CHEMICAL ENGINEERING TRANSACTIONS

VOL. 90, 2022

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Aleš Bernatík, Bruno Fabiano
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ISBN 978-88-95608-88-4; **ISSN** 2283-9216

DOI: 10.3303/CET2290013

Ignition and Self-heating Risk Assessment of Hydrocarbon Polluted Soils

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Polluted soils not only pose environmental problems, but can also have an impact on site remediation workers due to pollutant toxicity and flammability. Soil samples were extracted from a polluted site and tests were performed in order to determine their minimum ignition temperature (MIT) in cloud and their self-heating behavior. Their water and volatile contents were also determined. Moreover, soil samples were depolluted by thermal treatment (24 h at 400 °C), sieved and mixed with diesel or eicosane at different concentrations, ranging from 2 to 30 wt%. The influence of the mixing procedure was examined, as well as the effects of the particle size distribution and the pollutant content on the MIT in cloud and thermal stability.

It appears that the contaminated soil is prone to self-heating and critical temperatures ranging from 215 to 285 °C were obtained for 8000 to 125 cm^3 baskets, respectively. Pre-heating to 100 °C for 24 h leads to a slight decrease critical temperatures, e.g. 265 °C for 125 cm^3. The thermal conductivity of the powders was measured and the Frank-Kamenetskii model was used to extrapolate their self-heating behavior to larger storages. While their thermal stability is questionable, the likelihood of a dust explosion remains low, as their MIT was above 900 °C. However, by adding hydrocarbons to the depolluted sample, the MIT decreases upon introduction of 5 wt% pollutant and reaches 490 °C for 25 wt%. eicosane. The nature of the mixing process appears to have little impact on the ignition sensitivity of the samples. In contrast, the particle size distribution has a significant impact on the self-ignition temperatures of the soils. Such quantitative assessment should improve the process safety practices related to the operations of soil excavation, transportation, storage and thermal treatment operations. In addition, a better knowledge of the self-heating behavior of such soils may be useful in view of smoldering remediation.

1. Introduction

Human and industrial activities can lead to the release and introduction of harmful substances into soils. Considering only the EU Member States, an average of 3.6 sites with soil polluting activities have been identified per km^2. In France, the 'BASOL' database lists nearly 10,000 polluted or potentially polluted sites. The nature of soil contamination obviously depends on industrial activity, but hydrocarbons are one of the most common pollutants. For instance in France, hydrocarbons represent nearly 60% of the pollutants found in a soil, including 14% for chlorinated hydrocarbons and the same proportion for Polycyclic Aromatic Hydrocarbons (PAHs) (MEST, 2019).

Site remediation can be performed either in-situ (without removing the media, e.g. by bio or phytoremediation, for instance) or ex-situ (when removing the soil for off-site treatments) which involves the transportation and storage of large volumes of contaminated soil (van Hullebusch et al., 2020). Various remediation technologies can be used, from chemical fixation to physicochemical methods, such as thermal treatment (van Hullebusch et al., 2020). The risks associated with these techniques are mainly related to the toxicity and ecotoxicity of the pollutants or chemicals used to treat the soil (e.g., hydrogen peroxide, EDTA). However, fire and explosion risks should also be considered. Indeed, the presence of flammable hydrocarbons implies to consider such risks at different stages of the treatment: for instance, i) during the excavation of the soil, dusts containing

Paper Received: 19 December 2021; Revised: 18 March 2022; Accepted: 26 April 2022
Please cite this article as: Dufaud O., Janès A., Henrion J., Sigot L., Laubie B., Simonnot M.-O., 2022, Ignition and Self-heating Risk Assessment of Hydrocarbon Polluted Soils, Chemical Engineering Transactions, 90, 73-78 DOI:10.3303/CET2290013

hydrocarbons can be dispersed and form dense clouds, ii) during their transportation, iii) when stored before treatment, iv) on conveyor belts or vibrating grids, or v) during the thermal treatment itself (e.g. in rotative furnaces). If, beyond the legal requirements for the protection of employees, securing such sites and processes appears essential, none or very few studies have been performed on this subject.

