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Chapter 23

USE OF HIGH CONCENTRATION MAGNESIUM SULFATE SOLUTION TO REMEDIATE PETROLEUM IMPACTED GROUNDWATER

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Abstract: Anaerobic degradation is the dominant driving force in natural attenuation of petroleum contamination in the subsurface. The contribution to natural attenuation by electron acceptors other than oxygen, such as nitrate, iron III, manganese IV, sulfate, and even carbon dioxide, has been the subject of considerable research in recent years. Kolhatkar et al. (2000), Wiedemeier et al. (1999), and Wilson et al. (2002) have shown that of these natural anaerobic processes, sulfate reduction accounts for most of the degradation. The use of these alternative electron acceptors has been shown to have many potential advantages over the traditional approach of attempting to add dissolved oxygen to the plume. The case studies presented will demonstrate the benefits of using high concentrations of Magnesium Sulfate solution (>1,000 mg/l) to stimulate the biodegradation of petroleum contaminants in groundwater under field conditions at various sites. Many of these sites have had other technologies applied prior to applications. Graphics depicting the historical concentrations and reduction trends will be provided. In addition to the relatively rapid degradation of petroleum compounds such as benzene, toluene, ethylbenzene and xylenes (BTEX), this technology is quite cost effective in comparison to other currently available remediation techniques. A description of the technology, site selection criteria, dosage determination, and field scale performance results demonstrating contaminant concentration reductions in groundwater of more than 90% within a few months at some sites will be presented. Magnesium Sulfate was selected for use due to availability, low cost, high solubility and the relative safety associated with handling. This technology has advantages over others for many sites where physical limitations (buildings, utilities, etc.) preclude other technologies.

Key words: Groundwater remediation, petroleum, sulfate.

1. INTRODUCTION

The use of natural processes to remediate petroleum impacted groundwater in-situ is generally accepted practice. However, the length of time needed to reach regulatory required cleanup criteria is sometimes unsatisfactory. Enhancing natural processes to speed the rate of degradation would be very desirable. Anaerobic degradation is the dominant driving force in natural attenuation of petroleum contamination in the subsurface. The contribution to natural attenuation by electron acceptors other than oxygen, such as nitrate, iron III, manganese IV, sulfate, and even carbon dioxide, has been the subject of considerable research in recent years. Kolhatkar et al. (2000), Wiedemeier et al. (1999), and Wilson et al. (2002) have shown that of these natural anaerobic processes, sulfate reduction accounts for most of the degradation. The addition of these alternative electron acceptors has been shown to have many potential advantages over the traditional approach of attempting to add dissolved oxygen to the plume. Successful applications of relatively low concentrations of sulfate solution (<1,000 milligrams per liter (mg/l)) have been previously reported (Anderson et al., 2000; Cunningham et al., 2001). A process using high concentrations of sulfate solution (>1,000 mg/l) has
been developed to accelerate remediation and site incident closure. The case studies presented in this paper demonstrate the benefits of using high concentrations of Magnesium Sulfate Heptahydrate (MgSO₄) solution to stimulate the biodegradation of petroleum contaminants in groundwater under field conditions at various sites. In addition to the relatively rapid degradation of petroleum compounds such as BTEX, this technology is quite cost effective in comparison to other currently available remediation techniques. Magnesium Sulfate was selected for use due to availability, low cost, high solubility and the relative safety associated with handling. This technology has advantages over others for many sites where physical limitations (buildings, utilities, etc.) preclude other technologies.

2. MATERIALS AND METHODS

2.1 Misconceptions

While advocating this technology at various sites with regulatory agencies in many different states within the USA, we encountered many misconceptions about the technology. The following is a summary of these misconceptions and an explanation of why they are misconceptions.

2.1.1 Misconception # 1: Biodegradation requires aerobic conditions.

While many traditional remediation technologies have focused on increasing the available subsurface oxygen supply to stimulate aerobic degradation, anaerobic conditions exist at the majority of petroleum impacted sites (Chappell, 2000; Wiedemeier et al., 1999). This is because oxygen is quickly depleted on the upgradient side of the plume and indigenous anaerobic bacteria, which are almost universally present in the shallow subsurface (Ghiorse and Wilson, 1988), will bloom in the absence of oxygen. Anaerobic biodegradation has been documented to be the dominant mechanism for natural attenuation at many sites (Kolhatkar et al., 2000).

