TREATING PETROLEUM CONTAMINATED SOIL AND SLUDGES USING PLASMA

R.N. Szente*, L. B. Souza, H. Pasquini
TSL Environmental Corporation
411 Funchal, 7th Floor, São Paulo – S.P. - Brazil
* corresponding author
Email: roberto@tslambiental.com.br; Fax: (55) 11 30497401; Phone (55) 11 91584935

Abstract

Traditional processes, such as incineration, cement kiln processing, centrifuging and others, used for treating soil contaminated with petroleum, oil, diesel, etc and or for treating oily sludges (generated from the exploration, production and refining of petroleum), present several environmental, technical and economical restrictions. A new process, based on the use of a plasma system, was developed for treating those materials, including petroleum contaminated soil and oily sludges. The process is based on the use of a plasma system, to transfer energy to the material being treated. The contaminated material is heated in a controlled ambient, without the presence of oxygen, up to 1,200 ^{0}C, using a plasma torch operating at temperatures around 15,000^{0}C. The organic compounds volatilize under those conditions and leave the reactor; the vapors are cooled in condensers, recovering the organic compounds in the form of a light oil. The oil can be readily reused. The soil after the treatment presents less than 0.01% in weight of hydrocarbons (legal limit for discarding it is 1%); similar results were obtained when treating sludges containing up to 90 % hydrocarbons. Nil or almost nil off gases are generated in process. A demonstration unit was built (200 kg/h capacity) and industrial units are being designed and constructed for treating up to 5,000 kg/h of those materials.

I. Introduction

Soils contaminated with petroleum or different types of oils, caused normally by accidental spills or during normal maintenance of oil transportation pipes, are commonly found materials, specially in areas located inside or close to petrochemical or refinery plants. It is common to find soil contaminated with more than 25 % in weight of petroleum or oil. The spilled petroleum or oils may cause serious treat to the environment, endangering different vegetal and animal species, including human beings. In the same category, it can be included soils, sludges and similar materials contaminated with other organic compounds, such as pesticides and insecticides. In this case the amount of contamination could vary from tens of ppm (parts per million) to few percents. In all contamination cases mentioned above there is a considerable risk to the environment if the toxic or hazardous organic compounds are not removed from the soil or sludge and then properly treated.

There are several possible manners to treat contaminated soils containing organic compounds. The most commonly used processes include incineration, the use of centrifuges and bioremediation. However, those processes present considerable drawbacks as shown below.

a) Incineration

In the incineration process, the contaminated soil is normally fed into a rotating furnace that contains proper lining. Gas or oil burners are used to maintain the temperature inside the furnace in the range of 500 to 1,000 ^{0}C; air is allowed inside the furnace. The combination of the oxygen from the air and the temperature inside the furnace result in the partial or complete combustion of the contaminating organic compounds. The result of the process is material that in principle would be free of organic toxic or hazardous compounds. The process is conducted in dedicated incineration units or in cement kilns.

The problems associated with the incineration process are the following:

i) Large volume of effluent gases that need to be properly treated (the effluent gases are the summation of entrained air for the process, the gases resulted from the combustion of the organic toxic compounds, the gases from the burners and water vapor), since the gases can contain toxic compounds; although dedicated incineration units present off gases cleaning systems, the same is not the case of cement kilns (normally only a removal of entrained particulate material is conducted), which increases the problem.

ii) Poor energy efficiency, since a great deal of the energy resulted from the oil/gas burners leave the furnace with the off gases, with typical energy efficiencies of less than 30 % for the overall process;

iii) No recovery of the initial organic materials is possible, since the organic compounds are burnt in the furnace; in the case of oil or petroleum contaminated soil, for instance, it could represent a significant loss of raw materials;

iv) Large costs and environmental risks associated with the transportation of the material to dedicated incineration plants (the contaminated soil needs to be properly placed inside drums or other vessels in order to be carried to the incineration site);

b) Centrifuges

The use of centrifuges to treat contaminated soil or sludges is also a common practice. In this process the contaminated material, containing variable amounts of organic toxic or hazardous compounds and eventually water, is fed into a centrifuge. In the centrifuge vessel, due to centrifuge forces resulted from the rotation at high speeds, the liquid organic compounds contaminating the soil or sludges and eventual water are separated from the solid materials, using different types of screens. The result of the process would be in principle material (soil or sludge) free of liquid organic contaminants and water, making it possible the recovery of such organic liquids in a separate vessel.

