CHLOROCARBON TRANSPORT OUT OF CONTAMINATED SOIL PARTICLES

by

Shuxiang Han

B.S., Civil Engineering
Tsinghua University, China, 1984

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Signature of Author.

Certified by

Visiting Professor Maria Flytzani-Stephanopoulos
Department of Chemical Engineering
Thesis Advisor

Certified by

Professor Adel F. Sarofim
Department of Chemical Engineering
Thesis Advisor

Thesis reader

Professor Duvvuru Sriram
Department of Civil & Environmental Engineering

Accepted by

Joseph M. Sussman
Chairman, Departmental Committee on Graduate Studies
The adsorption and desorption of toluene ($C_7H_8$), monochlorobenzene ($C_6H_5CL$), dichlorobenzene ($C_6H_4CL_2$) have been studied for two types of particles, montmorillonite and Spherocarb, the representative of a clay soil and the other of a strong sorbent. The nature of particles is the key factor in the decontamination. The retained final monolayer organic molecules, which stick to the solid surface more tightly, correlate with the microporous area in the solids. The controlling mechanisms of desorption is proposed to be the higher activation energy on the micropore wall surface. The chemical composition of the contaminants have a significant effect on the amount adsorbed under isothermal conditions. The polarity of organic chemical is believed to be responsible for this phenomenon. Heating the particles is an effective method for achieving complete desorption. The experimental results indicate that each combination of contaminant-particle has a different required minimum temperature for complete desorption. The nature of the particles and contaminant contribute to the minimum temperature.

The desorption kinetics were studied. Desorption was found to be controlled by an activated process. Surface diffusion is the main transport phenomenon when the contaminants desorb from small pores. From the experimental results, it is suggested that the diffusion model is not sufficient to describe the rate of desorption in this study. A new kinetic model is used to describe the desorption process. It is found that the activation energy distribution of the solid surface is close to the Gaussian distribution.
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CHAPTER 1. INTRODUCTION

With the development of industrial technology, the utilization of chemical materials and energy is accompanied by an increasing flux of organic chemicals to the environment. Solving the problem of hazardous waste is imperative (1-6).

Solids are important contributors to hazardous wastes in the United States (6). Traditional way of handling hazardous waste is disposal to a landfill site (7). Studies have found that organic compounds may be released from waste landfills and contaminate soil, groundwater and air. Each year, there are millions of tons of residues produced by industrial processing and treatment of other wastes. And millions to billions of tons of contaminated soils are found in numerous, and widely distributed abandoned landfill sites. Each location may contain numerous exposed or buried drum of wastes, and hundreds to thousands of tons of contaminated soils, posing an immediate threat to the environment and human health. Therefore, cleanup of contaminated soils is critical to national remediation of hazardous wastes.

One common method for the cleanup of contaminated soils is redistribution (3), where the contaminated soil is redisposed in an approved landfill site. In resent years, because the landfill costs increasing and regulations on land filling become more strict, thermal incineration is an attractive technology for decontaminating hazardous solids.
Incineration is an engineered process that uses decomposition of organic matter by thermal oxidation at high temperature (usually 900°C or greater) to destroy the hazardous constituents in the waste (5). For incineration, an applicable disposal must be combustible. Therefore, wastes with organic content are considered appropriate for incineration. There are four most common incinerator designs: liquid injection, rotary kiln, fixed hearth, and fluidized bed incinerators.

A typical incineration system for solids hazardous wastes consists of a primary combustor (8), where the contaminants are primarily desorbed from solid, and the secondary combustor, or afterburner, where the major thermal destruction takes place. Rotary kilns are the more versatile and common incinerators that they are applicable to the destruction of solid wastes, slurries, and containerized waste as well as liquids.

A rotary kiln is a cylindrical-lined shell that is mounted at a slight incline from the horizontal plane (8). Rotation of the shell provides for transportation of the waste through the kiln and for enhanced mixing of the waste with the combustion air. The residence time of waste solids in the kiln is generally 1 to 1.5 hour that is controlled by the kiln rotation speed (1-5 revolutions per minute), the waste feed rate. The primary function of the kiln is to desorb the hazardous matter from solid surface to gas state, which occurs through a series of volatilization, destructive distillation, and partial combustion. An afterburner is needed to complete the gas-phase combustion reactions. The afterburner is connected
directly to the discharge end of the kiln, where the gases exit the kiln. Both kiln and afterburner are usually equipped with an auxiliary fuel firing system to maintain the desired operated temperatures.

Because the inorganic compounds of hazardous wastes are not destroyed by incineration, following incineration of hazardous wastes, combustion gases may need to be further treated in an air pollution control system. An ideal incinerator for hazardous solids would expose all the solids to sufficient time, temperature, and oxidizing agent (air) to assure their complete oxidation (combustion). For some conditions, because a major portion of the volatiles combustion process occurs as a temporary and immediate extension of devolatization, there may be some toxic substances generation from secondary reactions of contaminants which are of public concern as health hazardous. The materials exiting the incineration system are either as bottom ash from the combustion chamber, as contaminants in scrubber wastes and other air pollution control residues, and in small amounts in the air emissions from the stack.

Technically speaking, any waste with a hazardous organic fraction, no matter how small, should be a candidate for incineration. Properly designed and operated thermal destruction systems offer the prospect of destroying the hazardous organic components of waste streams (5). Many existing data indicate that well-operated hazardous waste incinerators and other thermal destruction facilities are capable of achieving high levels of organic
hazardous material destruction which equal or exceed current RCRA performance standards (5, 9). However, even under good combustion conditions, incomplete combustion byproducts may be emitted. One of the concerns expressed by some scientists, environmentalists and the public regarding thermal destruction of hazardous waste is the possible impact on human health and the environment of emissions of potentially hazardous products of incomplete combustion (5, 6). The volatile compounds tend to be detected more often and in significantly higher concentrations than the semivolatile compounds.

When a rotary kiln operates in a batch mode, transient phenomena involving rapid release of waste vapor into the kiln environment may occur (6, 11). Such phenomena of transient waste vapor generation, so-called puffs, are frequently encountered when fresh waste is introduced to the incineration chamber too rapidly or in too high a concentration. Puffs can disrupt normal operation or may reduce the chamber temperatures, causing volatile or char combustion to be quenched. The experimental results show that puffs are readily generated even when feeding small quantities of waste at 100% excess air. Puff generations increase with the kiln temperatures increases , apparently by the liquid evaporation rates increasing.

In a rotary kiln environment, the charged solid is as a bed composed of many layers of particles. Hence, both intraparticle and interparticle effects contribute to the desorption process (1-4, 7). It is evident that a fundamental study of the adsorption and
desorption of contaminants on soil particles can contribute significantly to the understanding of the transport and diffusion of hazardous chemicals in soils and lead to the optimization of the operation of a rotary kiln.
A number of efforts have been made to evaluate the cleanup of contaminated soil with selected constituents (1-4, 7). A more desirable option is to desorb the contaminants from soil at lower temperatures and then expose the off-gas to a high-temperature afterburner for decomposition of the hazardous compounds. DeLeer and co-workers (12), who focused on low-temperature desorption of contaminants from soils, found that, in an indirectly-heated laboratory reactor, the concentration of PAHs was below the detection limits (0.01mg/kg) at temperatures of 300°C-350°C and a residence of time 30 minutes. In Dev's experiments (13), the recovery of tetrachloroethylene from a sandy soil was 95% at temperatures between 90°C-130°C (3). Lighty, et al (1-4) performed studies of the chemical and physical processes of several contaminants removal from soil beds, with very high cleanup efficiencies at temperatures of 100°C-400°C. The results obtained by these investigators show the possibility of contaminants desorption to a satisfactory limit at modest temperature. These achievements are significant to optimize the incinerator operation parameters, especially for reducing volatile puffs and the high cost of incineration systems.

