

## Thermal remediation of oil polluted sands from black tides: The fluidized bed option

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### Abstract

Following the oil spills due to the accidents involving the oil tankers Erika and Prestige on the Atlantic coast, thermal remediation of oil polluted sands in a fluidized bed was studied. A thermal process is proposed as an alternative to the physico-chemical washing that has been carried out with the Erika wastes. The study consists of: choice of the polluted wastes; air fluidization behavior of oil polluted sands in a cold fluidized bed; depollution characterization in a hot fluidized bed; design and engineering of an industrial scale furnace and investment and operating cost evaluation of such a remediation unit.

Polluted sands were prepared for different combinations of sand particle diameter, oil and water content. Fluidizability of oil polluted sands was checked in a cold model fluidized bed facility. Hot tests showed that combustion started as soon as the fluidized bed temperature was equal to or higher than 700 °C. The remediation of the polluted sand was good in all the cases with a remaining pollution in the sand of about 50 mg/kg. Flue gas emissions were within the regulatory limits. There was no danger of any ash fusion noticed even in the long duration tests.

An industrial scale furnace was then designed based on the measured limits of fluidizability and the evaluated time necessary to get an almost complete remediation of the oil. Fluidized bed treatment costs were then evaluated and compared to the physico-chemical separation that has been used in the case of Erika oil spill and the thermal treatment in a rotating furnace. Fluidized bed combustion appeared to be one of the best options with a cost of only 80 €/t of polluted waste.

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### 1. Introduction

Oil slick is a marine pollution receiving much attention all over the world due to its frequency of occurrence, magnitude and the extent of damage it can inflict on the environment. Oil slicks usually happen in the accidents involving oil tankers and ships as Erika's accident in the Atlantic Ocean near the French coast [1]. The ship 'Erika' carrying 31,000 t of heavy oil (No. 6

Fuel Oil) broke up into two on 12 December 1999 spilling about 15,000 t of the fuel oil into the Atlantic and polluted the Brittany coast (France) for about 450 km. On 13 November 2002, one of the tanks of Prestige burst before sinking completely into the depth of the Atlantic. About 63,000 t of oil polluted the coast of Galicia, Spain and France.

This paper presents the remediation of oil contaminated sand in a fluidized bed combustor (THERMER project carried out under the framework of RITMER, a research network funded by the French authorities). It investigated the suitability and feasibility of fluidized beds for dealing with oil polluted sand. Cold model experiments were carried out using coarse and fine sands

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for different combinations of heavy and light oils with and without water to assess the variation of the minimum fluidization velocity ( $U_{mf}$ ) in the ambient air. It also established the limits of oil pollution in the sand beyond which the fluidization quality deteriorated drastically. Hot tests were carried out in a fluidized bed with sands polluted with light and heavy oils mixed with water and also with the original waste from the Prestige accident collected from the beaches. The self-ignition temperature of these polluted sands was evaluated from the flue gas analysis. The complete combustion time was evaluated during the batch experiments. The quality of remediation was assessed by the measurements on the unburnt total hydrocarbon content of bed particles and also by the quality of the flue gas. Long duration tests with Prestige wastes were also carried out to assess the occurrence of ash fusion and defluidization of the bed that might result from the salt content from the seawater. Models were developed to predict the operating conditions of an industrial reactor for efficient remediation of the polluted sand and the quantity of natural gas addition in the fluidized bed as a function of the required bed temperature level, the type and level of the pollution of sand. This paper discusses then the engineering of a dedicated industrial size fluidized bed combustor for the remediation of oil polluted sand and its economics in comparison with the other remediation routes.

## 2. Experimental

Cold model experiments were carried out to assess the feasibility of fluidizing the oil polluted sand and to establish the maximum pollutant concentrations possible. Hot model experiments were mainly aimed at evaluating the efficiency of the whole process based on the flue gas emissions and the pollution abatement.

### 2.1. Fluidization of oil polluted sands

Materials for the cold studies were chosen based on the characteristics of the real wastes collected from the oil polluted beaches considering the varying nature of oil that can be involved in marine pollution. A few polluted sand models were defined for this study based on the waste characteristics collected from the beaches after the Erika accident.

Two kinds of raw sand were used for the tests: coarse sand of average harmonic (or Sauter (13)) diameter 0.43 mm (particle size distribution from 0.1 mm to 4.0 mm) and fine sand of average harmonic diameter 0.10 mm (particle size distribution from 0.04 mm to 0.315 mm). Both sands had a particle density of 2650 kg/m<sup>3</sup>.

Four kinds of pollution were simulated with heavy oil (No. 6 Fuel Oil), diesel and water by mixing them in different proportions (Table 1). Light oil was obtained by mixing heavy oil and diesel at a ratio 25:75. Emulsions (mixtures of oil and water) were prepared using a mechanical mixer and then they were mixed with the appropriate quantity of dry raw sand manually in the proportion of 95% raw dry sand +5% pollutant. Mixing was continued to get uniform polluted sand without agglomeration. For the experiments having water content, it was fixed

Table 1  
Polluted sand models chosen for the experiments

Model no.	Raw sand (95%)	Oil pollutants (5% by weight)
1	Coarse	Heavy oil alone (100%)
2	Coarse	A mixture of heavy oil (70%) and water (30%)
3	Coarse	Light oil alone (100%)
4	Coarse	A mixture of light oil (70%) and water (30%)
5	Fine	Heavy oil alone (100%)
6	Fine	A mixture of heavy oil (70%) and water (30%)
7	Fine	Light oil alone (100%)
8	Fine	A mixture of light oil (70%) and water (30%)

at 30% by weight as it was the usual moisture content of the polluted sand collected from the seashore.

