Integrated Physical - Chemical – Biological Remedial Strategy for TPH Impacted Groundwater: significant benefits of augmenting an extractive remedial system with *RegenOx*™

Introduction

This document summarises the combined use of physical, chemical and biological remediation approaches to synergistically increase treatment rate and efficiency, save costs, and meet an inflexible remedial deadline on a UK project. The use of the specific technologies in combination for the first time in this project provides benefits that none of the technologies used alone could achieve. Central to this was the novel exploitation of a feature of the *RegenOx*™ product that was initially designed for an alternative purpose. The success of this is demonstrated in the pioneering 'treatment-train' case study presented below. The principle is now being widely exploited in a variety of additional projects.

Project Background

Geo^2 Remediation Ltd. carried out the remediation of a former service station following historic leakage from underground storage tanks (UST's), which had resulted in total petroleum hydrocarbon (TPH) contamination of the groundwater. Concentrations were significant near the source area, with plume migration down-gradient towards the edge of the property. A fixed-price remediation strategy was agreed with the client against a fixed and inflexible development deadline.

Ex situ Physical Remediation

The initial works comprised the UST's being made safe and removed, after which some of the most impacted soils were excavated from around the tank base and walls.

In situ Physical Remediation

In April 2006, a Dual-Phase Vacuum Extraction (DPVE) system was installed to recover residual LNAPL and reduce the TPH concentration within the groundwater. Over one year's operation, contamination levels across the site had been reduced but the system had reached asymptotic levels commonly observed in physical abstraction-based systems. The DPVE unit was then shut down to allow for rebound monitoring which showed that the free-phase contamination had been successfully removed. However, the dissolved phase TPH concentration had not reduced to below the site specific target levels (SSTL's) as agreed with the regulatory authorities.

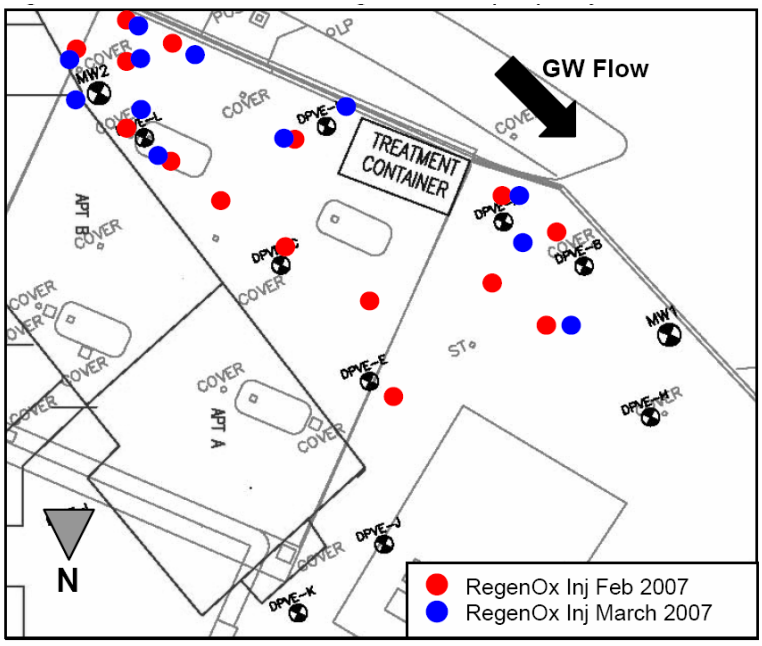

Figure 1. RegenOx Injection Locations

Combined *in situ* Physical Remediation and Chemical Oxidation

At this point it was decided to begin the next phase of the remedial strategy and apply *in situ* chemical oxidation (ISCO), using the Regenesis product *RegenOx*™, in order to augment the DPVE system and improve the contaminant abstraction efficiency. *This approach was novel, and previously untried, and was based on features of the RegenOx product designed for other purposes.* This is described briefly below.