"Puff" phenomena has been studied by Wendt, et al from an experimental and theoretical point of view (14). A transient vaporization/fragmentation model was developed to give a good
mechanistic understanding. The results showed that a high kiln temperature and rotation speed exacerbate puff generation. Hence, lowering the operation temperature for complete desorption is very beneficial for a rotary kiln system.

Studies have pointed out that desorption of contaminants in the soil particles is the key step during incineration (1-4, 7). Lighty and co-workers studied incineration of hazardous solid waste materials in a rotary kiln environment (1-4). The charged solid is a bed composed of many layers of particles that are being slowly stirred in chamber. Hence, the contaminants may exist either adsorbed onto the internal pore structure of the particles, or adsorbed onto the external surface of the particles or as a liquid phase within the bed. In their study, they observed that temperature was the dominant independent parameter in the desorption process. Even above the boiling point of the organics used (e.g. p-xylene), the amount of contaminant remaining in the soil was high and the rate of removal leveled off with time, indicating that a threshold concentration remaining in the soil would evolve very slowly. It is suggested that contaminant desorption, not intraparticle transport, is the probable rate-limiting step at long times in the evolution of the contaminant from soil particles, which necessitated heating well above the boiling point of the organic compound. And the last monolayer of contaminant molecules may be tightly bound to the soil, thus requiring high temperatures to ensure adequate cleanup. The results indicated that:
a) desorption rate is a strong function of soil types. Porous chemically active soils, such as clay and peat, may require longer residence times or higher temperatures to reach lower cleanup limits than impervious sands.

b) heavier hydrocarbons are more difficult to remove than lighter compounds.

c) in complex hydrocarbon mixtures, the lighter compounds will be selectively desorbed first.

d) increasing the local temperature increases the desorption rates.

e) moisture has two effects on desorption. First, the water replaces sites that would have had contaminant physically adsorbed, therefore, contaminant is more easily desorbed. Secondly, the contaminant is "steam distilled" with the water as the desorption takes place.

M. Flytzani-Stephanopoulos and co-workers (7, 15) studied the isothermal adsorption and desorption of contaminants from a single soil particle by using EDB (the Electrodynamic Thermogravimetric Analyzer) to simplify the desorption environment. The interparticle transport is removed for this device because there is no external diffusion. In their study, toluene and carbon tetrachloride were tested at ambient temperature on three types of soil particles: Spherocarb, montmorillonite, and Carbopack. The workers invoked that the formation of liquid may block the micropores, and therefore
inhibit further penetration of the organic compound inside the pores. They also attributed the main mechanism for adsorption and desorption to surface diffusion in the monolayer. During desorption, the process which takes place is evaporation, first from the larger pores and then from the smaller capillaries. The results suggested effects of soil types, contaminants, concentration of organic matter, and temperature on desorption process. This study pointed out that the desorption of a monolayer of adsorbate on soil particles is the key step for complete decontamination.

Many investigators have studied the kinetics of the desorption phenomena (16-19). Pore diffusion is commonly considered as the limiting step in the soil particle desorption. Hence, Fick's diffusion law is usually employed to describe the desorption mechanism. But the complexity of pore distribution in soil particles increases the uncertainty of diffusion coefficient. People often assume homogeneity among the pores, which leads to a significant oversimplification for microporous sorbents. For the diffusion coefficient, the study by H. Kopsinis suggested a time-dependent apparent diffusivity (19). And the effective diffusivity changes from $10^{-7} \text{ cm}^2/\text{sec}$ to $10^{-9} \text{ cm}^2/\text{sec}$, values much lower than the organic molecular diffusivity in air. Capillary condensation in the micropores ($<30\text{Å}$) and surface diffusion were employed to explain the behavior. In the adsorption process, the adsorbed molecule may be desorbed into the gas or be readsorbed onto the pore wall in its transport journey. So, the migration time will increase with the surface area increase due to the increase in adsorption sites.
J. Farrell and M. Reinhard (18) studied the desorption of halogenated organic from soil for unsaturated conditions. The desorbed organic molecules must diffuse through the water in the pores and then out of the soil particle. The solid/solution distribution coefficient, $K_d$, and solid porosity effects are considered in determining the effective diffusivity. The experimental results indicated that the solid diameter has little effect on the desorption rate, not as high as expected from the diffusion model, especially for the later (slow) desorption branch. So, the particle diameter is not considered the length scale for the slow diffusion. The experiments also show that the effective diffusivity, $D_e$, decreases with the contaminant removal. They suggest that two different mechanisms appear to control the rate of organic desorption. At the beginning, and for the major portion of adsorbed organic molecules, pore diffusion controls the contaminant desorption. When the desorption process enters the second period, e.g., slow desorption period, adsorption in micropores is consistent with the slow released fraction.

A recent study (18) showed that adsorption of contaminants in micropores may limit the complete desorption for soil cleanup because it increases the effects of steric hindrance, sorption energies and surface area, all of which contribute to reduce desorption rates.

Although there are several studies of soil decontamination both experimental and theoretical regarding the adsorption and desorption of organics soils, the effects of soil characteristics and
organic chemical properties are needed for complete understanding and for optimizing the thermal decontamination system.
In the adsorption of gases on solids, the shape of the adsorption isotherm may vary substantially depending on the nature of the adsorbent and the adsorbate. The structure and distribution of solid pores are important. The existence of pores increases the area of solid exposed to the environment. Hence, there are more adsorbed sites, which lead to higher adsorbed amounts.

For mesoporous solids, the typical gas adsorption curve at different vapor pressure is as Figure 3-1 (20). The essential characteristic of mesopores in the isotherm curve is the capillary effect, which is responsible for the hysteresis loop. The lower portion of the loop is traced out on adsorption, the upper portion on desorption. Studies found that the general form of the loop is independent of the adsorbate and arises from the porous structure of the adsorbent. And the steep portion of the desorption branch occurs at a relative pressure that depends on the nature of the adsorbate. At the initial step of the curve, the adsorption is restricted to a thin layer on the wall of pores, until at a certain stage, capillary condensation will occur in the finest pores. On thermodynamic grounds, the equilibrium vapor pressure, $P$, over a concave meniscus of liquid, must be less than the saturation vapor pressure $P_0$ at same temperature. This means that a vapor molecule will be able to condense to a liquid in the pores of a solid even when its pressure is less than $P_0$. As the vapor pressure is progressively
increased, wider and wider pores are filled. Because of higher volume to surface ratio of wider pores, adsorption amount increases faster with vapor pressure increase when condensation occurs in wider pores. The pressure range responsible for condensation phenomena is very large due to the mesopore range from 20-500Å. Therefore, the presence of mesopores brings about an increase in adsorption due to the capillary condensation, while solids possessing only macropores show little or no capillary effects.

If a solid contains micropores, which are no more than a few molecular diameters in width (<20Å), this results in the adsorption curve of Figure 3-2 (20).

