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Thermal Technologies Applications for Soil Remediation

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***Abstract*—**This paper discusses the importance of having a good initial characterization of soil samples when thermal desorption has to be applied to polluted soils for the removal of contaminants. Particular attention has to be devoted on the desorption kinetics of the samples to identify the gases evolved during the heating, and contaminant degradation pathways. In this study, two samples coming from different points of the same contaminated site were considered. The samples are much different from each other. Moreover, the presence of high initial quantity of heavy hydrocarbons strongly affected the performance of thermal desorption, resulting in formation of dangerous intermediates. Analytical techniques such TGA (Thermogravimetric Analysis), DSC (Differential Scanning Calorimetry) and GC-MS (Gas Chromatography-Mass) provided a good support to give correct indication for field application.

***Keywords*—**Desorption kinetics, hydrocarbons, thermal desorption, thermogravimetric measurements.

I. Introduction

CONTAMINATION of soils by petroleum products has become a major environmental issue in many industrialized countries. It was found that almost 500,000 sites in Europe require decontamination and approximately 3.5 million sites are potentially polluted [1]. Therefore, many different technologies have been developed for remediation of contaminated soils: biological treatment, soil washing, air stripping, thermal desorption, incineration, etc.[2]. Among the various processes, thermal desorption is considered the best option. It is commonly considered, due to its reliability, high capacity and destruction of contaminants; [3]-[5].

In Situ Thermal Remediation (ISTR) refers to technologies including Steam Enhanced Extraction (SEE), Thermal Conduction Heating (TCH), and Electrical Resistance Heating (ERH) that have been demonstrated at >50 sites to be effective options for difficult-to-treat source zones contaminated with organic chemicals [6]. They are well suited to redevelopment and remediation of sites associated with small and medium enterprises in urban areas, as they afford the ability to treat source zones in settings with access limitations, rapidly and completely, without excavation.

The use of ISTR is often reported in literature; for example, a lot of work refers good performances held by the In Situ Radio Frequencies coupled with Soil Vapor Extraction for BTEX and Hydrocarbons removal [7], [8].

This paper investigates the possibility to remediate a soil contaminated by BTEX, light, heavy and chlorinated hydrocarbons. Laboratory tests have been performed using a static kiln in order to obtain the treatment operating parameters, (i.e. time and temperature) for the design of an in situ thermal remediation technique. Particular attention was posed on the desorption kinetics of the samples, to identify the gases evolved during the heating, and the contaminant degradation pathways. In fact, non-controlled temperatures, may cause the formation of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) during the destruction process, with the consequence of an increased toxicity of soil after thermal treatment [9], [10].

II. Materials and Methods

The soil used in the tests came from an industrial area in the north of Italy; samples were collected from two different points of the contaminated site. The samples were collected in Geoprobe mode, obtaining a hollow punch sealed at the ends to prevent the dispersion of contaminants. They were named SI3 and SI4. Values of concentration of the contaminants are initially very high; they are given in Table I.

TABLE I
Quantities of Contaminants in Soil Samples before Thermal Treatment

	SI3	SI4
	mg/kg	mg/kg
Benzene	1580	0.75
Ethylbenzene	4600	176
Stirene	<0.001	<0.001
Toluene	3400	68
Xilene	8400	257
BTEX	16400	501
C≤12	19200	970
C>12	207	446
VC	5.5	<0.001
1,2-DCA	6700	1.32
TCE	43000	165
PCE	18200	710
1,2-DCE	1750	0.133
1,2-DCP	135	0.125
1,1,2-TCE	192	3.6

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The experimental design consisted, initially, in TGA (Thermogravimetric Analysis) measurements using a Mettler-TGA/DSC (Differential Scanning Calorimetry) apparatus. These measurements allowed the identification of temperatures for successive testing in static tubular oven. Such temperatures were identified in the thermograms in correspondence of the main weight losses of each sample. Some thermogravimetric measures were coupled with GC-MS (Gas Chromatography-Mass) analysis for the identification of the evolved gases during the warming-up.