RegenOx™ Basics

RegenOx™ is a proprietary two-part chemical oxidation product developed and sold by Regenesis for *in situ* groundwater treatment. It combines the use of a controlled-release percarbonate-based oxygen compound with a proprietary multi-part catalyst to generate surface-mediated free-radical generation and contaminant oxidation (e.g. perhydroxyl radical, hydroxyl radical and superoxide radical), with reactive power comparable to that of Fenton's reagent but with greatly facilitated handling and subsurface delivery / longevity (up to 30 days). This provides an effective contaminant oxidation reaction without violent exothermic reaction, and can therefore be handled using a wide range of standard field equipment (e.g. direct push injection rigs) or applied directly to excavations. Furthermore, it is alkaline and can therefore be used in calcareous formations in addition to sands and gravels etc.

[1]*RegenOx*-enhanced Contaminant Desorption

RegenOx has been designed as a bespoke remediation product to provide advantages in usage and application over commodity chemical products used for ISCO (e.g. permanganates, persulphates, peroxides). One of the design features it includes is reduced losses onto the aquifer matrix, commonly known as the matrix Natural Oxidant Demand (NOD). This is achieved by *RegenOx* through a powerful desorption / surfactant effect of the combined product (principally the catalyst) that draws the contaminant off the soil surface and into solution / onto the catalytic surface where localised free-radical generation occurs leading to focussed contaminant destruction. This restricts the oxidant losses onto tightly bound and heavier soil organics such as humics, roots, and other natural or immobile fractions. At the same time, *RegenOx* is purely inorganic therefore adding no organic surfactant to the system that may prevent a competitive oxygen sink to on-going contaminant biodegradation.

The present project makes use of this product feature to combine in situ *chemical oxidation with enhanced physical mass recovery. RegenOx-desorbed contaminant mass and partially oxidised (more soluble) organic species are recovered via groundwater abstraction using the DPVE system, whilst further contamination is destroyed* in situ *by oxidation.*

Augmentation of the DPVE System Using *RegenOx* – Procedure

Once the results from the DPVE treatment were shown to be asymptotic, *RegenOx* was applied by direct push injection into the residual contaminant plume. The abstraction lances of the DPVE system were raised above the groundwater level in order to provide ongoing soil vapour extraction (SVE) whilst the chemical oxidation process was completed. The *RegenOx* fully oxidised some of the TPH in the groundwater, but also produced more soluble intermediate products by partial oxidation and temporarily increased the desorption of TPH sorbed to the formation. This meant that, after two

[1] Standard *RegenOx* treatment typically comprises a sequence of applications, approximately one month apart, progressively desorbing and oxidising contaminants. This process is often followed by enhanced-bioremediation using Regenesis slow-release electron donors / acceptors (e.g. ORC®, HRC®).

weeks, the DPVE lances could be lowered into the groundwater once more in order to remove the partially oxidised products and the desorbed fraction produced by the *RegenOx* application, thus significantly increasing the extraction efficacy of the DPVE system.

In situ Chemical Oxidation

Once the DPVE treatment had removed the dissolved phase contaminants made available by the *RegenOx* application, the lances were raised above the groundwater and a second application of *RegenOx* was completed. Whilst the DPVE lances were used to provide SVE, the second *RegenOx* application was used to chemically oxidise the residual dissolved phase TPH contamination to below the site-specific treatment levels (SSTL's). The DPVE liquid extraction was shut off at the time of the second *RegenOx* application (one month after the first).

In situ Bioremediation / Natural Attenuation

The site was broadly brought intto compliance through the above procedures, but with the exception of a residual area in the region of well DPVE-N which remained above compliance. However, the TPH in this region continued to drop steeply following the second RegenOx application for a period significantly longer than the 3 – 4 week reactive duration of the *RegenOx* (7,300 µg/L dropping to 4,680 µg/L (35% reduction) at 50 days post-application). The observed continued reduction was attributed to enhanced biodegradation arising through:

- Increased contaminant bio-availability (*RegenOx*-enhanced desorption);
- Increase contaminant biodegradability (partial contaminant oxidation to less recalcitrant species – e.g. alkanes converted to alcohols, carboxylic acids etc.);
- Creation of temporary (1 – 2 month) aerobic / high redox conditions through *RegenOx* application accompanied by resultant oxidation of aquifer mineral species (e.g. iron and manganese) which will contribute as electron acceptors to enhance biodegradation for a further period post oxygen depletion.