The main problems associated with that process are:

i) The impossibility of complete removal of the organic compounds; the soil or sludge after the treatment with centrifuges still contains typically more than 5 % in weight of organic contaminants (the legal limit for discarding hydrocarbon containing material is less than 1 %);
ii) Constant maintenance of the centrifuges required;
iii) Chemical agents need to be added to the charge regularly in order to improve the separation of the oil and the other components; this increase the costs of the process and the treatment of the recovered materials.

c) Steam extraction

The extraction of organic compounds from contaminated soil using steam consists in injecting saturated steam directly in the soil, resulting in a localized heating of the same, volatilizing, oxidizing and dissolving the organic compounds.

That process presents some problems:

i) Low removal efficiency, resulting in longer treatment periods;
ii) The off gases from the soil need, in principle, to be cleaned, since they may contain some organic compounds; the cleaning of the gases presents a difficult task.
iii) Some organic compounds will not be volatilized or oxidized by steam, remaining in the contaminated area.

d) Bioremediation

There are several variations of the bioremediation process, but all of them consist in the consumption of the organic compounds, present in the contaminated soil, by microorganisms or bacteria, resulting carbon dioxide and water vapor from the process.

Bioremediation presents some restrictions:

i) Can be used in cases where the contamination of the soil is not above 1 %;
ii) The soil can not present harmful compounds to the microorganisms (such as heavy metals);

iii) Normally only few types of organic compounds can be consumed by the microorganisms; in the cases of several organic compounds exist, some of them will not be eliminated by the process.

As shown above, all the existing processes for treating contaminated soil present technical and/or economical and/or environmental restrictions. A new process for treating contaminated soil (soil contaminated with petroleum, oil, gasoline, diesel, benzene, toluene, organo-chlorinated compounds, mercury, etc) or petroleum sludges was developed; the process uses a plasma system in a clean and efficient manner as shown below. The process was developed in a joint collaboration between TSL Environmental Corporation and the Technological Research Institute of São Paulo.

II. PLASMA PROCESS

A brief description of plasma is given below, followed by a description of the plasma process developed for treating contaminated soil and similar materials.

a) Thermal Plasmas

Thermal plasmas have been applied increasingly to industrial processes, in different areas. Thermal plasmas can be understood as an ionized gas, at high temperatures (above 10,000 ^{0}C) when compared to temperatures normally found in combustion or using electrical resistance heating. Thermal plasmas are produced using an electric arc, that strikes between two (metallic) electrodes, inside an equipment called plasma torch. When a common gas, such as air, argon, nitrogen, steam and many others, are injected into the plasma torch, the molecules / atoms of the gases collided with the electrons present in the electric arc (the electrons are being produced in one electrode, accelerated and collected in the other electrode). The result of that process is the heating and ionization of the gas, producing a (thermal) plasma jet, that reaches very high temperatures as mentioned above. .

Thermal plasmas have been used for:

i) Environmental applications, such as for the treatment of industrial residues (1), treatment of hospital wastes (2), vitrification of incineration ashes (3), treatment of radioactive materials (4), recovery of aluminum from drosses (5) and others;
ii) Metallurgy applications, such as for tundish heating for continuous casting (6), ferroalloys production (7), blast furnaces (8) and others;
iii) Materials applications, such as the production of titanium oxide (9), zirconia (10) and several nitrites and carbides (11).

A thermal plasma process was developed for the treatment of contaminated soil and similar materials. The plasma process utilizes a plasma torch, operating at approximately 15,000 ^{0}C, for volatilizing the organic compounds present in the contaminated soil, in a controlled ambient; the volatilized organic compounds are recovered in the form of an oil, and can be readily reused. The process presents several advantages when compared to conventional technologies, as described below.

b) Process Description

The developed plasma process can be understood as a controlled volatilization of the organic compounds initially present in the contaminated soil, in an ambient that does not contain oxygen. The energy for the process is provide by a plasma torch; a plasma gas, such as argon or nitrogen (not containing oxygen), is used in the torch. The organic vapors that leave the plasma reactor, with the plasma gas, passes through a series of condensers; the vapors after cooling, are recovered in the form of a light oil (diesel type) that is 100 % reusable. The plasma gas can be recycled in the process.

