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Large scale and long term application of bioslurping: The case of a Greek petroleum refinery site

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Abstract

This paper presents the course and the remediation results of a 4-year application of bioslurping technology on the subsurface of a Greek petroleum refinery, which is still under full operation and has important and complicated subsurface contamination problems, mainly due to the presence of light non-aqueous phase liquids (LNAPL). About 55 wells are connected to the central bioslurping unit, while a mobile bioslurping unit is also used whenever and wherever is necessary. Moreover, there are about 120 additional wells for the monitoring of the subsurface of the facilities that cover a total area of 1,000,000 m². An integrated monitoring program has also been developed and applied on the site, including frequent LNAPL layer depth and thickness measurements, conduction of bail-down and recovery tests, sampling and chemical analysis of the free oil phase, etc., so as to evaluate the remediation technique's efficiency and ensure a prompt tracing of any new potential leak. Despite the occurrence of new leaks within the last 4 years and the observed entrapment of LNAPL in the vadoze zone, bioslurping has managed to greatly restrict the original plume within certain and relatively small parts of the refinery facilities. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

Bioslurping is a relatively new subsurface remediation technology that combines elements from three different remediation techniques: vacuum-enhanced pumping, soil vapour extraction and bioventing [1], achieving simultaneous remediation of soil and groundwater – through LNAPL removal – and of soil gas – through indirect oxygen provision and bioremediation stimulation.

A "bioslurping well" has a "slurp tube" of adjustable length, which is lowered into the LNAPL layer and is connected to a vacuum pump. Through this tube free product along with limited groundwater and soil gas are removed from the subsurface. When LNAPL levels decline in response to pumping, the slurp tube can only extract vapors (soil vapor extraction), allowing the renewal of the soil gas from the atmosphere through the soil surface and therefore an increase in the oxygen content and consequently in the rate of aerobic biodegradation is noticed.

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0304-3894/\$ - see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2007.06.110 The pumped mixture (free oil product, groundwater and vapors) from the slurp tube is led to a liquid/vapor separator and an oil/water separator. Fig. 1 presents the components of a typical bioslurping system.

The main advantages of the bioslurping technology include [2,1]:

- high free phase recovery efficiency,
- minimization of groundwater and free oil phase mixing, due to the absence of pump cone creation and the prevalence of horizontal free phase flow towards the slurp tube,
- minimization of the pumped liquid volume, due to minimum groundwater pumping,
- stimulation of the biodegradation process in the unsaturated zone of the subsurface,
- ability to be applied using a mobile unit,
- capability to avoid soil vapor treatment, when low pumping rates are applied,
- good control of the free phase mobility expansion.

The study area of this paper comprises the facilities of a Greek refinery, which is situated near a coastline and a lake of important ecological value. This petroleum refinery covers an area of



Fig. 1. Typical bioslurping system components.

 $1,000,000 \text{ m}^2$ and has been operating for more than 20 years. As far as the hydrogeological characteristics of the refinery's site are concerned, the surveys conducted showed intense heterogeneity of the site. In general, the geology of the site consists of limestone and dolomite, forming the nearby hills, with unconsolidated alluvial deposits filling the lower elevations. Normal faulting is responsible for the formation of the existing hills and provides abrupt lithologic changes to the unconsolidated material along the flanks of the hills. The groundwater flow is controlled by these lithologic changes and occurs in the poorly sorted unconsolidated deposits that consist of sand, gravel, and clay [3].

The first signs of leaking and subsurface contamination appeared almost 15 years ago, when light petroleum products were found at the nearby coast and lake. Several wells (more than 120) were drilled within the area of the refinery to monitor the groundwater and the soil of the area (Fig. 2). Finally, the existence of a wide and thick free oil phase on the surface of the aquifer was determined [4] and bioslurping was applied in 1998. Large quantities of leaking petroleum products had to be removed from the subsurface for many years [2], in order to achieve a satisfying improvement of groundwater quality.

