.10
	n	0.24	11.2
Anthracene-Fluorene Contaminated Sand 250°C	a	1.99	0.92
	b	0.13	9.31
	n	0.26	29.8
Anthracene-Fluorene Contaminated Sand 320°C	a	1.99	0.80
	b	1.80	8.99
	n	0.10	28.1
Anthracene-Fluorene Contaminated Sand 350°C	a	1.99	0.56
	b	2.03	8.62
	n	0.12	22.5
Naphthalene-Phenanthrene Activated Carbon 150°C	a	4.93	1.30
	b	0.03	29.9
	n	0.75	9.76
Naphthalene-Phenanthrene Activated Carbon 250°C	a	4.93	7.19
	b	0.10	27.3
	n	0.48	31.9
Naphthalene-Phenanthrene Activated Carbon 350°C	a	4.93	1.41
	b	0.18	11.1
	n	0.56	5.81

### 6.3.2 Temperature Dependence of Parameter b

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 6-18 shows parameter b as a function of desorber temperature for all three prepared samples. To show the relationship between contaminant boiling point and changes in parameter b, the PAH bubble points at 0.5 atm, the operating pressure of the BTR, are included in Figure 6-18. Both of the prepared sand samples show a tremendous increase in the value of b from the lowest temperature to the two higher temperatures. The value of b for the naphthalene-phenanthrene sand treated at 150°C was 0.20. By 250°C, the value of b had jumped to 1.87, and further increased to 2.12 at 350°C. Similarly for anthracene-fluorene sand, b jumped from 0.048 at 250°C, to 1.80 at 320°C and 2.02 at 350°C. For both sand samples, b was a polynomial function of temperature.

The third prepared sample, naphthalene-phenanthrene activated carbon, shows a perfectly linear relationship between b and temperature. Parameter b varied between 0.021 at 150°C and 0.175 at 350°C. Although parameter b was around the same value at the lowest temperature for all three prepared samples, 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 in b with temperature. While a linear relationship between desorber temperature and desorption rate was found for the contaminated activated carbon, it is not likely that a similar relationship would have been identified for the sand had melting not occurred, since desorption is a strong function of temperature.

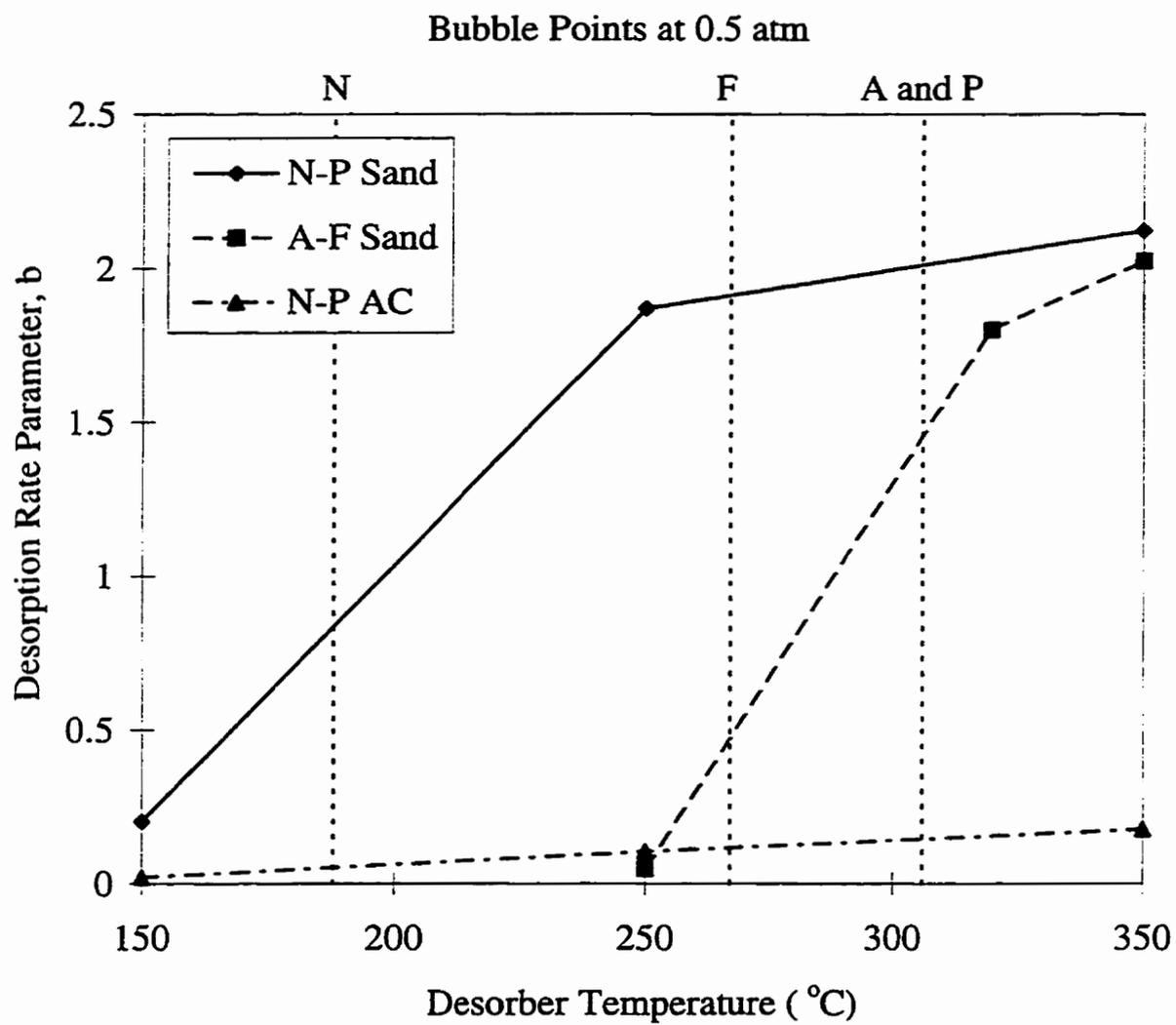


Figure 6-18: Temperature Dependence of Parameter  $b$  in Prepared Samples

#### **6.4 Comparison of Industrial and Prepared Samples**

Certain comparisons can be made between the results from the industrial samples and those from the prepared samples, although the purpose for treating the two types of samples was quite different. The industrial samples were treated at temperatures of 400 and 500°C to see if Alberta Tier 1 Criteria could be achieved. While a greater degree of remediation would have been achieved at higher desorber temperatures, the prepared samples were used to investigate the effects of contaminated sample characteristics and BTR operating characteristics on desorption.