Due to the small size of pores, the potential fields from neighboring walls will overlap and the interaction energy of the solid with a gas molecule will be correspondingly enhanced (18, 20). This will bring about a complete filling of pore at quite low pressure. The evidence for that is the rapid increase of adsorption amount at lower vapor pressure stage. It is pointed that for the microporous solids, the amount of vapor adsorbed on the exterior surface with increasing value of $P/P_0$ is small relative to that adsorbed in pores. For the plateau in the curve, the explanation is that the pores are so narrow that they can not accommodate more than a single molecular layer on their wall.

Aside from increased adsorption at lower vapor pressure due to the higher adsorption energy, there are two additional contributions to reduced transport rates in micropores. The first
Figure 3-1 The Adsorption Isotherm of Solid with Mesopores

Figure 3-2 The Adsorption Isotherm of Solid with Micropores
contribution is that steric hindrance increases greatly as the pore size approaches the organic molecular size. The second contributing factor is that as pore size decreases, the ratio of pore surface area to pore volume increases. Therefore, smaller pores lead to higher internal retardation.
4.1 Experimental Procedure

A TGA (Thermogravimetric Analyzer) was used as a "single-layer" multi-particle reactor to measure the relative variation of the soil particle weight during adsorption and desorption of organic vapor. It consists of a Cahn 2000 electrobalance, Micricon temperature controller, and Data acquisition system. The schematic diagram is seen in Figure 4-1.

The Cahn 2000 electrobalance is a very sensitive weight and force measurement instrument ($10^{-6}$g). It contains of a balance beam, a torque motor coil, sample suspension fixtures, a beam position sensor system and controls, circuitry and indicators. When the weight of sample changes, a torque is formed about the axis of rotation from both sides of the beam. An electric current flowing in the torque motor coil produces a torque about the axis of rotation. When these two torques are balanced, the electric current is a direct measure of the combination of forces changed in the sample. The Micricon system controls the heating rate and temperature of the furnace. It can be programmed to provide various rate of heating as well as isothermal heating. The sample temperature is monitored by a thermocouple and displayed on the Micricon screen. The signals of the temperature from Micricon controller and the electric current
balancing the sample change from the electrobalance are converted by Cahn 2000 and then are accepted by the data acquisition system.

A thin layer of quartz wool, that permits the gas flowing through, filled the chlorimet wire loop. A layer of soil particles was positioned on the quartz wool. Then the sample loop with the soil particles on the quartz wool was installed into the TGA chamber, in which the desired N$_2$ gas (99.9% pure) and purge gas flowed through. The particles were dried before adsorption runs by heating at 250°C for two hours.

After drying, the temperature of the TGA chamber was lowered to room temperature. Dried particle weight was measured. Then, the N$_2$ stream with contaminant vapor was switched into the chamber, the adsorption process began. N$_2$ flowrates were kept unchanged before and after the valve opening. When the particle weight reached a stable value, the adsorption process was at equilibrium. The desorption experiment was carried out immediately after the adsorption runs by stopping the contaminated N$_2$ stream and introducing pure N$_2$ gas.

In the whole processes of adsorption and desorption, the drag force effect was removed by keeping the gas flow rate unchanged.

4.2 Contaminant Vapor

In the work we performed, the contaminant vapor stream was produced by introducing the pure N$_2$ flowing through the saturator,
in which the pure contaminant liquid was put in. A gas distributor was installed at the inlet of the saturator to spray the gas evenly. The vaporizing molecules of the contaminant were carried out of the saturator by N$_2$ stream.

We could change the temperature of the saturator to get different contaminant concentration in the N$_2$ stream. For this purpose, the saturator was put into a water bath. Three sets of experiments were done by changing the water temperature in the bath:

a: Room temperature: keeping the water temperature in the bath at 21°C

b: 0°C: putting ice into the bath to make a mixture of ice and water at a temperature of 0°C

c: -21°C: putting dry ice (solid CO$_2$) and NaCL into the bath to keep the water temperature at -21°C

Therefore, we can get three different concentrations in the N$_2$ stream for each contaminant.

In order to calculate the concentrations of the contaminants C$_7$H$_8$ (toluene), C$_6$H$_5$CL (monochlorobenzene), and C$_6$H$_4$CL$_2$ (dichlorobenzene) in the N$_2$ stream, the Antoine equation is used:

$$\ln P = A - \frac{B}{C + T}$$

where:
P: the organic vapor partial pressure in the \( N_2 \) stream (mmHg)

T: the temperature of the saturator (K)

A, B, C: Antoine constants

For \( C_7H_8 \): \( A=16.0137 \) \( B=3096.52 \) \( C=-53.67 \)

\[ C_6H_5CL \] \( A=16.0676 \) \( B=3295.12 \) \( C=-55.60 \)

\[ C_6H_4CL_2 \] \( A=16.2799 \) \( B=3798.23 \) \( C=-59.84 \)

Therefore, the partial pressures for different contaminants at different temperatures are:

For \( C_7H_8 \):

\( T=21^\circ C \) \( P=22.86\text{mmHg} \)

\( T=0^\circ C \) \( P=6.66\text{mmHg} \)

\( T=-21^\circ C \) \( P=1.49\text{mmHg} \)

For \( C_6H_5CL \):

\( T=21^\circ C \) \( P=9.45\text{mmHg} \)

\( T=0^\circ C \) \( P=2.49\text{mmHg} \)

\( T=-21^\circ C \) \( P=0.49\text{mmHg} \)

For \( C_6H_4CL_2 \):

\( T=21^\circ C \) \( P=1.06\text{mmHg} \)

\( T=0^\circ C \) \( P=0.21\text{mmHg} \)
4.3 The Solid Particle Properties

In this study, montmorillonite and Spherocarb are employed as surrogate soil particles. The physical properties of the materials are reported in Table 4-1.

Table 4-1. Physical properties of Solid Materials

<table>
<thead>
<tr>
<th>material</th>
<th>diameter (μm)</th>
<th>surface area (m²/g)</th>
<th>intrusion volume (cm³/g)</th>
<th>bulk density (g/cm³)</th>
<th>porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spherocarb</td>
<td>125-150</td>
<td>860.0</td>
<td>0.83</td>
<td>0.63</td>
<td>0.525</td>
</tr>
<tr>
<td>montmorillonite</td>
<td>90-125</td>
<td>192.3</td>
<td>1.24</td>
<td>0.65</td>
<td>0.802</td>
</tr>
</tbody>
</table>

The surface area of solids was determined with the Flowsorb 2300 by measuring the quantity of N₂ that adsorbs as a single layer of molecules, a so-called monolayer, on the sample. The obtained surface area includes all the pore wall surface area which has pore diameter larger than the N₂ molecular diameter (3.64 Å) and flat surfaces. And the other properties in Table 4-1 were obtained by the Miromeritics Autopore 9200 mercury porosimeter. The device measures the volume distribution of pores in materials by mercury intrusion. It is based on the capillary law governing liquid
penetration into small pores. Pore surface area is calculated from the summation of the incremental pore volume area based on the mean diameter and the volume increment. For this mercury porosity measurement, only pore diameter larger than 30Å was measured. The distribution of the pore size for the two materials are shown in Figures 4-2 and 4-3.
Figure 4-2 Cumulative Surface Area vs. Pore Diameter

Spherocarb
Total Area 860 m²/g

Log (pore diameter) (Å)