Experiments were carried out in a cold fluidized bed (Fig. 1) of cross-sectional area 0.2 m × 0.2 m. A blower supplied the fluidization air and the flow was measured by a mass flow meter (capacity 0–100 N m<sup>3</sup>/h, Brooks) and a velocity meter (hot wire from Dantec) according to the range of flow rate. The fluidization air distributor was a perforated plate with 2 mm diameter holes spaced at 10 mm centre to centre for the coarse sand and 1 mm diameter holes spaced at 12 mm centre to centre for the fine sand [2]. Pressure fluctuations were measured using pressure transducer (ESP-32HD from PSI at 200 Hz) and data acquisition system (Fluke 2086 used at 1 Hz) as shown in Fig. 1.

A bed inventory of 6 kg of raw unpolluted dry sand was placed in the reactor to initiate each series of experiments. Then quantities of polluted sand previously prepared was mixed thoroughly to the bed until given levels of oil pollution in the sand were reached. The experiments were thus carried out starting with a bed of raw dry sand (6 kg) and increasing the percentage of pollution in the bed by adding polluted sand containing 5% pollutants.

At every increase of the percentage of pollution in the bed,  $U_{mf}$  was evaluated: pressure drop across the bed was determined and was plotted against the velocity for both increasing and decreasing airflow rates.  $U_{mf}$  was estimated from the decreasing air velocity part of the plot (defluidization curves) [2].

Defluidization curves tended to look like the defluidization curve obtained with dispersed solids or binary mixtures when the pollution fraction was increasing, and were characterized by a large intermediate state between the beginning of defluidization at high gas velocities and the almost totally defluidized bed when decreasing gas velocity. This extended transient intermediate regime between the fixed bed and the fluidized bed may be observed when particle size distribution is large [3] or becomes large by agglomeration or by sticking [4], or when the bed is composed of a mixture of jetsam and flotsam particles [5]. In the present study, sticking of particles together, because of the presence of oil on their surface, was clearly observed and have undoubtedly increased the particle size distribution of the raw sand.

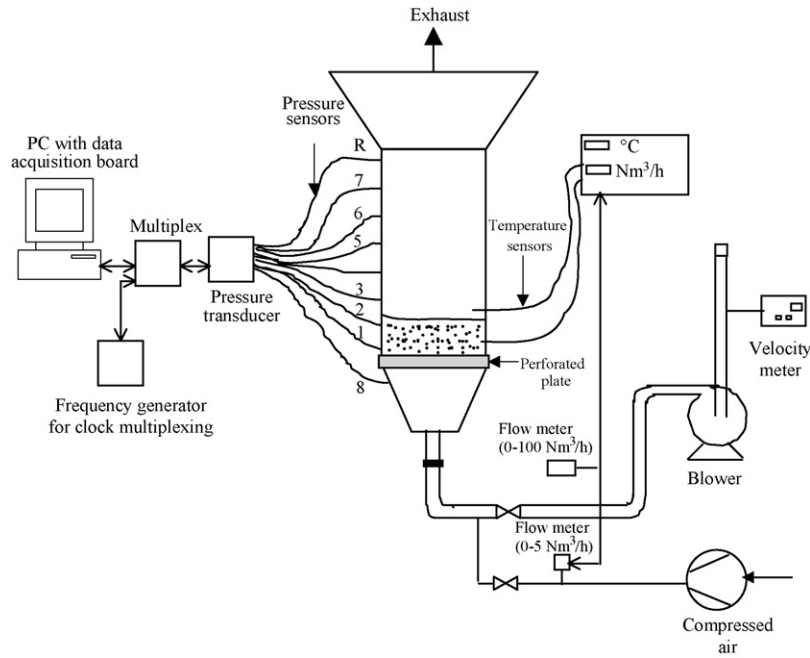


Fig. 1. The cold fluidized bed experimental facility.

Fig. 2 presents the normalised  $U_{mf}$ , that is the  $U_{mf}$  of sand for varying pollution contents divided by the  $U_{mf}$  of the corresponding raw unpolluted sand. At low pollution percentage, the increase of  $U_{mf}$  was slow; then, beyond certain level of pollution, the  $U_{mf}$  increased rapidly with the pollution content in the bed. For each type of pollutant, a critical pollutant content corresponding to the change of slope of the  $U_{mf}$  curves was then determined by fitting two straight lines to a curve and their intersection [6] as observed by Seville et al. who showed the evolution of  $U_{mf}$  of a fluidized bed containing sintering product as a function of temperature [7]. Benesse and Delebarre also observed these two different trends in the study of  $U_{mf}$  of scrap wood particles as a function of their moisture [8]. Critical concentrations of different pollutants for both coarse sand and fine sand are given in Fig. 3. Both sands exhibited more or less similar

behavior when polluted with heavy oil. However, with light oil, the bed of coarse sand was fluidizable at higher pollutant concentrations than for the fine sand. With light oil + water, the bed was not fluidizable at concentration above 0.17%. With heavy oil + water and heavy oil alone, the fine sand bed was fluidizable up to 0.86% and 1.25% of pollution, respectively. The presence of water, for both coarse and fine sands, with heavy oil or light oil, decreased the fluidizability of the bed.