2.1.2 Misconception # 2: This is in-situ direct oxidation (Persulfate Radical).

This process does not utilize persulfate. The generation of Persulfate Radicals is an entirely unrelated process. The technology presented in this paper is a process to enhance natural biodegradation by replenishing a locally depleted electron acceptor (Sulfate).

2.1.3 Misconception # 3: Anaerobic Biodegradation is too slow to be feasible.

In fact, for the majority of petroleum impacted sites anaerobic biodegradation is the dominant component of natural attenuation whether enhanced or not (Kolhatkar et al., 2000). Monitored Natural Attenuation is an accepted remedial approach by many regulatory agencies within the USA. The process presented in this paper is predicated on the enhancement of this ongoing natural process.

2.1.4 Misconception # 4: Hydrogen Sulfide gas will be generated.

While Sulfide is a byproduct of the reaction, under typical field conditions there are adequate concentrations of dissolved metals, such as Ferric Iron, to bond with the Sulfide. Hydrogen Sulfide gas generation has not been an issue at any of the sites where this technology has been utilized, but if it is a concern it should be monitored.
2.1.5 Misconception # 5: Addition of the application material will result in increased plume migration.

The use of a higher concentration solution results in the application of lower volumes to introduce the desired mass of Sulfate to the contaminant plume. Typical site application volumes are on the order of 500 to 1,000 gallons applied over a period of four to eight hours. Since the typical fluid volume in the target area of the aquifer is greater than 100,000 gallons, the MgSO₄ solution added is less than 1% of the aquifer volume. Post application monitoring performed has not documented contaminant plume migration to previously unimpacted areas on any sites where this technology has been utilized.

2.1.6 Misconception # 6: This technology will result in a lingering sulfate contaminant plume in the groundwater.

The feasibility evaluation process for this technology is intended to assure that favorable conditions exist for the utilization of Sulfates by the existing bacteria population. Applications are made in iterative steps to minimize the potential for applying more Sulfate than is required to adequately degrade the contaminants.

2.2 Technology Description

The material utilized in this process is a custom-blended, aqueous solution of agricultural grade MgSO₄, or simply hydrated magnesium sulfate, which is commonly known as Epsom Salts. Our supplier is Livingston Fluid Services, Inc. of Howell, Michigan. For the case studies discussed in this paper, the solution applied contained a target concentration of approximately three pounds of MgSO₄ per gallon. Analytical testing of several batches of the application material indicates a typical Sulfate concentration of 140,000 mg/l. The use of this relatively high concentration application material minimizes the volume of solution needed to introduce the desired amount of Sulfate to the contaminant plume which reduces potential transportation costs. Another benefit of using a relatively highly concentrated application solution is that less time is required on site to complete the application. The application material was delivered to the case study sites by bulk tanker truck, in steel drums, or in plastic containers.

2.3 Site Selection Criteria

The potential for applicability of this technology at a given site is based on a limited number of readily determined factors. Most important is an evaluation of the concentrations of electron acceptors within and outside of the extent of the contaminant plume. If the electron acceptors within the plume are depleted in comparison to non-impacted background locations, there is a clear indication that the existing bacterial population is capable of degrading the contaminants and the limiting factor is the availability of electron acceptors. Therefore, the addition of sulfates is likely to increase the degradation of contaminants.

In the event that the site contains an appreciable quantity of liquid phase product (LPH), it may be more cost effective and expeditious to initially use other techniques to address the highly impacted source material. Once the majority of the LPH has been removed, sulfate addition may be a cost effective method to address the residual impact.

Sulfate addition may not be suitable as the only remediation technique if site conditions indicate that hydraulic plume control is warranted or if a sensitive receptor, such as a drinking water supply, is immediately threatened.
2.4 Dosage Determination

Site specific dosage is estimated by first calculating the desired volume of impacted groundwater to be treated and then determining the mass of sulfate needed to raise the average concentration within this volume by 250 mg/l. An experience based site specific demand factor of one to five is then used to develop the site specific dosage. The site specific demand factor is based on the relative degree of impact, groundwater flow velocity, results of previous site sulfate applications or pilot studies, proximity of sensitive receptors, and background sulfate concentrations.

2.5 Application Techniques

2.5.1 Surface Applications

Sulfate exists naturally in most groundwater. It is highly soluble compared to other electron acceptors and has a high capacity to reduce contaminant mass. Sulfate is a key factor in the degradation of contaminates in matured plumes. Sulfate is relatively less expensive than other treatment technologies and for select sites may be significantly less costly based on the advantages identified above.