A.Thermogravimetric Analysis

TGA analysis was performed with a TGA/DSC instrument (TGA/DSC1, Mettler Instrumentation). 50 mg of soil samples were placed into an alumina crucible and heated from 25 to 900°C at 10°C/min in airflow, to best represent the conditions potentially applied in the field, or in N_2 in the case of coupling to TGA-GC-MS. In both cases, flow rate was 30 ml/min.

B.GC-MS Analysis

The GC-MS analysis was carried out according to the following analytical protocol:

- Extraction of 5 g of soil with 20 ml of n-hexane in a TURBULA® Shaker-Mixer for 2 hours;
- Subsequent separation of the extract from the soil by centrifugation (15 min, 3000 rpm);
- Repetition of the previous points for two more times;
- Concentration of the extract under N_2 flux, using a TurboVap by Zymark;
- Analysis.

This method was previously validated in comparison with Soxhlet US EPA standard method 3540C [11].

Quantified analytes were BTEX, C<12, C>12, Vinyl-Chloride (VC), 1,2-Dichloroethane (1,2-DCA), Trichloroethylene (TCE), Tetrachloroethylene (PCE), 1,2-dichloethylene (1,2-DCE), 1,2-dichloropropane (1,2-DCP) and 1,1,2-Trichloroethane (1,1,2-TCE). Analysis were made according to the following instrument conditions: GC Agilent 6890, MS Agilent 5973 equipped with a DB-5MS column (60*250*0.1), oven program 40 °C for 5 min, from 40 °C to 150 °C at 15 °C/min, from 150 °C to 320 °C at 10 °C/min and 320 °C for 10 min.

GC-MS analyses were performed on sample in their unaltered state and after thermal treatment.

C.Thermal Tests

Desorption tests were performed in a tubular static kiln, an LFT-TUBE-FURNACES-1200 °C made by Lenton Thermal Designs Limited. A resistance wire wound onto the quartz tube heats the oven. The regulation of temperature is managed by a thermocouple. For each test, about 50 grams of soil were placed inside a quartz pan and then inserted inside the oven fluxed with air. Performed tests are reported in Table II.

TABLE II
PERFORMED DESORPTION TESTS

	150°C 1h	150°C 2h	150°C 3h	150°C 5h	350°C 1h	350°C 2h
SI3	X	X	X	X	X	X
SI4	X	X	X			

III. RESULTS AND DISCUSSION

Thermogravimetric curves of the two soil samples are reported in Fig. 1. Samples exhibit a substantial loss in weight between 25 °C and 150 °C, due to water and light contaminants evaporation, and between 700 °C and 800 °C. From 25 °C to 150°C the weight loss is about 30 % and 18 %, respectively for samples SI3 and SI4; this is in good agreement with data reported in Table I where sample SI3 resulted in more contamination than SI4. Otherwise SI3 has a second loss with maximum at 330 °C and ending at 350 °C. The difference between the samples is also detected in the DSC curves (Fig. 2), where all the samples have a first endothermic peak (A) between 50 °C and 150 °C coming from the evaporation processes and one exothermic shortly after 400 °C (B). Only for SI3 was observed the presence of a second exothermic peak with maximum at 330 °C (C). In correspondence of these events, the GC-MS spectrum of the evolved vapors were registered to well understand the desorption pathway. In particular, for SI3 at 330 °C desorption of hydrocarbons from 10 to 13 carbon atoms was detected as in Fig. 3; the same peaks were not detected in the other sample. That difference was the first indication of the different response of samples when subjected to heat treatment. Therefore, tests in a tubular airflow oven were then carried out at 150 °C for all samples and 350 °C only for the SI3. In the first line of Table III is indicated the weight loss measured by weight difference between the initial and the treated sample. At 150 °C, there is no difference between the treatment performed for two hours and three. There is also good agreement between the weight losses recorded with the TGA and those relating to thermal testing.