The normal operating temperatures of the proposed plasma process is from 800 to 1,200 ^{0}C, in order to volatilize all the hydrocarbons contained in the treated material. The contaminated soil or sludge is continuously fed into the reactor from one end, while the oil free soil is removed from the other end of the reactor. The contaminated material, as it travel through the reactor, becomes increasingly free of organic contaminants; and it is clean once it has reached the outlet chute for removal from the reactor. The atmosphere inside the plasma reactor is maintained neutral or reducing in order to prevent the oxidation of the hydrocarbons and to permit their recovery after volatilizing them inside the reactor and condensing the hydrocarbons outside the plasma reactor.

The developed process presents several interesting characteristics and advantages when compared to conventional technologies, such as:

i) Higher energy efficiency, since the plasma jet is at much higher temperature than, for instance, the flame produced by oil or gas burners employed in incineration (typically 15,000 ^{0} C for the plasma jet and 2,000 ^{0} C for the oil or gas flame), so that the heat transfer, dependent on the temperatures of the energy source and the heated substance, is significantly higher in the plasma process, increasing substantially the energy efficiency of the plasma process. A typical energy efficiency above 80 %, is achieved with the plasma process as compared to around 20 % for the normal gas or oil burners);
ii) Possibility of recovering the organic compounds that were initially contaminating the soil, which can be a significant asset for the process specially when the soil or sludge contains more than 10 % in weight of hydrocarbons;
iii) Nil or almost nil off gases are produced in the process, since the plasma torch can operate with small amounts of gases (and the plasma gases can be recycled in the process) and the volatilized organic compounds are condensed and recovered.
iv) Soil after the plasma treatment contains less than 0.01 % in weight of hydrocarbons, even when treating soil containing more than 50 % organic

compounds;which is less than 100 times the legal limit for discarding or reusing the soil.

v) Continuous operation process.

A schematic representation of the equipment can be seen in Figure 1 below.

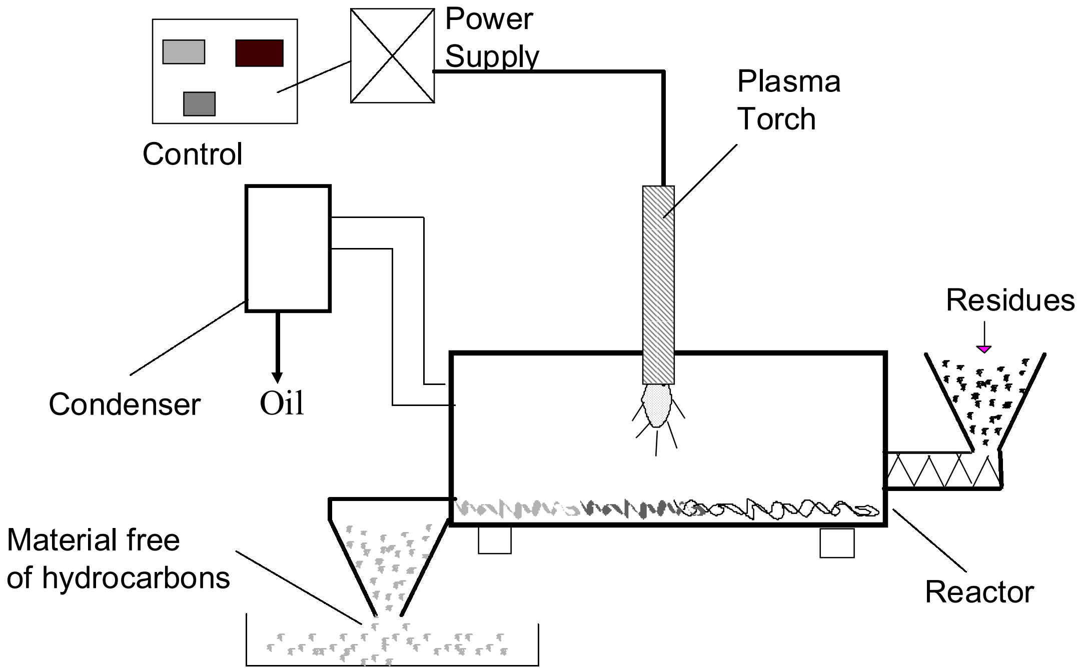

Figure 1 – Schematic representation of the plasma process

III. Results and Discussion

Several experiments were performed in a demonstration unit capable of treating up to 200 kg/h of contaminated material. Different materials were treated in the plasma unit, including soil containing from 1 to 50 % hydrocarbons (petroleum) and 25 % water in average. A summary of those results is given below.