## 2.2. Efficiency of thermal remediation in a fluidized bed

The same raw fine sand of average harmonic diameter of 0.10 mm was used for the hot model experiments. Four kinds of pollution were simulated with heavy oil, diesel and water by mixing them as shown in Table 1. Some sand polluted with 10% of Prestige oil (containing around 60% of seawater) was also tested in the same apparatus.

The experimental set-up consisted of a dense fluidized bed reactor with an inner diameter and a height of reactor of 105 mm

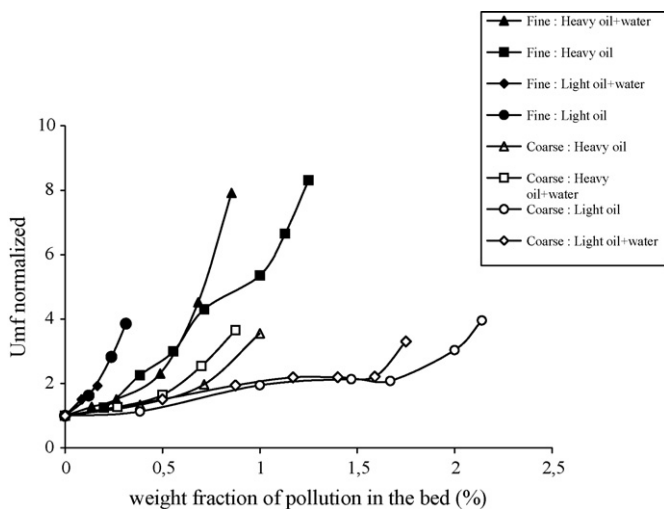


Fig. 2.  $U_{mf}$  (normalised) for fine and coarse sands.

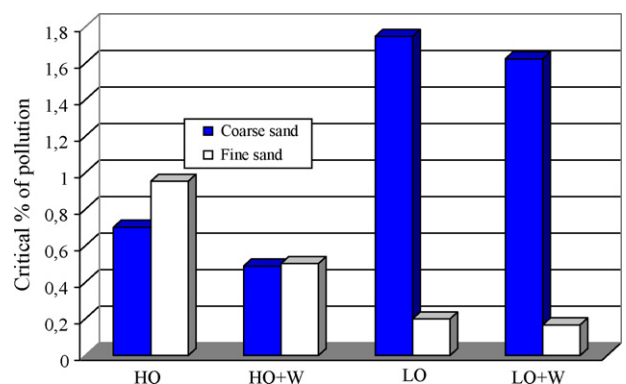


Fig. 3. Critical content of pollution (HO: heavy oil, LO: light oil, W: water).

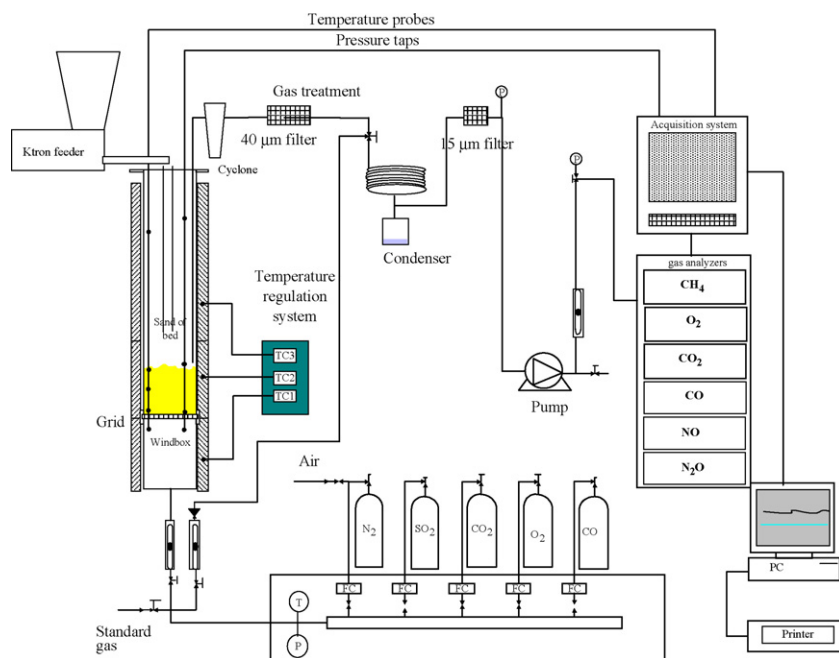


Fig. 4. Schematic drawing of the fluidized bed furnace.

and 1420 mm, respectively. The height of the initial bed was about 190 mm corresponding to a mass of 1.5 kg of sand. Unburnt fraction of the bed was measured by weighing the sample before and after heating at 815 °C. Total combustion time was estimated by introducing a sample in the reactor at a given time having a sufficient mass to obtain a significant decrease of O<sub>2</sub>.

