



ELSEVIER

Thermochimica Acta 325 (1999) 77–87

thermochimica
acta

Effect of oxidizing gas pressure on laboratory-scale decontamination of soils polluted by hydrocarbons

V. Risoul^{a,b}, G. Trouvé^a, W.A. Peters^c, P. Gilot^{a,*}

^a *Laboratoire Gestion des Risques et Environnement, Ecole Nationale Supérieure de Chimie Mulhouse – Université de Haute-Alsace, 25 rue de Chemnitz, 68200 Mulhouse, France*

^b *Trédi, Département Recherche, Technopôle de Nancy-Brabois, B.P. 184, 54505 Vandoeuvre lès Nancy, France*

^c *Energy Laboratory and Center for Environmental Health Sciences, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge MA 02139, USA*

Received 21 March 1998; accepted 29 September 1998

Abstract

Three standard European soils were artificially contaminated with hexachlorobenzene, 4-chlorobiphenyl, and naphthalene. Small piles (ca. 30 mg) of contaminated soil, or neat soil in control runs, were then heated in the crucible of a thermogravimetric analyzer from room temperature to ca. 450°C at 5°C/min. To investigate effects of ambient gas pressure on contaminants removal, soil specimens were subjected to closely similar heating schedules under either 0.1 or 0.01 MPa pressure of air. The lower pressure augmented decontamination, reducing by as much as 20–45°C the temperature necessary for a given extent of pollutant removal, and increasing the maximum rate of decontamination. The precise magnitude and duration of such pressure-induced improvements in decontamination varied with pollutant and soil type. Predictions of a contaminant evaporation-diffusive transport model were in reasonable agreement with experimentally observed pressure trends. Higher diffusion coefficients for pollutant vapor under reduced pressure are believed to be responsible for the observed pressure effects. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The discovery of the best strategies and techniques for soil amelioration remains a difficult challenge [1]. Thermal processes manifested in different technologies such as rotary kilns [2–5], thermal augers [6] and fluidized beds [7] are frequently used for clearing contaminated soils. In the decontamination of soils polluted by hydrocarbons or their derivatives, evaporation of the contaminant has been shown, both by experiment and modeling, to play an important role

[8]. Thus, the vapour pressure of the contaminant will be important for the thermal treatment protocol, i.e. temperature or temperature range, heating rate, and heating time, necessary to achieve high extents of pollutant removal [9]. Although the nature of the soil is also important, the volatility of the contaminant is an especially important parameter in soil cleanup. The total external pressure strongly affects the evaporation of hydrocarbons. Thus, the effect of this parameter on soil thermal decontamination needs to be systematically investigated.

Relatively few results have been reported in the literature about the effect of operating pressure on soil thermal remediation [10]. Potentially, pressure can

*Corresponding author. Tel.: +33-03-89-32-76-55; Fax: +33-03-89-32-76-61.

affect the release of the contaminant from the soil particle, as well as secondary chemical reactions (e.g. pyrolysis) of contaminants as they are transported away from the soil. The vacuum pyrolysis of hydrocarbon-contaminated soils was investigated by Roy et al. [10], using a laboratory-scale batch reactor and a prototype process development unit. Operating pressures of 0.5–1.0 kPa were used for each case, respectively. No carrier gas was used and the vapours resulting from pyrolysis were condensed with high efficiency. The main characteristic of the vacuum pyrolysis process was the small quantity of pyrolytic gas produced, mainly composed of simple molecules such as CO, CO₂, H₂, CH₄. The contaminant vaporization temperature was reduced by 50–75°C on reducing the pressure.

The main objective of the present paper is to investigate if, at laboratory scale, thermal treatment of hydrocarbon polluted soils under pressure of 10⁴ Pa will significantly decrease the temperature range for achieving high extents of decontamination. Another goal is to assess if a mathematical model will reliably predict the effect of pressure on the decontamination process.

2. Experimental

Three standard European soils [11,12], supplied by the Environmental Institute (Joint Research Centre, European Commission) at Ispra, Italy, were artificially contaminated according to a previously described procedure [13]. The soils S₁ (75% clay), S₂ (60% CaCO₃) and S₃ (75.5% silt) were contaminated with hexachlorobenzene (HCB). The sedimentary soil, S₃, was also separately contaminated with naphthalene (Naph) and 4-chlorobiphenyl (4-CBP). The mass of the contaminant was chosen in order to obtain a contamination level of ca. 4% by weight of uncontaminated soil.

The soil thermal decontamination was studied by thermogravimetric analysis (TGA). Soil samples of ca. 30 mg were placed into the quasi-hemispherical crucible of a CAHN 121 thermobalance and submitted to a preselected temperature–time history under two different operating pressures i.e. either 10⁴ or 10⁵ Pa ($\leq \pm 3\%$). The ambient carrier gas was air and the flow rate 83 cm³ min⁻¹ (standard conditions). The partial vacuum (minimum value of 10⁴ Pa) was obtained by

use of a membrane pump, continuously pumping during the experiment.