Cumulative Area/Total Area

Figure 4-3 Cumulative Surface Area vs. Pore Diameter

Montmorillonite
Total Area 192 m²/g

Log (pore diameter) (Å)
CHAPTER 5. EXPERIMENTAL RESULTS AND DISCUSSION

The transient adsorption and desorption behavior for toluene, monochlorobenzene, dichlorobenzene on montmorillonite and Spherocarb are investigated at room temperature and high temperature. In the present work, N₂ flowrate is 300cc/min. The changes of soil particle weight in the adsorption and desorption processes are recorded, in which, MA is the total amount of contaminant adsorbed by soil particles at adsorption equilibrium; Mad, the amount of contaminant stayed in particles at time t; and M₀, the dried pure soil particle weight just before adsorption begins. Therefore, at any time t, the weight of soil particles recorded by data acquisition is:

\[ W = \text{Mad} + \text{M₀} \]

Typical desorption process is shown in Figure 5-1. At initial time, the desorption is rapid and then falls off. For toluene-montmorillonite and monochlorobenzene-montmorillonite, the desorption time for 90 percent of initial amounts adsorbed is about two hours or longer (Table 5-1). At room temperature, the desorption time is over 15 hour-long and no complete desorption is observed. It is obvious that the last retained organic will take very long time to completely desorb from the soil particle. The desorption time will be much longer for Spherocarb. For this type of particles, less than 50 percent of adsorbed monochlorobenzene is desorbed in about two hours. The retained amount of organic by
Figure 5-1a  Adsorption of C₆H₅CL on Montmorillonite Particles

Figure 5-1b  Desorption of C₆H₅CL from Montmorillonite Particles
Table 5-1 Adsorption and Desorption Ammonut and Corresponding Characteristic Time

<table>
<thead>
<tr>
<th>Materials</th>
<th>Saturator Temperature (°C)</th>
<th>MA/M0 (g.liquid/g.solid)</th>
<th>t0.5a (min)</th>
<th>t0.9a (min)</th>
<th>t0.5d(min)</th>
<th>t0.9d(min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite-C7H8</td>
<td>-21</td>
<td>0.0457</td>
<td>0.82</td>
<td>2.8</td>
<td>5.6</td>
<td>&gt;120</td>
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<td></td>
<td>0</td>
<td>0.0999</td>
<td>0.96</td>
<td>22.1</td>
<td>4.1</td>
<td>124</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>0.2172</td>
<td>1.44</td>
<td>15.1</td>
<td>8.5</td>
<td>89.1</td>
</tr>
<tr>
<td>Sphero-carb-C7H8</td>
<td>-21</td>
<td>0.3350</td>
<td>0.9</td>
<td>1.97</td>
<td>94</td>
<td>&gt;140</td>
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<td></td>
<td>0</td>
<td>0.3325</td>
<td>0.5</td>
<td>0.9</td>
<td>&gt;140</td>
<td></td>
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<tr>
<td></td>
<td>21</td>
<td>0.3772</td>
<td>0.3</td>
<td>0.65</td>
<td>&gt;120</td>
<td></td>
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<tr>
<td>Montmorillonite-C6H5CL</td>
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<td>0.0414</td>
<td>3.8</td>
<td>30.1</td>
<td>11.2</td>
<td>127</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0.1042</td>
<td>2.1</td>
<td>29</td>
<td>8.2</td>
<td>&gt;100</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>0.3124</td>
<td>3.8</td>
<td>38.4</td>
<td>17.7</td>
<td>101</td>
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<tr>
<td>Sphero-carb-C6H5CL</td>
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<td>0.4017</td>
<td>2.2</td>
<td>5</td>
<td>&gt;140</td>
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<td>0.4142</td>
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<td>0.8</td>
<td>1.5</td>
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<td>Montmorillonite-C6H4CL2</td>
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<td>5.7</td>
<td>60</td>
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<tr>
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<td>28</td>
</tr>
<tr>
<td>Sphero-carb-C6H4CL2</td>
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<td>0.75</td>
<td>1.47</td>
<td>&gt;150</td>
<td></td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>0.5569</td>
<td>0.76</td>
<td>1.7</td>
<td>&gt;140</td>
<td></td>
</tr>
</tbody>
</table>
solid corresponds to a coverage less than a monolayer. It is understood that some adsorbed molecules in the monolayer is more strongly bound to the solid surface.

5-1. Effect of Initial Concentration for Desorption

In this research, we have conducted three sets of adsorption experiments by keeping the saturator separately at 21°C, 0°C, and -21°C. It is expected that a different adsorbed amount for each pair contaminant-solid at equilibrium can be reached (Figure 5-2 and Figure 5-3) due to the different vapor pressure in the gas stream. During the whole process, the TGA chamber temperature was kept at room temperature.

An observation has been found in the desorption process of monochlorobenzene from montmorillonite that there is no appreciable variation in the desorption rate \((\text{Mad/MA})\) (Figure 5-4) although the initial amounts of the contaminant adsorbed are different at the beginning of desorption process. This means that the relative desorption rates \((\Delta(\text{Mad/MA})/\Delta t)\) are weak function of initial contaminant concentration. The same situation has been found in the desorption of toluene from montmorillonite (Figure 5-5) and Spherocarb (Figure 5-7), and also for the desorption of \(\text{C}_6\text{H}_5\text{Cl}\) from Spherocarb (Figure 5-6).

The data of Figure 5-4 are further analyzed in regards to the slow desorption segment. The two curves corresponding to 0.312 (T=
Figure 5-2 Adsorption of C₆H₅Cl on Montmorillonite Particles for Different Saturator Temperature

Figure 5-3 Adsorption of C₇H₈ on Montmorillonite Particles for Different Saturator Temperature
Figure 5-4  Desorption of C₆H₅CL from Montmorillonite Particles

Figure 5-5  Desorption of C₇H₈ from Montmorillonite Particles
Figure 5-6  Desorption of C₆H₅CL from Spherocarb Particles

Figure 5-7  Desorption of C₇H₈ from Spherocarb Particles
21°C) and 0.1043 (T=0°C) adsorbed amounts are replotted from the point corresponding to 0.0414 and 0.0478 adsorbed amounts left in the particles. This is almost equal to the third initially adsorbed amount MA (at T=-21°C). We take these amounts as the new MA to compare the desorption rates from montmorillonite with the same starting amount of contaminant. The results are shown in Figure 5-8. We can see that there are large differences in Mad/MA for the three cases. The fastest desorption rates occurs for the least initially adsorbed amount 0.041, and the slowest desorption for the highest initially adsorbed amount 0.312. This shows the importance of soil pore structure.

Figure 5-8 Desorption of C₆H₅CL from Montmorillonite Particles
The soil particles we used are not homogeneous. From the pore size distribution, we know that there exist micropores, mesopores, and flat surfaces. The site of adsorbed molecule determines whether it is easy or difficult to desorb from the solid surface. Theoretically, the gas molecules are likely to adsorb on the sites with higher adsorption energy. The gas molecules would bind stronger on micropore walls due to strong adsorption energy caused by the overlap interaction of pore walls. The adsorption should take place on the micropore walls at first and then on mesopores and flat surface. According to this view point, the desorption rates should be different for the different initially adsorbed amounts, which they should be similar for the same adsorbed amount left in the particles. This is not the case as clearly shown by the data of Figure 5-4 and 5-8, respectively.

