

## Theme: D REMEDIATION CONCEPTS & TECHNOLOGIES

Lecture Session (LeS): LeS D.13 Soil treatment & other brand new ideas

### THERMOPILES® – A NEW THERMAL DESORPTION TECHNOLOGY FOR RECYCLING HIGHLY ORGANIC CONTAMINATED SOILS DOWN TO NATURAL LEVELS

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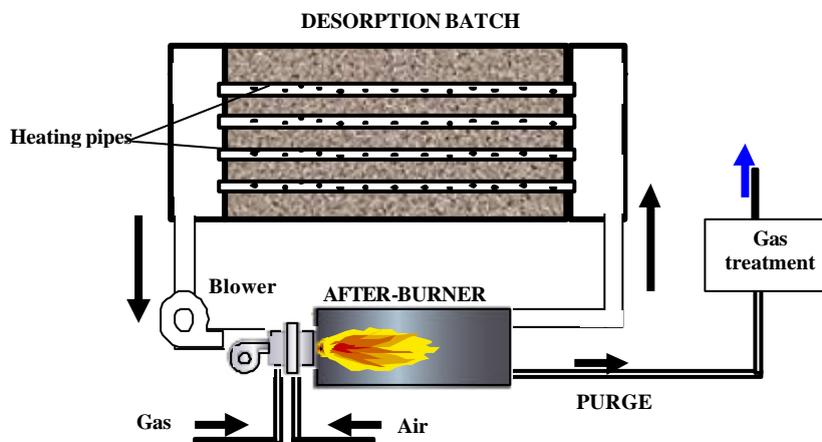
#### Principle

The Thermopile® technology, developed by Deep Green, provides an implementation system allowing to treat hydrocarbon and PAH contaminated materials down to natural levels or down to levels where they are treatable with a traditional thermal desorption unit, in a controlled batch system. The materials are indirectly heated while a substantial part of the energy is reused to heat the pile of soil. The system differs from most of the indirect thermal desorption systems by its very high energetic efficiency as well as its ability to be set-up remotely.

The system does not face preferential path problems, since the heating medium is only conduction, which is very indifferent with regard to soil type (clay, sand, silt, etc.). That property is critical to an in-depth clean-up with a batch system.

Other systems, based on heat, are mostly sending heat vectors (gasses, hot air, steam, etc.) through the soil, which implies preferential paths, which are the main cause for not completely cleaning the soil with most batch technologies (down to natural levels).

The following drawing presents a schematic view of principle of DEEP-GREEN's THERMOPILE process (Patent pending : EP 04447142.3).



The soil to treat is placed in a pile or in a modular container in which perforated steel pipes are installed along a hexagonal pattern.

During treatment those pipes are heated by hot gases (about 600°C) coming from the afterburner. Consequently the soil reaches the contaminant's desorption temperature. The desorbed pollutants are then drawn by convection and diffusion into the heating pipes via the perforations.

Once in the pipes the desorbed gases are mixed with the heating gases. They are sucked by the ID fan and sent to the afterburner. The hydrocarbons in gaseous phase are then oxydized in the afterburner. In this manner, they provide a part of the energy needed to heat the soil itself. The pilot unit is also equipped with a purge that allows the evacuation of a part of the gases circulating in the system (after the afterburner => clean gases). Different additional gas treatments can be applied as required by the type of contaminants and the emissions limits imposed.

A side phenomenon, which occurs most of the time while treating high energetic content soils, is internal soil combustion. This phenomenon reduces the treatment duration while increasing the treatment efficiency as the soil reaches high temperatures (up to 700°C).

The THERMOPILE concept has been tested and proved efficient by several field tests, as described hereafter.

## **TEST 1**

### **Materials and methods**

This test consisted in an attempt to clean a pile of 15-20 tons (metric) of soil polluted with PAH's (2000 mg/kg) and oils (5000 mg/kg) The soil came from an ancient cokeworks site . The soil also contains coal dust.