a) Material (soil) after treatment:
Less than 0.01 % hydrocarbon when treating soil containing up to 50 % hydrocarbons;

b) Off gases
Less than 1 % of the amount of gases that would be generated if the soil containing hydrocarbons would be burnt in an incineration, for all the experiments and

conditions; gas analysis indicated only the presence of water vapor, carbon dioxide, nitrogen, oxygen and argon (plasma gas); no sulfur or chloride compounds detected.

c) Recovered oil
Diesel type for petroleum contaminated soil or petroleum sludge (analysis conducted by Petrobras – brazilian national oil company);

d) Specific energy for the process
0.5 kWh/kg.

The developed plasma process is well adapted for treating soil contaminated with several other compounds and elements, including mercury, organic chlorinated compounds and others. Economical evaluation of the process, based on the energy requirement and investments for the plasma units, indicate that the developed process can be even less costly than the existing technologies, without the environmental and technical limitations that those processes have as mentioned above.

Industrial units are being planned for treating contaminated soil on the site; those units will be able to process from 100 kg/h up to 5,000 kg/h (up to 2,000 kg/h the units are mobile; above that, the units are semi-mobile).

IV. Conclusions

A new process was developed, using a plasma system, for treating contaminated soil. The process removes the contaminants to a level several orders lower than the minimum required by environmental standards, at the same time that the organic contaminants can be recovered in the form of a light oil, completely reusable, reducing to almost zero the off gases that would be generated if the residues would be incinerated. The plasma units can be made mobile, treating in situ the contaminated area, avoiding therefore the risks and costs of transportation of toxic materials. Economical evaluation indicates that the process is very competitive with existing technologies, without presenting the environmental and technical limitations of those processes.

References

1) R.N. Szente, R.A. Schroter, M. G. Garcia, O.W. Bender; “ Thermal Plasma Treatment of Galvanizing Residues”, Journal of The Minerals, Metals & Materials Society - JOM, pg. 32-35, July 1998.
2) G.W. Carter, A.V. Tsangaris, “ Plasma Gasification of Biomedical Waste”, Proc. Internationa. Symposium on Environmental Technologies: Plasma Systems and Applications, Georgia, USA, October 1995.

3) N. Cerqueira, I. Ghiloufi, C. Vandensteendam, J.M. Baronnet, “ Heavy metals volatility modeling for fly-ash plasma vitrification”, Proc. International Symposium on Plasma Chemistry, Orleans, France, July 2001.
4) C. Girold, B. Barthelemy, N. Cerqueira, C. Vandensteendam, J.M. Baronnet, “ Medium level burnable radioactive waste incineration/vitrification under oxygen trasnferred arc plasma”, Proc. International Symposium on Plasma Chemistry, Orleans, France, July 2001.
5) R.N. Szente, M. Garcia, R. Schoeter, O Bender, L. Barbosa, “Recovering Aluminum via Plasma Processing”, Journal of The Minerals, Metals & Materials Society - JOM, pg. 52-55, November 1997.
6) Z. Yamazaki, H. Hashimoto, First International EPRI Plasma Symposium, California, USA, 1990.
7) D.R. MacRae, “ Application of Plasma Technology to Ferroalloy Processing”, Plasma Technology in Metallurgical Processing, Jerome Feinman Editor, Iron and Steel Society, 1987.
8) S.Santen, L. Bentell, B. Johansson, P. Westerlund, “ Applications of Plasma Technology in Ironmaking”, Plasma Technology in Metallurgical Processing, Jerome Feinman Editor, Iron and Steel Society, 1987.
9) R.N. Szente, " Industrial Applications of Thermal Plasmas", AAIP Conf. Proceedings, n. 345, p. 487-494, 1995.
10) G. Clarke, Materials Edge, September-October, 1987.
11) E. Bouyer, M. Muller, G. Schiller, “ Thermal plasma synthesis of ceramic materials from liquid precursors”, Proc. International Symposium on Plasma Chemistry, Orleans, France, July 2001.