An explanation for these observation is given in the following. Although there is higher energy of micropore walls, the small pore size also increases the difficulty for gas molecules to enter the micropores due to the higher steric hindrance. At lower P/P₀, because the difference of vapor concentration in the gas outside and inside of micropores is lower, the gas molecules are more difficult to diffuse into the micropores. Hence, at lower vapor pressure, although the adsorption amount at equilibrium is less than monolayer, not all the adsorbed molecules are trapped by micropores. From the experimental results above, we deduce that the distribution of the adsorbed vapor molecules among the micropores, mesopores and flat surfaces are nearly same, which
leads to no appreciable variation in the desorption rate for the three P/P_0 cases (Figure 5-4). After long time desorption at room temperature, there is a portion of contaminant left in the micropores of the particles, because once the gas molecules are trapped by micropores during adsorption, they are more difficult to be desorbed. In addition to energetics, the steric hindrance also slows down the diffusion of the molecules out of micropores. Thus, when 0.041 adsorbed amount is left in the particles initially containing 0.312 amount of C_6H_5CL, this is all in the micropores and comes out at a slower rate than the equivalent amount initially adsorbed at the lower P/P_0 (Figure 5-8).

5.2 Effect of Soil Type

Two types of solid particles, montmorillonite and Spherocarb, are compared in this work. The results show that the soil type has a strong effect on adsorption and desorption (Figure 5-9 - Figure 5-22).

For monochlorobenzene, the adsorbed amounts at equilibrium exhibit bigger difference for different P/P_0 (saturator at 21°C, 0°C and -21°C) on montmorillonite than on Spherocarb (Table 5-1). This can be explained from the physical properties of the two types of soil particles. For Spherocarb, the surface area is 96.5 m^2/g by mercury porosimetry. From Figure 4-2, we know that this area corresponds the pore diameter greater than 30Å. From BET analysis, the surface area of Spherocarb is 860 m^2/g. The nitrogen diameter
is 3.681Å. This means that a great portion of surface area (860 m²/g-96.5 m²/g=763.5 m²/g) is contributed by pore sizes of 3.681Å to 30Å. For montmorillonite, this contribution is much less, only 192.3m²/g-151.9m²/g=40.4m²/g. Hence, the latter consists mainly of mesopores. Its surface to volume ratio is less than that of Spherocarb. So, when same vapor pressure changes occur to the two types of particles and capillary condensation takes place, more gas molecules are condensed into the pores for montmorillonite. Hence, the adsorption isotherm for montmorillonite is similar to the theoretical mesopore adsorption curve (Figure 3-1 and Figure 5-23), and that of Spherocarb more similar to the theoretical micropore adsorption curve (Figure 3-2 and Figure 5-24). Thus, the pore structure of solids is significant to the adsorption phenomena.

For Spherocarb, the adsorption reaches equilibrium faster than montmorillonite (t₀.₉ₐ in Table 5-1). A gas molecule bound on a solid surface experiences repeated adsorption and desorption processes during the whole run. This phenomenon is related with the energy possessed by adsorbed molecule and adsorption sites. When adsorption site has higher energy, the adsorbed molecule is more difficult to desorb. Hence, the adsorbed molecules are easier to reach a stable state if they are trapped by micropores. For Spherocarb particles, the area of micropore walls (d<30Å) is the main portion of the total surface area (about 88%). Thus, shorter time is needed for Spherocarb to reach equilibrium.

For montmorillonite, the micropore wall area is only about 20 percent of the total area. The main portion is contributed by the
mesopores (d≥30Å) and flat surfaces. The molecules adsorbed and desorbed from mesopores and flat surfaces will affect the total adsorption process. Because of lower energy for mesopore and flat surface adsorption, the adsorbed molecules are easier to desorb/adsorb. Therefore, it will take a longer time to reach equilibrium.

Another phenomenon in the adsorption process is that there is a higher adsorbed amount of contaminant for Spherocarb than montmorillonite at equilibrium. We change the adsorption amounts MA/M0 to molecules per unit surface area (Figure 5-25 and Figure 5-26). It seems that more molecules are adsorbed on Spherocarb at lower vapor pressure and more molecules on montmorillonite at higher vapor pressure. The solids pore structure and distribution contribute to this phenomenon. At lower vapor pressure, e.g. saturator at -21°C, the adsorption amounts are less than monolayer. Because more adsorption sites on Spherocarb have higher energy and are easier to trap the gas molecules, maybe some fine pores experience the condensation. From the pore distribution, Spherocarb has a higher portion of fine pores. Hence, condensation in fine pores at lower vapor pressure will greatly increase the adsorption amount. With the vapor pressure increases (near P₀), bigger pores are filled with contaminant liquid. For montmorillonite, the ratio of volume to area is higher than that of Spherocarb. As discussed above, montmorillonite consists largely of mesopores. When the vapor pressure is higher, e.g. saturator at 21°C, the adsorption amount on montmorillonite increases greatly due to condensation.
occurring in big pores. With the saturator at 21°C, the adsorbed amounts correspond to multilayer. This verifies that condensation takes place in mesopores.

The soil type has the greatest effect on desorption process. At room temperature, the desorbed amount for montmorillonite is over 90 percent in about two hours. But for Spherocarb, the desorption amount is only about 20-50 percent for two hours. At room temperature, most molecules adsorbed on Spherocarb do not have enough energy to break away from the solid surface. The steric hindrance to diffusion out of micropores could be important. But, from the experimental results, we can see that it appears to be a secondary factor here because there is a big difference between adsorption and desorption time for Spherocarb.

For montmorillonite, the area of flat surfaces (pore diameter greater than 500Å) is only about 5 percent of the total area. The mesopores contribute the greatest portion of total area (about 75% of total area). Hence, for the higher adsorption amount, e.g., saturator at 21°C, most adsorbed molecules correspond to mesopore wall adsorption or mesopore condensation. For this portion of adsorbed molecules, it is shown from the experimental results that they are easier to be desorbed than that from micropores. So, at room temperature, a higher fraction of adsorbed molecules is desorbed than from Spherocarb.
Figure 5-9 Adsorption of C₇H₈ on Different Materials

Figure 5-10 Desorption of C₇H₈ from Different Materials
Figure 5-11 Adsorption of C$_7$H$_8$ on Different Materials

Figure 5-12 Desorption of C$_7$H$_8$ from Different Materials
Figure 5-13 Adsorption of C$_7$H$_8$ on Different Materials

Figure 5-14 Desorption of C$_7$H$_8$ from Different Materials
Figure 5-15 Adsorption of C₆H₅CL on Different Materials

Figure 5-16 Desorption of C₆H₅CL from Different Materials
Figure 5-17 Adsorption of $C_6H_5CL$ on Different Materials

![Graph showing adsorption of $C_6H_5CL$ on different materials.](image)

Figure 5-18 Desorption of $C_6H_5CL$ from Different Materials

![Graph showing desorption of $C_6H_5CL$ from different materials.](image)
Figure 5-19 Adsorption of C₆H₅CL on Different Materials

Figure 5-20 Desorption of C₆H₅CL from Different Materials
Figure 5-21 Adsorption of C₆H₅CL₂ on Different Materials

Figure 5-22 Desorption of C₆H₅CL₂ from Different Materials
5.3 Effect of Contaminants

In the present work, toluene and chlorobenzenes are examined. The experimental results indicate that there are differences between these compounds in the adsorption and desorption from soil particles. From the Table 5-1, it is seen that the adsorption amount at equilibrium is larger for chlorobenzenes than for toluene. We change the adsorbed amounts to the molar number per soil gram (Figure 5-27 and Figure 5-28). It shows that dichlorobenzene is more likely to adsorb onto the particles than monochlorobenzene and toluene at same vapor pressure. The phenomenon is similar for both Spherocarb and montmorillonite particles.

