PRESENT ENVIRONMENT AND SUSTAINABLE DEVELOPMENT, VOL. 7, no. 1, 2013

EVALUATION OF THE NON-OXIDATIVE THERMAL TECHNOLOGY FOR REMOVAL OF PETROLEUM PRODUCTS FROM CONTAMINATED SOILS

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Key words: pyrolysis, soil, total petroleum hydrocarbons, efficiency

Abstract. The present paper illustrates results obtained at laboratory scale in order to assess the efficiency of the non-oxidative technologies used to decontaminate polluted soils. The experiments were carried out using a laboratory device: a calcinations oven, electrically heated, that operates in a discontinuous way. The soil samples used for the present research were collected from a real area contaminated with petroleum hydrocarbons. Experimental campaigns were conducted at different pyrolysis temperatures (350°C, 500°C, 650°C and 800°C) and focused on two main aspects: the influence of the process temperature on the decontamination efficiency and volatile quantity generated during pyrolysis treatment. The results of the experiments have shown that the process parameters have an important influence on the remediation of total petroleum hydrocarbons (TPHs) from contaminated soil. The efficiency of the pyrolysis treatment has significantly increased while process temperature has risen. It was observed the same order of magnitude on removing TPHs from soil when the pyrolysis time has been increased.

Introduction

One accepted definition for the pollution is introduction of elements, compounds or energy into environment at levels that impair its functioning or that present an unacceptable risk to humans or other targets that use or are linked to that environment. There is a wide range of soil contamination: rupture of underground storage links, application of pesticides, and percolation of contaminated surface water to subsurface strata, oil and fuel dumping, leaching of wastes from landfills or direct discharge of industrial wastes to the soil. The most common chemicals involved are petroleum hydrocarbons, solvents, pesticides, lead and other heavy metals. Oil spills due to accidents or careless oil handlings are frequently TPHs (Total Petroleum Hydrocarbons) polluting factors for soils. People can be affected

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by contaminated soils through dermal contact, ingestion, food consumption or inhalation of dusts or vapours (Merino and Bucalá, 2007).

The European Environmental Agency has estimated approximately 250.000 sites that require to be clean up and that more than 80.000 sites have been cleaned up during the last 30 years in EU countries. It is also expected that number of sites needing remediation will increase by 50% by 2025 (EEA, 2007). Many industrial sites and oil refineries contain soils contaminated with petroleum hydrocarbons, soils considered as hazardous wastes if the concentration of those pollutants is significantly (Code of Federal Regulations).

Over the past decade, concerning the remediation of sites polluted with hydrocarbons, the thermal decontamination technologies have become a topic of high interest (Nathanail and Earl, 2001). These have been extensively used for the treatment of soil, sludge and sediment containing different kinds of pollutants. In order to understand the fundamentals of contaminant release from soils several independent analyses have been performed (Lighty et al., 1988, 1989, 1990; Tognotti et al., 1991; Maguire et al., 1995; Cabbar et al., 1994; Gilot et al., 1997; Bucalá et al., 1994; Larsen et al., 1994; Risoul et al., 2002) and different laboratory and pilot-scale equipments have been used. To establish an optimal technology for decontamination of the polluted soil it is needed to adopt a systematically and organized approach in order to obtain optimal results. The objective of the present laboratory research was to study the influence of the thermal treatment operational conditions on remediation efficiency in case of a soil polluted with petroleum products.

1.Materials and methods

For the present work, soil from Central Romania was the subject of the experimental study. This area was historically polluted due to human activities related to the petroleum processing. The samples were collected from 9 points of the surface area, at equal distances one from each other. The excavation depth was 20 cm and 40 cm, respectively. The collected soil was mixed and after, soil samples were extracted for chemical analyses and experiments. In order to work with a uniform mass, the soil was size-fractionated by a cutting mill. The elemental composition of the contaminated soil, presented in table 1, showed 13.36% of organic carbon, that which is believed to decompose to light gases during thermal treatment (US EPA, 1989, Saito et al., 1998). Other properties of the contaminated soil are included also in the next table.

In order to identify the TPHs content in soil, the extraction procedure was used following the rules of the Romanian standard (SR 13511, 2007). The extraction method was carried out using two kinds of laboratory equipments:

Soxhlet and rotary evaporator. The solvent used for analysis was dichloromethane for GC residue analysis, stabilized with ethanol, with 99.8% purity.

Tab. 1: Properties of the contaminated soil

Contaminated soil properties	Value	Unit
Humus amount	39.2	[%]
C_{org}	13.36	[%]
Density	1.5	[g/cm3]
Umidity	16	[%]
TPH	71 000	[$mg/kg_{dry\ soil}$]

2. Thermal Facility

The pyrolysis experiments were performed in a calcinations oven. Its principle scheme is presented in fig. 1. The contaminated soil feeding of the equipment was manually carried. Every sample of contaminated soil has been placed in the oven without a previous treatment. The temperature range of the experiments was between 350ºC and 800ºC.

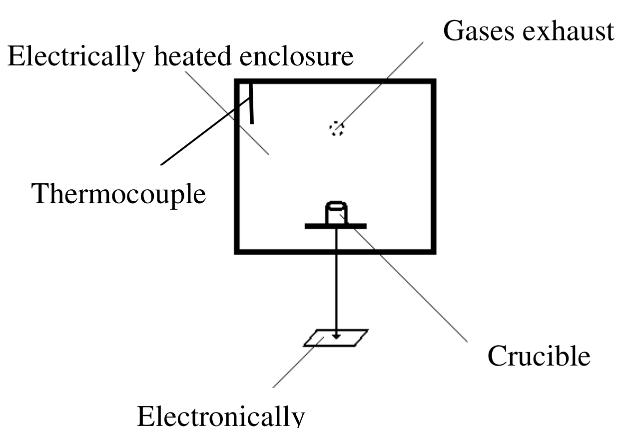

Fig.1: Principle scheme of the calcinations oven

For all thermal treatment experiments, the mass of the polluted soil was maintained in furnace for two retention times: 15 and 30 minutes.