This study focuses on the thermal stability of soil storages and on the minimum ignition temperature of dust clouds generated by the handling of polluted soil. In order to study the influence of the particle size distribution and pollutant content on the former safety parameters, depolluted soils were mixed with hydrocarbons and their ignition sensitivity was compared to that of soils extracted from a contaminated industrial site.

2. Description of the samples and methods

Soil samples were prepared to fit the criteria for standardized analyses.

2.1 Soils samples

Soil samples were extracted from a polluted site, a former coking plant located in the 'Grand-Est' region (France), now occupied by an experimental platform for the study of polluted site remediation (GISFI). They were sieved to 5 mm to remove centimeter-sized rocks, incompatible with standardized experiments (Figure 1a). The remaining soil (Figure 1b) was either tested as is, or was depolluted by thermal treatment at 400 °C for 24 h (Figure 1c).

The depolluted soil was then mixed with diesel or eicosane ($C_{20}H_{42}$), a surrogate for heavy hydrocarbons, at different concentrations, ranging from 2 to 30 wt%. Eicosane was chosen as it is solid at room temperature (melting point: 36-38 °C) and can be added to the samples either as a powder, or as a liquid after heating. Mixing was performed using a chaotic stirrer (Turbula) to ensure homogeneity of the mixtures. In the standardized tests aiming at determining the minimum ignition temperature (MIT), the depolluted soil was sieved to 500 µm and the mixing process was carried out before testing. The particle size distributions were analyzed by laser diffraction (Helos/Vario - Sympatec GmbH).

Figure 1: a) Non-passing fraction of the 5 mm sieve, b) sieved hydrocarbons polluted soil, c) depolluted soil

2.2 Thermal stability

The self-heating behavior of the soil samples was characterized by combining tests in a Grewer oven (2 $K.min^{-1}$ with a maximum temperature of 400 °C) and in isothermal baskets according to EN 15188 standard (ECS, 2020). Their water and volatile contents were also determined. The effect of a pre-heating treatment on the soil thermal stability was also studied.

Isothermal basket tests were performed to determine the critical ignition temperatures for a series of four basket sizes, ranging from 15.6, 125, 1000 and 2744 cm^3. As requested by EN 15188 standard, a thermocouple was placed at the center of the sample. Two additional thermocouples were placed in the soil sample, at its surface and at one-third of the height, to better identify the location of self-heating. Ignition criteria were met if the soil temperature exceeded the oven temperature by 60 K during the test (24 h) or if an inflection point was observed over the oven temperature. Tests were repeated by lowering the oven temperature until no ignition occurred.

The self-heating behavior of the samples was modeled by the Frank-Kamenetskii theory (Bowes, 1984). The Frank-Kamenetskii dimensionless parameter δ_c was set at 2.569. By representing $\ln\left(\frac{T_A^2\delta_c}{r^2}\right)$ as a function of $1/T_A$ for the four basket sizes r (half-length of the cube, m), the activation energy E_a ($J.mol^{-1}$) of the combustion reaction of the pollutants can be estimated. Being a key parameter for thermal stability, the thermal conductivity λ was determined using a CTi thermal conductivity analyser (CTherm) at 0.12 and 0.10 $W.m^{-1}.K^{-1}$ for 5 mm and 500 µm soil samples, respectively.

2.3 Minimum ignition temperature

Tests were performed to determine the minimum ignition temperature (MIT) of the soil samples, using a Godbert-Greenwald furnace and according to ISO/IEC 80079-20-2 standard (ISO, 2016). Ignition criterion was met when a flame was observed. Both the sample weight and the powder injection pressure were varied to determine the MIT for a given pollutant concentration.