### **The gas loop**

The oxidiser temperature is programmed to be around 800-900°C. Hot gases are collected at the exit of the oxidiser stack and drawn to the entrance of the pile through a 8 meters long, 273 mm (10") diameter steel pipe, insulated with 40 mm insulation. 9 stainless steel flexibles pipes (1.5m, 88.9 mm (3") diameter, non insulated) are connected to this steel pipe and supply 9 steel heating screws buried in the pile (6m long, 88.9 mm (3") pipe dia, 200 mm screw dia). A 10<sup>th</sup> screw is placed on the top of the pile but isn't connected to the hot gases entry. This screw is only connected to the "exit of pile" pipe and is used to suck gases between the soil pile and the insulation in order to avoid fugitives.

15 mm holes are drilled every 200 mm in these screws (on 2 diametrally opposed line and alternated). The screws are connected at their end to 10 stainless steel flexibles pipes, which bring the gases to a 273 mm (10") diameter steel pipe (with partial insulation). Then the gases are drafted through this pipe to the oxidiser.

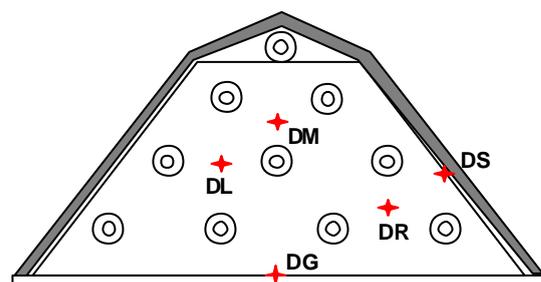
### **The soil pile**

We built a 6 meters long soil pile as shown in fig A. The screws are placed in the soil pile in an equilateral triangle pattern

The pile was covered with 40 mm insulation covered with aluminium sheet and also build on an insulation layer (between ground and soil).

### **Temperature measurements**

The temperature reached by the soil was a very important parameter for the evaluation of the



**Fig A : Thermocouples positions (front view)**

cleaning potential of the THERMOPILE technology, since it is the determinant factor for pollutants desorption.

In order to measure the temperatures reached by the soil in different places, we placed K type thermocouples in different points. These places are detailed in the figures A and B. All the measurement of the thermocouples have been recorded with a data logger (ModuLogger™, Logic Beach Inc.), with a sampling rate of 1 sample every 30 minutes.

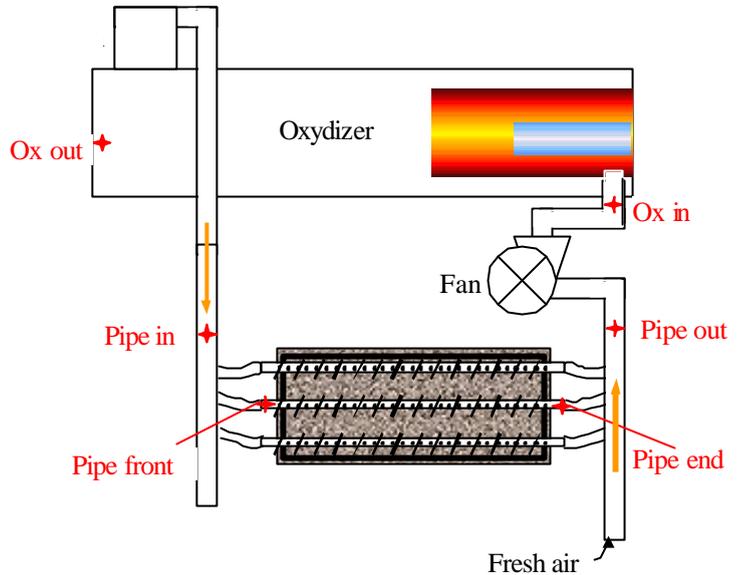
We placed 15 thermocouples in the soil pile, at 3 different distances from the front side:

- 1 m: Front (Dirt Middle F, Dirt Left F, D Ground F)
- 3 m: Middle (DMM, DLM...)
- 5 m: End (DME, D Right E...)

We also placed two thermocouples in the middle (3m) of the central screw: one on the pipe ("Screw in") and one at the extremity of the screw cutting ("Screw out").

6 thermocouples have been placed to record the gas temperatures at different places of the gas loop. These thermocouples are shown in the figure E

The pipe front and pipe end thermocouples are placed on the central screw.