The dense fluidized bed reactor was fed by a K-tron feeder (T20 model) at a rate of a few grams/minute and was fitted with a gas-analysis equipment and a computer as illustrated in Fig. 4. The reactor vessel was made of type Z12CN25-20 stainless steel. Thermocouple probes and pressure taps were positioned at intervals along the length of the reactor to measure axial temperature and pressure profile. The reactor was heated electrically by three heaters: one for the wind box, one for the reaction zone and another for the freeboard. The fluidization grid was a stainless steel sintered plate to ensure uniform flow distribution.

Gas mixture samples withdrawn above the top of the bed were conditioned (quenched, filtered and dried) before introducing into the analytical equipment consisting of: CO<sub>2</sub> analyzer (Maihak UNOR 6N 0–15%, infrared), O<sub>2</sub> analyzer (Rose-

mount OXYNOS 100 0–25%, paramagnetic), SO<sub>2</sub> analyzer (Maihak UNOR 610 0–5000 ppm, infrared), CO analyzers (Maihak UNOR 610 0–5000 ppm, infrared; Rosemount BINOS 100 0–5%, infrared), NO analyzer (Maihak UNOR 6, infrared) and N<sub>2</sub>O analyzer (Maihak UNOR 610 0–1500 ppm, infrared). The signals generated from the gas analyzers, thermocouples and pressure transducers were converted to the digital form by a data acquisition system and then stored in the hard disk.

### 2.2.1. Self-ignition temperature

Self-ignition temperature was investigated to select the most appropriate range of temperatures necessary for the onset of combustion of the oil fraction on the polluted sands. Polluted sands were fed continuously into the bed having a controlled temperature in the range of 400 °C to 850 °C. Fig. 5 illustrates two examples of combustion curves at 450 °C and 800 °C for the Prestige polluted sand. It shows that, greater the bed temperature, greater is the CO<sub>2</sub> signal and the lowest is the O<sub>2</sub> signal [9]. From the flue gas analysis signals of the various tests conducted, it was found out that self ignition of polluted sands is as low as 600 °C and complete combustion takes place at bed temperatures above

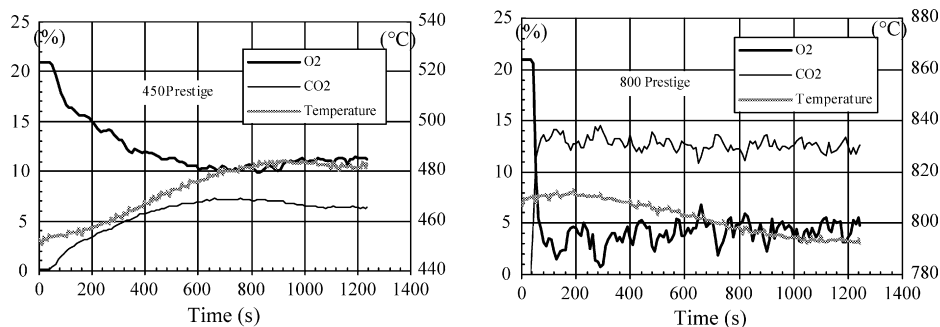


Fig. 5. Examples of self-ignition test signals for Prestige oil at 450 °C and 800 °C.

Table 2  
Complete combustion time after SO<sub>2</sub> signals

Fluidized bed temperature (°C)	Combustion time (s)
650	35
700	31
800	31
850	34

700 °C whatever was the pollution. However it was noticed that, Prestige oil polluted sand had a 50 °C delay on its ignition temperature compared to the heavy and light oils tested in this study [9]. All raw data are available in the Final Report of THERMER project available at the library of IFREMER, Brest, France.

### 2.2.2. Complete combustion time by batch experiments

Time to complete the combustion at different fluidized bed temperatures was measured during the batch experiments carried out with sand polluted by Prestige oil at 10%. O<sub>2</sub>, CO<sub>2</sub>, CO and

SO<sub>2</sub> flue gas analyses gave nearly the same duration, a little more than 30 s (Table 2). This evaluation includes the combustion of the volatiles as well as the char and it intrinsically accounts for the unburnt fraction. It is the total time required to complete the combustion of what may possibly burn.