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. The magnitude of the effect of these two desorber operating parameters on remediation is a function of the contaminant and sample characteristics. While it is not possible to quantify the effect of these two characteristics based on these results, they clearly show that lower molecular weight, relatively volatile hydrocarbons are more easily removed by thermal desorption, and that sample characteristics such as porosity reduce the desorption rate.

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 the same slow desorption rate curve that prepared activated carbon did. The temperature dependence of parameter  $b$  could not be determined, because experiments were only performed at 400°C, however, the value of  $b$  for the sludge at this temperature was 0.242. Both the CanOxy soil and the Amoco activated carbon showed similar desorption rates to those of the prepared sand samples. Although no melting was observed from the industrial samples, desorption of light contaminants off these samples was akin to the removal rate due to melting. Parameter  $b$  for Amoco activated carbon varied from 1.90 at

400°C to 2.06 at 500°C. For the CanOxy soil, the variation of  $b$  with increasing temperature was more significant, the parameter more than doubling from 1.19 at 400°C to 3.08 at 500°C. These two industrial samples show an even stronger parameter  $b$  temperature dependence than did the prepared sand samples, even though the sample characteristics more closely resemble those of the prepared activated carbon.

## **6.5 Design and Scale-Up Considerations for a Commercial Desorber**

The detailed design of a commercial thermal desorber to be built by BM Ecos and based loosely on the BTR has not yet been finalized. Although the commercial unit will likely still be indirectly heated, with the volatilized contaminants swept from the desorption chamber under vacuum, several modifications to the BTR design could be proposed. The most significant of these changes includes the incorporation of a pre-heat zone, and changing the auger design so that the desorber could operate either batch-wise or continuously. Studies on a pilot scale desorber, which accurately replicates the commercial unit will be needed to ensure that remediation goals can still be achieved. In the following section, a scaled-up thermal desorption system, which would be effective for managing hydrocarbon contaminated soils, is proposed and discussed. The proposed system is based on the experimental results from the BTR and on other thermal desorber designs.

A schematic diagram of the proposed thermal desorber is shown in Figure 6-19. The desorption system consists of two indirectly heated thermal screws, both of which are inclined to increase residence time, and operated under vacuum. Screened and pre-treated soil is fed through an air lock valve into the primary soil pre-heat desorber, operating at slightly above 100°C. Pre-treatment such as aggregation or blending is vital to ensure the flowability of the soil sample and prevent plugging of the auger. In soil pre-heat desorber, water and other light compounds are removed and directed to the primary condenser. The