The desired operating pressure was obtained in the TGA chamber by adjusting the carrier gas flow rate with a fine control leak valve. After an initial equilibration period the chamber pressure was very stable, exhibiting a drift of only 3% over 3 h of continuous operation, as measured with an active strain gage. However, the pressure adjustment created unsteady air flows which disturbed the TGA crucible. To stabilize the carrier gas flow and the crucible, a period of 5 min was imposed before initiating the TGA heating program. During this period, contaminated soil specimens underwent weight losses of ca. 1.5 and 0.5% at pressures of 0.01 and 0.1 MPa, respectively. To correct for these losses, the time origin of the TGA thermograms was taken at the end of this 5-min equilibration period. Likewise, the initial mass of sample was taken as the sample mass at the conclusion of this period. Control experiments were performed by subjecting uncontaminated (neat) specimens of the same soils to the temperature–time histories (heating schedules) as those used in the decontamination runs. To assure that the neat soil specimens constituted a reliable control for the polluted soils, the neat soil samples were also subjected to the same solvent treatment and evaporation procedure used in artificially contaminating these soils, except that no contaminating was dissolved in the solvent.

The percentage of initial (i.e. at time=0) contaminant removed from the soil at any time throughout the heating protocol, was determined from a mathematical analysis [8] of the TGA thermograms for neat and contaminated soils. The effect of reducing the operating pressure from 0.1 to 0.01 MPa was determined for each of the five soil/contaminant systems given in Table 1, together with the initial mass of soil, the soil contamination level after correcting for changes during the 5-min pressure conditioning period (CL₀), and the percentage of contamination that would just cover the soil BET surface area with one monolayer of the pollutant (CL_{res}). Methods of determining these quantities are discussed in more detail in Ref. [14].

3. The mathematical model

A mathematical model for removal of a volatilizable organic contaminant from thin soil beds (piles)

Table 1

Experimental conditions, contamination levels CL_i , CL_0 , CL_{res} (see text) and extent of decontamination DL_{lim} expected to be controlled by evaporation for the different soil/contaminant systems

| Contaminant Soil | HCB | | | | | | Naph. | | 4-CBP | |
|----------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| | S_1 | | S_2 | | S_3 | | S_3 | | S_3 | |
| | 10^5 | 10^4 | 10^5 | 10^4 | 10^5 | 10^4 | 10^5 | 10^4 | 10^5 | 10^4 |
| Contamination level CL_i (wt%) | 2.4 | 3.1 | 3.1 | 3.7 | 4.1 | 4.4 | 2.1 | 2.1 | 2.7 | 4.1 |
| Contamination level CL_0 (wt%) | 2.1 | 3.3 | 3.3 | 3.5 | 4.3 | 4.1 | 2.3 | 1.7 | 3.0 | 3.0 |
| Soil mass at time 0 (mg) | 30.108 | 30.499 | 29.244 | 29.431 | 30.520 | 30.819 | 28.547 | 29.592 | 30.187 | 30.229 |
| CL_{res} (wt%) | | | 1.62 | 1.62 | 2.18 | 2.18 | 0.74 | 0.73 | 0.84 | 0.84 |
| DL_{lim} (wt%) | | | 49 | 53 | 47 | 45 | 68 | 56 | 71 | 72 |

undergoing heating in a TGA has been described [8]. This model assumes that decontamination occurs without chemical reactions, by evaporation of the pollutant from the soil particles, followed by diffusion of contaminant vapor through the void spaces of the soil pile, and then through a gas-phase concentration boundary layer between the top of the soil pile and the ambient carrier gas. This model was adapted for use in the present studies of the effect of operating pressure. Although air was used as the carrier gas in the present experiments it is assumed that chemical reactions with oxygen occur at temperatures higher than those for which most of the contaminant release occurred, and thus that a non-reactive transport model is reasonable.

This model represents the TGA crucible as a right circular cylinder of cross-sectional area $6.36 \times 10^{-5} \text{ m}^2$. The soil piles are also described by a right circular cylinder, with cross-sectional areas of 4.6×10^{-5} , 4.5×10^{-5} , 4.4×10^{-5} , and $4.1 \times 10^{-5} \text{ m}^2$ for S_2 /HCB, S_3 /HCB, S_3 /4-CBP, and S_3 /Naph, respectively. In this model, decontamination kinetics are assumed to be governed by concentration (i.e. Fickian) diffusion of the contaminant vapor away from the soil particles and then through the soil pile and a concentration boundary layer between the top of the soil pile and the carrier gas. Intraparticle diffusion of contaminant was not considered in the present model. Even at 0.01 MPa, it is reasonable to consider the present mixtures of air and contaminant vapor as hydrodynamic fluids where contaminant transport occurs by Fickian rather than Knudsen diffusion. Calculations found the Knudsen number, i.e. the ratio of the mean free path of contaminant to the mean diameter of the void volumes in the soil pile to be small; conservatively it is <0.05 .

The concentration of contaminant vapor, C_v , was determined by the partial pressure of contaminant vapor, P_v , i.e. assuming the ideal gas law, by the relation $C_v = N_v/V = P_v/RT$. Thus, at the surface of each soil particle, assuming equilibrium between condensed phase contaminant and contaminant vapor, the partial pressure of contaminant is given by its vapor pressure P_{vp} , which typically varies exponentially with temperature, but shows little effect of total external pressure (unless, somewhat unlikely in the present case, the molar volume of a contaminant in its condensed phase becomes comparable to the molar volume of its vapor, i.e. there is a strong Poynting correction). Thus, in the present situation, pressure effects on decontamination are primarily manifested in terms of the effects of pressure on the coefficient of diffusion, D , for contaminant vapor. This quantity scales inversely with pressure so that at any pressure, P , $D(P)$ is related to the diffusion coefficient D_0 at atmospheric pressure, P_0 by:

$$D = D_0 \frac{P_0}{P} \quad (1)$$

with

$$D_0 = aT^{1.5} \quad (2)$$

The values of a for the three contaminant vapors are given in Ref. [14].