### 2.3. Environmental efficiency of fluidized bed thermal remediation

Table 3 presents the flue gas composition during the steady state continuous tests conducted at four different temperatures with different pollutants. NO has greater concentrations with heavy oil than in the cases of Prestige oil and light oil. NO<sub>2</sub> concentrations were at their maximum at 800 °C. The presence of water generally increased NO<sub>2</sub> content. SO<sub>2</sub> emissions were in the range of 1300–2000 mg/N m<sup>3</sup> at 6% of O<sub>2</sub> for heavy and light oils; but were much higher in the case of Prestige waste (sulfur content of Prestige oil was 2.63%) [9]. Addition of limestone at a relatively small Ca/S molar ratio of 1.1 reduced the SO<sub>2</sub>

Table 3  
Emissions during continuous combustion tests

	Temperature (°C)			
	650	700	800	850
<b>Heavy fuel</b>				
O <sub>2</sub> (%)	5.82	5.48	6.54	6.11
NO as NO <sub>2</sub> (mg N m <sup>-3</sup> at 6% O <sub>2</sub> )	260	275	315	302
SO <sub>2</sub> (mg N m <sup>-3</sup> at 6% O <sub>2</sub> )	2050	2032	1893	2011
N <sub>2</sub> O (mg N m <sup>-3</sup> at 6% O <sub>2</sub> )	26	23	4	0
CO (mg N m <sup>-3</sup> at 6% O <sub>2</sub> )	406	217	65	95
<b>Heavy fuel + water</b>				
O <sub>2</sub> (%)	5.32	6.03	5.70	5.62
NO as NO <sub>2</sub> (mg N m <sup>-3</sup> at 6% O <sub>2</sub> )	259	297	331	316
SO <sub>2</sub> (mg N m <sup>-3</sup> at 6% O <sub>2</sub> )	1733	1806	1727	1834
N <sub>2</sub> O (mg N m <sup>-3</sup> at 6% O <sub>2</sub> )	26	15	0	0
CO (mg N m <sup>-3</sup> at 6% O <sub>2</sub> )	654	561	87	168
<b>Light oil</b>				
O <sub>2</sub> (%)	5.13	5.35	5.89	6.26
NO as NO <sub>2</sub> (mg N m <sup>-3</sup> at 6% O <sub>2</sub> )	224	232	239	234
SO <sub>2</sub> (mg N m <sup>-3</sup> at 6% O <sub>2</sub> )	1330	1389	1292	1439
N <sub>2</sub> O (mg N m <sup>-3</sup> at 6% O <sub>2</sub> )				
CO (mg N m <sup>-3</sup> at 6% O <sub>2</sub> )	1555	1852	470	704
<b>Light oil + water</b>				
O <sub>2</sub> (%)	5.34	6.35	6.48	6.24
NO as NO <sub>2</sub> (mg N m <sup>-3</sup> at 6% O <sub>2</sub> )	201	227	253	246
SO <sub>2</sub> (mg N m <sup>-3</sup> at 6% O <sub>2</sub> )	1430	1496	1319	1545
N <sub>2</sub> O (mg N m <sup>-3</sup> at 6% O <sub>2</sub> )				
CO (mg N m <sup>-3</sup> at 6% O <sub>2</sub> )	972	1110	182	284
<b>Prestige oil</b>				
O <sub>2</sub> (%)	2.91	6.10	5.70	4.50
NO as NO <sub>2</sub> (mg N m <sup>-3</sup> at 6% O <sub>2</sub> )	282	344	290	269
SO <sub>2</sub> (mg N m <sup>-3</sup> at 6% O <sub>2</sub> )	3752	3596	3688	3978
N <sub>2</sub> O (mg N m <sup>-3</sup> at 6% O <sub>2</sub> )	3	13	0	0
CO (mg N m <sup>-3</sup> at 6% O <sub>2</sub> )	5696	1710	1137	1249
<b>Prestige oil + limestone</b>				
O <sub>2</sub> (%)	8.73	7.34	5.28	
NO as NO <sub>2</sub> (mg N m <sup>-3</sup> at 6% O <sub>2</sub> )	383	346	285	
SO <sub>2</sub> (mg N m <sup>-3</sup> at 6% O <sub>2</sub> )	866	1119	1568	
N <sub>2</sub> O (mg N m <sup>-3</sup> at 6% O <sub>2</sub> )	30	7	0	
CO (mg N m <sup>-3</sup> at 6% O <sub>2</sub> )	3608	934	788	

Table 4  
Remediation quality obtained during the tests

	Unburnt (% on dry basis)							
	Bed product				Fly ash			
Temperature (°C)	650	700	800	850	650	700	800	850
Heavy fuel	0.06	0.06	0.09	0.07	5.3	1.63	1.94	3.22
Heavy fuel + water	0.06	0.05	0.07	0.04	9.57	1.84	2.01	2.33
Light oil	0.06	0.08	0.08	0.09	1.08	1.70	7.77	4.61
Light oil + water			0.06	0.06			2.27	2.75
Prestige oil	0.05	0.06	0.05	0.04			2.04	1.62
Prestige oil + limestone	0.17	0.12	0.15		4.01	6.15	1.88	

emissions by 60–75%. CO emissions were generally decreasing with an increase in the temperature up to 800 °C. Heavy oil polluted sand produced less CO than the light oil polluted sand. Presence of water increased the CO content of the flue gas for heavy oil; but reduced it for the light oil. High CO emissions for Prestige oil at 650 °C may be attributed to its high self-ignition temperature. However, when it was efficiently burning, the composition of the Prestige oil flue gas was like that of the light oil. N<sub>2</sub>O emissions were always low and even disappeared at 800 °C and above. This is quite different from the situation encountered during coal combustion for which N<sub>2</sub>O emissions are generally of the same order of magnitude of the NO<sub>2</sub> emissions.

