Development of a Treatability Study Work Plan for Testing Nanoparticles at a US DOE Superfund Site

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Abstract

This paper introduces the basic requirements for developing a treatability study work plan for implementation of a remediation technology at a Superfund site. Specifically, the application of nanoparticle technology for remediation of a TCE plume at the Paducah Gaseous Diffusion Plant in western Kentucky is discussed.

Site Description

The Paducah Gaseous Diffusion Plant (PGDP) is the only active uranium enrichment facility in the United States. Located in the western part of McCracken County, KY, the facility is approximately 10 miles west of Paducah and 3.5 miles south of the Ohio River (Figure 1). The plant is located on a US DOE reservation that encompasses approximately 3,500 acres, including property leased to the state of the Kentucky to augment the West Kentucky Wildlife Management Area (WKWMA). The WKWMA provides an effective buffer around the 748 acres that comprise the plant's main industrial operations (DOE, 2006).

US DOE property is bordered to the north by the Tennessee Valley Authority (TVA) Shawnee Steam Plant which, along with another facility in Missouri, provides electricity to the PGDP. US DOE property is bordered to the south and west by the WKWMA. Several private properties directly border US DOE property to east. Residential and agricultural properties to both the plant's east and west have been affected by a TCE groundwater plume (Figure 2). An additional Technetium-99 (Tc99) plume also exists, but all concentrations above MCLs currently are contained within US DOE property boundaries. Surface water from the PGDP is discharged into a series of drainage channels east and west of the plant; these channels flow into Little Bayou and (Big) Bayou creeks as shown in Figure 2 (KRCEE, 2007).

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Currently, three distinct TCE groundwater plumes emanate northeast, northwest and southwest of the PGDP (see Figure 2). The northeast plume, which is beyond the DOE property, includes both TCE (at concentrations above MCLs) and Tc99 (at concentrations below MCLs); however, only TCE has been detected in the northwest and southwest plumes. The northeast and northwest plumes currently are managed by separate pump and treat facilities, as shown in Figure 3. Groundwater from the northeast plume is pumped back to the PGDP, where it is air stripped using existing cooling towers. Groundwater from the northeast plume is pumped from both pumping fields back to the PGDP, where the water is treated before being discharged into Little Bayou Creek. Importantly, as a result of the site's geology, parts of the northeast plume have been found to migrate to the surface, where it then discharges into Bayou Creek through a series of springs.

Site History

In 1988, the Kentucky Cabinet for Human Resources (CHR) Radiation Control Branch (RCB) discovered Technetium-99 (99 Tc) in private drinking-water wells northwest of the Paducah Gaseous Diffusion Plant (PGDP). Technetium-99, a man-made radioisotope that is a by-product of nuclear fuel rod fissioning, was introduced to the PGDP enrichment process through spent nuclear fuel rods from the US DOE Savannah River nuclear facility. The discovery of 99 Tc and, subsequently, Trichloroethylene (TCE) in drinking-water wells led US EPA and US DOE to enter into a formal Administrative Consent Order (ACO) under Sections 104 and 106 of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). The ACO required that US DOE investigate and address the nature and extent of the PGDP-related contamination and its potential impacts on human health and the environment.

On May 13, 1991, the Commonwealth of Kentucky and US DOE signed an Agreement in Principle (AIP). This non-regulatory program provides funding for independent, impartial, and qualified assessments of past, present, and future environmental and health issues related to but not addressed by CERCLA and other regulatory programs at contaminated US DOE sites. Agreements in Principle were initiated by US DOE to provide funding for additional data collection and assessments in response to potential public distrust of the agency related to cleanup of existing sites.

On August 19, 1991, Kentucky issued US DOE a Resource Conservation Recovery Act (RCRA) permit for the treatment and storage of hazardous PGDP wastes. The RCRA permit requires US DOE to comply with environmental laws and regulations in the cradle-to-grave management of hazardous wastes, worker safety, record keeping, emergency planning and prevention, and protection of public health and the environment.