In May 2003, the Laboratory of Toxic and Hazardous Waste Management of the Department of Environmental Engineering of the Technical University of Crete took over the application of a complete subsurface remediation and monitoring program on the account of the refinery's administration. This program mainly included the recovery of the existing free phase layer, as well as the monitoring of the subsurface for the proper operation and evaluation of the installed bioslurping system and the tracing



Fig. 2. Ground plan of the refinery's facilities, where the existing wells and the different defined areas are noted.

of any new potential leak. Fig. 3 shows the existing free phase layer plume in May 2003.

2. Bioslurping application

2.1. Installed systems

The main installed bioslurping system is a typical one (Fig. 4), as it is presented in Fig. 1. It is located in the central east part of the facilities, where the main free phase layer plume has been allocated.

The system is connected to 55 wells (Fig. 5), while a mobile bioslurping unit is also used in order to achieve free phase

recovery from remote parts of the refinery and/or deal with new leaks.

2.2. System operation

The installed bioslurping system has been operating for 16 h per day and for 5 days per week (except weekends). The applied vacuum is about 0.4 bars, depending on the number and the characteristics of the connected wells. The daily recovered free product volume is recorded.

2.3. Monitoring

The main activities of the monitoring stage include:



Fig. 3. Free phase layer thickness (m) spatial distribution in the subsurface of the refinery in May 2003.

- measurement of the thickness of the free oil phase in different wells (points) in the whole area of the refinery,
- conduction of bail down tests for the evaluation of the free phase flow and the extent of the leakages in certain areas of the refinery,
- conduction of productivity tests for the estimation of the available free phase quantities in the subsurface of the refinery,
- frequent sampling and analysis of free phase, soil, soil gas and groundwater samples from several points of the facilities.

During the period May 2003–February 2006 several measurements of the thickness of the present free oil phase have been made. Special equipment has been used in order to acquire precise results and create a satisfying image of the variation of the thickness of the free phase layer in connection with space and time. Pollutant distribution maps of the refinery have been created to develop a graphical representation of the existing free oil layer and to assess potential changes of the position and the extent of the plume. Bail down tests, as well as productivity tests, have also been conducted in several wells of the refinery to reflect the flow of the free phase on the aquifer and estimate the available free product in the subsurface.



Fig. 4. View of the installed bioslurping system.



Fig. 5. Bioslurping wells network within the facilities of the refinery.



Fig. 6. Free phase layer thickness (m) distribution progress.

3. Results and discussion

3.1. Free phase layer distribution

As it can be clearly concluded from the free phase layer thickness measurements and the monthly distribution maps that have been created, bioslurping has managed to greatly restrict the existing plume. Not only did it prevent the "exit" of the plume outside the refinery's boundaries (towards the nearby lake and sea), but it also reduced the plume area within the refinery. Fig. 6 presents several representative free phase layer distribution maps of the period May 2003–November 2006.

During the 4-year application of bioslurping, the existing plume has followed a restrictive course. However, there were periods that limited expansion or appearance of the plume at a previously "clean" part of the refinery was noticed (Fig. 6b). This was mainly attributed to new leaks, that through the dense existing well system they were rapidly located and dealt with effectively by appropriate adjustments of the bioslurping system. Of course, groundwater table variations and certain meteorological conditions (such as heavy rain events) also influence both the bioslurping system's efficiency and the free phase layer thickness.

3.2. Free phase layer recovery

As it has already been mentioned, the daily recovered free phase volume has been recorded, in order to acquire a reliable image of the available free phase quantities in the subsurface. This availability consists a very good indicator of a new potential leak, especially when it concerns previously "clean" wells.

Fig. 7 presents the recovered free phase quantities during the period January 2004–November 2006. Increased recovered quantities do not necessarily coincide with expended free phase plumes (as they are depicted in the created free phase layer thickness distribution maps), provided that the system is



Fig. 7. Recovered free phase volume (January 2004-November 2006).

well monitored and quickly adjusted to any new event. The recent increased measured values (October–November 2006) have been found to be related to a new leak.