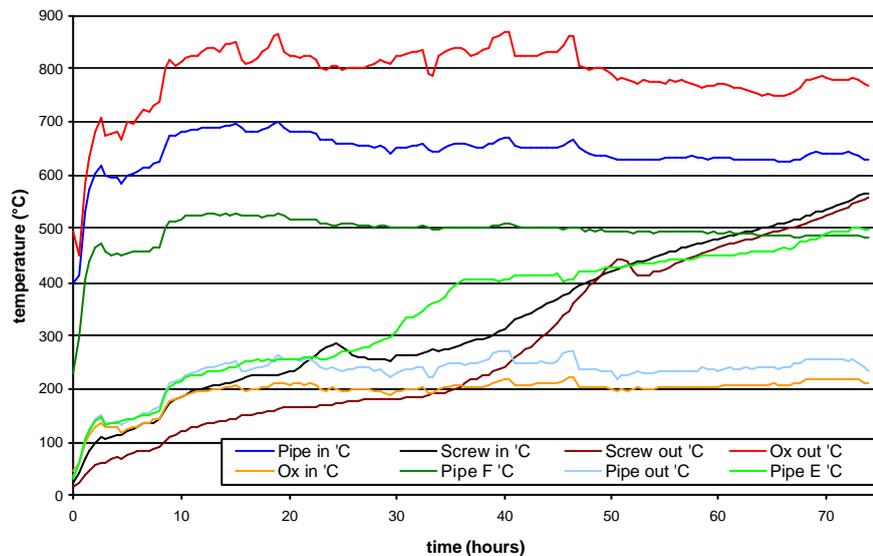
**Fig B:** Global view of THERMOPILE pilot and thermocouples positions

### Results

We ran the machine during 4 consecutive days. Outside temperature were ~7 to 12°C day and ~ -2 to +3°C night, with a little bit of rain.

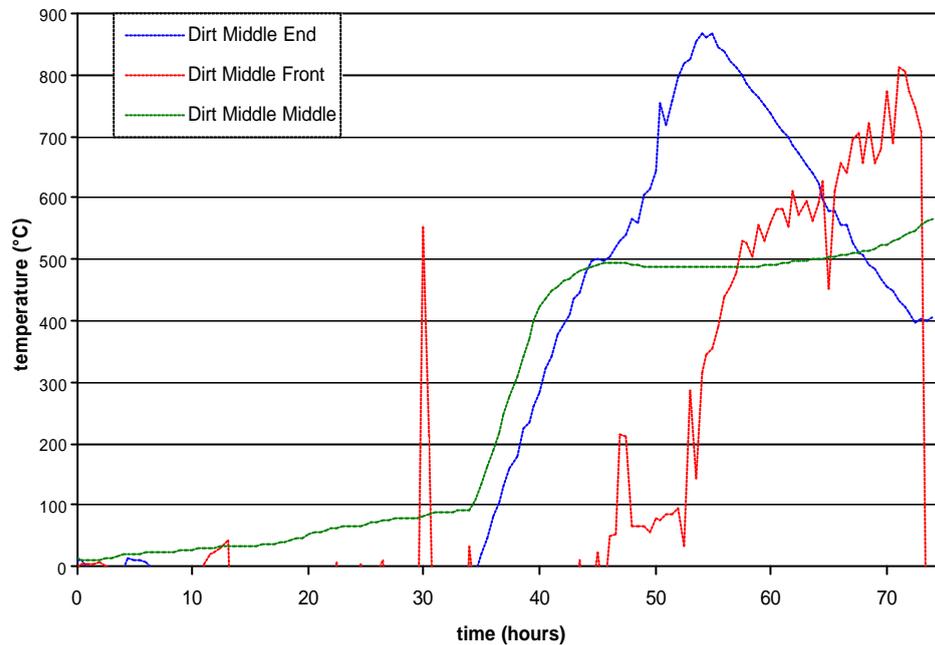
### Gas temperatures

The figure C shows the evolutions of the gas temperature recorder by our thermocouples while running test.