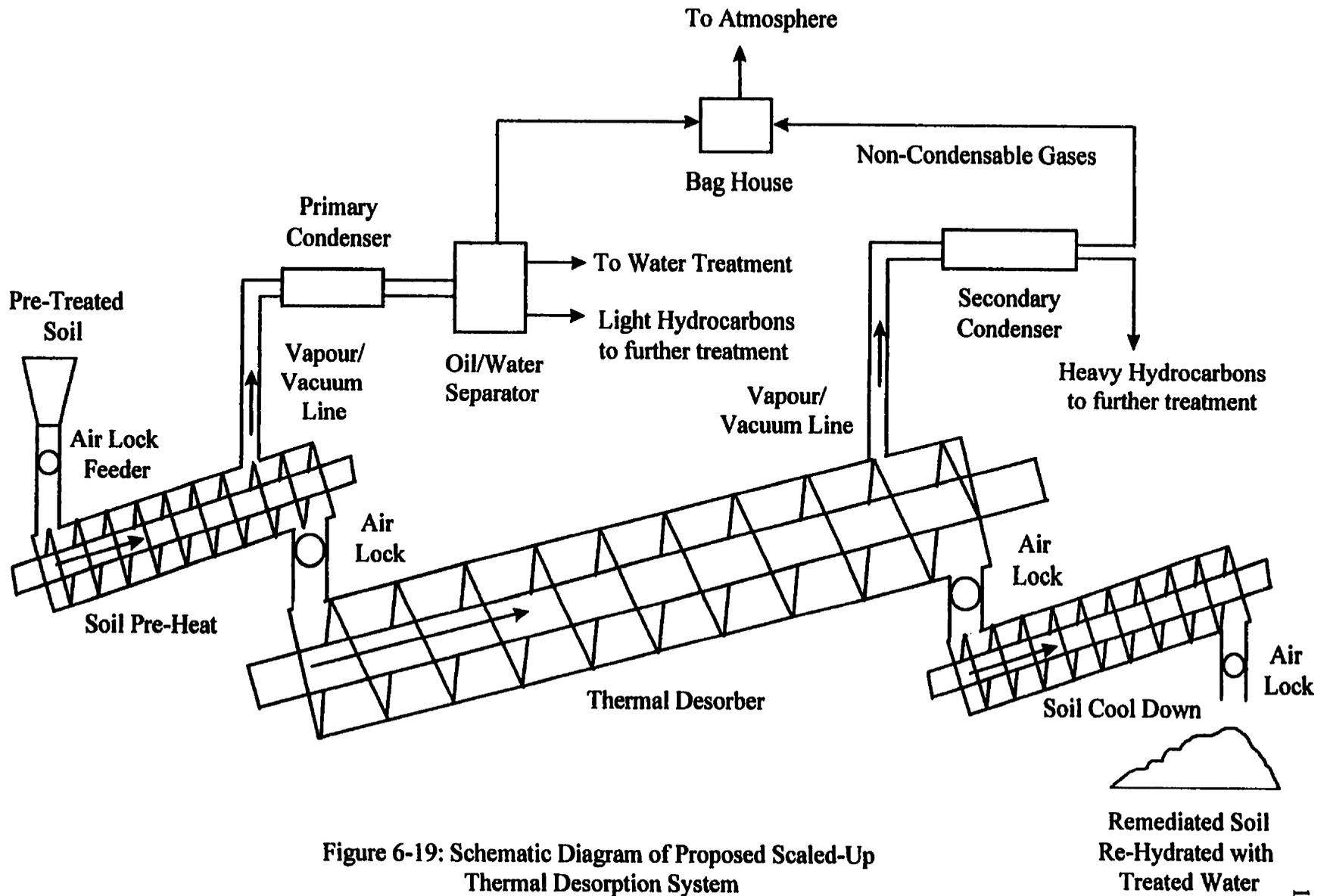


Figure 6-19: Schematic Diagram of Proposed Scaled-Up Thermal Desorption System

soil is then fed to the main thermal desorber through a second air lock valve, isolating the two desorbers. The main desorber, operating at temperatures up to 500°C, which is the upper limit for most thermal desorbers, separates the bulk of the heavy hydrocarbon contaminants. Volatilized hydrocarbons are drawn into the secondary condenser under vacuum. The hot treated soil is then moved through an air lock valve to a third screw, the soil cool down, in which heat is exchanged with the pre-heat desorber, and the soil is cooled prior to discharge. Finally, the remediated soil is re-hydrated, in order to suppress dust formation, with treated water desorbed from the soil.

In order to achieve operating temperatures of 500°C in the main desorber, it will need to be heated either electrically or by circulating hot oil. Traditionally, thermal screw desorbers are narrow to improve heat transfer to the soil, and long to increase residence time while maintaining a reasonable rotational speed of the screw to promote mixing. Soil residence time is governed by the incline of the desorber and the screw rotational speed, however, the main desorber is capable of rotating in reverse as well. The ability to rotate the screw in both directions provides excellent mixing like that in the BTR, and significantly increases the residence time possible inside the desorber. The soil pre-heat, which is operated at slightly above 100°C, could conceivably be heated by combustion of desorbed hydrocarbons recycled from the contaminated soil. Unfortunately, this would require a large gas treatment unit to manage the combustion gases and would lead to greater air emissions from the system. Therefore, the heating requirements of pre-heat desorber are provided by exchange with the treated soil in the cool down screw, which exits the main desorber at about 500°C. When necessary, heat is provided either by circulating hot oil or a band heater. Both the pre-heat and cool down screws operate only in a single direction.

Water and light hydrocarbons volatilized in the pre-heat desorber are drawn into the primary condenser under vacuum. The condensed material is then sent to an oil-water separator, from which the water fraction is directed to a water treatment unit and the light

hydrocarbons are collected for further treatment. Non-condensable gases, if any are formed, are sent to a bag house for particulate removal and are then vented to atmosphere. Clean water from the water treatment unit is later sprayed on the remediated soil. Heavy hydrocarbons volatilized in the main desorber are sent to the secondary condenser. Since water was separated in the pre-heat desorber, the material exiting the secondary condenser will consist primarily of hydrocarbons, which are collected for further treatment, recycling or disposal. Any non-condensable gases formed in the desorber are again sent to the bag house prior to venting.

There are several benefits to this proposed desorption system design. In the proposed system, which is an indirectly heated desorber operated under vacuum like the BTR, volatilized compounds alone are drawn out of the desorber. In comparison to other thermal desorber designs, which use an inert sweep gas, the volume of material exiting the desorber is significantly reduced. By operating under vacuum, the size of downstream treatment units are reduced, there are little or no emissions to the atmosphere, and the combustion of desorbed contaminants is minimized. The main desorber design, in which the screw is capable of rotating in both directions, allows the desorber to operate batch-wise as well as continuously in order to increase soil residence time if necessary. Finally, the incorporation of a pre-heat desorber and cool down screw, which transfers heat to the pre-heat unit, will result in a more energy efficient system. Typically high moisture content soils are expensive to treat by thermal desorption, since the water must be heated to desorption temperatures along with the soil and hydrocarbon contaminants. The pre-heat desorber removes the water from the soil at a relatively low temperature and then the remaining material can be treated at higher temperature in the main desorber to volatilize the hydrocarbons. In addition, separation of desorbed materials is achieved by the dual system, since water and light hydrocarbons will be separated by the pre-heat unit, and the heavy hydrocarbons by the main desorber.

Regardless of the design selected for the commercial scale desorber, the unit must have as close to ideal heat transfer and mixing characteristics as possible. Although a continuous thermal screw could not replicate the excellent mixing achieved in the BTR with the auger rotating in both directions, the unit must be carefully designed to avoid the existence of 'dead spots', which will significantly affect desorption efficiency. Additionally, heat transfer to the soil must be quite good in order to minimize sample heat up time. The effective residence time of the sample is reduced by poor heat transfer, since less time is spent at the selected desorption temperature. While efficient mixing and heat transfer are very important, for all desorber designs, contaminant desorption rates are dictated by contaminant and soil characteristics such as contaminant molecular weight, sample porosity and humic content. Therefore, the generation of desorption rate expressions such as equation 6-2:

$$\ln c = \ln a - bt^n \quad (6-2)$$

is a valuable tool for evaluating any desorption system. The residual contaminant concentration  $c$ , can be identified at any residence time  $t$  within the limits of those studied, given the initial contaminant concentration  $a$ , and the appropriate experimentally evaluated parameters  $b$  and  $n$ .

## CHAPTER SEVEN

# CONCLUSIONS AND RECOMMENDATIONS

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The conclusions drawn from the results presented in this thesis are summarized in this chapter, and recommendations for future work are suggested.

### 7.1 Conclusions

Thermal desorption experiments were performed using a novel, bench scale batch thermal desorber, developed by Bromley Marr Ecos Inc., the Batch Thermal Reactor (BTR). A treatability study on five contaminated industrial samples was followed by a fundamental study of the thermal desorption process using three prepared samples contaminated with binary mixtures of polynuclear aromatic hydrocarbons. The results gathered from both the industrial and prepared samples were used to generate desorption rate curves, a simple parameter which is useful for determining how the system might operate on a larger scale.

Five industrial samples were obtained by BM Ecos to investigate the feasibility of treating several typical waste types using the BTR. The goal of these experiments was to explore the treatability of these samples and determine whether they could successfully be treated to comply with Alberta Environment Tier 1 Criteria for Contaminated Soil Assessment and Remediation using a combination of pre-treatment and thermal

desorption. It was found that CanOxy chlorinated organic contaminated soil, treated at 400°C for 30 minutes, Amoco activated carbon, treated at 500°C for 60 minutes, and several PanCanadian produced sand samples met Tier 1 Criteria after thermal treatment. Despite aggressive pre-treatment of the Domtar flare pit sludge, the sample was not successfully treated to Tier 1 Criteria. The sample had a contaminant concentration eight times the legislated limit after treatment at 400°C for 60 minutes. The sludge will likely need to be treated by some other method, or by desorption followed by stabilization. The fifth sample, Weyerhaeuser pulp sludge, was not suitable for treatment in the BTR, because the pulp fibers ignited on introduction into the desorber.

