Brownfields

4. Microbiological remediation of soil contaminated with thermo oil in Extremadura, Spain

LOCATION	Extremadura, Spain
POLLUTANT	HTF consisting of biphenyl and biphenyl oxides
SOURCE	Oil accidentally spilt from solar field
GENERAL CLEAN UP OBJECTIVES	Reduce groundwater and soil contamination
REMEDIATION ACTIONS	Excavation, liquid phase extracted with vacuum pumps, waste material stored in 5 compilations, heterotrophic bacteria digestion in ex-situ dynamic biopiles
SITE/END USE	Concentrated solar power station
SOCIAL-LEGAL ISSUES	Land reclamation
KEY LEARNING/ EXPERIENCE TO SHARE	New method tested fo the first time: thermal oil microbiological degradation of biphenyl and biphenyl oxide on site treatment using biopiles

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View of the Solar Plant

The study case

In December 2011 thermo oil was accidentally spilt in the solar field of a PTS (Thermo-Solar Plant) in the Autonomous Community of Extremadura, where this fluid is used as a heat carrier. In this PTS cylindrical - parabolic technology is used. The technology is based on converging solar rays in reception tubes of high thermal efficiency, located in the focal line of the trough-shaped parabolic mirrors. Inside the tubes the sunrays heat the HTF (Heat Transfer Fluid) to approximately 400ºC. The heated fluid is then pumped through a series of heat exchangers in order to produce superheated steam. Conventional steam turbines convert the heat carried by the steam to electricity. The spilled thermo oil used as heat carrier consists of a mixture of two organic compounds, biphenyl and biphenyl oxide. The volume spilled was estimated to be $70m^3$, contaminating an area of $12,000m^2$ of soil. DGMA (General Direction of Environment) evaluated the area where the accident took place with the objective of identifying the causes of the spillage as well as the scale of the environmental damage. Taking the data obtained and also the environmental legislation into account, it was agreed to initiate an environmentally responsible course of action at the expense of the responsible party. The aim of this administrative action was to specify the quantitative extent of the environmental damage and to assess the significance of this damage.

The problem

In the course of DGMA´s environmental requirements the party responsible for the environmental affection took a number of measures in order to prevent the situation from becoming more dangerous. Also the soil quality and the associated risks had to be analysed. As a first means of recovery the solid phase of the HTF was removed from the contaminated soil and the liquid phase was extracted with a vacuum pump. Subsequently the first layer of affected soil (where the contamination was visible for the naked eye) was excavated and the remaining area was covered with a polyethylene film. A volume of 1,752t of soil proved to be highly contaminated and was directly delivered to a waste disposal site for hazardous materials. The rest of the excavated soil (1,755t) was spread out on high density polyethylene sheets inside the plant. After analytical characterization of the excavated soil and the realization of an QRA (Quantitative Risk Analysis), target values were obtained (see table right column *page 86*). These target values set the maximum allowed concentration of pollutant which could remain in the soil remaining after excavation and the excavated soil after the recovery treatments. Based on the QRA results, DGMA declared the environmental damage at the site of the accident to be significant, requiring the organization responsible for the damage to present a project to ensure environmental recovery. The project presented was approved by the DGMA. In the development of the project specific environmental conditions, such as monitoring the environmental aspects, controlling the degradation in the biopiles, ensuring the quality of the air around the site and ensuring that more than 90% of the contaminated soil would be treated according to the proposed technique, were established.

The strategy

Excavation

After an initial urgent excavation, a second excavation was carried out in order to isolate the total amount of affected soil. The excavation was executed selectively to ensure that no clean soil was mixed with contaminated soil. So only polluted material was treated and the cost of the recovery could be kept to a minimum. This goal was achieved by using organoleptic differentiation and a Photoionization Detector (PID). Once the target values for the soil quality were achieved, the soil remaining after excavation was analyzed by taking samples from the walls and the bottom of the pit. Those samples were analyzed in a laboratory according to the ISO 17025 norm. If the results were found to be below the target values determined previously in the QRA, the excavation was regarded as finished and the refilling of the pit would be started.