3. Results and discussion

3.1 Thermal stability of polluted soil from an industrial site

More than 30 self-heating tests were performed on the polluted soils. For the smallest basket (15.6 cm^3), no ignition was observed, even at 400°C i.e. the maximum temperature of the furnace. Figure 2 shows an example of a self-heating test performed on the largest volume available (8000 cm^3). At around 80 °C, the sample temperature levels off and reaches a plateau (energy sink). Exhaust gas samples were collected and analysed by gas chromatography: no light hydrocarbons were observed. This step can be considered as the drying of the sample. Self-heating was first visible at one-third of the basket before reaching its center. This behaviour is typical of oxygen diffusion limitation: from a thermal point of view, the likelihood of a self-heating is greater at the center of the sample; however, the oxygen content is rapidly limited and self-heating occurs closer to the surface. This phenomenon obviously depends on the storage porosity.

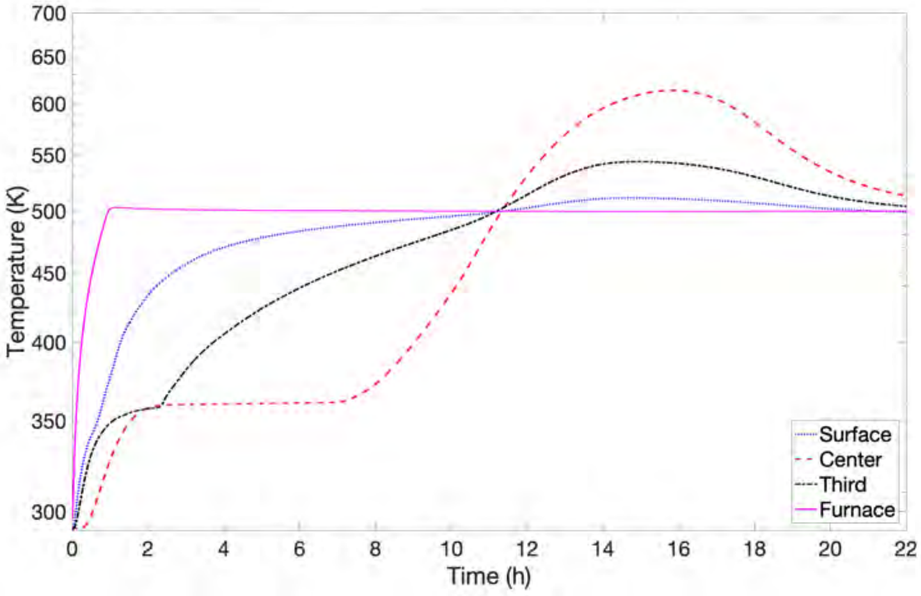

Figure 2: Example of a self-heating test on a soil polluted by hydrocarbons in a 8000 cm^3 basket at 230 °C

A similar thermal behaviour of the polluted soils was observed by performing tests with a Grewer oven. Endothermic peaks were recorded at around 100 °C, confirming the water evaporation process. Then, exothermic reactions were observed at about 423 and 498 K (150 and 225 °C), for soil samples sieved to 5 and 2 mm, respectively. The latter result raises the question of dependence of the pollutant content on the particle size distribution of the soil. In order to obtain comparable results, the self-heating tests were therefore carried out with powders sieved to 5 mm. It should also be kept in mind that the soil porosity can influence the internal thermal transfers and heat accumulation.

Table 1 sums up the results obtained for the self-heating tests. As expected, the critical temperature at which the self-ignition is observed decreased as the storage volume increased. Therefore, one of the most effective and obvious methods to prevent self-heating of soil storage is to limit their size. In order to highlight the influence of their water content on their thermal stability, the soil samples were subjected to a thermal pre-treatment at 100 °C for 24 h. In addition to drying, such treatment can modify the pollutant chemical availability in the soil, notably by improving its desorption. Table 1 shows that, for a given storage size, the critical temperatures were slightly lower when a pre-treatment was applied to the polluted soil. Even if the critical temperature is relatively high (628 K – 355 °C), self-ignition of a storage as small as 15.6 cm^3 is then possible. The maximum temperatures of 750 K (477 °C) were reached at the samples center during the tests.