Experiments were performed on three prepared samples to investigate the effect of sample porosity, contaminant molecular weight, desorber residence time and desorber temperature on contaminant removal. Sand and activated carbon, chosen as porous and non-porous model solids, were artificially contaminated with 50:50 weight mixtures of PAHs with different boiling points. Both sand and activated carbon were contaminated by the naphthalene-phenanthrene mixture, while only sand was contaminated by the anthracene-fluorene mixture. Increasing desorber temperature and residence time both resulted in greater PAH desorption. Based on the proportions of PAHs condensed in the primary trap, it was found that the lighter PAH desorbed preferentially. Sample porosity had a very pronounced impact on desorption, reducing the rate of contaminant removal. Pore sorption onto the activated carbon prevented melted PAHs from draining off the sample as they do off the non-porous sand sample. While it was found that PAHs were removed from the activated carbon by desorption alone, the loss of contaminants off the sand samples at temperatures above the PAHs melting points led to artificially low contaminant concentrations, particularly at higher desorber temperatures.

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 developed here is applicable to any type of desorption

system. Given equation parameters  $b$  and  $n$ , which can be experimentally determined using the BTR or similar equipment, and the initial contaminant concentration,  $a$ , the residual hydrocarbon contamination can be accurately determined for residence times between 10 and 60 minutes. Therefore, it is possible to interpolate the desorption data to determine the residence time required to meet Alberta Tier 1 Criteria.

For the industrial samples, it was found that the rate of contaminant desorption for Domtar flare pit sludge fell to a prohibitively low value, and would require an extremely long residence time to achieve Tier 1 Criteria. The desorption rates for both the CanOxy chlorinated organic soil, and Amoco activated carbon were faster at 500°C than at 400°C, and remained relatively high even at low hydrocarbon concentrations. In both cases, the initial rate was extremely high, indicating that the sample contained light hydrocarbons, which were easily desorbed. The prepared sand samples showed a dramatic difference between the desorption rate curves at the lower temperatures, and those at the two higher temperatures. This result was due to removal of PAH contaminants by melting instead of by desorption. The activated carbon sample showed the lowest desorption rates because contaminants most likely had to diffuse through the activated carbon pores prior to desorbing off the surface of the particles.

The temperature dependence of parameter  $b$  in the exponential decay equation for the prepared samples was also investigated. It was found that a linear relationship between  $b$  and temperature existed for the activated carbon, while a second order polynomial relationship was found for both contaminated sand samples. Finally, a design for a commercial scale desorption system, based on the results from the BTR and on other commercial desorber designs, was proposed.

## 7.2 Recommendations for Future Work

The feasibility of treating other industrial samples using the BTR could be investigated, however, the five samples considered in this work are representative of several common waste types. Further work should be directed toward the investigation of sample treatment in a pilot scale desorber. Since the BTR depicts an idealized desorber, with excellent mixing and heat transfer, it is well suited to fundamental studies of the desorption process, and to studies on the effects of sample pre-treatment. Bearing this in mind, the following recommendations are made:

1. Further experiments using prepared samples contaminated with relatively heavy polynuclear aromatic hydrocarbons, such as chrysene or benzopyrene, which have normal boiling points of 468 and 495°C respectively, should be considered. These compounds have higher melting and boiling points than any of the four PAHs considered here, so contaminant loss due to melting would be less significant. The effects of sample porosity, desorber temperature and desorber residence time would be more apparent, and perhaps quantifiable using heavier PAH contaminants. An additional operational variable, level of desorber vacuum, could also be investigated using the BTR.
2. The development of a pilot scale thermal desorber, which replicates the design of the commercial scale desorber, should be undertaken. Since the proposed designs of the full scale desorber differ significantly from the bench scale unit, many of the operating parameters will not be the same. Therefore, a pilot scale study is necessary in order to ensure that remediation goals can still be achieved. In addition, the effect of a pre-heat zone on desorption efficiency should be investigated.

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**APPENDIX A:**  
**INDUSTRIAL SAMPLE ANALYSES**

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**CHEMEX Labs Alberta Inc.**

Calgary: 2021 - 41st Avenue N.E., T2E 6P2, Telephone (403) 291-0077, FAX (403) 291-0488  
 Edmonton: 8031 - 48th Street, T6B 2R4, Telephone (403) 485-9577, FAX (403) 485-3332

Sample Description : EAST POND SLUDGE  
 Sample Date & Time : N/A N/A  
 Sampled By :  
 Sample Type : GRAB  
 Sample Received Date: June 25, 1996  
 Sample Station Code :

PRELIMINARY COPY

**BROMLEY-MANN ECOS INC.**  
 ATTENTION : PETER MOHAMMED

SAND/SLUDGE

Chemex Worksheet Number : 96-06864-2  
 Chemex Project Number : BROMD10-0502  
 Sample Access :  
 Sample Matrix : SLUDGE  
 Report Date : July 5, 1996  
 Analysis Date : July 3, 1996

PARAMETER DESCRIPTION	NAQUADAT CODE	UNITS	R E S U L T S	DETECTION LIMIT
Hot Water Soluble Boron		ug/g	2.77	0.05
Hexavalent Chromium	NOT DONE			
Total Mercury - (CVAA)		ug/kg	365.	20.
Barium (ICP)		ug/g	951.	1.
Beryllium (ICP)		ug/g	0.5	0.1
Chromium (ICP)		ug/g	1180.	0.2
Cobalt (ICP)		ug/g	4.5	0.3
Copper (ICP)		ug/g	9.7	0.1
Lead (ICP)		ug/g	17.	2.
Molybdenum (ICP)		ug/g	46.7	0.3
Nickel (ICP)		ug/g	13.1	0.5
Vanadium (ICP)		ug/g	19.0	0.2
Zinc (ICP)		ug/g	410.	0.1
Cadmium (ICP-MS)	NOT DONE			
Thallium (ICP-MS)	NOT DONE			
Arsenic (ICP-MS)	NOT DONE			
Selenium (ICP-MS)	NOT DONE			
Saturation Percent		%	2.	1.
pH (Saturated Paste)			7.7	0.1
Electrical Conductivity	NOT DONE			
Soluble Sodium	NOT DONE			
Soluble Calcium	NOT DONE			
Soluble Magnesium	NOT DONE			
Soluble Potassium		mg/L	45.7	0.1
Sodium Adsorption Ratio (SAR)	NOT DONE			
Theoretical Gypsum Requirement	NOT DONE			