On May 31, 1994, US EPA placed the PGDP on the Superfund National Priorities List (NPL), which identifies contaminated sites across the nation that US EPA has designated as high priority based on potential threats to human health and the environment. Following a site's addition to the NPL list, federal law requires that responsible state and federal agencies enter into a Federal Facilities Agreement (FFA) outlining the agencies' roles and responsibilities. These include investigation and implementation of corrective measures, as well as the integration of state and federal cleanup requirements into an effective and comprehensive process. After four years of negotiation, US DOE, US EPA, and the Commonwealth of Kentucky formally signed the FFA in 1998.

As part of the FFA agreement, management of clean-up efforts first involved characterization of all potential sources of contamination into solid waste management units (SWMUs) or Areas of Concern (AOC). This process included a qualitative evaluation of contaminant types and concentration, release mechanisms, likely exposure pathways, estimated points of exposure, and potential receptors based on current and reasonably foreseeable future land and groundwater uses. These sources were then grouped into one of five media-specific Operable Units (OUs):

- Groundwater OU
- Surface Water OU
- Soils OU
- Burial Grounds OU
- Decontamination and Decommissioning OU
- Comprehensive Site OU

Subsequent management activities associated with each OU typically involve several phases including: 1) remedial investigation, 2) baseline risk assessment, 3) feasibility studies, 4) record of decision/selection of a particular remedial action, 5) remedial design, and 6) remedial action. In most cases, management of each OU involves several different projects that address the contamination/risk issues associated with one or more SWMUs or AOCs. For example, the Groundwater OU includes several different projects: 1) on-site TCE source remediation, 2) the northwest and northeast plumes, 3) the southwest plume, and 4) potential sources associated with two off-site landfills. Specific timelines for each of these projects are established and tracked via the FFA and an annual Site Management Plan developed by US DOE. Assurance of project performance is provided by a CERCLA five-year review process.

KRCEE

The Kentucky Research Consortium for Energy and Environment was created in 2003 as part of a US DOE federal earmark appropriation facilitated by Senator Mitch McConnell. The consortium was created to help address myriad technical issues associated with PGDP clean-up activities by leveraging university expertise, both within Kentucky and regionally, to supplement the work of specific DOE laboratories and contractors. To date, KRCEE has overseen nearly 30 separate research projects -- many involving actual work at the site -- that have addressed such disparate concerns as seismic issues, groundwater contamination, surface water and sediments, volumetrically contaminated metals, and sensor technologies.

This paper summarizes ongoing efforts to field test the use of bi-metallic nanoparticles to remediate several large TCE plumes that radiate north and west from the PGDP toward the Ohio River (see Figure 2). To date, more than 44 applications of nanoparticles for groundwater remediation have been documented at various contaminated sites, both within the US and internationally (Karn, 2009). This paper focuses on the regulatory requirements associated with such implementations and, specifically, on regulations associated with conducting a treatability study at an active US DOE Superfund site.

Treatability Studies

A treatability study typically includes a series of laboratory, bench, pilot, and/or field tests that provide critical data for the evaluation of the technical, regulatory, and economic feasibility of a particular remediation technology. Several factors influence the practicality, level, and scope of the tests, including the particular phase of the remediation process (e.g., remedial investigation and feasibility study versus record of decision and remedial action), technology-specific factors, and site-specific factors (e.g., the magnitude of pollution, depth of the groundwater aquifer, in-situ versus ex-situ treatment, etc).

A key issue in the implementation of a new technology at a Superfund site is insuring that the technology has been tested and accepted prior to reaching a critical point in the existing site management plan. The timeline for the dissolved phase component currently allows for an examination of different possible treatment technologies, including the use of nanoparticles (DOE, 2009).

Levels of Treatability Studies

Three different levels of treatability studies are typically performed prior to incorporation of a particular remediation technology into the final record of decision at a Superfund site. These levels are summarized in Table 1. Remedy screening normally is used to determine the feasibility of a particular technology. Remedy selection is then used to develop performance and cost data. Finally, if feasible, RD/RA is used to develop detailed design and cost data and to confirm full-scale performance.