The thickness of the concentration boundary layer above the soil pile, δ , is needed to implement the present decontamination model. This quantity does vary with TGA geometry and contaminant type, and interestingly, to some extent with pressure. Methods for estimating δ , for the present contaminants and TGA are presented in [14]. These methods were

employed to compute values of δ for the two operating pressures of current interest, for a mean temperature relevant to the range of temperatures responsible for most of the decontamination in the present experiments. The resulting values of δ for each contaminant and pressure are specified in the captions to Figs. 3–6.

On account of the possibility of strong pollutant–substrate interactions, pure evaporation is not expected to represent release of the last monolayer of contaminant from a soil particle adequately. Consequently, the model calculations of percentage decontamination, as a function of temperature, were terminated when only one monolayer of contaminant was calculated to remain sorbed on the soil surface. This was accomplished by forcing the computational routine to stop further release of contaminant from any local region within the soil pile that exhibited a residual contamination level (in wt% of contaminated soil) corresponding to one monolayer of pollutant molecules [9]. The amount of contaminant that can be held by a given soil particle within a single monolayer was determined by dividing the BET surface area per unit mass of each soil, by the estimated cross-sectional area of the relevant pollutant molecule (see [14]). This quantity, CL_{res} , is called the residual con-

tamination level for a given soil/pollutant combination. Values of CL_{res} , and of the corresponding level of soil decontamination when the pollutant loading has been reduced to one monolayer, DL_{lim} , are presented in Table 1. The units of DL_{lim} are a percentage of the initial contaminant loading (CL_0) released up to that point. The quantity DL_{lim} represents the maximum percentage decontamination expected to be reliably predicted by the present pure evaporation model.

4. Results

Fig. 1 shows the wt% loss as a function of time and temperature when uncontaminated and HCB-contaminated specimens of soil S_2 were subjected to TGA at two different operating pressures of 10^4 and 10^5 Pa, at a heating rate of $5^\circ\text{C}/\text{min}$. In this figure, time 0 corresponds to the moment when the samples were placed within the crucible, before the 5 min at room temperature necessary to set the pressure at the desired value. During these 5 min, both uncontaminated and contaminated soil samples lost ca. 0.5 and 1.5 wt% under 10^5 Pa and 10^4 Pa of pressure, respectively. During this period, the weight loss was higher for

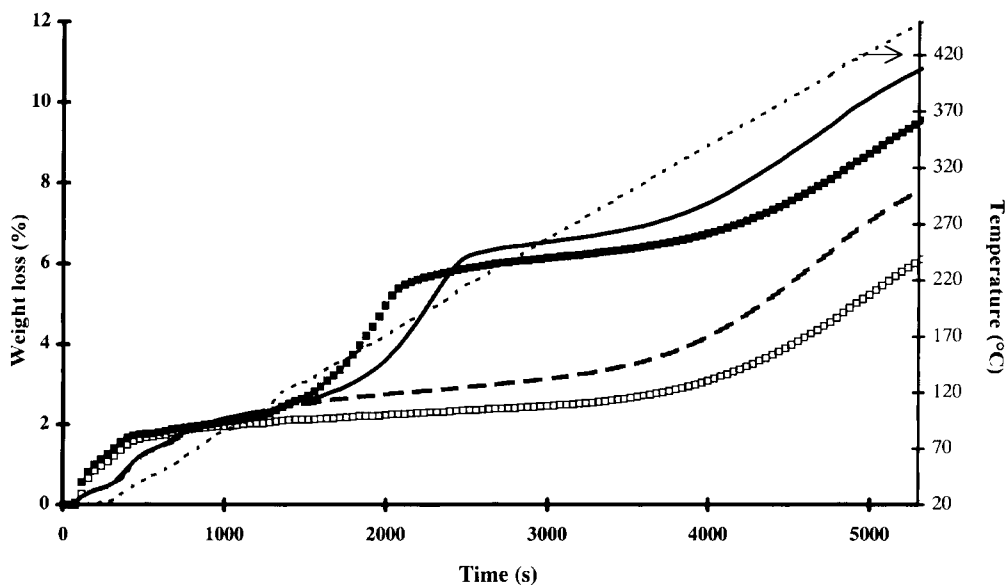


Fig. 1. Thermograms of soil S_2 contaminated by HCB and uncontaminated soil S_2 under two different pressures. Heating rate of $5^\circ\text{C}/\text{min}$. (—) Soil S_2 contaminated, 10^5 Pa, initial mass of 30.324 mg. (---) Soil S_2 uncontaminated, 10^5 Pa, initial mass of 30.253 mg. (■) Soil S_2 contaminated, 10^4 Pa, initial mass of 29.791 mg. (□) Soil S_2 uncontaminated, 10^4 Pa, initial mass of 29.839 mg. (· · ·) Temperature.

the contaminated sample, meaning thereby that some contaminant was already released. After 1000 s, the operating pressure slightly affected the release of volatiles from the neat soil. More volatiles were released under 10^5 Pa. This is probably due to some reactions between soil components and oxygen, and hence greater reactivity of the soil under the higher partial pressure of oxygen. An experimental proof of this fact is that the soil weight loss was shown to be higher, at a given temperature, when air was used instead of nitrogen (data not shown) under 10^5 Pa of pressure. Regarding the contaminated sample, between 1200 and 2500 s, the weight loss was higher under 10^4 Pa of pressure, corresponding to a higher rate of volatile release. This period was mainly devoted to the release of the contaminant since the weight loss of the soil itself remained small during this period. The contaminant release started at 125°C under 10^5 Pa and at ca. 110°C under 10^4 Pa. Thus, a reduced pressure clearly favors the soil decontamination process. After 2500 s, the weight loss was higher under 10^5 Pa of pressure, due to a dominating effect of the weight loss from the soil itself, which is favored under 10^5 Pa of pressure. During the later portion of the heating, i.e. after 4000 s, the curves corresponding to the uncontaminated and contaminated soils, for a given pressure, remained parallel for both pressures, meaning that the decontamination process was over.