Sulfate can be applied by three primary application methods. Because of this flexibility, it is applicable to a wide range of sites. The three primary application techniques include surface or dry application, application in designated application wells that intersect the target groundwater treatment zone, or liquid application through infiltration trenches that distribute the sulfate over a target area.

Surface, or soil mixing, application can be very effective for select applications. Selected applications where sulfate, supplied as Calcium Sulfate (Gypsum), has been mixed with backfill material, approximately 1% by volume, have been proven to aid in the degradation of residual contamination that may remain at the limits of the excavation. The cost for this material is minimal and the onsite application is simple and does not represent additional hazards to workers. Surface applications have also been performed over vegetated areas where shallow groundwater contamination is targeted. Application via surface application requires a few key site conditions to improve effectiveness. The rate at which the sulfate can reach the contaminant will be dependant on the soil porosity, groundwater movement, and dispersion. In the presence of oxygen, the sulfate reducing microorganisms are less active and there would be an expected delay in the degradation rate of the contaminant. In most cases, this has not been observed to significantly effect the overall time.

In all case study sites, degradation under sulfate reduction already appears to be the primary driver and the lag time by introducing oxygen through infiltration of rain or application of backfill material appears limited.

2.5.2 Application Wells

Application of high concentration solution through application wells has been demonstrated to be effective for remediation of dissolved contaminant plumes. Application wells are installed and screened across the target zone. Dose applications can be derived based on the treatment area and mass of contaminate. Premixed solution is delivered to the site and can be directly discharged into the application wells. Application rates will vary depending on the porosity of the soil which directly affects the ability of the well to disperse the solution into the contaminated area. Because this can be a factor on many sites with tight soils, higher concentrations of sulfate solutions are less expensive to apply than would be a more dilute solution. We have observed that it is not practical to field mix these batches to meet selected application rates. The monitoring well network surrounding the application well is a critical component to this type of application. The objective is to apply a sufficient amount of sulfate to be consumed by the degradation of the contaminant while at the same time reducing the amount of introduction water that may have an adverse effect on the plume.
2.5.3 Application Trenches

The third application technique involves the construction of an infiltration trench with a header system to increase the area of the application. A trench backfilled with porous material serves as a below grade engineered distribution system. The granular backfill being more porous than the target soil serves to improve the application rate, reducing the amount of time to introduce the target sulfate addition, and also increase the distribution during the application. Trench dimensions are determined by the estimated amount of individual applications, physical site restrictions, and dimensions of the plume. A header system to distribution piping is typically constructed to aid in uniform distribution in the trench initially but also serves to facilitate targeting areas where additional applications may be required. This approach requires more surface construction than application wells but may ultimately reduce the number of site applications.

3. RESULTS

There are many benefits to providing sulfate as the terminal electron acceptor. As anaerobic conditions naturally prevail under petroleum impacted sites, this technology enhances processes that are already occurring. The high solubility of sulfate provides an engineering option that reduces cost and minimizes hazards. The lower energy reactions also require less nutrient supplementation and produce less secondary precipitates which can be costly to manage. Since one mole of sulfate has twice the oxidizing capacity of oxygen, sulfate is extremely efficient at target area reduction. This is the primary benefit that makes this a cost feasible option.

The injection of MgSO$_4$ is an in-situ remedy which promotes anaerobic biostimulation. Biostimulation refers to the manipulation of environmental conditions to enhance and accelerate biological degradation of contaminants through microbial respiratory metabolism. This process occurs through the oxidation of an organic compound, such as petroleum constituents, with the reduction of an inorganic compound (electron acceptor). Aerobic respiration utilizes oxygen as the terminal electron acceptor, while anaerobic respiration utilizes nitrate, sulfate, ferric iron, manganese oxide, and/or carbonate as the terminal electron acceptor. When the availability of these electron acceptors is limited in subsurface conditions and groundwater flow is not effective in replenishing the depleted electron acceptors, providing an additional source is often the most effective form of remediation. The distribution and availability of electron acceptors controls the rate of biodegradation. As mentioned above, these acceptors are depleted at a rate significantly higher than can be naturally replenished.