Regulatory Closure

Based on these principles, the observed contaminant reduction trend and the isolated nature of the residual contamination, regulatory closure of the project was secured – on time and on budget – and the development of the site proceed on schedule.

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Results Summary

Project results are summarised in the following tables. A summary of the overall programme in the principal impacted well is illustrated graphically in Figure 2.

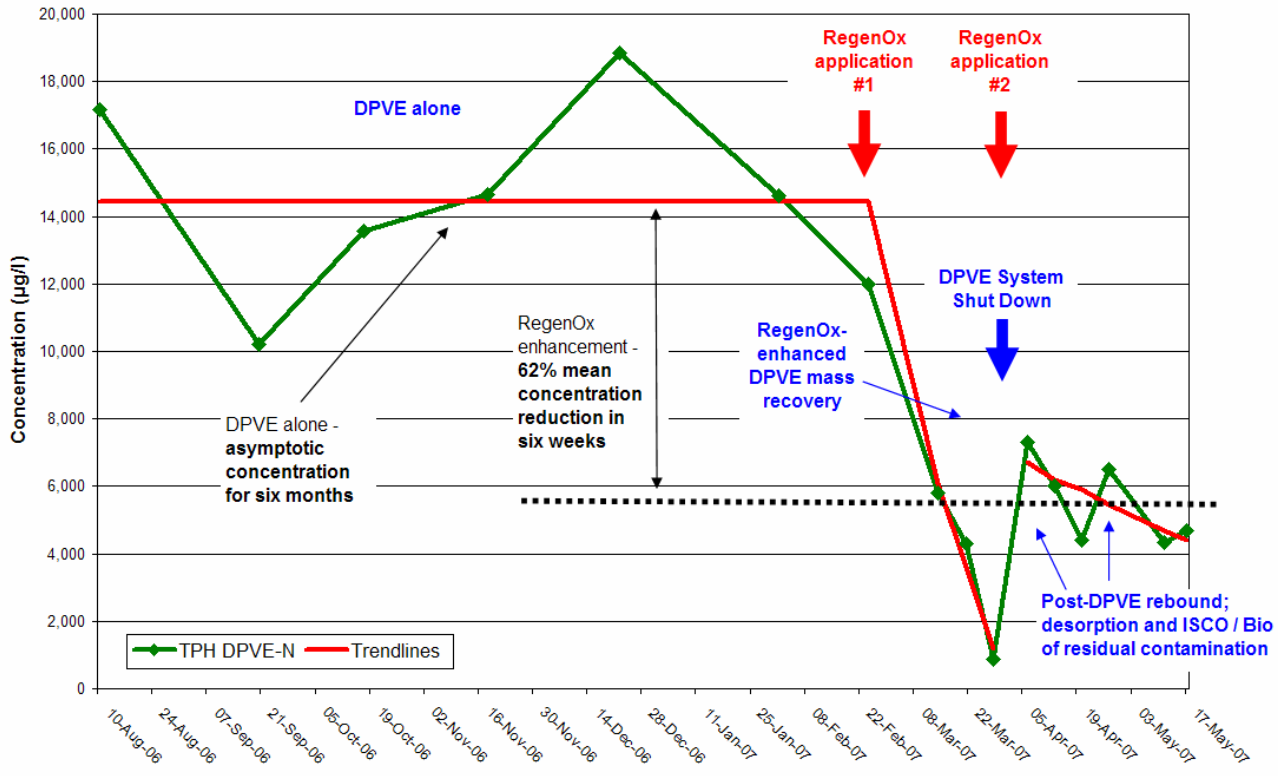
Table 1. Groundwater TPH Concentrations during the Treatment Program (µg/L)