This paper focuses on the requirements to develop a treatability study that addresses the remedy selection phase of proposed implementation. Previous bench scale research using both media and contaminated groundwater from the site already have demonstrated the potential applicability of the proposed technology at the site (Meyer, et. al., 2008). The basic CERCLA evaluation criteria for proposed technology are summarized in Table 2 (USEPA, 1992).

Components of a Treatability Study

All treatability studies consist of the three basic components that are summarized in Table 3 (USEPA, 1992). This project currently is focused on the completion of Phase I. In general, the treatability work plan will include several different sections as summarized in Table 4 (EPA, 1992). Critical to its development is the Data Quality Objectives Development Process (see Table 5). The treatability study’s ultimate objective is to gain an understanding of the feasibility and effectiveness of the proposed technology. This information is then summarized in a final treatability study report. An example of the typical contents of such a report is provided in Table 6 (EPA, 1992).

Table 1. Levels of Treatability Studies (EPA, 1992)

Level	Scale	Waste Stream Volume	Time Required	Potential Cost Range $
Remedy Screening	Bench Scale (off –site)	Batch	Days	$10,000 to $50000
Remedy Selection	Bench or Pilot	Batch or Continuous	Days/ Weeks	$50,000 to $100,000
	Pilot or Full Scale (on site)	Continuous	Weeks /months	$50,000 to $250,000
RD/RA	Full Scale (on-site)	Continuous	Weeks /months	$250,000 to > $1,000,000

Table 2. CERCLA Evaluation Criteria for Remediation Technologies (EPA., 1992)

I.	**Threshold Criteria**
1.	Overall Protection of Human Health and the Environment
2.	Compliance with Applicable or Relevant Appropriate Requirements (ARARs)
II.	**Primary Balancing Criteria**
1.	Long-term Effectiveness and Performance
2.	Reduction of Toxicity, Mobility, and Volume through Treatment
3.	Short-Term Effectiveness
4.	Implementability
5.	Cost
III.	**Modifying Criteria**
1.	State Acceptance
2.	Community Acceptance

Proposed Treatability Studies

Two treatability studies associated with the PGDP northeast plume currently are under consideration. The northeast plume was chosen for several reasons, including: 1) the pre-existence of a pump and treat system that provides the possibility of replacing an existing treatment cell with a cell that contains the proposed technology, 2) an abundance of geologic and monitoring data, 3) confinement of most of the plume underlying either the WKWMA or the TVA property, and 4) access to the northern extent of the plume

Table 3. Treatability Study Protocol (EPA, 1992)

Phase I: Develop the Treatability Study Work plan
1. Establish the data quality objectives for the study
2. Identify all relevant ARARs
3. Assemble all the needed technical information for the proposed technology

4. Assemble the needed site data for the study
5. Identify all relevant waste management issues
6. Identify the experimental procedures and design the experiment
7. Prepare the final work plan
Phase II: Prepare the Supporting Plan Documents
1. Prepare the Sampling and Analysis Plan
2. Prepare the Health and Safety Plan
3. Prepare the Community Relations Plan
Phase III: Execute the Plan
1. Execute the treatability study, with emphasis on collecting and analyzing data
2. Conduct community relations activities in support of the study
3. Comply with regulatory requirements for testing and residuals management
4. Analyze and interpret the data, including a discussion on statistical analysis methods
5. Report the results in a logical and consistent manner

Table 4. Typical Components of a Treatability Study Work plan (EPA, 1992)