From these thermograms, the decontamination was assumed to be complete at a temperature of 450°C . The weight loss WL_{CT} (wt%) of the contaminated soil and the weight loss WL_{NCT} (wt%) of the uncontaminated soil, observed at 450°C from the thermograms, were then used to estimate the initial contamination level CL_i of the soil [8]. The same procedure, using the same temperature of 450°C , was used for every soil/contaminant system.

Table 1 gives, for every soil/contaminant system, the initial contamination level CL_i (wt% of the soil only) calculated from the thermograms, accounting for the total weight loss occurring from the moment at which the sample was placed inside the crucible. For some systems, (S_1/HCB , S_2/HCB , S_3/Naph and $S_3/4\text{-CBP}$ at 10^5 Pa) these contamination levels are lower than the expected values by ca. 4%. They are also slightly smaller than the corresponding values obtained one year before [9] when experiments were

performed with the same samples of contaminated soils under 10^5 Pa of pressure.

The contamination levels CL_0 , corresponding to the contamination remaining after the 5-min conditioning period for establishing the operating pressure, are also supplied in Table 1. These contamination levels CL_0 are used as inputs for modeling, together with CL_{res} and the masses m_0 of the contaminated samples at time 0. The contamination levels CL_0 can be less than CL_i since both soil volatiles and contaminant are released during the 5-min period.

From the thermograms, the instantaneous values of the weight losses $WL_{\text{CT}}(t)$ and $WL_{\text{NCT}}(t)$ were determined and used to estimate the decontamination level $DL(t)(\%)$ at any time during the decontamination process [8]. Figs. 2–6 present the experimental decontamination levels (%) as functions of temperature at 10^5 and 10^4 Pa, for a heating rate of $5^\circ\text{C}/\text{min}$. In these figures, time 0 corresponds to the end of the five-minute conditioning period, i.e. to the start of the temperature program.

Clearly, a lower pressure allows a given extent of decontamination to be achieved at a lower temperature. For a decontamination level of 50%, the corresponding temperatures are 32° , 30° , 38° , 45° and 20°C lower under 10^4 Pa of pressure for S_1/HCB , S_2/HCB , S_3/HCB , $S_3/4\text{-CBP}$ and S_3/Naph , respectively. This temperature reduction seems to be only slightly affected by the nature of the soil ($30\text{--}38^\circ\text{C}$) for the contaminant HCB. However, it seems to be more dependent on the contaminant type since, for the soil S_3 , the temperature lowering ranges from 20°C (in case of Naph) to 45°C (in case of 4-CBP). This temperature reduction appears to be almost constant between 20 and 80% of decontamination. The last part of the experimental decontamination curves (last 20%) must be considered as highly uncertain owing to the very small contaminant release during this part of the heating schedule.

Soil decontamination behavior during nonisothermal heating can be characterized in terms of temperature ranges for achieving prescribed rates or extents of soil cleaning. Pressure effects on decontamination can, in turn, be conveniently studied by examining how these temperature ranges vary with pressure. Two useful temperature ranges [9], are those where the soil decontamination rate exceeds one tenth, and one half its maximum decontamination rate, i.e. $0.1 V_{\text{max}}$ and

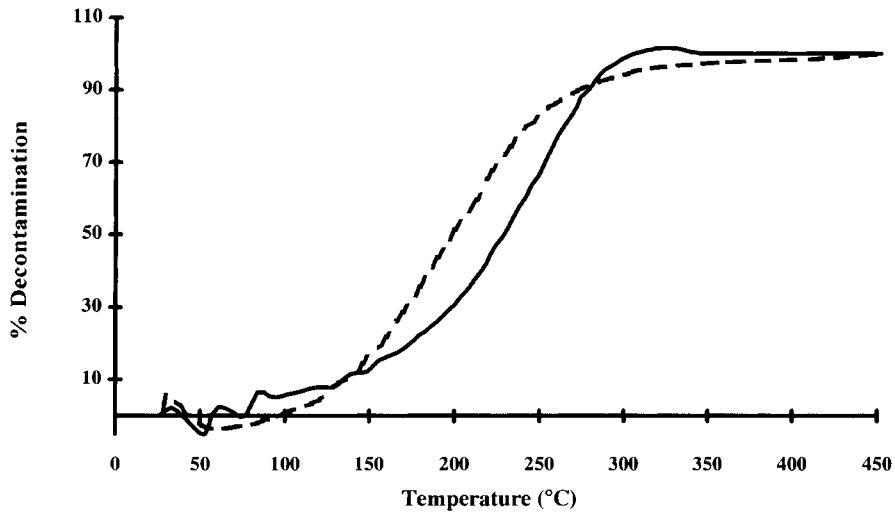


Fig. 2. Decontamination level as a function of temperature for soil S_1 contaminated by HCB under two operating pressures. Heating rate of $5^\circ\text{C}/\text{min}$. (—) 10^5 Pa, experiment; (---) 10^4 Pa, experiment.