3.3. Free phase availability

Bail down tests have been conducted weekly for the evaluation of the free phase flow in certain parts of the refinery. These tests include total removal of the free phase in specific wells and record of the time needed for the free phase layer to reappear and obtain its usually observed thickness.

Bail down tests show a relatively high flow of the free phase in certain wells of the examined refinery. The measured flow is of course depended on several factors, such as the existence of nearby leaking tanks, local hydro-geological conditions, etc. This is confirmed by the noticeable deviation between the acquired recovery rates of the examined wells in different parts of the facilities. In general, bail down tests show relatively short free phase reappearance time and important thickness of the free phase layer in certain wells (Fig. 8).

On the other hand, productivity tests, that include continuous pumping of the existing free phase for the estimation of the available volume, have shown that there are no large quantities of free petroleum product in the subsurface of the refinery. Even in wells where high free phase layer thickness is appeared, very small amount of free product (1-5 L) can be recovered under continuous pumping, indicating low free phase availability (Fig. 9).



Fig. 8. Bail down tests results in selected wells in May 2006.

3.4. Free phase layer composition

Analytical procedures, like gas chromatography in conjunction with data analysis and interpretation techniques for revealing the affiliation of a certain sample to a group of chemically similar objects (chemical fingerprinting), have been applied for the free phase layer composition determination. By determining the free phase layer composition, it is possible to achieve source identification of a spill. Briefly, the results of the free phase sampling and analysis are the following [5]:

- the existing free oil phase consists of three main groups: light distillates like gasoline and reformate, heavy distillates like diesel and mixtures of them,
- the detected hydrocarbons are shown to be composed of two sources: one from gasoline and the other from a heavy petroleum product,
- toluene and xylene have maximum mass percentage in most of the samples, while other present volatile substances are paraffines, naphthalenes and olefines (*n*-C5 to *n*-C8), which show a maximum content in most of the samples (heavier substances with a molecular weight of *n*-C9 could be found in a less content),
- according to the product composition of the majority of the free phase samples, which shows that most of the plume components are volatile substances, there is a high risk for the emission of combustible gases.



Fig. 9. Productivity tests results in selected wells in May 2006.

4. Conclusions

The application of bioslurping technology has so far led to a significant reduction of the free phase layer thickness within the study area. However, the residual free phase volumes in the subsurface, as well as new leaks still contaminate the unsaturated and saturated soil zone. Although there is a minimized free phase volume on the groundwater table, the residual layer is causing an ongoing groundwater contamination.

On the other hand, the identified significant contamination of the groundwater cannot be minimized by the free phase recovery, because groundwater is not directly treated with this technology and therefore the application of an appropriate groundwater remediation technology (such as air sparging) is strongly recommended, since it has already proved that it can have very positive remediation results on the specific site [6].

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References

- F.I. Khan, T. Husain, R. Hejazi, An overview and analysis of site remediation technologies, J. Environ. Manage. 71 (2004) 95–122.
- [2] E. Gidarakos, J. Thomas, Detailed Chemical Characterization of Subsurface Contaminants in Support of Remediation Activities, Battelle Report, 2001.
- [3] E. Gidarakos, J. Thomas, I. Gaglias, D. Lamprinoudis, Bioslurping treatment for subsurface contamination, Petrol. Technol. 6 (2001) 43–49.
- [4] K. McCarthy, A. Uhler, T. Naymic, E. Gidarakos, Identification of Subsurface Hydrocarbon Products Using Fingerpsinting, Battelle Report, 2001.
- [5] N. Pasadakis, E. Gidarakos, G. Kanellopoulou, N. Spanoudakis, Identifying sources of oil spills in a refinery by gas chromatography and chemometrics. A case study, Environ. Forensics, in press.
- [6] M. Aivalioti, E. Gidarakos, Air Sparging, Demonstration in a contaminated petroleum refinery site, International Conference on Bioremediation of Soil and Groundwater, Krakow, Poland, 2004.