Well	Following Free-Phase Removal (August 2006)	Before 1st RegenOx Injection (February 2007)	Following 2nd RegenOx Injection (April 2007)	Final Validation Concentrations (May 2007)
MW-1	1,064	<10	<10	580
MW-2	2,806	1,300	550	910
DPVE-K	841	<10	<10	350
DPVE-N	17,167	12,000	6,500	4,680

Table 2. Summary of RegenOx System-Enhancement Performance

Well	Pre-RegenOx *Asymptotic* Average (µg/L)	Post-RegenOx Average (µg/L)	Reduction
MW1	1,341	530	60%
MW2	1,961	944	52%
DPVE-K	877	350	60%
DPVE-N	14,432	5,538	62%

Figure 2. Groundwater TPH Concentrations Over Time (Well DVPE-N)



"Project Brunel" – Supporting Notes for BBRIA Entry

These notes accompany the project case study description with which they are submitted.

Title:

Integrated Physical – Chemical – Biological Remedial Strategy for TPH Impacted Groundwater: Significant benefits of augmenting an extractive remedial system with *RegenOx*™

Submission Categories

3: best use of combined treatment systems
5: most innovative remediation method

Specified Criteria

a) This submission represents best rather than good or average practice.

The approach described is unique and unprecedented, and therefore cannot be considered average or indeed good practice. Further, it can be considered 'best' practice as it draws upon the optimal features of the combined technologies achieving benefits to time and cost none of the technologies could achieve alone.

b) Cost-effectiveness and durability over the period of operation.

Cost effectiveness: this was a fixed time and fixed price project – the combined technologies achieved concentration reductions across the site in the order of 60% and regulatory closure in a six-week period following six months of limited reduction / asymptotic conditions post-free product removal. Without this approach, closure would not have been secured, the system would be on-going at best and the development delayed – the cost effectiveness of the approach is therefore evident. (Cost of the two RegenOx applications = £ 6,000; cost of ongoing DPVE operation = £ 5,000 per month; cost of project deadline failure = min. £ 200/day plus construction hold-up of 40 number £ 180k - £ 250k flats).

c) Significant reduction in pollution burden rather than transferral.

The combined treatments added *in situ* chemical oxidation (ISCO) and biotreatment / natural attenuation to DPVE alone. Although much of the contamination was removed through DPVE and enhanced DPVE recovery (principally in solution), a significant component of the contamination was addressed through ISCO and *in situ* bio / natural attenuation. The balance of this cannot however be quantified from the available data, as the project was a commercial remediation activity and not a formal pilot or technology evaluation endeavour.

d) Community and stakeholder acceptance.

Stakeholder acceptance demonstrated through securing regulatory remedial closure on budget and on schedule – all stakeholders most satisfied.

e) Compliance with health and safety.

No reportable H&S incidents through the project. Reagents employed present lower hazard / risk than other common ISCO agents and are supplied with MSDS's. Application in accordance with formal work plan method statements and COSHH assessments.

f) Genuine novelty.

These technologies have never been combined before. The enhanced mass-recovery benefit of RegenOx has not been commercially exploited before this time. The combined approach – ideally designed into projects from the onset – enables a powerful and effective segue between physical, chemical and biological treatment processes with attendant savings to cost and schedule whilst maximising the clean-up that can be achieved.

g) Represents a significant technological advance for the industry, with the opportunity for widespread application.

Opportunities for exploitation of this approach are as widespread as asymptotic pump-and-treat systems – the flexibility of design, dosage and variable emphasis on component technologies provides opportunities to apply the technologies in a wider range of soil types (high / low permeability, fractured systems), project conditions and contaminant concentrations than any component technology alone. Multiple project designs have followed this in the UK and elsewhere in Europe. The first of these to be approved are now underway.

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