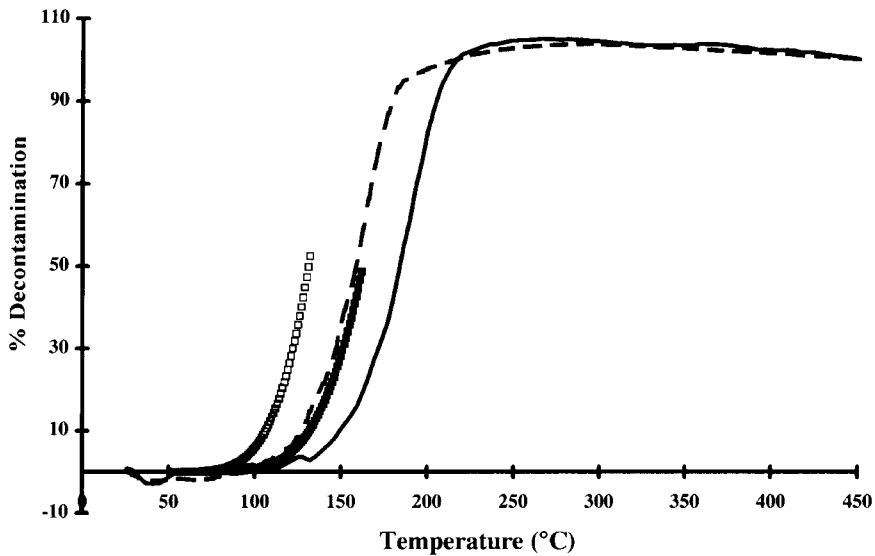


Fig. 3. Decontamination level as a function of temperature for soil S_2 contaminated by HCB under two operating pressures. Heating rate of $5^\circ\text{C}/\text{min}$. (—) 10^5 Pa, experiment; (■) 10^5 Pa, model, $\delta=5.6$ mm; (---) 10^4 Pa, experiment; (□) 10^4 Pa, model, $\delta=6.1$ mm.

$0.5 V_{\max}$, respectively. Fig. 7 summarizes experimentally determined information on these two temperature ranges for the five soil/contaminant systems and two pressures studied. Except for S_2/HCB and S_3/HCB , both temperature ranges are generally slightly more narrow when decontamination is carried out under the lower pressure of 0.01 MPa. More importantly, for all

the five systems, the upper temperature bound for these ranges is lower at 0.01 MPa. The largest reductions in temperature ranges, ca. 60°C , were observed for $0.1 V_{\max}$ for the S_1/HCB and $S_3/4\text{-CBP}$ cases. The contaminants HCB and Naph, which sublime, seem to be less affected by operating pressure for S_3 and/or S_2 , but significant reductions in both the 0.1 and $0.5 V_{\max}$

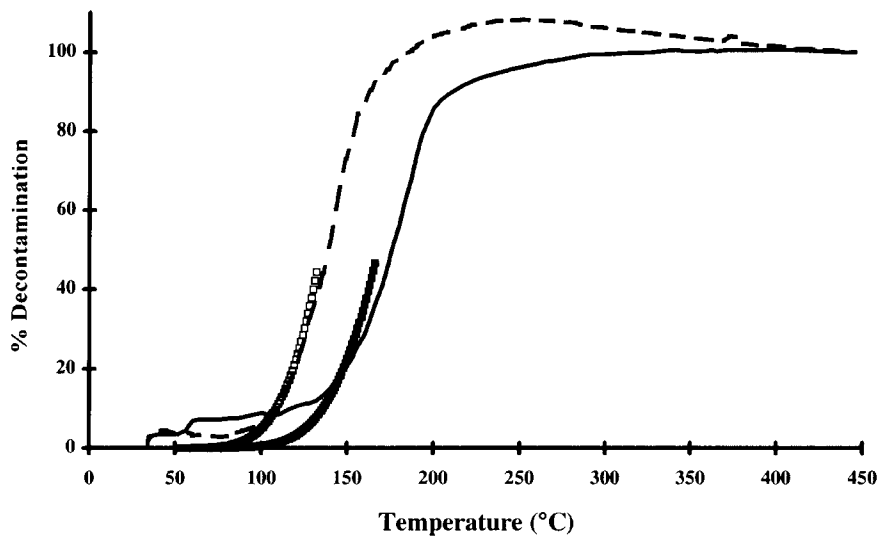


Fig. 4. Decontamination level as a function of temperature for soil S_3 contaminated by HCB under two operating pressures. Heating rate of $5^\circ\text{C}/\text{min}$. (—) 10^5 Pa, experiment; (■) 10^5 Pa, model, $\delta=5.6$ mm; (---) 10^4 Pa, experiment; (□) 10^4 Pa, model, $\delta=6.1$ mm.