The remediation efficiency was evaluated by measuring the unburnt fraction, and in an eight cases, the total hydrocarbon fraction of the sand that was withdrawn from the bed during steady state operation (Table 4). Unburnt fraction measurements were also performed on the dust collected at the filter but dust was generated in very small quantities during the tests. The small amount of unburnt or hydrocarbon fractions measured in the bed sand, and their reasonable agreement one to each other for given samples made it possible to consider the unburnt fraction (cheaper and easier analysis compared to total hydrocarbon fraction) as the one to be compared to the imposed maximum fraction after remediation. The analysis showed that, the pollution concentration in the bed was always lower than 50 mg/kg, much below 2500 mg/kg imposed by the specific limit imposed by local French authorities to the company responsible

for the remediation of Erika's polluted sand before its disposal (Table 5).

### 3. Modeling and engineering of the fluidized bed furnace

#### 3.1. Modeling the polluted sand remediation in fluidized bed

A model was developed that could predict the remaining pollution in the bed at any time, with the following assumptions. All processes (volatilization and combustion of the volatiles and char) follow first order kinetics [10,11]. Oil covering the sand particles is first transformed into volatiles whilst some char remains on the sand particles. Volatiles burn in the gaseous phase and char burns on the surface of the sand particles [12]. This char layer is supposed to be very thin so that the burning solid particles have an unchanging size.

Volatiles (burnt or not) and burnt char are gaseous and are no longer in the bed, while unburnt char is still remaining on the sand particles. The remaining pollution in the bed at any time  $t$  will thus be the mass of the unvolatilized oil and the mass of the unburnt char:

$$m_p(t) = m_{oil}(t) + m_{unburnt\_char}(t) \quad (1)$$

Assuming that volatilization and char combustion follow first order kinetics given by their respective constant ( $k_{oil}$ ) and ( $k_{char}$ ),

Table 5  
Prediction of remediation obtained with 2 reactors in series and various conditions

Reactor 1 (R1)				Reactor 2 (R2)	
Initial pollution fraction (%)	Complete combustion time (mn)	Mean residence time R1 (mn)	Pollution fraction outlet R1(%)	Mean residence time R2 (mn)	Final pollution fraction outlet R2 (%)
1	1	30	0.016	30	0.000
2	1	30	0.033	30	0.001
3	1	30	0.049	30	0.001
4	1	30	0.066	30	0.001
5	1	10	0.242	10	0.012
5	1	30	0.082	30	0.001
5	1	60	0.041	60	0.000
15	1	10	0.726	10	0.035
15	1	30	0.247	30	0.004
15	1	60	0.124	60	0.001
5	5	30	0.394	30	0.031
5	15	60	0.576	60	0.066

VMI the volatile matter index of oil for the operating conditions of the bed and  $m_{p0}$  the initial pollution fraction present in the bed, then the pollution fraction in the bed is given by

$$m_p(t) = m_{p0} e^{-k_{oil}t} + (1 - \text{VMI})m_{p0}(1 - e^{-k_{oil}t})e^{-k_{char}t} \quad (2)$$

The burnt pollution at any time  $t$  was expressed as a function of the already cited kinetic constants  $k_{oil}$ ,  $k_{char}$  as well as  $k_v$  characterizing the kinetics of volatile matter combustion. All three constants were then determined by fitting with batch experiments at respective temperature. Residence time distribution was then taken into account in order to calculate the mass of the remaining pollution in the bed at any time  $t$  in a continuous process. The fluidized bed reactor was considered as a perfectly mixed reactor [13], so that the steady state bed pollution fraction in the bed is given by

$$m_{\text{average-p}}(t) = \int_0^\tau m_{p0}(e^{-k_{oil}t} + (1 - \text{VMI})(1 - e^{-k_{oil}t})e^{-k_{char}t}) \times \frac{1}{t_m} e^{-(t/t_m)} dt \quad (3)$$

where  $\tau$  is the complete combustion time and  $t_m$  the mean residence time.

Calculations showed that, for an initial pollution of 50,000 mg/kg (as in the case of Erika accident), remediation to 2500 mg/kg requires a residence time of nearly 6 min at any temperature between 600 °C and 850 °C [9]. If a remediation level of 500 mg/kg is to be reached, the residence time needed becomes 20 min.

The above-mentioned model allows to calculate the bed pollution content in steady state conditions knowing several empirical parameters characterizing the pollution combustion [14]. Alternatively, a simpler model might consider that the oil transformation as gaseous products is similar to particle drying where particle size does not change [13]. If the oil fraction on the sand particles fed into the furnace is  $Q_i$  and their complete remediation time equal to  $\tau$ , then, the remaining pollution at any time  $t$  (for the time interval  $t$  between 0 and  $\tau$ ) can be given by

$$\frac{Q(t)}{Q_i} = 1 - \frac{t}{\tau} \quad (4)$$

Assuming that the fluidized bed is perfectly mixed and a mean particle residence time  $t_m$ , the average fraction of pollution  $Q_{\text{average}}$  of the bed inventory is given by

$$Q_{\text{average}} = \int_0^\infty Q(t) \frac{1}{t_m} e^{-(t/t_m)} dt \quad (5)$$

Accounting that the function  $Q(t)$  is equal to 0 for time values above  $\tau$ , the average pollution in the bed at steady state conditions is

$$Q_{\text{average}} = Q_i \left( 1 - \frac{1 - e^{-(\tau/t_m)}}{\tau/t_m} \right) \quad (6)$$

If the complete remediation time is considered to be 1 min (twice the measured time) and the mean residence time equal

to 30 min, then the average pollution in the bed and thus the remediation quality of the withdrawn sand from the reactor is only 2% of the initial pollution of the sand. For an initial pollution of 5%, the sand exiting the furnace will have a remaining oil content of 0.1% [14].