Table 1: Results of self-heating tests carried out on hydrocarbon-polluted soils with/without pre-treatment

Basket volume (cm^3)	15.6	125	1000	8000
Critical temperature (K) - as is	-	558	508	488
Critical temperature (K) - pre-treated	628	538	498	468

Figure 3 shows the influence of thermal pre-treatment on the thermal stability of polluted soils. It confirms that hydrocarbon-polluted soils are more prone to self-heating after preheating. For instance, the critical temperature is lower than 100 °C for storage dimensions of 1 meter (half cube length) after pre-heating, whereas it reaches 130 °C for polluted soil. It should be noted that the sample water content was determined by weighting the sample before and after drying at 100 °C for 24 h. An average mass loss of 17% was observed based on 5 tests. After thermal treatment at 400 °C, the overall mass loss (with regard to the polluted soil) reached 25%, which means that about 8 wt%. of the sample was combustible contents, i.e. the pollutants. Similar mass losses were recorded with the Grewer oven.

These results are notably very promising in the context of smoldering remediation, a depollution technique based on flameless combustion of a polluted porous medium (Pironi et al., 2011). Indeed, after preheating to 100 °C, large stockpiles of polluted soils can be treated by the phenomenon of self-ignition at relatively low temperatures, i.e. with less energy consumption than with the conventional processes.

From the point of view of process safety, self-ignition risk remains acceptable near room temperature (even for temperatures up to 40 °C), as the dimensions of an aerated static pile must exceed 5 m to generate such phenomenon.

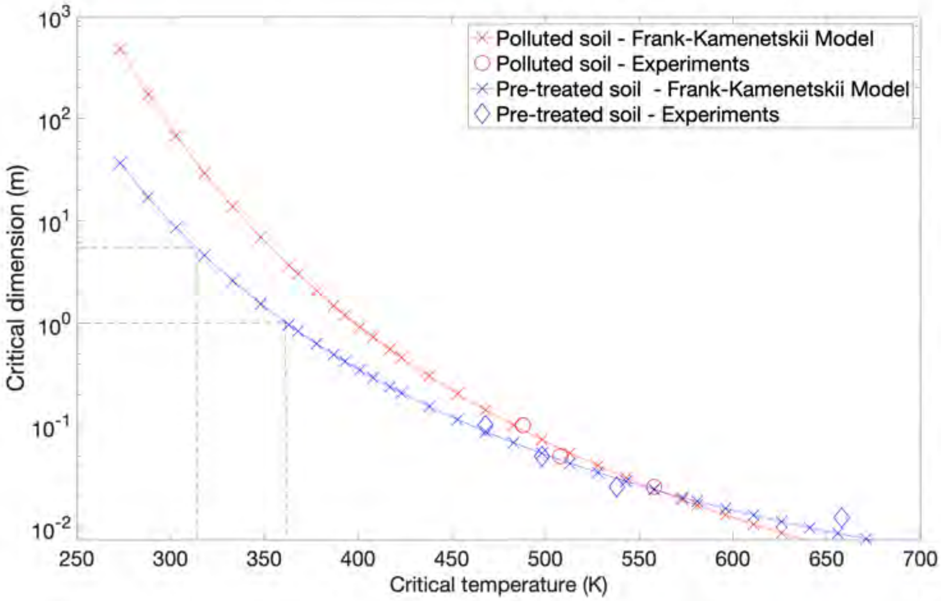

Figure 3: Comparison of the thermal stability of hydrocarbon polluted soils with/without thermal pre-treatment

3.2 Thermal stability of polluted soils: influence of the nature of the pollutant

As the chemical nature of the original pollutant was unknown, additional tests were performed. After thermal treatment and depollution at 400 °C, soil samples were homogeneously mixed with 10 wt%. diesel using a chaotic stirrer. This percentage was chosen as recent studies have shown that for classical contaminated soils with 0 to 20 wt%. diesel contents, a maximum value of 12.6 wt%. of hydrocarbons was retained (Hernández-Mendoza et al., 2021). Self-heating tests were performed with three different basket sizes.