Compound	Maximum Conc. (mg kg-1)	Target Value (mg kg-1)
biphenyl oxide	22.000	540
biphenyl	7.400	72
benzene	251,7	50

Database/KEPLER

Target and maximum allowed values of the analyzed compounds

Treatment of the excavated soil

Before the excavated material was treated microbiologically, it was stored in 5 compilations which had previously been conditioned and which were isolated by polyethylene tarp. Dimensions and volumes of every single compilation were determined using a topographic survey; also considered was the level of contamination which had been analytically evaluated for each of them. In addition to the conditioning of the excavated material, the base for the construction of the biopiles was prepared. For this purpose an area of 5,430m^2 was levelled and aggregate was spread in two separated zones: one measuring 3,450m^2 and one 750m^2. Those two zones formed Biopile 1 and Biopile 2 respectively as well as Biopile 3 later on. Within these areas two longitudinal ditches were excavated in order to collect liquids which could possibly leach from the soil treated. The aggregate was then levelled out again as well as compressed. Also a slope of 1% was incorporated in order to ensure that the leaching liquids could be collected in perimetral drains. A geotextile sheet was applied directly on top of the aggregate layer and a double-layer of high density thermally sealed polyethylene (1,5mm thickness) was spread on top of the geotextile. The polyethylene served to make the base of the biopile waterproof. Two tanks of 1,000L capacity were installed at the end of the drainage system to collect the leaching liquids: one for Biopile 1 and the other one for Biopile 2. The leaching liquids were purified using an activated carbon filter and were reused in the plant for biological treatment of soil which was set up next to the biopiles.

Assembling of the biopiles

Once the base for the biopiles was set up, the soil collected for recuperation was transferred to the site. Biopile 1 had a volume intake of 2,640m^3 of contaminated soil, Biopile 2 of 1,111m^3 and finally Biopile 3 of 98m^3. During the course of the assembly of the biopiles the soil was turned a first time to homogenise the material.

Dismantling of the biopiles and relocation of the material

The depolluted soil was used for the recreation of a protecting wall of earth around the solar panels in order to decrease the impact of wind inside the installation. Once all the earth had been used in that way a new set of samples was taken for the last analysis. For this purpose 16 samples were analysed regarding the concentrations of biphenyl, biphenyl oxide, Hydrocarbon Oil Index (HOI), phenol and benzene. The analytical results are presented in the table *Mean concentrations,* right column *page 87.* Taking those values into account, it becomes clear that none of the concentrations exceeded the target value for soil quality.

SEPTEMBER 2014		
Pollutant	**Mean Value , mg kg^{-1}**	**Target Value , mg kg^{-1}**
HOI	<0,1	-
Benzene	<0,1	50
Phenol	<0,01	-
Biphenyl	4,7	72
Biphenyl oxide	15,3	540

Database/KEPLER

Mean concentrations in the protecting wall

Ambient actions after the soil recovery had taken place

Once the recovery of the soil polluted with thermo oil was carried out, the restoration of the site where the accident had taken place was the next step. All the means and materials used for the waterproofing of the zones of storage and treatment as well as the activated carbon employed in the purification of the leaching liquids - generally all the residues generated during the progress of the project were handled and disposed of according to the current legislation and its compulsory rules.
In order to ensure that the soil quality in the treatment zones was not altered, soil samples, not only of the zones where the treatment had taken place but also of the zones of storage, were taken and analysed. The results allowed the verification of the efficiency of the actions taken to protect the environment.
To reinstall the site to its original form, the ditches and accesses constructed

Positioning of the 1.5mm high density polyethylene sheet

Detail of the plant for soil treatment

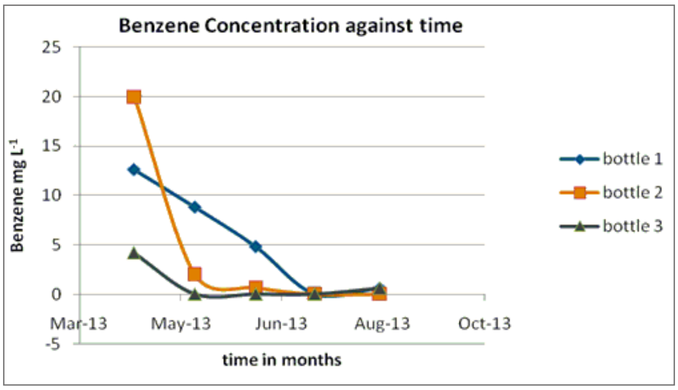
were filled up and compacted.