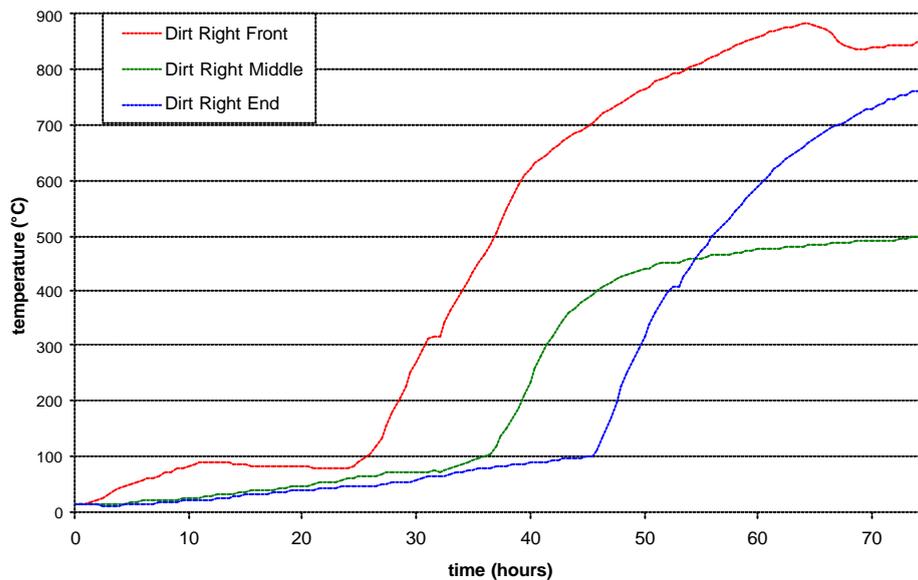
**Figure C:** Evolution of gases and screw temperatures during the test (Oxidiser burning)

## Soil temperature



**Figure D:** Evolution of soil temperature during the test, D.M. thermocouples.

Figure D shows that the soil temperature in the middle of the pile slowly increase to reach 100°C during the first 34 hours and then suddenly increase in the following 7 hours, to reach ~500°C and stabilise at this temperature until the 63rd hour, when it start to increase again. The explanation for this sudden temperature increase is the ignition of soil after all the water contained by the soil has been vaporized. This soil ignition is due to the presence of organic materials, especially coal.



**Figure E:** Evolution of dirt temperature during the test, D.R. thermocouples.

The figure E shows the same pattern of temperatures evolution as fig D: slow increase until 100°C and then quick increase (straight line with the same gradient). We also find higher temperatures recorded by the extremities thermocouples, which confirm our hypothesis of better combustion due to higher oxygen concentration.

We can also note that the maximum temperatures reached are the same: DMF~DRF~DME~DRE ~ 800-900°C; DMM~DRM ~ 500°C

The quick increase of temperature happens approximately at the same time for DMM and DRM.

### Gas emissions during test

During the test we monitored the emissions of SO<sub>2</sub>, CO, NO<sub>x</sub>, NO and O<sub>2</sub>, at the bleed.

At the afterburner stack	+10h	+50h	+70h
Gas T	719°C	711°C	700°C
O <sub>2</sub>	4,1 %	4,1 %	4,0 %
NO <sub>x</sub>	62 mg/m <sup>3</sup>	66 mg/m <sup>3</sup>	70 mg/m <sup>3</sup>
NO	65 mg/m <sup>3</sup>	65 mg/m <sup>3</sup>	62 mg/m <sup>3</sup>
CO	42 mg/m <sup>3</sup>	10 mg/m <sup>3</sup>	0 mg/m <sup>3</sup>
SO <sub>2</sub>	5 mg/m <sup>3</sup>	4 mg/m <sup>3</sup>	5 mg/m <sup>3</sup>

Table 1: Summary of the emissions measurements during test.

### Evolution of hydrocarbons concentrations

Composite samples of the dirt have been realized and analysed before and after treatment.

Analysis results are given in the following table

	Beginning of test	End of test
Dry Material %	82,5 to 84,3 %	99,8 to 100 %
Total hydrocarbons (C <sub>10</sub> -C <sub>40</sub> ) ppm	3200 to 5300 ppm	<10 to 13 ppm
Total PAH's (16 EPA) ppm	1800 to 2200 ppm	n.d. to 8,9 ppm
Mercury (Hg) ppm	1,8 to 2,1 ppm	<0,1 to 0,2

Table 2: Summary of the dirt analysis results, before and after treatment.

