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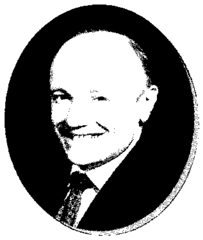
The Application of Innovative Strategies for Addressing Petroleum Impacted Groundwater



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유류에 의해 오염된 지하수와 지반의 처리시 오염 정도와 향후 부지 사용 목적에 따라 적절한 처리 기준을 정하는 것이 선행되어야 한다. 미 메사추세츠주에서는 오염물의 음용수에 대한 노출 정도에 따라 지하수의 오염처리 기준을 세분하는데, 그 중 가장 엄격한 것이GW-1 기준이고 반대로 가장 관대한 것은UCL 기준이다. 본 컬럼은 이 두 기준을 각각 적용한 사례연구를 통해 유류오염 지하수 및 지반 처리 기술을 소개하고 있다. – 김윤승(편집간사)

1. Introduction

The remediation of petroleum contaminated soil and groundwater continues to be a technical and regulatory challenge in the Northeastern portion of the United States. Regulations have changed in the recent few years that allow consideration of a property's use and location in developing a remedial strategy. However, this in turn has lead to challenges, on the one hand, in establishing what level of cleanup is necessary for a non-sensitive location and use and, on the other hand, in identifying strategies that will allow closure for a sensitive use and location. Massachusetts has a regulatory program that provides such consideration.

In Massachusetts, in areas where groundwater is and may be used for drinking water purposes attainment of very stringent drinking water standards (Maximum Contaminant Levels (MCLs)) must be reached. MCLs have been developed by the United

States Environmental Protection Agency for several specific compounds. For petroleum, these compounds include certain mono-aromatic compounds (i.e., benzene, toluene, ethyl benzene and xylenes) as well as a polyaromatic compound (benze(a)pyrene).

2. GW-1 and UCL

Beyond these federally promulgated standards, Massachusetts has developed a number of standards applicable to drinking water exposures for other compounds. These are known as GW-1 standards. GW-1 standards have been developed for a variety of compounds. Most notably for petroleum, GW-1 standards have been developed for specific fractions. These fractions are known as the volatile petroleum hydrocarbon (VPH) fractions (determined through a purge and trap/ gas chromatographic (GC) flame ionization detector (FID) method) and the extractable petroleum hydrocarbon (EPH) fractions (determined through a solvent extraction GC-FID method). GW-1 standards have been developed for six EPH/VPH fractions based on aromaticity and on the number of carbon atoms . For example, the C5 - C8 aliphatic hydrocarbon fractions includes all of the aliphatic hydrocarbons with between five and eight carbon atoms. The standards were developed by utilizing attributes for representative compounds for the fraction range (e.g., hexane for the C5 - C8 aliphatic fraction).

The current GW-1 standards for the EPH/ VPH fractions are :

VPH fractions:
- C5 - C8 aliphatic hydrocarbons - 400 ug/l
- C9 - C12 aliphatic hydrocarbon - 4,000 ug.l.
- C9 - C10 aromatic hydrocarbons - 200 ug/l

EPH fractions:
- C9 - C18 aliphatic hydrocarbons - 4,000 ug/l
- C19 - C36 aliphatic hydrocarbons - 5,000 ug/l
- C11-C22 aromatic hydrocarbons - 200 ug/l

In addition to these fractions, GW-1 standards have been developed for several individual constituents of petroleum (e.g., naphthalene).

At the other extreme, for sites in very non-sensitive exposure environments, Massachusetts has developed criteria referred to as Upper Concentration Limits (UCLs). UCLs have been developed for both soil and groundwater for a number of petroleum constituents including the EPH/ VPH fractions described above. Under the regulations, if the average concentration of a particular compound in either soil or groundwater exceeds the relevant UCL, then a significant potential risk to public welfare and the environment exists. In these instances it is not possible to attain a Permanent Solution. Thus, to reach a Permanent Solution the average concentration must be below the UCL.

The regulations also define a separate type of UCL which is applicable to petroleum. Specifically, the regulations state that :

The presence of non-aqueous phase liquids (NAPL) having a thickness equal to or greater than $\frac{1}{2}$ inch in any environmental medium shall be considered a level which exceeds Upper Concentration Limits.

From a practical standpoint for petroleum, this criterion requires that the average thickness of separate phase hydrocarbons (SPH) measured in monitoring wells at a site be below $\frac{1}{2}$ inch in order to attain a Permanent Solution.

The above criteria, in general, bracket the extremes of remedial requirements for groundwater at petroleum sites. For sites in very sensitive environments, GW-1 standards drive remediation, while for sites in non-sensitive environments, the UCL and, in particular, the requirement to attain an average thickness of $\frac{1}{2}$ inch SPH in monitoring wells is the driver.