The contaminant chemical nature contributes to this phenomena. Chlorobenzenes are more polar due to their chlorides than toluene. The polarity strength sequence of the compounds are dichlorobenzene, monochlorobenzene, toluene. When the gas molecules interact with solid surface, different chemical affinity is exhibited between the contaminants and solid. For more polar contaminant, besides the van der Waal's force, there will be the induced dipole:dipole force. Hence, stronger attraction force exists for polar chemicals, and then more molecules will be adsorbed on the solid surface.
Figure 5-23  Adsorption Amount of C7H8 on Different Materials vs. Vapor Pressure

Figure 5-24  Adsorption Amount of C6H5CL on Different Materials vs. Vapor Pressure
Figure 5-25  Adsorption Amount of C\textsubscript{7}H\textsubscript{8} on Different Materials vs. Vapor Pressure

Figure 5-26  Adsorption Amount of C\textsubscript{6}H\textsubscript{5}Cl on Different Materials vs. Vapor Pressure
Figure 5-27 Adsorption Amount of Different Contaminants on Montmorillonite vs. Vapor Pressure

Figure 5-28 Adsorption Amount of Different Contaminants on Spherocarb vs. Vapor Pressure
5.4 The Effect of Particle Size

Two montmorillonite particle sizes, 45-53µm and 90-125µm, were compared to study the effects of particle size on the desorption process. Figure 5-29 and 5-30 show the comparison of toluene and monochlorobenzene desorption from the two particle sizes.

The experimental results indicate that there is little effect on the adsorption amounts for the two particle sizes. The desorption rates are also nearly identical. In the initial stage of desorption process, the adsorbed organic molecules are released from flat surfaces and large pores first. The desorption rate initially depends on evaporation of adsorbed molecules from adsorption sites. Hence, the particle size has little effect on the initial desorption stage. When the desorption proceeds to later stage, however, the desorption mainly occurs from small pores. Pore structure and pore size are the main factors affecting the desorption. If pore diffusion is important, bigger particles imply longer traveling distance, so that smaller particles are expected to have a faster desorption rate. From Figure 5-29 and Figure 5-30, it is seen that the later stages of desorption process are also nearly identical for the two particle sizes. Two points are suggested to explain this behavior. First, for the desorption from fine pores, especially micropores, the first step is that the adsorbed molecules must have enough energy to break away from the attraction of pore wall. Due to the overlap of energy field of small pore wall, the adsorbed molecules are more difficult to release from the adsorption sites than from flat surfaces and
Figure 5-29  Desorption of C₆H₅CL from Montmorillonite with Different Particle Size

Figure 5-30  Desorption of C₇H₈ from Montmorillonite with Different Particle Size
larger pores. This step is determined by pore sizes, which give different adsorption energy among the adsorption sites, not by particle size. Second, bigger particle size should have longer pore length than that smaller particles, which increases the adsorbed molecules diffusion distance. Thus, when the molecules in small pores diffuse out, the bigger particles should exhibit longer desorption times. But, in the adsorption process, the adsorbed molecules also have diffusion resistance when they diffuse into the small pores. Hence, the adsorbed molecules in small pores are likely to stay near the pore entrance. Although the pore length increases with particle size increases, the final effect on desorption process is not as large as expected from the pore diffusion model.

5.5 Effect of Temperature on Desorption Process

Heating the chamber is an effective method to decontaminate the solids to a limited level. At room temperature, there is no observation of complete desorption for tested pairs of solids and contaminants. Especially for Spherocarb, most of the adsorbed molecules are left in the particles after two hours of desorption at room temperature.

The experimental results (Figure 5-31 and Figure 5-36) show that raising the chamber temperature can achieve complete desorption. Once the temperature of the chamber increases, the desorption rate \(\frac{d(M_{ad}/MA)}{dt}\) abruptly increases. From the step-heating experiment, Figure 5-36, the result shows that it is
difficult to achieve the complete desorption from soil particles before the temperature reaches the required minimum temperature for complete desorption. When the temperature is held at 100°C, the desorption rate is very low. In the heating process, the desorption rate is related to the heating rate and the temperature, especially the local temperature. For monochlorobenzene and dichlorobenzene, we can make the following conclusions:

a) The temperature that is needed complete desorption is a strong function of soil type. Desorption is an activated process. For Spherocarb, because a higher amount of adsorbed molecules is trapped by fine pores, more energy is needed to activate desorption. The complete desorption of monochlorobenzene from Spherocarb is about 150°C, a little higher than its boiling point of 132°C, while from montmorillonite, it is about 80°C, much below its boiling point.

b) Different contaminants have different minimum temperature for complete desorption. For Spherocarb, dichlorobenzene needs higher temperature than monochlorobenzene to reach complete desorption due to its higher adsorption energy (as analyzed in 5.3) and boiling point. Higher boiling point means that a molecule needs more energy to break away from the attraction by other molecules in liquid state to enter gas state. Hence, higher boiling point compounds will require higher temperature for complete removal.
c) The heating history has a little effect on the desorption process and the required temperature for complete desorption. Three sets of heating experiments, fast heating, slow heating, and step heating, were performed. As shown in Figures 5-31 - 5-36, there is no obvious shift on the final temperature at which the contaminant is completely desorbed. At constant temperature during the holding period of the temperature program, from the experimental results (Figure 5-36) we can see that the desorption rate is much lower than that in the heating period. The energy possessed by the contaminant molecule and adsorption site is considered to be the key step for the desorption process. When the adsorbed molecule obtains enough energy, it can get out of the trap of solid surface and enter the gas state. Hence, for the examined contaminants and solid particles, heating is an effective method to decontaminate the soil.
Figure 5-31  Desorption of C₆H₅CL from Montmorillonite at High Temperature

Figure 5-32  Desorption of C₆H₅CL from Spherocarb at High Temperature
Figure 5-33  Desorption of C₆H₄Cl₂ from Montmorillonite at High Temperature

Figure 5-34  Desorption of C₆H₄Cl₂ from Spherocarb at High Temperature
Figure 5-35  Desorption of C₆H₄CL₂ from Spherocarb at High Temperature

Figure 5-36  Desorption of C₆H₄CL₂ from Spherocarb at High Temperature
CHAPTER 6. KINETIC STUDY

Pore diffusion model is often employed to describe the desorption mechanism of gas from porous solid because the diffusion of vapor into or out of the fine pores is considered the limiting step. Homogeneity among the pores and whole particle is assumed to simplify the complexities and heterogeneity of the natural system. If the particles are taken as spheres, the Fick's second law of diffusion within the particle can be expressed as:

\[ \frac{\delta C}{\delta t} = \frac{D_e}{r^2} \frac{\delta}{\delta r} \left( r^2 \frac{\delta C}{\delta r} \right) \]  \hspace{1cm} (6-1)

where \( D_e \) is the effective diffusivity.