3.1 Case Studies

3.1.1 Potterville, Michigan

Magnesium sulfate was applied by surface spreading in the vicinity of the former UST cavity and dispenser islands (Figure 1) at a vacant retail gasoline site in Potterville, Michigan. The UST systems were removed from the site in 2001. Confirmed releases were reported in 1992 and 2001. Historically, remediation has been unsuccessfully attempted with the use of various techniques including a High Vacuum Extraction system, monitored natural attenuation (MNA), bioaugmentation, and oxygen diffusion. Approximately 1,200 pounds of magnesium sulfate were applied to the site by surface spreading of dry material during four events which occurred between October 2002 and March 2004. In addition, liquid applications of 525 gallons in July 2004, 501 gallons in August 2004 and 651 gallons in September 2004, were completed.
The geological setting at the site is predominately silty clay with granular fill material within the former UST cavity. Groundwater is perched approximately one to two feet below the ground surface. The pavement at the site has been removed. Liquid phase hydrocarbons have been encountered as recently as March 2003.

The following three graphs depict the relatively rapid degradation of the BTEX constituents once the sulfate concentration was enhanced. In all three cases, the toluene concentrations appear to be most rapidly depleted. The graphs also substantiate that the concentrations of contaminants were permanently reduced even after the sulfate concentrations were depleted. Post application monitoring of observation wells surrounding the impacted area did not indicate any migration of the contaminant plume or any increase in sulfate concentrations which further substantiates that the significant reductions in contaminant concentrations are due to degradation and not dilution.
Figure 2. OW-4
Figure 3. OW-18
3.1.2 Midland, Michigan

Magnesium sulfate was applied to the subsurface by a series of 10 dedicated application wells (Figure 5) at a former retail gasoline site in Midland, Michigan. The site has been developed as a shared parking area for the local municipality and a neighboring church. Confirmed releases were reported in 1988 and 2000. Historically, remediation has been unsuccessfully attempted with the use of various techniques including a groundwater recovery system, monitored natural attenuation (MNA), and bioaugmentation. Four applications were completed as follows: 660 gallons in September 2003; 735 gallons in May 2004; 767 gallons in July 2004; and 527 gallons in September 2004.
The geological setting at the site consists of six to eight feet of predominately fine grained sand overlying clay. Groundwater is perched on top of the underlying clay and is encountered approximately six to eight feet below the ground surface.

Similar to the graphs from the other case studies, the following graphs depict the relatively rapid degradation of the BTEX constituents once the sulfate concentration was enhanced. In this case, the concentrations of all of the BTEX constituents have been reduced to near or below the method detection limits. At the OW-3AR location benzene, toluene and xylene concentrations diminished quickly post application. Ethylbenzene degradation proceeded at a slower pace, but eventually degraded as well. Post application monitoring of observation wells surrounding the impacted area did not indicate any migration of the contaminant plume or any increase in sulfate concentrations which further substantiates that the significant reductions in contaminant concentrations are due to degradation and not dilution.
Midland Michigan OW-19 B,T,E,X vs. Sulfate

Figure 6. OW-19
3.1.3 Indianapolis, Indiana

A magnesium sulfate solution was applied to an infiltration trench system at a former retail gasoline site in Indiana (Figure 8). The site is currently operated as a commercial bank and coffee shop. The trench was installed prior to site construction. This is a historical release site that has had a groundwater recovery system and over excavation activities completed in mid 1990’s and early 2000. Three separate applications have been completed including 1,850 gallons in June 2004, 1,860 gallons in July 2004, and 2,500 gallons in October 2004.
Biostimulation through anaerobic respiration was selected to address residual petroleum hydrocarbon impacts that exceeded the approved natural attenuation targets. Access to contaminated areas in shallow groundwater was restricted due to the current use of the property. Other remediation alternatives were evaluated including oxygen enhancements and system installation. The cost of the sulfate applications was approximately half of the modeled oxygen enhancement methods and 1/3 the estimated lifecycle system cost, if site constraints could be eliminated.

Sulfate concentrations were closely monitored in wells within the contaminated area and background wells assumed outside the influence of the release. This was important to understand the rate at which the sulfate was being consumed, to monitor elevated concentration migration and to determine if additional applications were required. Between May 2004 and January 2005, BTEX concentrations were significantly reduced. In many wells, the reduction was greater than 85%, representing a relatively rapid reduction over the affected area. Since January 2005, construction of confirmation wells and additional sampling have demonstrated that concentrations have been
remediated to a level that is consistent with MNA as a final remedial option. These levels were not reached through previous source area excavation and operation of a remediation system at this site.

Site information was collected to demonstrate that the addition of sulfate solution did not dilute or push the contaminant plume. Groundwater sample results as reported by the laboratory indicated that sulfate did influence the target application area and that BTEX concentrations during that same time were not being spread. Water levels in monitoring wells were studied to support the idea that the application was not flushing the contaminant plume. The total volume of solution represents about 9% of the assumed saturated volume in the aquifer, or about 1.5 inches of rain recharging the aquifer based on the impervious surface area available. This site receives approximately 40 inches of rain each year and prior to application the plume was demonstrated to be stable.