The following presents two case studies regarding the application of innovative remedial strategies to address petroleum impacts to groundwater in each of these extremes - i.e., a sensitive drinking water scenario and a non-sensitive non-drinking water scenario.

Case Study 1 – Remediation of Petroleum Hydrocarbons in a Drinking Water Scenario

This first case study involves the remediation of groundwater at a former gasoline station to attain GW-1 standards. The use of aggressive chemical oxidation was required to reach the stringent standards. In addition, analytical issues were encountered due to the reasonably low standards and interferences posed by the chemical oxidation process.

Background

GZA's client was interested in purchasing the site of a former gasoline station for redevelopment as an automobile dealership. Petroleum hydrocarbon releases associated with underground storage tanks (USTs) were reported for the site by the prior owner. Impacted soil and groundwater were removed during the removal of the USTs; however, residual levels of petroleum remained in one wall of the excavation - beneath a building foundation. The then current owner was unwilling to remediate the identified contamination prior to the property transfer and wished to place the responsibility for remediation on our client. (This served some of our client's interests, in that, if he assumed responsibility for remediation, he could perform it concurrent with redevelopment, allowing the redevelopment to proceed more quickly.)

Based on our review of the available site information, GZA concluded that residual contamination had migrated from the area beneath the building foundation to the former tank grave. The soil in this grave was granular in nature compared to the relatively tight till located outside of the tank grave. Thus, most of the contamination was located within a relatively small area, but was relatively deep- up to 20 feet below the ground surface. Remediation was further complicated by the location of the Site in a "GW-1 area," necessitating attaining GW-1 standards in all monitoring wells. Based on this information, GZA concluded that chemical oxidation would be the most cost-effective remedial option for the identified contamination. We subsequently issued a contract to our client for using chemical oxidation to achieve a Permanent Solution under the regulations. We also committed to reaching closure within 6 months of contract award.

Implementation

Once the property transferred, GZA initiated our remediation efforts. We first collected samples of soil and groundwater from the site and conducted a range of lab-scale studies to identify the best mix of reagents. Based on this study, we determined that Fenton's Reagent (utilizing a proprietary iron source) cost-effectively provided rapid and complete oxidation. Fenton's Reagent involves the generation of hydroxyl radicals from hydrogen peroxide with iron as a catalyst. The hydroxyl radical is a very aggressive oxidizing agent, promoting very rapid oxidation of petroleum hydrocarbons.

We then installed a series of unsaturated zone trenches to the water table in which we placed slotted pipe and risers. The trenches were backfilled with gravel. We also installed a number of injection wells into the saturated zone in the impacted area. The Fenton's Reagent was added serially. Initially, hydrogen peroxide was added without a supplemental iron source. Naturally occurring iron was present in the aquifer and provided the iron catalyst for the Fenton's Reagent. As the naturally occurring iron was consumed (i.e., oxidized to ferrous iron), which was determined through observation of less vigorous off

gassing in the field, we added the proprietary iron source. In general, the iron source and peroxide injections were separated by several days. An injection manifold was manufactured to: a) control the volume of added chemicals, and b) provide a water source to dilute the added chemical to within the pre-determined concentration, to quench a strong subsurface reaction and to disperse the added chemicals out of the gravel backfill of the injection trenches into the formation

Results

Following several months of injections (12,000 gallons of 17.5% peroxide), the residual levels of petroleum in most wells were reduced to below the drinking water standards. However, the reported concentration of one VPH fraction, the C9-C10 aromatic fraction, remained above the standard. In fact the concentrations in one well had increased. GZA reviewed the analytical data and determined that the gas chromatographic analytical method had inappropriately identified ketones (essentially nontoxic oxidation byproducts of naturally occurring organic matter in the soil) as included in this fraction. We addressed this issue by using gas chromatograph/mass spectroscopy techniques for estimating the residual concentration of this fraction in groundwater. The results of this analysis indicated that the GW-1 standards had been reached in all monitoring wells, allowing us to issue a Permanent Solution for the site - within the timeframes required by the client.

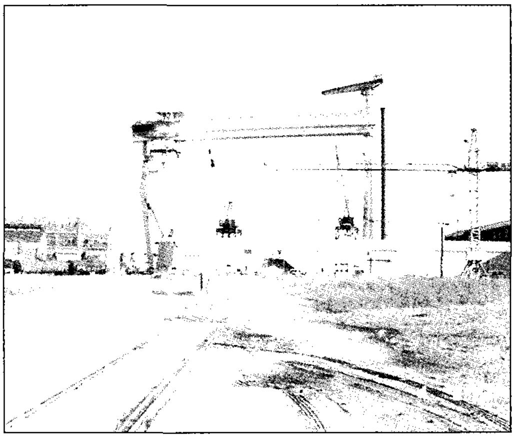
Case Study 2-Remediation of Petroleum Hydrocarbons in Groundwater in an Industrial Setting

This second case study involves the remediation of groundwater and more particularly SPH on the water table at a former shipyard to attain a Permanent Solution. The innovative application of pulse-pumping/ bioventing was employed to reach the UCL for SPH.