# CHEMEX Labs Alberta Inc.

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Sample Description : EAST POND SLUDGE  
 Sample Date & Time : N/A N/A  
 Sampled By :  
 Sample Type : GRAB  
 Sample Received Date: June 25, 1996  
 Sample Station Code :

PRELIMINARY COPY

BROMLEY-MANN ECOS INC.  
 ATTENTION : PETER MOHAMMED

SAND/SLUDGE

Chemex Worksheet Number : 96-06864-2  
 Chemex Project Number : BR0M010-0502  
 Sample Access :  
 Sample Matrix : SLUDGE  
 Report Date : July 5, 1996  
 Analysis Date : June 27, 1996

TOTAL EXTRACTABLE HYDROCARBONS METHOD MODIFIED ASTM D2887					
COMPONENT	mg/Kg	BOILING RANGE	COMPONENT	mg/Kg	BOILING RANGE
C 08	900.	98.5 TO 125.7	C 35	3700.	483.1 TO 491.0
C 09	2200.	125.8 TO 150.8	C 36	4400.	491.1 TO 498.0
C 10	3200.	150.9 TO 174.2	C 37	2500.	498.1 TO 505.0
C 11	2100.	174.3 TO 196.0	C 38	3100.	505.1 TO 512.0
C 12	4900.	196.1 TO 216.0	C 39	2900.	512.1 TO 519.0
C 13	11000.	216.1 TO 236.0	C 40	2700.	519.1 TO 525.0
C 14	6900.	236.1 TO 253.0	C 41	1900.	525.1 TO 535.0
C 15	17000.	253.1 TO 271.0	C 42	2300.	531.1 TO 537.0
C 16	11000.	271.1 TO 287.0	C 43	1600.	537.1 TO 543.0
C 17	12000.	287.1 TO 302.0	C 44	1900.	543.1 TO 548.0
C 18	12000.	302.1 TO 317.0	C 45	1200.	548.1 TO 554.0
C 19	10000.	317.1 TO 331.0	C 46	1100.	554.1 TO 559.0
C 20	8600.	331.1 TO 344.0	C 47	1000.	559.1 TO 565.0
C 21	6600.	344.1 TO 357.0	C 48	900.	565.1 TO 570.0
C 22	6000.	357.1 TO 366.0	C 49	810.	570.1 TO 576.0
C 23	5600.	366.1 TO 380.0	C 50	680.	576.1 TO 581.0
C 24	5300.	380.1 TO 391.0	C 51	660.	581.1 TO 584.0
C 25	5100.	391.1 TO 402.0	C 52	620.	584.1 TO 588.0
C 26	4400.	402.1 TO 412.0	C 53	390.	588.1 TO 592.0
C 27	4600.	412.1 TO 422.0	C 54	560.	592.1 TO 596.0
C 28	7100.	422.1 TO 432.0	C 55	530.	596.1 TO 600.0
C 29	5300.	432.1 TO 441.0	C 56	500.	600.1 TO 604.0
C 30	3600.	441.1 TO 449.0	C 57	330.	604.1 TO 608.0
C 31	4500.	449.1 TO 459.0	C 58	470.	608.1 TO 612.0
C 32	2800.	459.1 TO 468.0	C 59	470.	612.1 TO 615.0
C 33	4500.	468.1 TO 476.0	C 60	200.	615.1 TO 619.0
C 34	4600.	476.1 TO 483.0			

Average molecular weight : 276 AMU TOTAL HYDROCARBONS C8-C10 6300. mg/Kg  
 TOTAL HYDROCARBONS C11-C60 200000. mg/Kg

Surrogate recovery : 144% SLUDGE surrogate limits : 72% - 125%  
 MDL per component : 3. mg/Kg below C31 and 7. mg/Kg above C30  
 20. mg/Kg above C39 and 20. mg/Kg above C49

Results are reported in accordance with COME guidelines. All results are corrected for blank levels.  
 MDL - Method detection level. The reliable detection level is twice the method detection level.  
 ( ) - Bracketed results are values below the reliable detection level, and are subject to reduced levels of confidence.  
 Results are uncorrected for moisture unless otherwise noted.

COMMENTS : SAMPLE WAS DILUTED BY A FACTOR OF 3.  
 SURROGATE RECOVERY IS HIGH DUE TO C7 INTERFERENCE FROM THE SAMPLE.

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 Edmonton : 9031 - 48th Street, T6B 2P4, Telephone (403) 485-0677, FAX (403) 485-3332

Sample Description : EAST POND SLUDGE  
 Sample Date & Time : N/A N/A  
 Sampled By :  
 Sample Type : GRAB  
 Sample Received Date: June 25, 1996  
 Sample Station Code :

PRELIMINARY COPY

BROMLEY-MANN ECOS INC.  
 ATTENTION : PETER MOHAMMED

SAND/SLUDGE

Chemex Worksheet Number : 96-06864-2  
 Chemex Project Number : BROM10-0502  
 Sample Access :  
 Sample Matrix : SLUDGE  
 Report Date : July 5, 1996  
 Analysis Date : June 28, 1996

PARAMETER	VOLATILE ORGANICS ANALYSIS - BTEX CONC	EPA METHOD 8260 MODIFIED BLANK CONC	UNITS	MDL
Benzene	9.3	< 0.005	mg/Kg	1.1
Ethylbenzene	22.	< 0.005	mg/Kg	1.1
Toluene	81.	< 0.005	mg/Kg	1.1
m & p-Xylene	260	< 0.005	mg/Kg	1.1
o-Xylene	85.	< 0.005	mg/Kg	1.1
Total Purgeables (C3 to C10)	1300	0.16	mg/Kg	3.5
Total Purgeables (C11 to C12)	1100	(0.02)	mg/Kg	0.43

**NOTES :**

Results are reported in accordance with CCME guidelines, "Guidance Manual on Sampling, Analysis, and Data Management for Contaminated Sites, Volume 1". All results are corrected for blank levels.