The results are presented in Table 2. It appears that self-ignition occurs at relatively high temperatures, namely 583 and 523 K for 125 and 1000 cm^3 baskets, respectively. Moreover, no ignition was obtained for the smaller volume. One reason for this may be the rapid vaporization of diesel at temperatures above its boiling point (between 423 and 623 K as a function of the diesel type). The self-heating behavior of diesel-polluted soils was compared to that of organic soils (a mixture of peat and sand – 14 wt%. organic content OC) (Restuccia et al., 2017) and bituminous coal (García-Torrent et al., 2012) in Table 2. These results show that, while self-heating of diesel-polluted soils cannot be neglected and that precautions should be taken when storing them, its probability is still lower than that related to the self-ignition of peat, coal or the polluted soil of a former coking plant (Table 1).

Table 2: Results of self-heating tests carried out on diesel-polluted soils (10 wt%. diesel). Comparison with organic soils (Restuccia et al., 2017) and bituminous coal (García-Torrent et al., 2012)

Baskets volume (cm^3)	15.6	125	1000
Self-ignition temperature (K) / Diesel pol. soils	> 673	583	523
Self-ignition temperature (K) / Peat - 14% OC	-	470	452
Self-ignition temperature (K) / Bituminous coal	413	393	383

3.3 Ignition sensitivity of hydrocarbon polluted soils

During their extraction, transport, chemical or thermal treatment and more generally during their handling, polluted soil can be re-suspended and generate clouds, some of whose constituents may be combustible. Obviously, the temperature of the atmosphere during the dust dispersion will play an important role in the desorption of the pollutants and/or their vaporization. In order to assess the ignition risks associated with these potentially explosive atmospheres, the minimum ignition temperature in cloud of polluted soil was determined.
Tests carried out on polluted soil extracted from a former coking plant were all negative, i.e. no ignition was observed at temperatures of 900 °C or lower. Even after preheating at 100 °C for 24 h, the MIT of the samples remained above 900 °C. Therefore, the likelihood of a dust or hybrid mixture explosion during the remediation of such soil can be considered low.

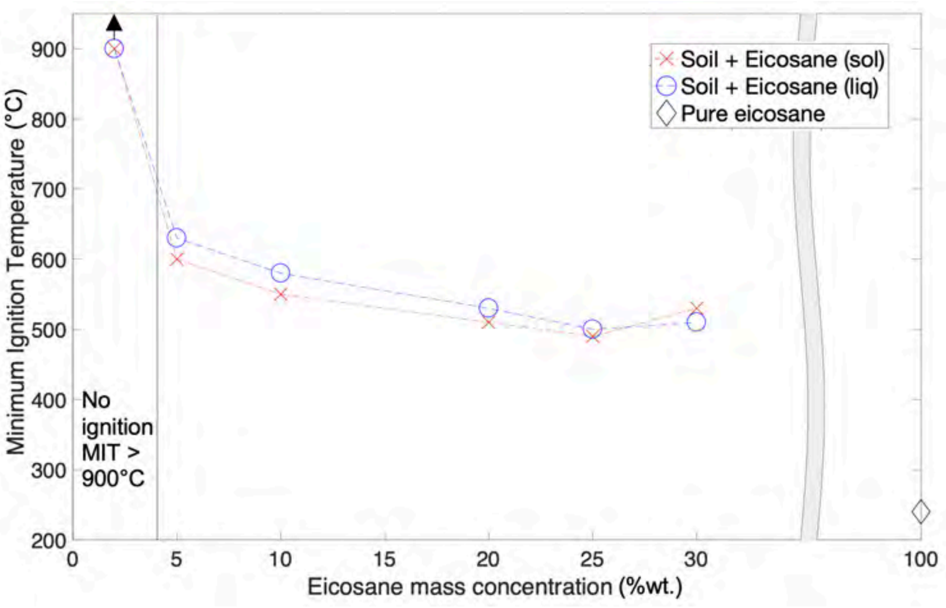

Figure 4: Evolution of the minimum ignition temperature in cloud of soil/eicosane mixtures as a function of their concentration and preparation mode