This result shows that the soil can be cleaned with this pilot unit. We have to stipulate the fact that this test was realized in special conditions (coal in the soil) that allows the soil to burn by itself and reach high temperatures (up to 800°C).

## **TEST 2**

This test is characterized by the use of a modular container instead of just a soil pile, this container allows an easier handling of the dirt. The heating elements used are steel pipes.

### Materials and methods

This test consisted in an attempt to clean a batch of 20 tons (metric) of soil polluted with tar. Average concentrations are : PAH's 3900 mg/kg and mineral oils 7500 mg/kg.

### The gas loop

The gas loop is the same than the previously described in test 1

### The soil batch

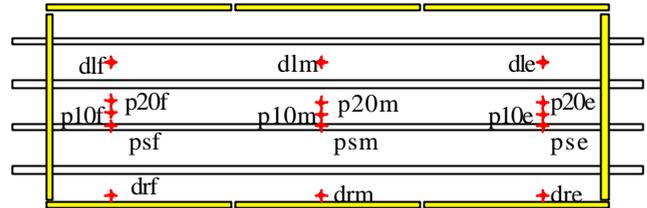
The modular batch is built of 8 steel plates (210x210cm) connected together. (see pic F)

The element of the front and the end of the batch are designed to allow an easy placing and easy removing of the pipes.

length of the container = 630cm

Space between heating pipes is 60 cm and pipes are organised in an hexagonal pattern.

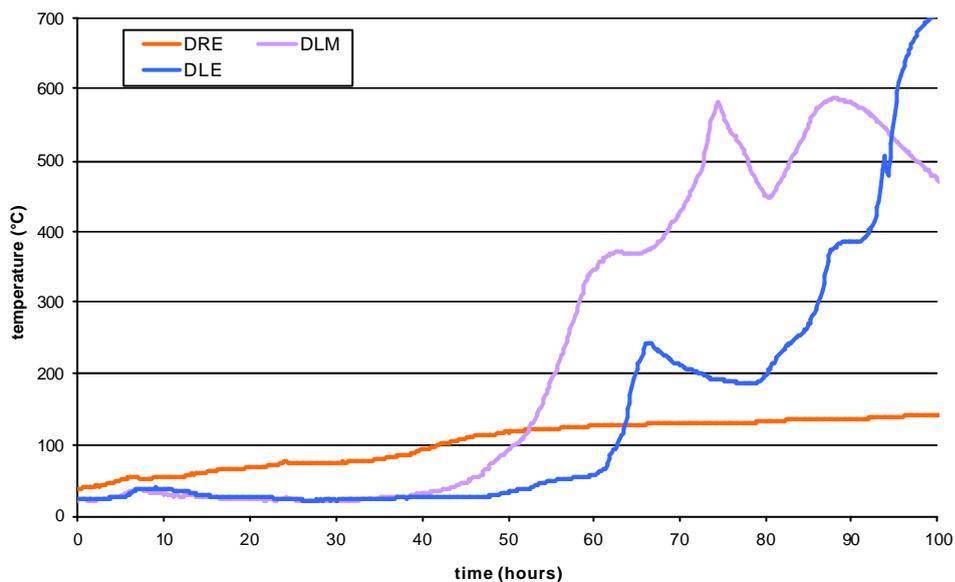
Insulation and sealing of the batch's top is done with 40 mm of rockwool covered with an aluminium sheet. The batch elements are insulated with a 40 mm rockwool layer.



**Figure F** : top view of the batch and thermocouples

### Results

#### Evolutions of soil temperatures



The DLM and DLE thermocouples reveal that a combustion occurs in the pile. However DRE indicate that this combustion occurs only in some places of the batch, at least during the experience duration considered.

#### Gas emissions during test

During the test we monitored the emissions of SO<sub>2</sub>, CO, NO<sub>x</sub>, NO and O<sub>2</sub>, at the bleed.