MDL - Method detection level. - Calculated on the basis of the instrument detection level, the dilution used, and the weight of the sample.

( ) - Bracketed results are values below the reliable detection level, and are subject to reduced levels of confidence. The reliable detection level is twice the method detection level.

**QA/QC SUMMARY**

All samples were spiked with a component whose recovery was monitored to maintain analysis accuracy. Guidelines from SW846 for suggested surrogate recoveries for each matrix are shown below. Results are uncorrected for moisture unless otherwise noted.

Instrument : GC/MS  
 Surrogate Recovery : 100% SLUDGE surrogate limits : 80% - 117%.

# CanOxy Soil Analysis

Parameter	Concentration	Tier 1 Criteria	CCME Res/Park Criteria
pH	7.6	6.5-8.5	6.5-8.5
EC (meq/100g)	5.4	2	2
<b>Metals (ppm)</b>			
Arsenic	10.0	10	30
Barium		600	500
Beryllium	0.8	5	4
Boron (hot wtr sol)	2.7	2	1000
Bromide (wtr sol)	5	20	
Cadmium		1	5
Chromium (+6)		5	8
Chromium total	61.2	100	250
Cobalt	9.1	20	50
Copper		80	100
Cyanide (wtr sol)	0.1	0.5	10
Cyanide total		5	50
Fluoride		200	400
Lead		50	500
Mercury	44	0.2	2
Molybdenum	0.6	4	10
Nickel		40	100
Selenium		2	3
Sulphur (elemental)		500	
Thallium		1	
Vanadium		100	200
Zinc	52	120	500
<b>Organics</b>			
Benzene		0.05	0.5
Ethylbenzene		0.5	5
Toluene		1	3
Xylene		1	5
Total Hydrocarbons (%)	1.8	1	0.5

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 Edmonton : 6331 - 48th Street, T6B 2P4, Telephone (403) 485-8877, FAX (403) 485-3332

Sample Description : PRODUCED SAND  
 Sample Date & Time : N/A N/A  
 Sampled By :  
 Sample Type : GRAB  
 Sample Received Date: June 25, 1996  
 Sample Station Code :

PRELIMINARY COPY

BROMLEY-MANN ECOS INC.  
 ATTENTION : PETER MOHAMMED

SAND/SLUDGE

Chemex Worksheet Number : 96-06864-1  
 Chemex Project Number : BRON010-0502  
 Sample Access :  
 Sample Matrix : SAND  
 Report Date : July 5, 1996  
 Analysis Date : July 3, 1996

PARAMETER DESCRIPTION	NAQUADAT CODE	UNITS	R E S U L T S	DETECTION LIMIT
Hot Water Soluble Boron		ug/g	1.19	0.05
Hexavalent Chromium	NOT DONE			
Total Mercury- (CVAA)		ug/kg	< 20	20.
Barium (ICP)		ug/g	22.7	1.
Beryllium (ICP)		ug/g	< 0.1	0.1
Chromium (ICP)		ug/g	3.0	0.2
Cobalt (ICP)		ug/g	1.3	0.3
Copper (ICP)		ug/g	0.6	0.1
Lead (ICP)		ug/g	5.	2.
Molybdenum (ICP)		ug/g	< 0.3	0.3
Nickel (ICP)		ug/g	4.7	0.5
Vanadium (ICP)		ug/g	4.7	0.2
Zinc (ICP)		ug/g	9.7	0.1
Cadmium (ICP-MS)	NOT DONE			
Thallium (ICP-MS)	NOT DONE			
Arsenic (ICP-MS)	NOT DONE			
Selenium (ICP-MS)	NOT DONE			
Saturation Percent		%	29.	1.
pH (Saturated Paste)			7.5	0.1
Electrical Conductivity	NOT DONE			

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Sample Description : PRODUCED SAND  
 Sample Date & Time : N/A N/A  
 Sampled By :  
 Sample Type : GRAB  
 Sample Received Date: June 25, 1996  
 Sample Station Code :

PRELIMINARY COPY

BROMLEY-MANN ECOS INC.  
 ATTENTION : PETER MOHAMMED

SAND/SLUDGE

Chemex Worksheet Number : 96-06864-1  
 Chemex Project Number : BROM10-0502  
 Sample Access :  
 Sample Matrix : SAND  
 Report Date : July 5, 1996  
 Analysis Date : June 27, 1996

TOTAL EXTRACTABLE HYDROCARBONS METHOD MODIFIED ASTM D2887					
COMPONENT	mg/Kg	BOILING RANGE	COMPONENT	mg/Kg	BOILING RANGE
C 08	< 1.	98.5 TO 125.7	C 35	140.	483.1 TO 491.0
C 09	3.	125.8 TO 150.8	C 36	160.	491.1 TO 498.0
C 10	11.	150.9 TO 174.2	C 37	120.	498.1 TO 505.0
C 11	32.	174.3 TO 196.0	C 38	120.	505.1 TO 512.0
C 12	78.	196.1 TO 216.0	C 39	120.	512.1 TO 519.0
C 13	260.	216.1 TO 236.0	C 40	110.	519.1 TO 525.0
C 14	220.	236.1 TO 253.0	C 41	81.	525.1 TO 535.0
C 15	370.	253.1 TO 271.0	C 42	110.	531.1 TO 537.0
C 16	340.	271.1 TO 287.0	C 43	77.	537.1 TO 543.0
C 17	360.	287.1 TO 302.0	C 44	98.	543.1 TO 548.0
C 18	420.	302.1 TO 317.0	C 45	72.	548.1 TO 554.0
C 19	380.	317.1 TO 331.0	C 46	68.	554.1 TO 559.0
C 20	370.	331.1 TO 344.0	C 47	66.	559.1 TO 565.0
C 21	320.	344.1 TO 357.0	C 48	40.	565.1 TO 570.0
C 22	310.	357.1 TO 366.0	C 49	84.	570.1 TO 576.0
C 23	350.	366.1 TO 380.0	C 50	56.	576.1 TO 581.0
C 24	240.	380.1 TO 391.0	C 51	59.	581.1 TO 584.0
C 25	320.	391.1 TO 402.0	C 52	40.	584.1 TO 588.0
C 26	190.	402.1 TO 412.0	C 53	62.	588.1 TO 592.0
C 27	250.	412.1 TO 422.0	C 54	40.	592.1 TO 596.0
C 28	350.	422.1 TO 432.0	C 55	66.	596.1 TO 600.0
C 29	340.	432.1 TO 441.0	C 56	67.	600.1 TO 604.0
C 30	180.	441.1 TO 449.0	C 57	70.	604.1 TO 608.0
C 31	210.	449.1 TO 459.0	C 58	50.	608.1 TO 612.0
C 32	120.	459.1 TO 468.0	C 59	76.	612.1 TO 615.0
C 33	190.	468.1 TO 476.0	C 60	54.	615.1 TO 619.0
C 34	140.	476.1 TO 483.0			