This equation describes the concentration of adsorbate as a function of time and position within the internal pores of a soil particle. In the equation, the driving force for diffusion is the concentration gradient. The effective diffusion coefficient, \( D_e \), reflects the rate at which the vapor appears to diffuse through the particle.

Physical adsorption can occur nearly as fast as molecules strike a surface. When a molecule in the gas phase strikes the solid surface and is adsorbed, there are two possible alternatives: desorption into gas, stay in the adsorbed position or movement to an adjacent active site. If the adsorbed site possesses low adsorption
energy, the adsorbed molecule is more easily to desorb into gas. This is the case for montmorillonite particles to take longer time to reach the adsorption equilibrium and to be desorbed easily.

In the small pore diffusion, the main mechanism is not Knudsen diffusion but surface diffusion. Such mass transport is an activated process, dependent on surface characteristic and the adsorbed molecules. In desorption processes, the adsorbed molecules in small pores diffuse out of the pores. At the beginning, because the adsorption amount is higher, there may be higher gradient of adsorbed molecules concentration, which move as a flow of the layers as a condensed phase. When the adsorption is monolayer, the adsorbed molecule can be desorbed into gas or move to an adjacent active site on the pore wall. If desorption occurs, the molecule can travel in the void space of the pore or be readsorbed again by the pore wall. For the finer pores, due to the pore size is less than the molecular free moving distance, the probability of a gas molecule striking the pore wall is higher. When most adsorption sites are occupied by vapor molecules, less bare sites are available for readsorption. Hence, the desorbed molecules can continue a longer time in their journey out of pores, and higher diffusivity appears.

With the desorption proceeding, the adsorbed amount left in solid decreases, the diffusion rate decreases very rapidly. There are two reasons for this phenomenon. First, the remaining adsorbed molecules are either the ones that possess lower energy or stick to the higher adsorption energy sites. It is difficult for the still
adsorbed molecules to break away from the attraction of solid surface to enter the gas state or move to another site. Second, due to more bare adsorption sites, the desorbed molecules can not travel long distances before readsorption. When a gas molecular moves in small pores with pore diameters less than the molecular mean free path, it can have more chances to strike the pore wall. Readsorption occurs on bare sites slowing down the diffusion of the molecules. This is why the final part of adsorbed molecules needs very long time to completely desorb.

When heating the soil particles, the adsorbed contaminant molecules get the energy with temperature increase. More molecules will break up the attraction of pore wall to enter gas state, which increase the vapor concentration in void space of pores. The diffusion flux will increase due to higher gradient of vapor concentration. With the higher temperature, the organic molecules obtain higher energy. Hence, when the desorbed molecules strike the pore wall in their diffusion journey in small pores, may be they could not be trapped by bare sites again due to the lower adsorption energy possessed by the bare sites than that by the diffusing molecules, or they are redesorbed immediately after continuing their diffusion movement. The surface diffusivity increases rapidly with temperature. So, as an effective method to reach the limited desorption, rising the temperature can enhance both the vapor concentration gradient of desorbed molecules in void space of pores and the effective diffusivity.
For pore diffusion model, the desorption rate is directly related to the particle diameter. $\frac{\delta C}{\delta t}$ decreases rapidly with the particle diameter. The experimental results show that the particle size has little effect on the desorption rate as analyzed in 5.4. Hence, for the porous particles, especially the particles with the higher portion of micropores, the particle diameter is not a good length scale for the diffusion model.

From the above picture, the mass transport for contaminant desorption is an activated process. Only the adsorbed molecules with higher energy than the energy of adsorption sites can desorb into gas. The activated energy for desorption from the solid surface depends on the solid surface characteristics, e.g., pore diameter, and the adsorbed organic molecules. Due to the heterogeneity of solid surface, the activated energy for adsorption is not uniform.

The energy of adsorbed contaminant molecules is of statistical nature. For physical adsorption, the increase in desorption time give the adsorbed molecules more attempts to overcome the desorption energy. So the probability of desorption over a higher energy barrier will increase. Then, it is expected that all the adsorbed contaminant molecules can be desorbed isothermally if the desorption time is long enough. In other words, although diffusivity is very low in the later part of the desorption process at constant temperature, the diffusion is still proceeding to complete desorption. But from the step-heating experimental results, the diffusion flux is very low at the holding period, which
means that the desorption time is very long for complete desorption at constant temperature.

For the final monolayer of adsorbed molecules, the effective method of speeding up the desorption process is to heat the soil particles to increase the energy possessed by the adsorbed molecules. Hence, the activation energy of distribution of adsorbed organic molecules is useful for the desorption process.

Because the solid surface is not homogeneous, the adsorbed organic molecules will possess a broad range of sticking energies. In the thermal desorption process, the adsorbed vapor molecules will exhibit different activation energy. The energy distribution function, \( f(E) \), is employed to describe the heterogeneity of solid surface, where \( f(E) \Delta E \) denotes the fraction of total adsorbed organic population with activation energy of desorption between \( E \) and \( E + \Delta E \). Hence, the integration of \( f(E) \) over all energy is:

\[
\int_{0}^{\infty} f(E) dE = 1 \quad (6-2)
\]

For the desorption of a monolayer of organic molecules from solid surface, the desorption rate is assumed to be proportional to the adsorbed amount with certain activation energy.

\[
\frac{d[O^*]_E}{dt} = -k_E [O^*]_{E,t} \Delta E \quad (6-3)
\]

Where, \( k_E \) is the rate constant (1/min), \( [O^*]_{E,t} \Delta E \) is the number of adsorbed organic molecules remaining on the solid surface with
activation energy between E and E+ΔE at time t, and \( \frac{d[O^*]_E}{dt} \) is the desorption rate of adsorbed monolayer molecules with activation energy between E and E+ΔE.

Du, et al (22) developed a method to determine the distribution of the surface complex in TPD (temperature-programmed desorption) for (CO) desorption (22). In this process, the distribution function is:

\[
f(E^*) = \frac{1}{[O^*]_{tot}} \frac{-d[O^*]/dt}{dE^*/dt}
\]  

(6-4)

Where, \( \frac{d[O^*]/dt}{dt} \) is the desorption rate determined from the experimental results. \([O^*]_{tot}\) is the total adsorbed amount of organic molecules. \( \frac{d[E^*]/dt}{dt} \) is the activation energy change rate with time (or with temperature proceeding). For the heating rate program of Figure (6-1), the parameters in determining \( f(E^*) \) are:

\[
T = \begin{cases} 
T_{(0)} & 0 \leq t \leq t_f \\
T_f & t > t_f 
\end{cases}
\]  

(6-5)

\[
\frac{dT}{dt} = \begin{cases} 
T_{(0)} & 0 \leq t \leq t_f \\
0 & t > t_f 
\end{cases}
\]  

(6-6)

\[
E^* = \begin{cases} 
RT \ln(k_o \frac{T}{T}) & 0 \leq t \leq t_f \\
RT_f \ln(k_o (t-t_f)) & t > t_f 
\end{cases}
\]  

(6-7)
The high temperature experiments for dichlorobenzene desorption from Spherocarb are conducted by using TGA. The temperature history and particle weight change are recorded by data acquisition. At first, the desorption is proceeding at room temperature. When the desorption rate levels off, the chamber temperature begins to rise. We take the adsorbed amount at this point as \( [O^*]_{0r} \), and the amount remaining on the solid surface as a monolayer.