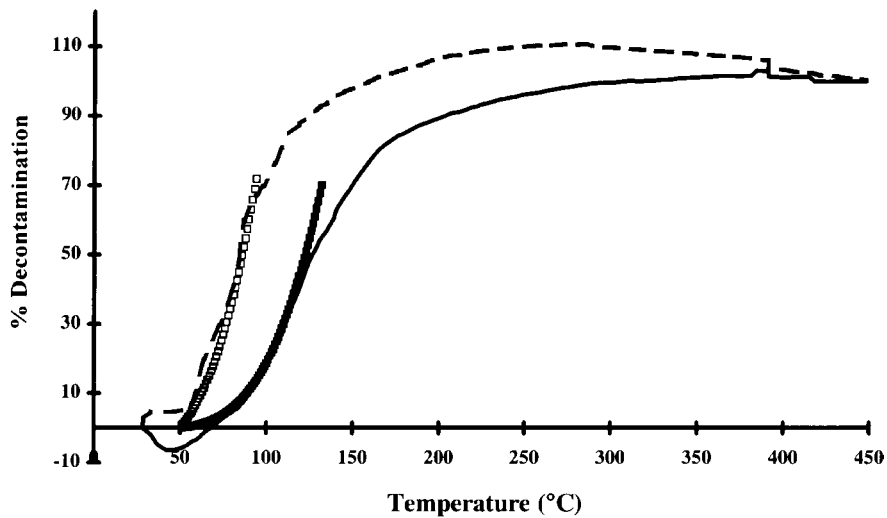


Fig. 5. Decontamination level as a function of temperature for soil S_3 contaminated by 4-CBP under two operating pressures. Heating rate of $5^\circ\text{C}/\text{min}$. (—) 10^5 Pa, experiment; (■) 10^5 Pa, model, $\delta=4.6$ mm; (---) 10^4 Pa, experiment; (□) 10^4 Pa, Model, $\delta=4.7$ mm.

temperature ranges are apparent for the removal of HCB from the clay soil (S_1). The systems S_2/HCB and S_3/HCB exhibit a shift of the lower boundary of the $0.1 V_{\text{max}}$ temperature range to a lower temperature, when the operating pressure is decreased to 0.01 MPa. However, at 0.01 MPa pressure, the lower limits of the $0.5 V_{\text{max}}$ temperature ranges are shifted toward lower

temperatures (by ca. 30°C) for all the soil/contaminant combinations except S_3/Naph , where the temperature reduction is only ca. 15°C . The temperatures at which maximum rates of decontamination are reached are lower under 0.01 MPa pressure, except for the S_1/HCB system which shows a slight increase (Fig. 8). The fractional increases in the maximum rates of

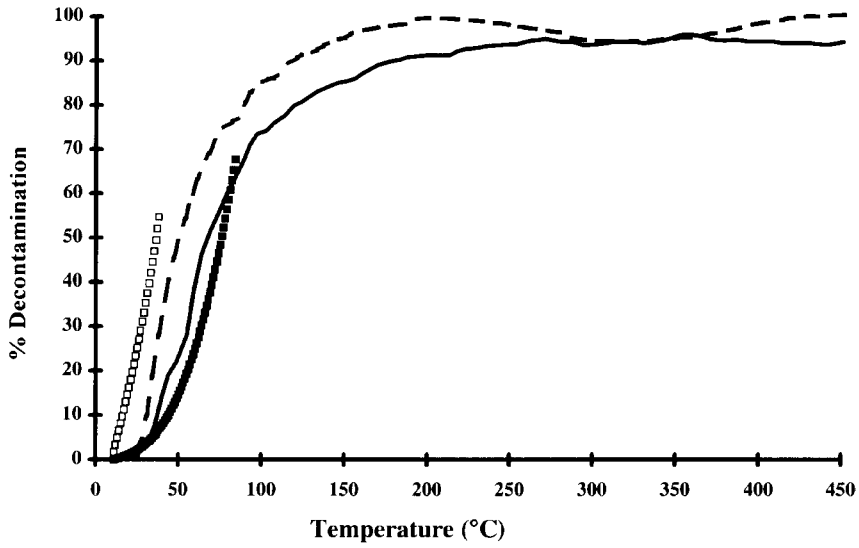


Fig. 6. Decontamination level as a function of temperature for soil S_3 contaminated by Naph under two operating pressures. Heating rate of $5^\circ\text{C}/\text{min}$. (—) 10^5 Pa, experiment; (■) 10^5 Pa, model, $\delta=5.5$ mm; (- - -) 10^4 Pa, experiment; (□) 10^4 Pa, model, $\delta=3.1$ mm.