At the afterburner stack	+10h	+50h	+70h	+95h
Gas T	717°C	718°C	715°C	721°C

O2	4,2 %	4,5 %	4,0 %	3,9 %
NOx	61 mg/m <sup>3</sup>	62 mg/m <sup>3</sup>	62 mg/m <sup>3</sup>	56 mg/m <sup>3</sup>
NO	60 mg/m <sup>3</sup>	55 mg/m <sup>3</sup>	58 mg/m <sup>3</sup>	58mg/m <sup>3</sup>
CO	22 mg/m <sup>3</sup>	15 mg/m <sup>3</sup>	3 mg/m <sup>3</sup>	4 mg/m <sup>3</sup>
SO2	6 mg/m <sup>3</sup>	5 mg/m <sup>3</sup>	5 mg/m <sup>3</sup>	5 mg/m <sup>3</sup>

Table 3: Summary of the emissions measurements during test.

### Evolution of hydrocarbons concentrations

Composite samples of the soil have been realized and analysed before and after treatment. Analysis results are given in the following table

	Before treatment	After treatment
Dry material %	86 %	100 %
Total hydrocarbons (C <sub>10</sub> -C <sub>40</sub> ) mg/kg	7500	320
Total PAHs (16 EPA) mg/kg	3900	110
Cyanides (CN) mg/kg	390	18

Table 4 : soil analysis results, before and after treatment.

These results confirm a significant decrease of the contaminants concentration. However those concentrations are not down to natural/background levels. This may be explained by an heterogeneity of the treatment efficiency due to the heterogeneous repartition of temperature in the batch during treatment. Some spot temperatures don't exceed 150°C (DRE).

### **TEST 3**

#### Materials and methods

This test consisted in cleaning a pile of approximately 250 tons (metric) of very polluted soil (non screened) containing a lot of tar. The pollution was very heterogeneous PAHs from 6.500 to 59.000 mg/kg, mineral oils 11.000 to 69.000 mg/kg.

#### The gas loop

The oxydiser temperature is programmed to be around 900°C. Hot gases are collected an the exit of the oxydiser stack and drawn to the entrance of the pile through a 15 meters long, 273 mm (10")diameter steel pipe, insulated with 40 mm insulation. 40 ceramic flexible hoses are connected to this steel pipe and supply 40 steel heating screws buried in the pile (6m long, 88.9 mm (3") pipe dia, 200 mm screw dia).

15 mm holes are drilled every 200 mm in these screws (on 2 diametrically opposed line and alternated). The screws are connected at their end to 40 ceramic hoses which bring the gases to a 273 mm (10") diameter steel pipe (with partial insulation).Then the gases are drafted through this pipe to the oxydiser.

#### The soil pile

The soil pile shape was the one shown in fig H.

The pile was covered with 40 mm insulation covered with aluminium sheet.

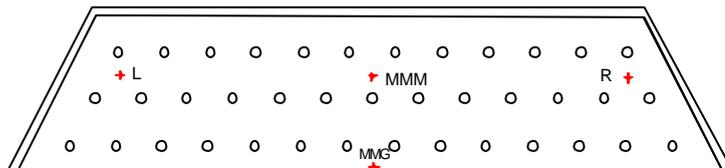


Figure H : Soil pile final

## Results

### Emissions monitoring during test

During the test we monitored the emissions of SO<sub>2</sub>, CO, NO<sub>x</sub>, NO and O<sub>2</sub>, at the bleed.

At the afterburner stack	+10h	+50h	+100h	+160h
Gas T	709°C	711°C	700°C	715 °C
O <sub>2</sub>	4,1 %	4,1 %	4,0 %	4,2 %
NO <sub>x</sub>	61 mg/m <sup>3</sup>	65 mg/m <sup>3</sup>	70 mg/m <sup>3</sup>	63 mg/m <sup>3</sup>
NO	55 mg/m <sup>3</sup>	55 mg/m <sup>3</sup>	57 mg/m <sup>3</sup>	60 mg/m <sup>3</sup>
CO	20 mg/m <sup>3</sup>	11 mg/m <sup>3</sup>	0 mg/m <sup>3</sup>	0 mg/m <sup>3</sup>
SO <sub>2</sub>	38 mg/m <sup>3</sup>	20 mg/m <sup>3</sup>	9 mg/m <sup>3</sup>	7 mg/m <sup>3</sup>

Table 5 : Summary of the emissions measurements during test.