I.	**Introduction**
1.	Background Information
2.	Regulatory Compliance
II.	**Treatability Study Goal and Objectives**
1.	Treatability Study Goal
2.	Treatability Study Objectives
3.	Data Quality Objectives
III.	**Description of Treatment Technology**
IV.	**Experimental Approach/Design**
V.	**Equipment Design and Experimental Procedures**
1.	Design Criteria
2.	Process Description
3.	Equipment Description
4.	Operations and Maintenance Requirements
5.	Experimental Procedures
6.	Sampling and Analysis
7.	Data Management
8.	Date Reporting
9.	Waste Management Plan

through the recharge zone in Bayou Creek. The first proposed study would involve an ex-situ evaluation of the proposed technology, substituting it in one of the treatment units associated with the northeast pump and treat system. In this case, the associated nanoparticles would be fixed physically to a series of membranes, thus insuring that they would not be discharged into Little Bayou Creek via treated groundwater. Should the results of this study prove promising, an in-situ test would be performed in which the proposed nanoparticles would be injected into one of many existing boreholes or monitoring wells; the resulting remediation efficiency would be evaluated using existing down gradient monitoring wells or by monitoring the discharge of the plume in Bayou Creek. Prior to the second treatability study, a detailed tracer study utilizing the proposed injection well would verify the hydraulic characteristics of the local aquifer and confirm the feasibility of the well for delivery of the nanoparticles.

Table 5. Data Quality Objectives Development Process (EPA, 1992)

	Stage 1
1.	Identify Data Users
2.	Consult Appropriate Databases for Relevant Information
3.	Develop a Conceptual Model of the Site
4.	Identify the Treatability Study Test Objectives and Performance Goals.
	Stage 2
1.	Identify Data Uses
2.	Identify Data Types
3.	Identify Data Quality Needs
4.	Identify Data Quantity Needs
5.	Evaluate Sampling and Analysis Options
6.	Review Precision, Accuracy, Representativeness, Completeness, and Comparability Parameters
	Stage 3
1.	Determine DQOs; Select Methods for Obtaining Data of Acceptable Quality and Quantity.
2.	Incorporate DQO's into the Work Plan and the SAP

Environmental Considerations and Alternative Implementation Strategies

Despite the successful application of nanoparticles in several remediation projects, there is growing concern among the environmental and regulatory community about the ultimate disposition of nanoparticles that are dispersed into the environment. This is especially true when such dispersement has the potential for subsequent exposure of nanoparticles to humans. These concerns were highlighted recently when Karn et. al. (2009) examined potential benefits and possible risks of using nanoparticles for in-situ applications. One purpose of the current study, however, is to demonstrate the feasibility of the proposed nanotechnology in either an ex-situ (within the current pump treatment system) or an in-situ situation. Given the physical characteristics of the groundwater aquifer (e.g., the discharge zone to the surface water body of Bayou Creek), it also may be possible to apply the nanotechnology in a membrane-bound form at the point of discharge. This may be done directly using the stream itself or, possibly, in combination with another technology known as a geo-siphon that is currently under consideration. Finally, additional research could lead to an in-situ application in which nanoparticles can be forced to precipitate out within the groundwater aquifer. This would be driven by modifying groundwater pH through the utilization of down gradient monitoring wells located between the possible injection point and the discharge zone of the Bayou Creek. The feasibility of this approach will be examined in future studies.

Table 6. Typical Contents of a Final Treatability Study Report

1. Introduction
1.1 Site Description
1.1.1 Site Name and Location
1.1.2 History of Operations
1.1.3 Prior Removal and Remediation Activities
1.2 Waste Stream Description
1.2.1 Waste Matrices
1.2.2 Pollutants/Chemicals
1.3 Treatment Technology Description
1.3.1 Treatment Process and Scale
1.3.2 Operating Features
1.4 Previous Treatability Studies at the site
2. Conclusions and Recommendations
2.1 Conclusions
2.2 Recommendations
3. Treatability Study Approach
3.1 Test Objectives and Rationale
3.2 Experimental Design and Procedures
3.3 Equipment and Materials
3.4 Sampling and Analysis
3.5 Data Management
3.6. Deviations from the Work Plan
4. Results and Discussion
4.1 Data Analysis and Interpretation
4.1.1 Analysis of Waste Stream Characteristics
4.1.2 Analysis of Treatability Study Data
4.1.3 Comparison to Test Objectives
4.2 Quality Assurance/Quality Control
4.3 Costs/Schedule for Performing the Treatability Study
4.4 Key contacts
REFERENCES
APPENDICES
DATA SUMMARIES
STANDARD OPERATING PROCEDURES