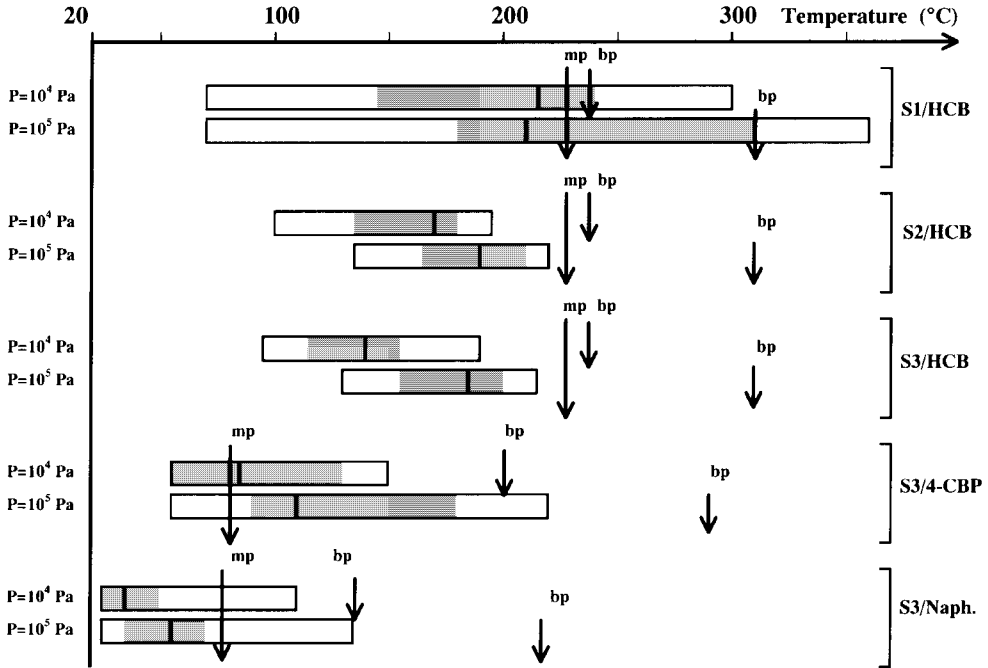


Fig. 7. Temperature ranges of decontamination for the different soil/pollutant systems, under two operating pressures. Heating rate of $5^\circ\text{C}/\text{min}$. □ $v > 0.1v_{\text{max}}$; ■ $v > 0.5v_{\text{max}}$; (l) temperature corresponding to the maximum rate of decontamination. m_p , melting point; and b_p , boiling point.

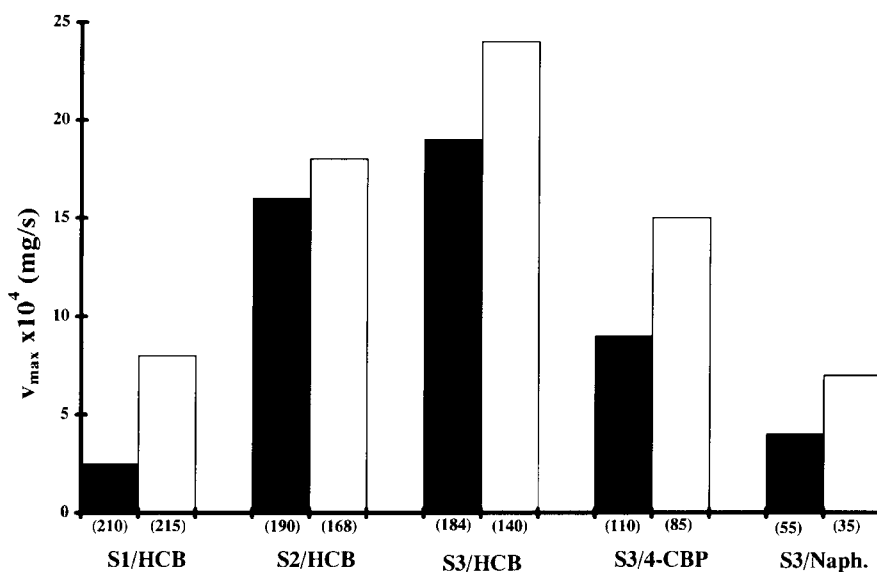


Fig. 8. Maximum decontamination rates and corresponding temperatures for the different soil/pollutant systems under two different operating pressures. Heating rate of 5°C/min. The temperatures are indicated between brackets. (■) 10^5 Pa; and (□) 10^4 Pa.

decontamination are especially significant for the S_1 /HCB, $S_3/4$ -CBP and S_3 /Naph systems (Fig. 8). In brief, the decontamination process is appreciably affected by reducing the operating pressure from 0.1 to 0.01 MPa, with given extents of decontamination being achieved at temperatures as much as 20–45°C lower at 0.01 MPa during the rapid phase of decontamination (Figs. 2–6) and maximum rates of decontamination always higher at the lower pressure (Fig. 8).

5. Discussion

Results obtained with the present model help inform the discussion. In Figs. 3–6, the decontamination levels predicted by the model are plotted vs. temperature for the two operating pressures, and can be easily compared to the corresponding experimental results. For the soil S_1 polluted by HCB (Fig. 2), the model is not used to predict the extent of decontamination as a function of temperature since all the contaminant molecules are expected to be adsorbed onto the surface of the soil particles in one monolayer. Thus, evaporation, which is the basis for contaminant release in the model, is not expected

to play a significant role for that particular clay soil.

The most important result from applying the present model is that the predicted reductions in the temperatures to achieve a given extent of decontamination, when pressure is reduced from 0.1 to 0.01 MPa, are generally in good agreement with the experimental observations. An exception is the S_3 /Naph system (Fig. 6), where the predicted temperature reduction, 45°C, is appreciably more than the 10–20°C observed experimentally. The reason for this disparity is not known, although it may be related to certain artifacts in the naphthalene experiments, namely condensation of some of this pollutant vapor on the wire used to suspend the TGA crucible. This would cause the experiments to underestimate the true extent of naphthalene removal. The 0.1 MPa data and model predictions are in reasonable agreement with the predictions generally showing less, not more, decontamination than the data. However, the agreement is not as good for the 0.01 MPa case, with the predictions showing greater decontamination than the data. Better agreement between model predictions and some of the experimental results could of course be desirable, e.g. in the case of the S_2 /HCB system (Fig. 3). Nevertheless, the ability of the present evaporation/diffusive

transport model to capture the overall trends in decontamination efficiency with decreasing pressure for four different soil/pollutant combinations is satisfying, and boosts confidence in the potential value of building upon the present mechanistic assumptions to construct more powerful decontamination models for applications to broader ranges of operating conditions.