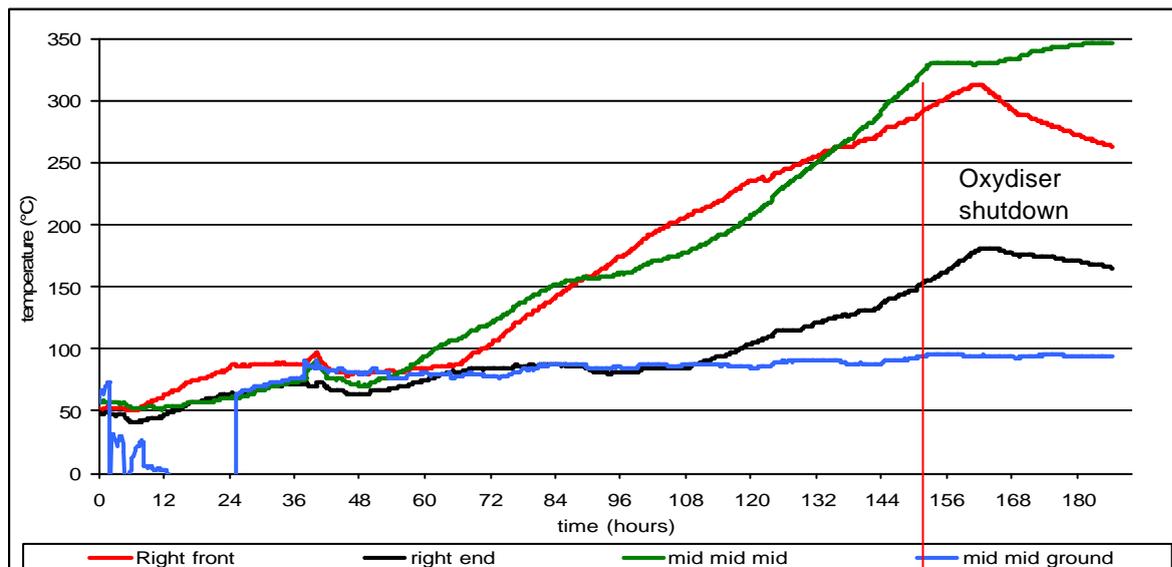
### Evolution of hydrocarbons concentrations

	Beginning of test	End of test	
		Cleanest sample	Dirtiest sample
Dry Material %	78,4 to 84,2 %	99,9 %	92,2 %
Total hydrocarbons (C <sub>10</sub> -C <sub>40</sub> ) ppm	11000 to 69000 ppm	< 10 ppm	5700 ppm
Total PAHs (16 EPA) ppm	6500 to 59000 ppm	2,2 ppm	1800 ppm
Mercury (Hg) ppm	1,0 to 2,0 ppm	< 0,1 ppm	1,0 ppm
Cyanides (CN) ppm	250 to 430 ppm	< 1 ppm	140 ppm

Table 6 : Summary of the dirt analysis results, before and after treatment.

These results reveal that the soil can be cleaned with this pilot unit but the cleaning efficiency is still very heterogeneous in space (and time). However, as the contaminants residual concentrations in the soil are low after the thermopile treatment, that soil can be totally cleaned by means of classical thermal desorption (rotary kiln).

As such the technology can be seen as a pre-treatment for high contaminated soils, after which it need traditional thermal treatment in order to reach backgrounds levels.



### **Production scale**

A production scale unit was set-up on a 2223 ton coal tar contaminated soil from a former cokeswork in France. The treatment showed the following results:

<i>Contaminant</i>	<i>Unit</i>	<i>Input</i>			<i>Output</i>		
		<i>Min</i>	<i>Max</i>	<i>Average</i>	<i>Min</i>	<i>Max</i>	<i>Average</i>
TPH	Mg/kg d.m.	2.645	94.545	64.507	<20	162	86
PAH (16)	Mg/kg d.m.	4.549	134.544	48.780	<2	720	92
CN	Mg/kg d.m.	142	5.822	3.465	<1	11	4.2
Moisture	%	12.6%	31.5%	24.1%	0.05%	1.5%	0.3%

*Table 7: Results for the treatment of 2,223 tons of coal tar soil for Arcelor (Bail Industrie)*

The average duration for each batch was 7 days.