Average molecular weight : 322 AMU TOTAL HYDROCARBONS C8-C10 14. mg/Kg  
 TOTAL HYDROCARBONS C11-C60 8400. mg/Kg

Surrogate recovery : 109% SAND surrogate limits : 72% - 125%.  
 MDL per component : 1. mg/Kg below C31 and 2. mg/Kg above C30  
 5. mg/Kg above C39 and 5. mg/Kg above C49

Results are reported in accordance with CCME guidelines. All results are corrected for blank levels.  
 MDL - Method detection level. The reliable detection level is twice the method detection level.  
 ( ) - Bracketed results are values below the reliable detection level, and are subject to reduced levels of confidence.  
 Results are uncorrected for moisture unless otherwise noted.

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 Edmonton: 9331 - 48th Street, T6B 2P4, Telephone (403) 485-8277, FAX (403) 485-3322

Sample Description : PRODUCED SAND  
 Sample Date & Time : N/A N/A  
 Sampled By :  
 Sample Type : GRAB  
 Sample Received Date: June 25, 1996  
 Sample Station Code :

PRELIMINARY COPY

**BROMLEY-MANN ECOS INC.**  
**ATTENTION : PETER MOHAMMED**

SAND/SLUDGE

Chemex Worksheet Number : 96-06866-1  
 Chemex Project Number : BROM010-0502  
 Sample Access :  
 Sample Matrix : SAND  
 Report Date : July 5, 1996  
 Analysis Date : June 28, 1996

PARAMETER	VOLATILE ORGANICS ANALYSIS - BTEX EPA METHOD 8260 MODIFIED			
	CONC	BLANK CONC	UNITS	MDL
Benzene	< 0.024	< 0.005	mg/Kg	0.024
Ethylbenzene	< 0.024	< 0.005	mg/Kg	0.024
Toluene	< 0.024	< 0.005	mg/Kg	0.024
m & p-Xylene	< 0.024	< 0.005	mg/Kg	0.024
o-Xylene	< 0.024	< 0.005	mg/Kg	0.024
Total Purgeables (C3 to C10)	11.	0.16	mg/Kg	0.08
Total Purgeables (C11 to C12)	61.	(0.02)	mg/Kg	0.02

**NOTES :**

Results are reported in accordance with CCME guidelines, "Guidance Manual on Sampling, Analysis, and Data Management for Contaminated Sites, Volume I". All results are corrected for blank levels.

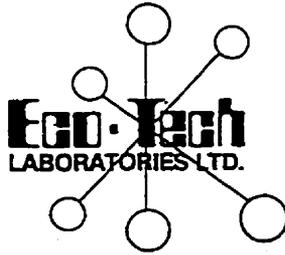
MDL - Method detection level. - Calculated on the basis of the instrument detection level, the dilution used, and the weight of the sample.

( ) - Bracketed results are values below the reliable detection level, and are subject to reduced levels of confidence. The reliable detection level is twice the method detection level.

**QA/QC SUMMARY**

All samples were spiked with a component whose recovery was monitored to maintain analysis accuracy. Guidelines from SM846 for suggested surrogate recoveries for each matrix are shown below. Results are uncorrected for moisture unless otherwise noted.

Instrument : GC/MS  
 Surrogate Recovery : 100% SAND surrogate limits : 80% - 117%.



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Meyerhaeuser Canada Ltd.  
Metals results

Report # E1267A

PARAMETERS	#1	#2	#3	#4
ALUMINUM %	.73	2.19	.91	.62
ANTIMONY	5	10	5	5
ARSENIC	15	<5	5	8
BARIUM	120	160	105	150
BISMUTH	<5	15	<5	<5
BORON	12	10	10	10
CADMIUM	4	<1	6	5
CALCIUM %	7.22	2.49	7.83	>15
CHROMIUM	85	75	128	102
COBALT	9	25	9	5
COPPER	148	50	151	118
IRON %	1.31	3.66	1.57	.92
LANTHANUM	<10	10	10	<10
LEAD	44	26	40	26
MAGNESIUM %	.59	1.38	.53	.37
MANGANESE	785	483	1291	1237
MOLYBDENUM	5	1	5	3
NICKEL	36	51	50	37
PHOSPHORUS	1800	1390	2450	3040
POTASSIUM %	.09	.33	.12	.08
SILVER	12.8	<.2	6.6	7
SODIUM %	.32	.11	.29	.26
STRONTIUM	96	66	89	160
TIN	<20	<20	<20	<20
TITANIUM	.05	.18	.04	.03
TUNGSTEN	<10	<10	<10	<10
URANIUM	<10	<10	<10	<10
VANADIUM	29	59	29	16
YTRIUM	7	19	7	7
ZINC	470	134	773	544
MERCURY *	.34	.61	.69	.73

NOTE: \* Awaited Results

All results in mg/kg on a dry weight basis unless otherwise noted.