A thermo-gravimetrical analysis was done using high precisions electronically balance. Monitoring the weight loss according to the temperature and the retention time followed the devolatilization process.

3.Results and discussions

Results of the experimental study revealed that the process parameter as temperature has an important influence on volatile compounds and also on TPHs concentration remained in solid residue after the decontamination process. Fig. 2 presents the variation of two pyro-products (solid residue – ash and volatile matter) as a function of the pyrolysis temperature. If the process temperature is rising, the ash quantity is decreasing, while the volatile matter quantity is rising, too. For a range of 350°C to 800°C, the ash mass have decreased from 81.43% in case of pyrolysis at 350°C to 73.59% for thermal treatment at 800°C. Alternately, if the pyrolysis temperature is rising from 350°C to 800°C, the volatile compounds mass has increased with 7.84%. Basic thermodynamic principle of the temperature effect indicates that high temperature would determine high rate of degradation, because the temperature will generate more energy necessary to break bonds from the hydrocarbons molecules (Saito et al., 1998).

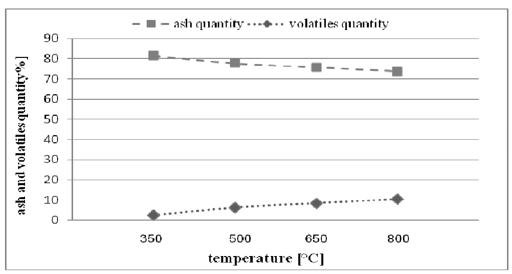

Fig. 2: Ash and volatile matter quantity as a function of pyrolysis temperature

Fig. 3 illustrates that high weight losses were obtained with increasing the process temperature. This is a consequence of the hydrocarbons volatilization from

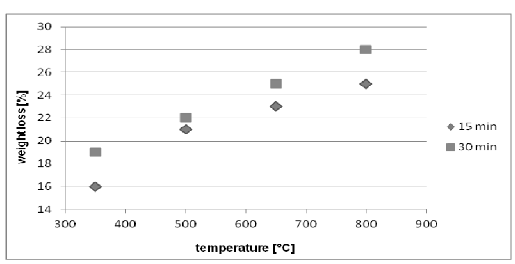

Fig. 3: Effect of the residence time on weight losses produced during pyrolysis treatments

the polluted soil during the non-oxidative thermal treatment. The final effect is the reduction of the TPHs concentration from the soil decontaminated by pyrolysis. This tendency was also demonstrated by another experimental research applied to the same contaminated soil, when the PAHs concentration from the pyrolysis ashes was evaluated (Bulmău et al., 2012). Both curves followed the same trend increasing with the process temperature and with the retention time. These important amounts of weight losses are obtained even for a short period of time of the non-oxidative thermal degradation. All pyrolysis process temperatures had produced low weight losses that oscillate between 1% and 3%, demonstrating that, it is not necessary to treat the contaminated soil for a long time in order to reduce TPHs from soils.

Figure 4 shows that the pyrolysis efficiency is increasing as the process temperature is rising. The experimental results demonstrated an increasing of decontamination level with 7% in case of non-oxidant thermal treatment at 500°C and with 1% to 2% for the rest of pyrolysis process temperatures (at 350°C, 650°C and 800°C, respectively).

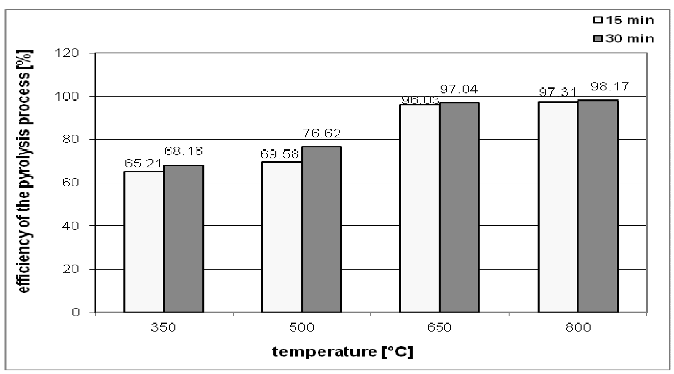

Fig. 4: Pyrolysis treatment efficiency function of the process temperature and retention time

Conclusions

The experimental results of the present study have demonstrated that process parameters have an important influence on removal of TPHs from the contaminated soil. The efficiency of the pyrolysis treatment increased more with the process temperature and less with the retention time.

Results obtained from the present experimental campaigns have shown that soil decontamination by pyrolysis treatments can exceed an efficiency of 98%, in case of 800°C pyrolysis temperature. Consequently, it was observed that the pyrolysis treatment represents a good technique for decontamination of soils polluted with TPHs.

Another important aspect is that increasing process temperature up to 650°C does not give reason for the energy consumption; efficiency increases only with approximately 1%. Using this method for polluted soil remediation an important decision it must to be taken: the range of the process temperature must be reduced correlating always with the process efficiency; that could be ensured at an important level even for low temperatures. In the future economical studies and interpretations concerning this topic will be done.

Acknowledgments

This work was partially supported under the Sectorial Operational Programme "Increase of Economic Competitiveness" POSCCE-A2-O2.1.2.-2009-2, RECOLAND ID519, SMIS-CSNR:11982, Nb. 182/18.06.2010 (2010-2013) and by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Romanian Ministry of Labour, Family and Social Protection through the Financial Agreement POSDRU/89/1.5/S/62557.

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