Microbiological treatment

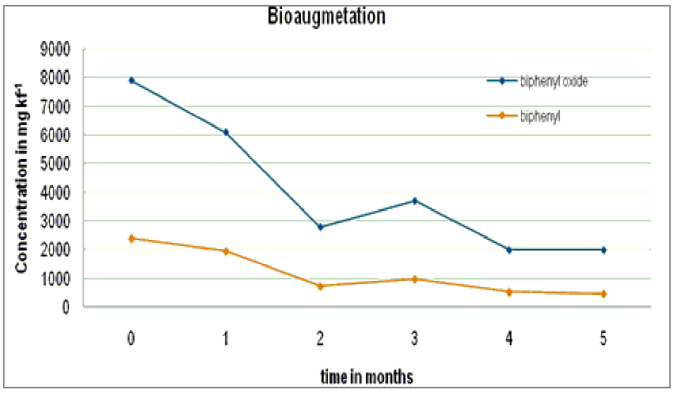
The thermo oil used in the thermal solar power plant as a heat carrier consists of a eutectic mixture of biphenyl (26.5%) and biphenyl oxide (73.5%). The two compounds are insoluble in water and toxic but not carcinogenic. It has to be pointed out that as a result of decomposition of this liquid, metabolites such as benzene and phenol can be formed which could also affect the environment at the site of treatment.
The biodegradation of the contaminant hydrocarbon compounds is a process in which microorganisms mineralize the chemical compounds. They transform them to more simple compounds of a lower molecular weight, so that a complete mineralization can take place. During this process the metabolites benzene, toluene, phenol and organic acids are formed. To ensure the degradation takes place, certain environmental conditions (availability of oxygen, moisture and nutrients) are necessary as well as an appropriate quantity of microorganisms. Those are generally native at the contaminated site and mostly aerobic.

Preliminary tests

Before beginning the treatment in-situ at the contaminated site, two tests were carried out on laboratory scale. Hence the efficiency of the treatment could be evaluated for the soil in question. Also a possible accumulation of benzene in the ambient air around the biopile during the turning of the soil could be studied. When the microcosms were tested, the degradation of biphenyl and biphenyl oxide against time was proven to be greater when using bio augmentation (degrading microorganisms and nutrients had been added) compared to a sample where the only parameter controlled was the humidity. Tests regarding volatilization allowed specifying the concentration of benzene associated with a contaminated soil sample in conditions simulating the ones in the biopiles. Even though the concentrations determined were below the maximum value specified in the law for prevention of risks at the workplace,



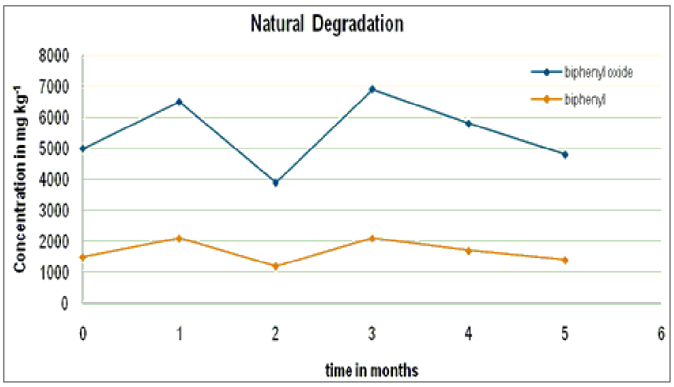
Benzene concentrations during a period of three months



Development of degradation, second tray (biodegradation)

Nº of the biopile	Compound	Mean Conc. Initial (mg kg^{-1})	Mean Conc. Final (mg kg^{-1})
1	Biphenyl	431	6,5
	Biphenyl Oxide	1161	18,6
2	Biphenyl	285	5,6
	Biphenyl Oxide	767	13
3	Biphenyl	218	35
	Biphenyl Oxide	1040	96

Values of the compounds of interest



Development of degradation first tray (natural degradation) bmp the DGMA considered it to be necessary to control and monitor the values from an environmental point of view. This also applied to the emissions of biphenyl and biphenyl oxide.