*[Signature]*

**ANALYSIS REPORT**  
**POLYCHLORINATED DIBENZODIOXINS AND DIBENZOFURANS**

**HIGH RESOLUTION GC/MS**

Client: Weyerhaeuser Canada

Our File: 2200

Sample ID: #1 North East - Sept 14

Axys ID: 2200-12

Sample Weight: 3.13 g dry

Date: September 17, 1993

Dioxins	Concentration pg/g	(SDL)	Furans	Concentration pg/g	(SDL)
T <sub>4</sub> CDD - Total	560	1.3	T <sub>4</sub> CDF - Total	5600	0.8
2,3,7,8	440	1.3	2,3,7,8	2800	0.8
P <sub>5</sub> CDD - Total	150	1.3	P <sub>5</sub> CDF - Total	460	1.0
1,2,3,7,8	38	1.3	1,2,3,7,8	76	1.0
			2,3,4,7,8	52	1.0
H <sub>6</sub> CDD - Total	750	1.3	H <sub>6</sub> CDF - Total	130	1.2
1,2,3,4,7,8	6.8	1.3	1,2,3,4,7,8	27	1.2
1,2,3,6,7,8	110	1.3	1,2,3,6,7,8	3.9	1.2
1,2,3,7,8,9	73	1.3	2,3,4,6,7,8	9.2	1.2
H <sub>7</sub> CDD - Total	990	1.7	1,2,3,7,8,9	6.2	1.2
1,2,3,4,6,7,8	490	1.7	H <sub>7</sub> CDF - Total	200	2.1
O <sub>8</sub> CDD	1300	1.4	1,2,3,4,6,7,8	66	2.1
			1,2,3,4,7,8,9	16	2.1
			O <sub>8</sub> CDF	78	1.4

SDL = Sample Detection Limit

ND = Not Detected

NDR = Peak detected but did not meet quantification criteria

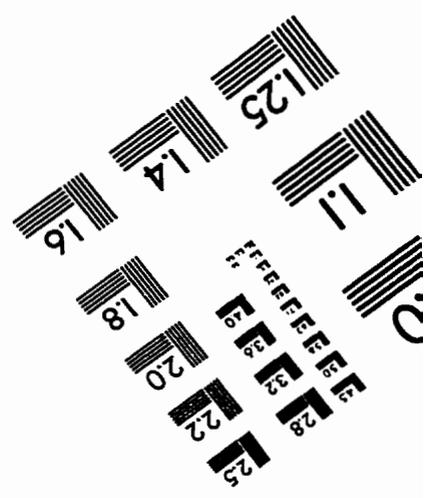
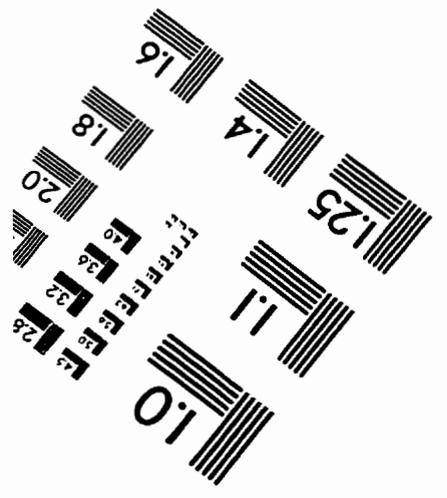
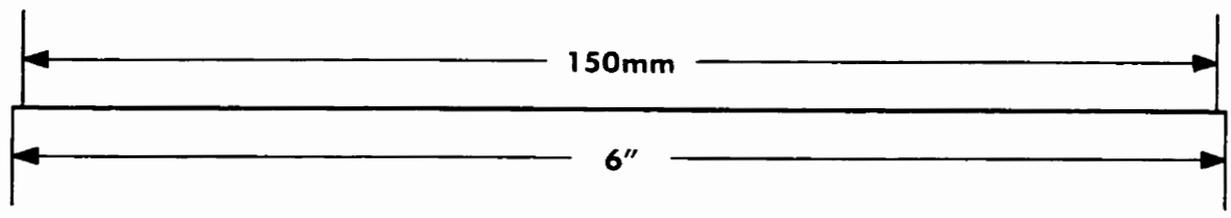
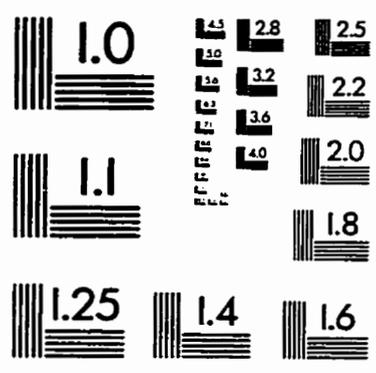
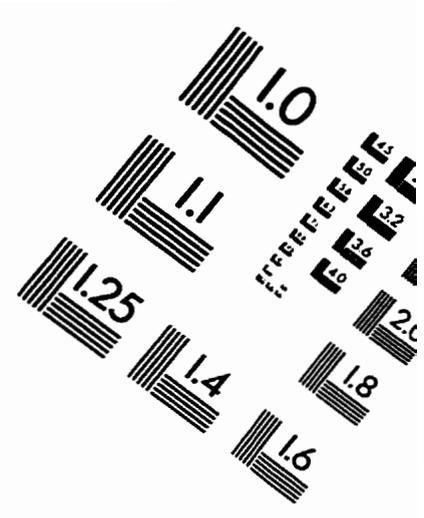
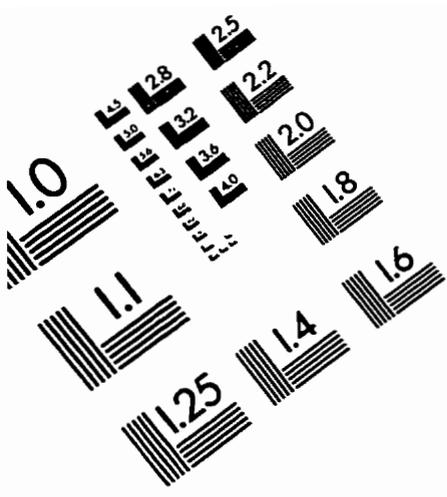
**Surrogate Standard Recovery (%)**

<sup>13</sup> C-T <sub>4</sub> CDD:	81
<sup>13</sup> C-T <sub>4</sub> CDF:	65
<sup>13</sup> C-P <sub>5</sub> CDD:	66
<sup>13</sup> C-H <sub>6</sub> CDD:	86
<sup>13</sup> C-H <sub>7</sub> CDD:	108
<sup>13</sup> C-O <sub>8</sub> CDD:	110

Approved by:

*M. Coreen Hamilton*  
M. Coreen Hamilton  
A. Dale Hoover

# TEST TARGET (QA-3)



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