The addition of a second reactor, fed by the solids overflow from the first bed, gives a significant improvement on the remediation level attained. It is possible to achieve a remaining pollution of only a few mg/kg in comparison with the legal requirements (2500 mg/kg cited above). Except in a very few cases, the remaining pollution in the bed is lower than the critical values of fluidizability measured in the cold model which means that the bed remains fluidized. In the very few other cases, the residence time would have to be increased by reducing the inflow of oil-polluted sands or by increasing the fluidized bed inventory until the average pollution fraction in the bed becomes smaller than the critical value to avoid defluidization.

### 3.2. Design details and auxiliary fuel requirement

Design and calculations of a fluidized bed furnace was then carried out in accordance with the French regulations for “incineration or co-incineration of dangerous wastes” dated 20 September 2002 [14].

If the sand to be treated in that plant is similar to the waste from the Erika oil spill, the temperature requirement of 850 °C for the furnace imposes energy addition that is supposed to be natural gas (mainly methane). In this case, the GEFIN model based on the work of Pre et al. [15] predicts that a natural gas addition of 500 kWh will be necessary to maintain 850 °C in the bed, instead of 731 °C that would have been the temperature achieved without any energy addition. Fig. 6 shows the predicted addition of auxiliary fuel and combustion product temperature as a function of the oil-pollution content of the sand. It can also be seen that, when fraction of pollution is above 7%, no natural gas addition is needed and thus temperature increases if pollution increases.

The furnace size explored for the following calculations were actually derived from the existing plants devoted to municipal solid waste incineration, in view of incineration in the existing

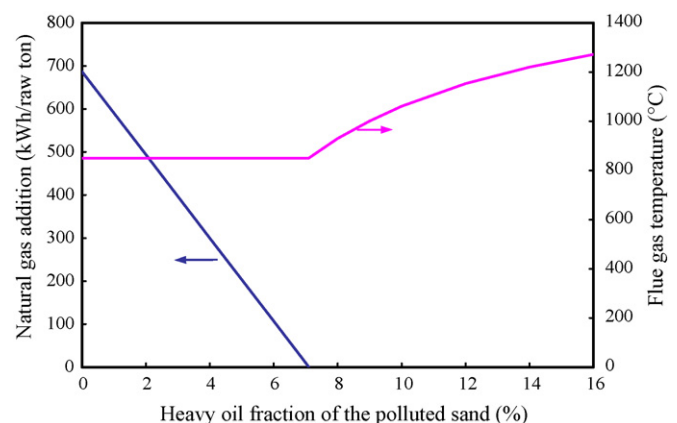


Fig. 6. Energy addition and flue gas temperature prediction vs. pollution fraction by GEFIN model to meet the 850 °C requirement.

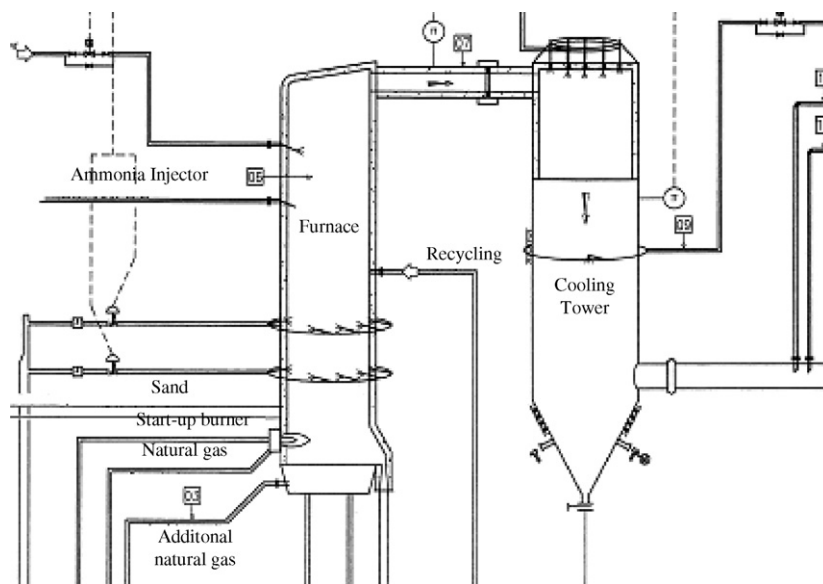


Fig. 7. Schematic drawing of the furnace and the boiler for gas cooling.

incinerators or of co-incineration of oil-polluted sands along with the municipal solid waste. As a matter of fact, RITMER had opined to avoid the building of dedicated plants for the polluted waste from black tides. For that reason, the furnace would have a bed cross-sectional area of  $6.4 \text{ m}^2$  at a fluidizing velocity of nearly  $1 \text{ m/s}$  and an entering sand flow-rate of  $5000 \text{ kg/h}$ . The sand feeding is an over-bed type, while the natural gas is to be fed into the bed itself for a better contribution of its combustion to the bed temperature elevation.