The temperature programs are from 298K to 573K. Three runs are performed to test the effect of heating history:

1. slow heating, which takes about 60 minutes to increase the temperature from 298K to 573K;

2. fast heating, which is about 20 minutes to reach 573K;

3. three-step heating, which first raises the temperature to 373K, maintains it at this value for about 35 minutes, then increases the temperature again to 473K, maintains it for 40 minutes, and finally increases the temperature to 573K.

Where \( k_0 \) is the Arrhenius equation preexponential factor.

\[
\frac{dE^*}{dt} \equiv \begin{cases} 
\frac{E^* T^{(t)}}{T^{(t)}} & 0 \leq t \leq t_f \\
\frac{E^*}{T_f} + \frac{(t-t_f)E^*}{RT_f} & t > t_f 
\end{cases} 
\] (6-8)
For the three runs, all desorption processes reached complete cleanup at or below the detection limit before the chamber temperature reaches 573K.

The results from the high temperature experiments are in Figure 5-31-5-36. On the basis of the information from the experiments, the activation energy distribution $f(E)$ for Spherocarb-dichlorobenzene corresponding to each run can be constructed according to above equations. The preexponential $k_0$ considered as $10^{10}$ 1/min (22) is a parameter during the calculation. The $f(E)$ for different temperature programs are presented in Figure 6-2.

From the results, we can see that $f(E)$ is insensitive to the temperature history. This verifies that $f(E)$ is an intrinsic property of the Spherocarb solid characteristics. For the adsorption of dichlorobenzene on Spherocarb, the adsorption energy is about 16-28 kcal/mol. Because desorption can occur at room temperature for a monolayer of adsorbed molecules, $f(E)$ is not zero at the beginning of the temperature-program run.

The obtained adsorption energy (16-28 kcal/mol in Figure 6-2) is higher than physical adsorption energy. It can be explained from two points. First is the value of the Arrhenius preexponential factor ($k_0$). For the surface desorption, $k_0$ has not been found a suitable value. From the results of Du (22), the value of $k_0$ has the effect on the value of activation energy. But, it does not affect the shape of the activation energy distribution. Secondly, repeated desorption and adsorption accompany the total desorption process. It will delay
the desorption. In the heating period, the retard time will lead to a higher temperature when the adsorbed molecule is finally desorbed away from the particle. And due to the repeated readsorption and redesorption, the effective Arrhenius preexponential factor $k_0$ will largely decrease.

We take the effective Arrhenius preexponential factor $k_0$ separately as $10^8$1/min and $10^5$1/min. The activation energy distribution are shown in Figure 6-3 and 6-4. From the results, it can be seen that the activation energy decreases with $k_0$ decrease, but it dose not change the distribution shape.

For the Spherocarb, the shape of $f(E)$ is found to very close to a Gaussian distribution (Figure 6-2). Therefore, the Gaussian distribution may be used to properly approximate the real solid surface energy distribution to simplify the situation. The desorption processes strongly depends on the desorption temperature. $E^*$ is governed by chamber temperature by equation 6-6 during heating period ($0 \leq t \leq t_f$) and during the holding period ($t > t_f$). For the heating period, $E^*$ increases rapidly with temperature rising. Hence, for the fast heating program, the adsorbed molecules are released quickly.

The desorption of monolayer organic molecules is an activated process. For a given adsorbed organic molecule, it must overcome the corresponding intrinsic energy barrier to be desorbed to gas. Due to the heterogeneity of solid surface, the adsorbed molecules have a variety of activation energy. The adsorbed molecules with energy
Figure 6-1 Typical Temperature Program

Figure 6-2 Distribution of Activation Energy of Spherocarb

\[ f(E) \times 100\% \text{ (mol/Kcal)} \]

- slow heating
- fast heating
- step-heating

\[ k_0: 10^{10} \text{ 1/min} \]
Figure 6-3 Distribution of Activation Energy of Spherocarb

Figure 6-4 Distribution of Activation Energy of Spherocarb
barrier lower than $E^*$ will be quickly desorbed; those adsorbed molecules with an energy barrier higher than $E^*$ do not have sufficient energy to break away from the attraction of solid surface. They will be desorbed by obtaining enough energy at higher temperature or taking long time to have more attempts to overcome the energy barrier at constant temperature.

During desorption, a molecule will have several times of desorption and readsorption. At constant temperature, the desorption time will be longer than that without readsorption. Hence, there may be an error in the equations for the holding period. In the heating period, the readsorbed molecules can be released again rapidly because they get higher energy as soon as the temperature rises to suitable values.
CHAPTER 7. CONCLUSION

The present work was performed to improve our fundamental understanding of adsorption and desorption of organic molecules from soil particles. The results suggest that several parameters affect the mass transfer process. For the tested organic chemicals (toluene, monochlorobenzene, dichlorobenzene) and two soil particles (montmorillonite, Spherocarb), the experimental data indicate that:

(1) Desorption process is a strong function of soil types, which affects the desorption both at room temperature and during heating. In the physical properties of soil particles, the surface area, porosity, pore size distribution, especially the micropores, are of great significance. The latter are directly related to the retained amount of contaminant at room temperature desorption and the temperature for complete desorption during heating. Mesopores are responsible for the liquid condensation at higher relative pressures during adsorption. Micropores are responsible for the slow desorption of the final monolayer of adsorbed molecules. For complete cleanup of contaminated soil, the micropores deserve more attention.

(2) Polar organic chemicals have more affinity to soil surface than non-polar organic matter. the polar organic chemical may introduced dipole-dipole force when adsorbed onto the soil particle
surface. Consequently, the attraction force may be higher than for non-polar organics.

(3) At room temperature, complete desorption will take very long time, especially for the soil particles with a higher portion of micropores. In the experiments, there is no observation of complete desorption for desorption time over 15 hours. After the initial rapid desorption period, the remaining portion of organic matter in the solids is a strong function of soil types. This is correlated to the portion of micropores in the solid.

(4) Increasing the temperature of the chamber is an effective way to speed up the desorption. The desorption process is of statistical nature. Thus, the physically adsorbed molecules can be desorbed isothermally with long enough desorption time to give them more attempts to overcome the desorption barrier. In the performed experiments, the contaminants were desorbed completely at temperatures close to their boiling points.

(5) The temperature of complete cleanup of contaminated soil is a strong function of soil type. For monochlorobenzene, the temperature for complete desorption is about 80°C and 220°C, respectively, for montmorillonite and Spherocarb. Micropores are responsible to this phenomenon due to their higher adsorption energy.

(6) For the porous particles, the pore diffusion model does not describe well the desorption rate. The particle diameter is not a good length scale for this situation.
(7) The desorption of the final monolayer of molecules is an activated process. Only the adsorbed molecules with higher energy than activation energy can be desorbed quickly. The energy distribution function \( f(E) \) is useful to determine the desorption rate and desorption temperature and time because the temperature history is filtered out.

These results suggest that the detailed knowledge of both the soil and organic compound characteristics is essential to optimize the operation of a cleanup system. The last monolayer of adsorbed organic molecules, which is tightly bound to the soil, is corresponding to the micropores of the solid. The micropores of soil particles will control the amount of last monolayer, complete desorption time, and temperature.
REFERENCES


20. S. J. Gregg, K. S. W. Sing, "Adsorption, Surface Area and Porosity".