Quantitative analysis of samples thermally treated at 150 °C demonstrate that SI3 samples have a different behavior from other samples as reported in Table III. For that sample an increase of one order of magnitude in C>12 was observed with values that exceed the initial one (Table I). This trend is strongly confirmed from the values obtained in the soil heated for five hours. This phenomenon could be due to the breakage of the large hydrocarbon chains, with the consequent formation of smaller chains, which are not desorbed from the soil in these conditions. While for SI4, one-hour treatment at 150 °C may be indicated for soil decontamination, for SI3 350 °C is required to avoid formation of non-desirable reaction intermediates. So, working desorption temperatures have to be well checked to define the operating field parameters.

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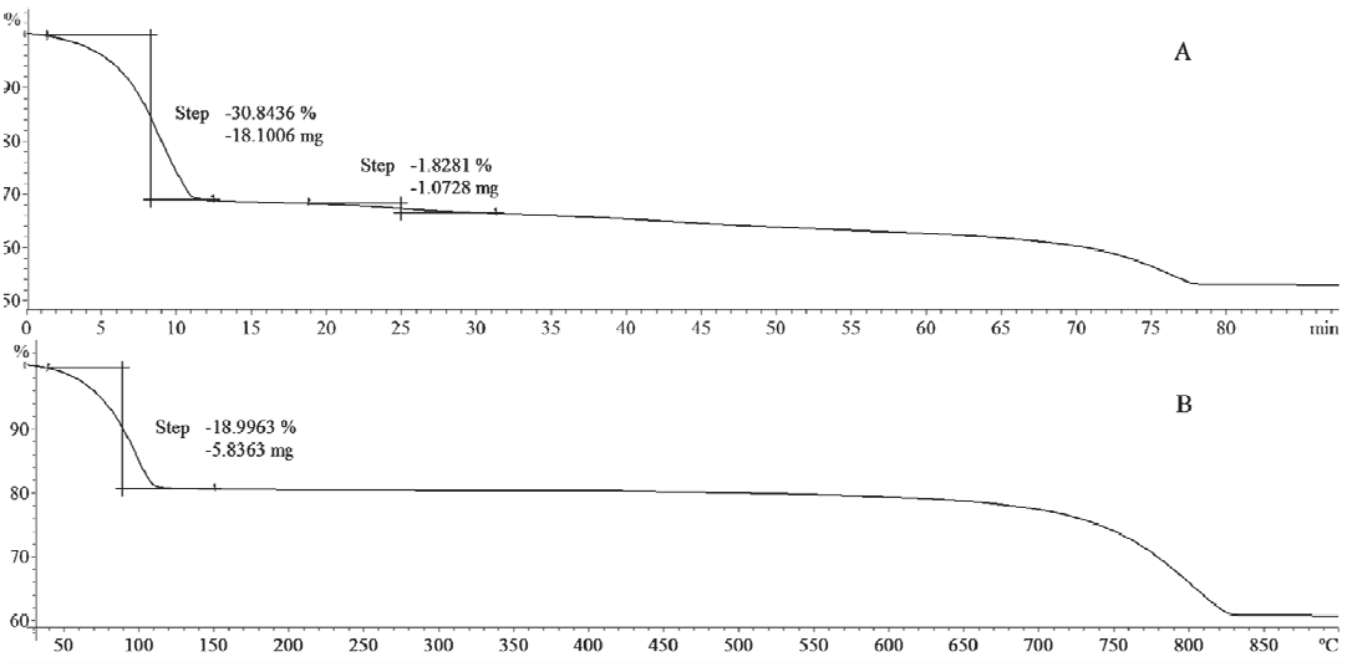


Fig. 1 TGA curves of sample SI3 (A) and SI4 (B)