The reactor was then designed with a combustion furnace surmounted by a post-combustion chamber (Fig. 7). Its volume is given by the regulation requirements for having at least  $2 \text{ s}$  of gas residence time at a temperature of  $850^\circ\text{C}$  and accounting for the total amount of flue gas combustion. The bed height chosen was  $40 \text{ cm}$  that yields a mean residence time of more than  $40 \text{ min}$ . The remediation efficiency in this case is about  $98\%$ . The bed was then supposed to be divided in two parts to get two reactors in series with a  $20 \text{ min}$  residence time in each. In this case, the remediation efficiency would be more than  $99.9\%$  that corresponds to  $30 \text{ mg/kg}$  of residual pollution in the sand. The flue gas treatment was then designed to meet the requirements imposed by the 20 September 2002 regulation. Accounting for the sulfur content of the oil-polluted sand, about  $97\%$  desulfurization efficiency would be necessary. This would be obtained by the combination of limestone addition into the furnace and a dry process treatment of the flue gas with lime after the furnace. The abatement of oxides of nitrogen would need a SNCR process and urea injection. Dioxins and furans would be captured by activated carbon injection into the furnace itself. A bag filter would complete the flue gas treatment to separate fly ash and fine particles.

#### 4. Technical-economic analysis

Investment and production costs of the fluidized bed remediation of oil polluted sand were then evaluated and compared to other existing processes such as thermal pyrolysis in rotating fur-

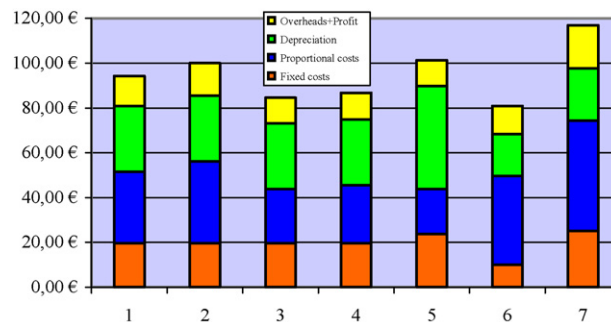


Fig. 8. Remediation cost of 1 t of oil-polluted sand vs. different processes: 1–4 in fluidized bed; 5 = physical-chemical treatment; 6 and 7 = rotating furnace; 1, 2 and 7 with a pollution fraction of  $15\%$ ; 3–6 with  $5\%$  pollution fraction. 1 and 3 flue gas treatment with limestone and lime; 2 and 4 flue gas treatment with lime only. From top to bottom: overheads + profit; depreciation; proportional costs; fixed costs.

naces and physico-chemical treatment process by washing with some fluxant and then rinsing it with water that was proposed by Brézillon and chosen by TOTAL for Erika's waste [1].

Fig. 8 presents the costs of remediation in euros for one ton of oil polluted sand. All costs are in the range of  $80\text{--}115 \text{ €}$ . However, the actual cost of option 5, i.e. the physico-chemical washing, was much more higher in the case of Erika wastes because of the presence of fine particles (smaller than  $25 \mu\text{m}$ ) dispersed by the river Loire on seashore [14]. These fine particles have considerably increased the investments and costs of water and sludge treatments. Moreover, the only possible solution to treat the cakes produced by water treatment was incineration. The cost of remediation for the  $270,000 \text{ t}$  of wastes from Erika by physico-chemical washing was slightly above  $200 \text{ €/t}$ .

#### 5. Discussion and conclusions

Presence of oil contaminants in sand changes its fluidization behaviour. There is a percentage of pollution in the bed above which the bed is not fluidizable, which varies with the type of



pollutants in the bed and the type of sand in use. While heavy oil pollution was critical for the coarse sand, the light oil pollution was critical for the fine sand. Presence of water worsened the scenario in all the cases.

Hot model studies in fluidized beds, using different sand particles and oil pollutants, clearly indicated the technical feasibility of de-polluting oil contaminated sand in a fluidized bed combustor. The emissions through the flue gas were found to be well within the regulatory limits. Remaining concentration of pollutant in the bed after depollution was negligible. Sticking, agglomeration, ash fusion involving defluidization and accretion to the reactor walls were not noticed during the hot tests. Ignition temperature of the oil waste was found to be about 700 °C, whilst the maintaining of a combustion temperature at the minimum requirement 850 °C imposes auxiliary fuel and that can be natural gas.

Incineration of oil-polluted sands has been proven to be economically feasible with an estimated expenditure of 80 €/t. This can be further reduced by its co-combustion with municipal solid waste. The fluidized bed incineration route of depollution is relatively fool proof, complete and environment friendly. This might be considered as a technically feasible and economically viable depollution route for dealing with the seashores polluted in oil spills.

### Acknowledgment

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