Microbiological treatment of the excavated soil

For carrying out a project using biopiles it is crucial to add sufficient amounts of oxygen. In this specific project, high oxygen levels were maintained by turning the soil with a backhoe equipped with a shovel for crushing and soil-turning. To maximise efficiency and to ensure that the nutrients, the water and the microorganisms would reach every gram of soil, the turning of the soil was carried out while the soil was sprayed with a water and microorganism solution. The needed levels of humidity, oxygen and nutrients were based on regular analysis of samples taken at the biopiles. The quantity of microorganisms added was determined as a function of the concentrations of degrading microbiota and pollution, as well as from the volume of soil to be treated. In order to produce and maintain the microorganisms in perfect conditions, an automatic fermentation plant was installed next to the biopiles. Also mixtures of water and/or nutrients and/or microorganisms could be prepared there and then be used in the biopiles. Once one treatment was finished, the biopiles were covered with thin sheets of polyethylene. This served the purpose of protecting the biopiles from an excess of humidity due to rainfall on the one side and it also prevented the contamination from escaping into the environment on the other side.

Controlling and monitoring of the biopiles

During the project the physical, chemical and biological conditions in the treated soil were monitored exhaustively. The objective of this monitoring was the optimisation of the treatment and the revelation of any problems during the course of the process. There is a specific protocol for the evaluation of the treatment. It consists of regularly taking samples of every section of the biopile. Following this the biphenyl, biphenyl oxide, benzene and phenol concentrations were analyzed. Each biopile is divided into sections of a

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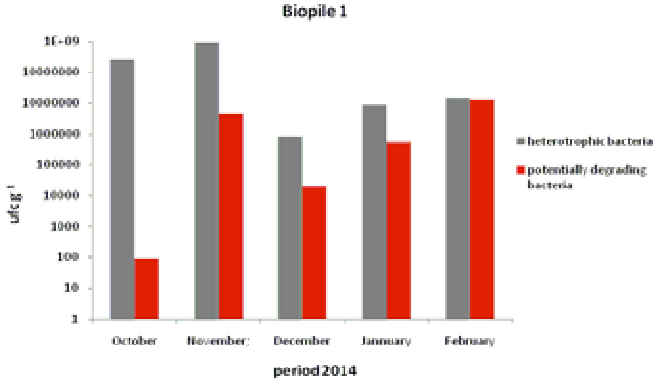
Soil turning and applying of the solution of nutrients and microorganisms.

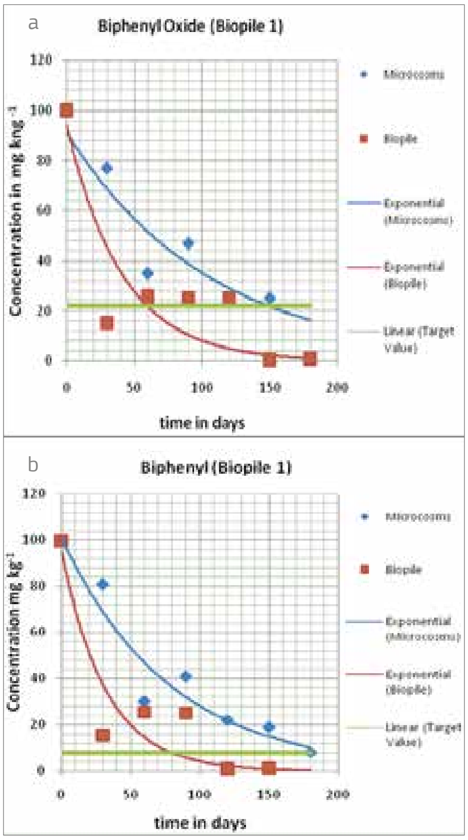
volume of 250m³. Each section is subdivided into three parts where soil samples are taken in each subsection. The three samples of each section are taken into account to obtain an average value for the section. Parameters analysed on the site are pH, temperature, redox, conductivity, saltiness and humidity. In the laboratory, concentrations of nutrients, biphenyl, biphenyl oxide, benzene phenol, the respirometry and the microbiologic count are analysed. In the table below the results for pollutant-concentrations obtained during the microbiological treatment corresponding to each of the biopiles are presented. In all cases the degradation of the pollutants exceeded 84% meaning that their mean final concentration was below the desired target value established. The monitoring of the population dynamics was carried out using a test tray in the laboratory. The objective was to determine the presence of heterotrophic and potentially degrading microorganisms in the biopiles and to find their number in units forming colonies per