Further tests were performed on mixtures of depolluted soils and eicosane at fuel concentrations ranging from 2 to 30 wt%. Eicosane was added either in solid form after grinding, or in liquid form after heating. The results in Figure 4 show that the introduction mode has little influence on the MIT in cloud of mixtures. On the contrary, the fuel concentration plays a significant role on the soil ignition sensitivity. Indeed, for fuel concentrations lower than 5 wt%, no ignition was observed, but for concentrations ranging from 5 to 30 wt%, the MIT in cloud was lower than 650 °C, with a minimum value reached at 490 °C for 25 wt% eicosane. It should be underlined that these MITs are much greater than that of pure eicosane, i.e. 240 °C. A similar trend was observed for diesel polluted-soil (Figure 5). The minimum fuel percentage leading to an ignition was 2 wt%, which was lower than for eicosane, but was consistent with the higher volatility of the hydrocarbon. The minimum MIT value, 550 °C, is reached for 10 wt% diesel. Unlike the polluted soil extracted from a former coking plant, these mixtures are flammable when dispersed in air and the explosion risk related to their handling must be thoroughly assessed.

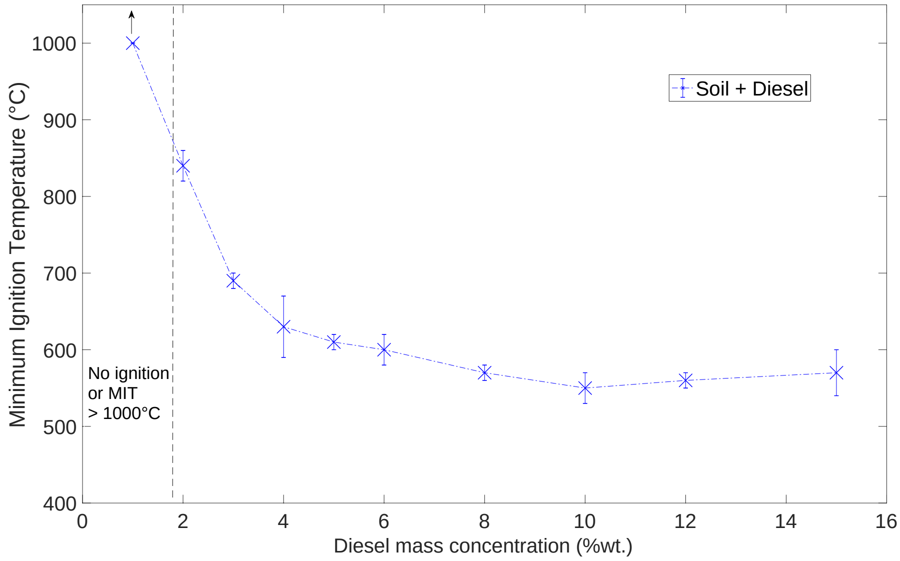

Figure 5: Evolution of the minimum ignition temperature in cloud of soil/diesel mixtures as a function of the diesel concentration

4. Conclusions

The risks of Ignition and self-heating of soils contaminated by hydrocarbons (diesel, gasoline, etc.) must not be overlooked. Adapted prevention measures must be considered, such as avoiding the accumulation of large deposits, reducing the storage duration, controlling the temperature of the pile or avoiding the soil dispersion during its excavation, transport and thermal treatment. In addition, it appears that a better knowledge of the self-heating behaviour of such soils can be useful in view of smoldering remediation.

Nomenclature

r – half-length of the basket, m
T_A – storage temperature, K
λ – thermal conductivity, W/(m.K)
δ_c – critical F-K parameter, -

Acknowledgments

This work was financially supported financially by the French Ministry for Solidarity and Health and the French Ministry of Higher Education, Scientific Research and Innovation. The authors would also like to thank the GISFI (Experimental Platform on Industrial Brownfield Redevelopment) for providing the soil samples.

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