The following graphs demonstrate the reduction in contaminate levels at this site.

![Figure 9. OW-3RR](https://scholarworks.umass.edu/soilsproceedings/vol12/iss1/24)
3.1.4 Illinois Pilot Study

A multi-site pilot study has been initiated in cooperation with the Illinois Environmental Protection Agency. Three of the sites included in the pilot study are Rantoul, Antioch and Springfield, Illinois. All three of these sites are retail gasoline stations with historical confirmed
Contaminated Soils- Remediation

Releases of gasoline. Geology at each site consists predominately of silty clay. Horizontal trenches were installed at each site to facilitate the distribution of sulfate solution. At the Rantoul site, 4,920 gallons of solution were applied in July 2005. Two applications were made at the Springfield site, 1,721 gallons in July 2005 and 2,723 gallons in October 2005. In November 2005, 4,920 gallons of solution were applied at the Antioch site.

The following graphs (Bruce and Kolhatkar, 2006) compare the attenuation rates before and after sulfate application. At the Antioch and Springfield sites, the addition of sulfate enhanced biodegradation of benzene, toluene and xylenes during the post application monitoring period. The toluene degradation rate was significantly increased at the Rantoul site.

Antioch, Illinois – MW-8 : BTEX Attenuation Rates
Before and After Sulfate Addition

![Graph of BTEX Attenuation Rates](image)

Note, the “NA” rate in this graph is an average from published data.

Figure 12. MW-8
Rantoul, Illinois – MW-1 and MW-11 Attenuation Constants
Before and After Sulfate Application

![Graph showing rate constants for MW-1 and MW-11 before and after sulfate application](image)

**Figure 13.** MW-1 and MW-11
3.1.5 New York Pilot Studies

A pilot study was conducted on a former retail gasoline station located in New York State from March 2006 to June 2006. Approximately 200 gallons of sulfate solution was applied through an application well during March 2006 and post application monitoring was conducted on a monthly basis for three months from surrounding wells. The following graph represents the data collected from observation well PT-4 which was located approximately 15 feet downgradient of the application well. The monitoring data indicates a reduction in each of the BTEX constituents, but the most significant reductions were noted in the Toluene and Xylene concentrations. While significant reductions in contaminant concentrations were noted, little change in sulfate concentrations was observed which is believed to be indicative of the utilization of the added sulfates prior to dispersion to the PT-4 location. Evaluation of the Pilot Study results was utilized to design a full scale remediation plan and to refine the site specific demand factor.
Figure 15. Clinton Site Map
4. DISCUSSION

Enhancement of biodegradation with the addition of sulfates is an exciting new option to safely, inexpensively and aggressively remediate petroleum impacted groundwater. Most historical release sites are already in an anaerobic reduction phase and are limited primarily by the lack of sulfate. The microorganisms are acclimated to this environment and the response has been quick on the pilot sites. The case studies clearly demonstrate that enhancement of the sulfate concentrations results in rapid decreases in BTEX concentrations. These sites were carefully selected and have geologies that promote the efficient application of the solution. Monitoring demonstrated that the contaminant plume was not simply diluted or displaced. Degradation was observed in the expected order, starting with the heavier end hydrocarbons. Sulfate concentrations were observed to be depleted and based on application calculations were consumed within the plume.

Utilization of a concentrated, aqueous solution of sulfate facilitates the distribution of this electron acceptor to the impacted aquifer with a variety of delivery techniques. Site geology is an important consideration in selecting any remedial alternative. Pre- and post-application monitoring is important to understand the application rates and as indicated in the pilot sites may be the most important variable in understanding the rate of reduction.

Toluene and xylene appear to be the easiest to degrade, but the case studies demonstrate that treatment to stringent standards is possible for all of the BTEX constituents.

5. CONCLUSION

When applied appropriately, the addition of sulfate to stimulate existing anaerobic bacteria can be a very effective remediation technique. This approach to site remediation involves the installation of

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Figure 16. PT-4

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a minimum of site infrastructure and avoids the typical pitfalls associated with ongoing operation and maintenance of mechanical remediation systems. While some of the BTEX compounds are preferentially degraded in the presence of sulfates, it appears that all are amenable to treatment with this technique and remediation to regulatory standards is achievable. The results demonstrated using this technology show great promise in expeditiously and cost-effectively remediating petroleum contaminant plumes.

REFERENCES