Database/KEPLER/2014

Concentrations of bacteria in biopile 1 over a period of 5 months (ufc g-1).

gram (ufc g-1). Considering the concentration of bacteria in biopile 1 during 5 months, it becomes clear that the concentration of microorganisms which are potentially degrading rose as the project went on. This fact points out that the exogenic microorganisms added to the soil during the treatment are capable of adapting to their surroundings and consequently to carry out the biodegradation. The unfolding of the degradation processes in the field (Biopile 1) and in the laboratory tests (microcosm) are illustrated and compared. Clearly the laboratory tests allowed optimizing the treatment in the field in such a way that the results obtained in the biopile were even better than in the laboratory. Once the target values of the microbiological treatment had been reached, an analysis of the toxicity of the recovered soil was carried out by taking two samples per biopile. The biological samples of toxicity are used on a regular basis to evaluate enviromental samples. Those tests are based on the natural bioluminescence of a marine bacterium called Vibrio fischeri in the presence



a) Comparison of the degradation of biphenyl in the laboratory and in the field (percentage of degradation in days of treatment).
b) Comparison of the degradation of biphenyl oxide in the laboratory and in the field (percentage of degradation in days of treatment).

of contaminating agents. The toxicity is expressed as the concentration of contaminating agent which generates the reduction of 50% of the initial luminescence (EC50). The results given by those biological tests of environmental toxicity showed that the toxicity was zero in all of the biopiles.

The results

The environmental recuperation works at the site were carried out during the course of 12 months, six of which were spent on microbiological treatment in the three biopiles. However they were not carried out simultaneously in each one of them. In Biopile 1 the targets were met within 5 months, in Biopile 2 in 5 months as well and in Biopile 3 in 4 months. The maximum concentrations of biphenyl and biphenyl oxide in Biopile 1 were initially measured to be 908mg kg-1 and 2,452mg kg-1, respectively. By applying the microbiological treatment the concentrations decreased to values below 7mg kg-1 of biphenyl and 19mg kg-1 biphenyl oxide. So the reduction of both compounds was close to 100%. In Biopile 2 the initial maximum concentrations were 327mg kg-1 of biphenyl and 889mg kg-1 of biphenyl oxide. Those values could be reduced to below 5 mg kg-1 for biphenyl and to below 13mg kg-1 of biphenyl oxide. This means a reduction close to 100% could be reached. The initial maximum concentrations for Biopile 3 were found to be 218mg kg-1 for biphenyl and 1,040mg kg-1 for biphenyl oxide. These concentrations were reduced to levels below 35mg kg-1 for biphenyl and below 96mg kg-1 for biphenyl oxide. This means the concentrations could be reduced by 84% and 90% of biphenyl and biphenyl oxide, respectively. In order to ensure the maximum security during the course of the soil turning works, an exhaustive monitoring of the ambient air around the biopiles was realized. This was due to an eventual accumulation of the metabolite intermediate benzene. However no significant benzene concentrations were detected in the active and passive sensors installed. The tests and analysis of micro organisms carried out in the laboratory allowed to optimize the microbiological treatment in the field. The efficiency of heterotrophic microorganisms for the degradation of biphenyl and biphenyl oxide has proven to be significant. Those micro-organisms were created in the laboratory of KUVIER and multiplied and maintained at the plant of biological treatment installed at the site. The treatment in-situ has made it possible to recover 4,046m^3 of affected soil in a short time. Hence its disposal could be avoided and an environmental benefit could be achieved. In the project described above a microbiological degradation of thermal oil composed of a mixture of biphenyl and biphenyl oxide has been achieved in an on site treatment by means of biopiles for the first time.

Further readings

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