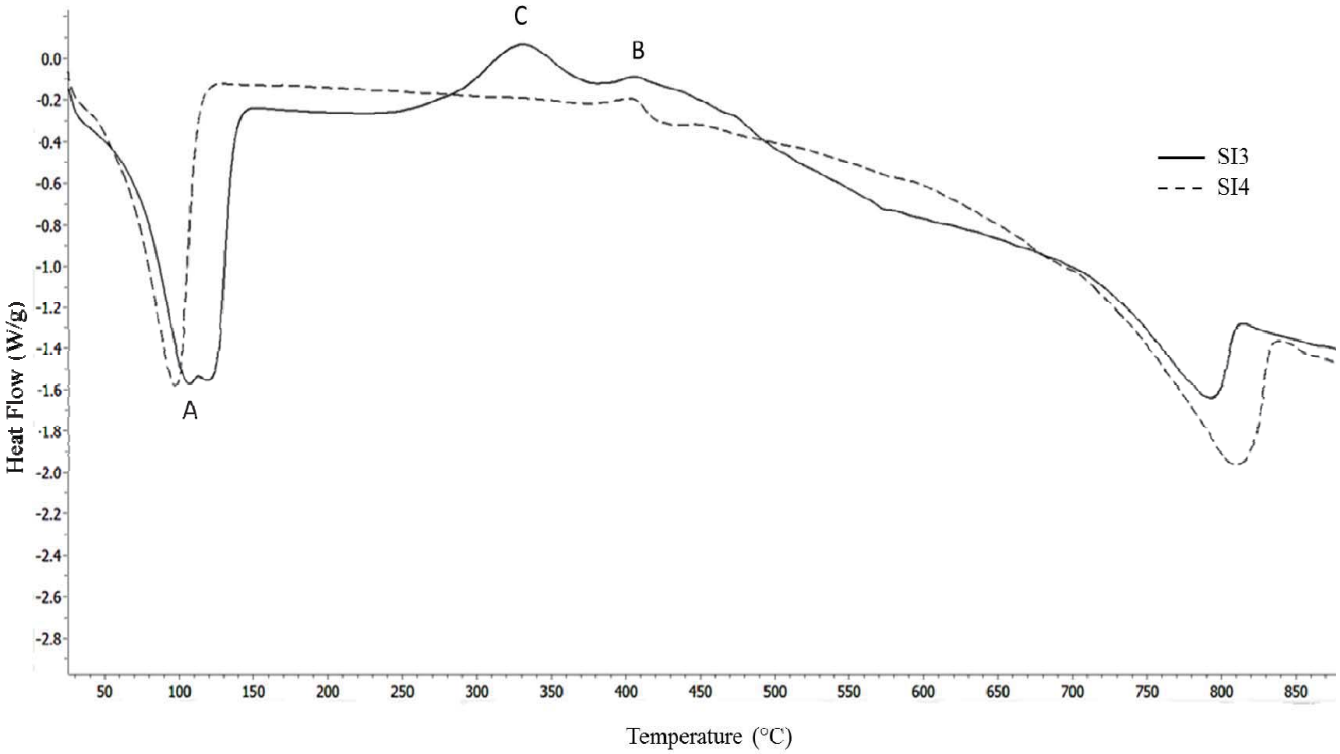


Fig. 2 DSC curves of sample SI3 (solid line) and SI4 (dotted line)