As noted above, the principal effects of pressure under the present conditions are exhibited in terms of the $1/P$ dependence of the diffusion coefficients for contaminant vapor away from the soil particles and through the soil bed and adjacent boundary layer. To reinforce this point, a sensitivity study was performed with the model as follows. All model input parameters, except the diffusion coefficient, were assigned to their values appropriate to a pressure of 0.01 MPa, while D_i was kept at its 0.1 MPa value. The model was then run and no effect of pressure was predicted. In a second such numerical experiment, where all input parameters except D_i were given their 0.1 MPa values, and D_i was assigned its 0.01 MPa values, the model predictions captured the experimentally observed effect of reduced pressure on decontamination. This suggests that, while all other factors remain the same, soil treatment methods that would accelerate pollutant vapor diffusion should give rise to augmented decontamination. This sensitivity study further implies that the changes in boundary layer thickness δ , with pressure (Figs. 3–6) are not a significant factor in explaining the improved decontamination with decreasing pressure.

6. Conclusions

Thermogravimetric analysis has been found to be a useful experimental technique to investigate effects of subatmospheric pressures of ambient gas, on the thermal removal of volatilizable organic pollutants from soil. Here, it was observed that when heating relatively shallow piles (ca. 30 mg) of soil at $5^\circ\text{C}/\text{min}$ in a TGA from room temperature to ca. 450°C , a ten-fold reduction in the ambient pressure of air (from 0.1 to 0.01 MPa) resulted in as much as $20\text{--}45^\circ\text{C}$ reductions in the temperatures needed to achieve a given extent of decontamination. Reduced pressure also gave rise to higher maximum rates of decontamina-

tion. The magnitude and duration of these pressure-induced improvements in decontamination depended upon contaminant type and soil type. A mathematical model describing decontamination in terms of pollutant evaporation from soil particles followed by concentration diffusion through the soil-bed interstices and then through a concentration boundary layer between the top of the soil pile and the ambient (carrier) gas, captured the major pressure-related trends, and gave reasonable quantitative predictions of decontamination efficiencies as affected by temperature for some soil/pollutant combinations and temperature ranges low enough to preserve at least a monolayer coverage of the soil with pollutant. Higher diffusion coefficients for pollutant vapor under reduced pressure are believed to be responsible for the observed pressure effects.

Acknowledgements

We thank TREDI and the French 'Ministère de l'Industrie' for financial support of this project. We thank the Environmental Institute of 'The Joint Research Centre, European Commission', at Ispra, Italy, for providing us standard European soil samples. NIEHS financial support of research at MIT on soil thermal decontamination, under Grant No. ESO4675 (MIT-Superfund Hazardous Substances Basic Research Program), is also gratefully acknowledged.

References

- [1] S. Johnson, in: Malcolm Pratt (Ed.), Remedial Processes for Contaminated Land, Institution of Chemical Engineers, Rugby, Warwickshire CV21 3HQ, UK, 1993, pp. 1–31.
- [2] W.L. Troxler, J.J. Cudahy, R.P. Zink, J.J. Yezzi, S.I. Rosenthal, Air and Waste 43 (1993) 1512–1525.
- [3] W.L. Troxler, S.K. Goh, L.W.R. Dicks, Air and Waste 43 (1993) 1610–1619.
- [4] D. Schneider, M.D. Beckstrom, Environ. Progress 9(3) (1990) 165–168.
- [5] R.C. Czarnecki, J.M. Czarnecki, in: P.T. Kostecki, E.J. Calabrese, M. Bonazountas (Eds.), Hydrocarbon Contaminated Soils; Lewis Publisher, USA, 1992, pp. 695–705.
- [6] M.M. McCabe, R. Abrishamian, in: P.T. Kostecki, E.J. Calabrese, M. Bonazountas (Eds.), Hydrocarbon Contaminated Soils; Lewis Publisher: USA, 1992, pp. 459–468.

- [7] J.V. Fletcher, M.D. Deo, F.V. Hanson, *Fuel* 74(3) (1995) 311–316.
- [8] P. Gilot, J.B. Howard, W.A. Peters, *Environ. Sci. Technol.* 31(2) (1997) 461–466.
- [9] V. Risoul, C. Pichon, G. Trouvé, W.A. Peters, P. Gilot, G. Prado, Submitted to *J. Hazardous Materials* 1998.
- [10] C. Roy, B. De Caumia, D. Blanchette, H. Pakdel, G. Couture, Schwerdtfeger, A.E. *Remediation* 1995, pp. 111–130.
- [11] G. Kuhnt, L. Vetter, A. Lattanzio, J. Loens, in: G. Kuhnt, H. Muntau (Eds.), *Euro-Soils, Identification, Collection, Treatment, Characterization*; Ispra, 1994, pp. 41–58.
- [12] G. Kuhnt, W. Koerdel, L. Vetter, N. Bruhn, F. Bo, G. Serrini, M. Bianchi, in: G. Kuhnt, H. Muntau (Eds.), *Euro-Soils, Identification, Collection, Treatment, Characterization*, Ispra, 1994, pp. 59–72.
- [13] R. Zaragoza, *Application des Fluides Supercritiques à l'Extraction de Composés Organochlorés dans des Matrices de Type Sol*. Ph.D. Thesis, INSA Lyon, France, 1993.
- [14] C. Pichon, V. Risoul, G. Trouvé, W.A. Peters, P. Gilot, G. Prado, *Thermochim. Acta* 306 (1997) 143–151.