Background

As part of facility closure activities, GZA performed an environmental site investigation of this 180-acre shipyard property where industrial activity dates back over 100 years. Our services included extensive field investigations (including soil borings, monitoring well installations, soil and groundwater sampling, and a full range of laboratory analysis); risk assessment of the observed contamination; and follow up studies to define the source and extent of the contamination.

Contaminants identified at the site included oil, PCBs, and solvents. Performance specifications were proposed for remediation of the contaminated areas. In particular, a release of over 400,000 gallons of No. 2 fuel oil was identified in an area of the site which is



now known as the Central Yard Oil Plume (CYOP). Another environmental firm was contracted to perform passive and then active product recovery in this area. Over the course of a twelve year period, they recovered 300,000 gallons of oil from this area.

However, at the end of this period, the recovery rates were relatively low while the residual thickness on the water table remained significant (i.e., on the order of a foot or more in certain monitoring wells ; compared to the regulatory remedial objective of inch in the environmental medium).

GZA was asked to identify possible remedial technologies to accelerate remediation and/or reduce cost. We developed a computer flow model of the groundwater system to optimize the groundwater extraction and treatment system. The model was used to assess the costbenefit relationship of flow rate versus time to clean up. Beyond this, we assessed the efficacy of a number of innovative technologies for accelerating remediation at the site. These technologies include:

- Pulse pumping/bioventing
- Radio frequency heating of the capillary fringe

We also participated in a field-scale study of radio frequency heating and conducted a laboratory-scale study of pulse-pumping/bioventing to assess the feasibility of these technologies as well as to generate design bases for full-scale implementation. Based on the results of these assessments as well as a log transformed linear regression analysis of the data, the client selected GZA to implement pulse-pumping/bioventing for the CYOP on a turnkey basis.

Implementation

Pulse pumping/ bioventing employs a combination of groundwater extraction and aerobic biodegradation to treat petroleum hydrocarbons in the subsurface. In this technology, groundwater extraction is utilized to depress the water table. As the water table is lowered, SPH on the water table is smeared across the dewatered zone. Soil vapor extraction or bioventing is then employed to pull fresh air through this freshly dewatered zone, increasing the oxygen content of the zone and stimulating the aerobic biodegradation of the smeared hydrocarbons in the zone. The carbon dioxide content of the extracted soil gas is monitored and used as an indication of when the smeared hydrocarbons have been biodegraded. Once the carbon dioxide concentration in the extracted soil gas decreases, the groundwater extraction system is shut down and the water table is allowed to return to its non-depressed elevation. The process is then repeated until the cleanup criterion is attained. Throughout the process, SPH that accumulates on the water table is also recovered separately.

GZA's implementation of pulse-pumping/ bioventing at the shipyard involved the following:

- Installing five groundwater extraction wells (in addition to the 8 wells that had been previously installed by others).
- Installing 10 bioventing wells including 3 installed beneath a building utilizing angle drilling techniques.
- Upgrading the groundwater treatment system with a more efficient oil-water separator to limit

overall operation and maintenance costs.

- Installing pneumatic pumps in select groundwater extraction wells to limit the potential for iron fouling.

Results

GZA began operation of the system. Based on monitoring of the carbon dioxide concentration in the extracted soil gas, we performed 3 "pulses" of the groundwater extraction system over the course of two years, at which time the remedial goals for the system had been reached - one year ahead of the previously predicted timeframe of 3 to 5 years and 13 years quicker than had been predicted for more traditional active product recovery.

Conclusion

Remediation of petroleum hydrocarbons in the subsurface can present both technical and regulatory challenges. Various in-situ technologies of bioremediation (such as biodegradation, bioventing or biosulrping), thermal remediation (such as radio-wave heating, steam enhanced extraction, or electrical resistance heating), and chemical oxidation are often employed in combination with direct pumping/ extraction and ex-situ treatment techniques for remediation of subsurface petroleum hydrocarbons. Identifying rational remedial objectives based on site use and location is the key step for developing remedial strategies that target those objectives and allow closure to be attained in a timely and cost-effective manner.

About GZA

Founded in 1964 as Goldberg-Zoino & Associates, Inc., a soils and foundations specialty consultant, GZA GeoEnvironmental, Inc. (GZA) has grown into a full-service company providing its clients with a wide range of geotechnical engineering, environmental consulting, and remediation services. GZA employs nearly 450 engineers, scientists, and technical support staff in more than 22 offices in the U.S.