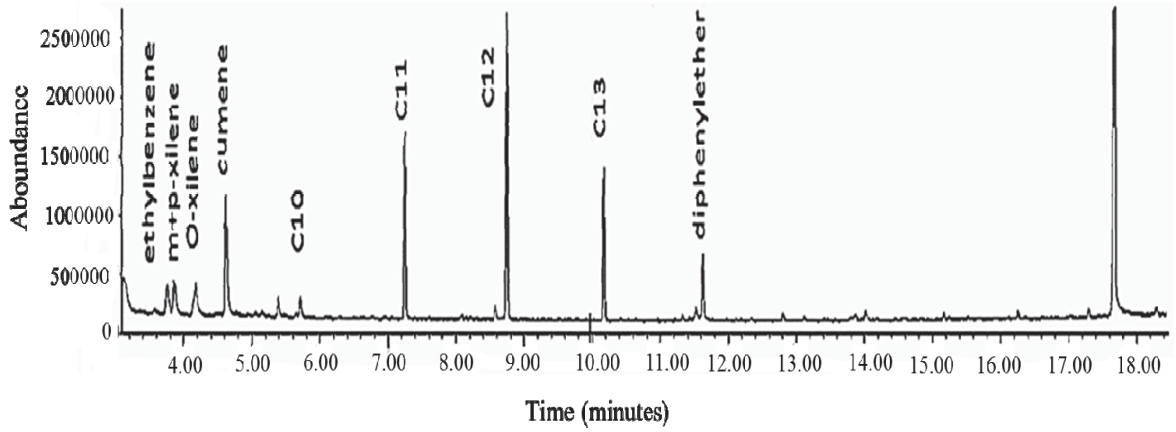


Fig. 3 GC-MS spectrum of evolved gas of SI3 at 330°C

TABLE III
QUANTITIES OF CONTAMINANTS IN SOIL SAMPLES AFTER THERMAL TREATMENT AT 150°C FOR DIFFERENT TIME

	Sample SI4			Sample SI3			Sample SI3			
	1h 150°C	2h 150°C	3h 150°C	1h 150°C	2h 150°C		3h 150°C	5h 150°C	1h 350°C	
Weight loss	18.4	19.5	20.6	32.9	33.3	Weight loss	33.3	33.1	35.9	
Benzene	ND	ND	ND	5.1	0.19	Benzene	0.098	0.028	0.05	
Ethylbenzene	ND	ND	ND	480	27	Ethylbenzene	6.5	0.32	0.47	0.59
Stirene	ND	ND	ND	ND	ND	Stirene	ND	ND	ND	ND
Toluene	ND	ND	ND	130	0.65	Toluene	3.4	0.112	0.223	0.37
Xilene	0.0015	0.0015	0.0015	910	68	Xilene	11.8	0.72	0.126	0.264
BTEX	0.003	0.003	0.003	1520	95.7	BTEX	21.7	1.15	0.82	1.22
C≤12	<1	<1	<1	357	45	C≤12	25.6	13.8	<1	<1
C>12	59	35	15.4	1770	3190	C>12	4050	8000	<5	<5
VC	ND	ND	ND	ND	ND	VC	ND	ND	ND	ND
1,2-DCA	ND	ND	ND	15.2	0.95	1,2-DCA	9.3	0.104	ND	0.17
TCE	ND	ND	ND	350	47	TCE	41	0.5	0.089	0.9
PCE	ND	0.015	0.020	810	36	PCE	18.1	0.36	ND	0.5
1,2-DCE	ND	ND	ND	0.731	0.2	1,2-DCE	3.23	0.001	ND	ND
1,2-DCP	ND	ND	ND	1.11	ND	1,2-DCP	0.155	ND	ND	ND
1,1,2-TCE	ND	ND	ND	ND	ND	1,1,2-TCE	0.33	ND	ND	ND

Concentration values are reported in mg/kg, ND values under detectable limits

IV. CONCLUSIONS

In this study attention was posed on the desorption kinetics of the samples, to identify the gas evolved during the heating, and the contaminant's degradation pathways. It was demonstrated that in a real case, where soils are not homogenous, temperature and time have to be evaluated with attention to avoid the formation of more hazardous intermediates.

The presence of high molecular weight hydrocarbons strongly affected the performance of thermal desorption and the knowledge of the degradation pathways is the key point for the optimization of the overall process.

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