Summary and Conclusions

This paper has provided a brief overview of the technical and regulatory issues associated with conducting a treatability study at an existing Superfund site. In this case, the use of bi-metallic nanotechnology to treat TCE-contaminated groundwater is under investigation. Two possible implementation approaches are under consideration: 1) an ex-situ application that would use an existing pump and treat system and membrane bound nanoparticles, and 2) an in-situ application in which nanoparticles would be injected into the contaminated aquifer.

The current research will provide new insights into the applicability of bi-metallic nanoparticle technology for treating contaminated groundwater plumes. This approach takes into consideration both technical challenges and growing environmental concerns about the use of such technologies in for groundwater remediation.

Acknowledgments

This work was supported by the DOE and KRCEE through contract DE-FG05-03OR23032 and by the NIEHS-SRP P42ES007380 and NIEHS-SRP P42ES007380-13S2. The content is solely the responsibility of the authors and does not necessarily represent the official views of the U.S Department of Energy nor the National Institute of Environmental Health Sciences or the National Institutes of Health.

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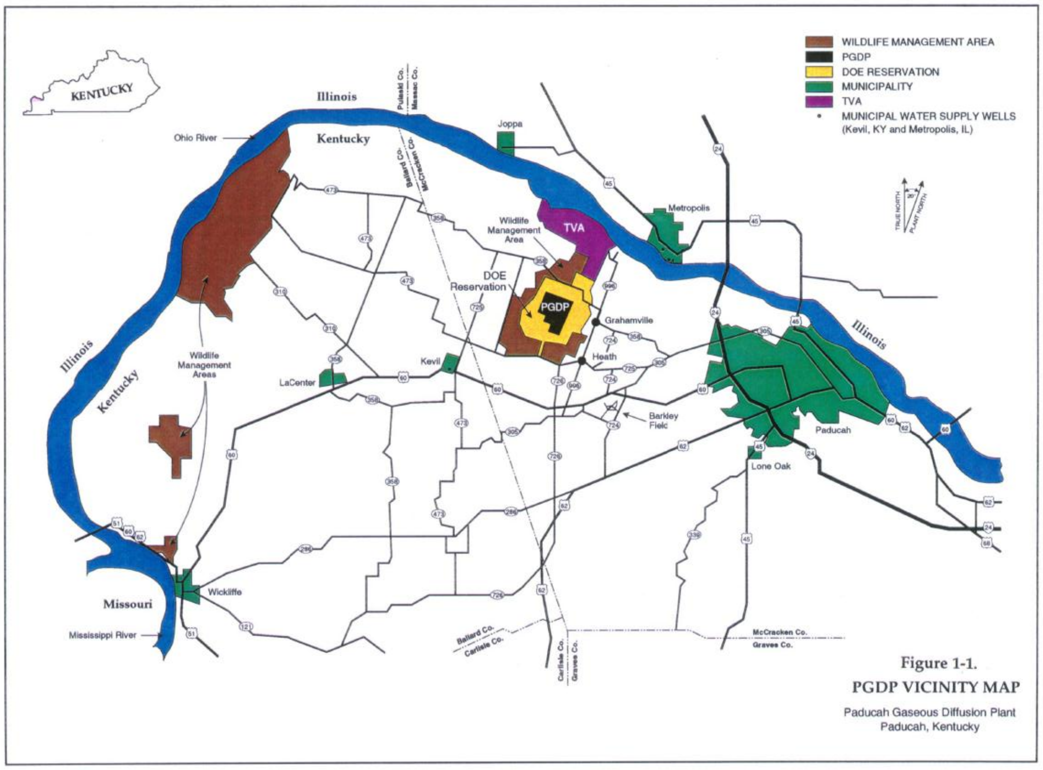

Figure 1. Location of the Paducah Gaseous Diffusion Plant (DOE,2001)

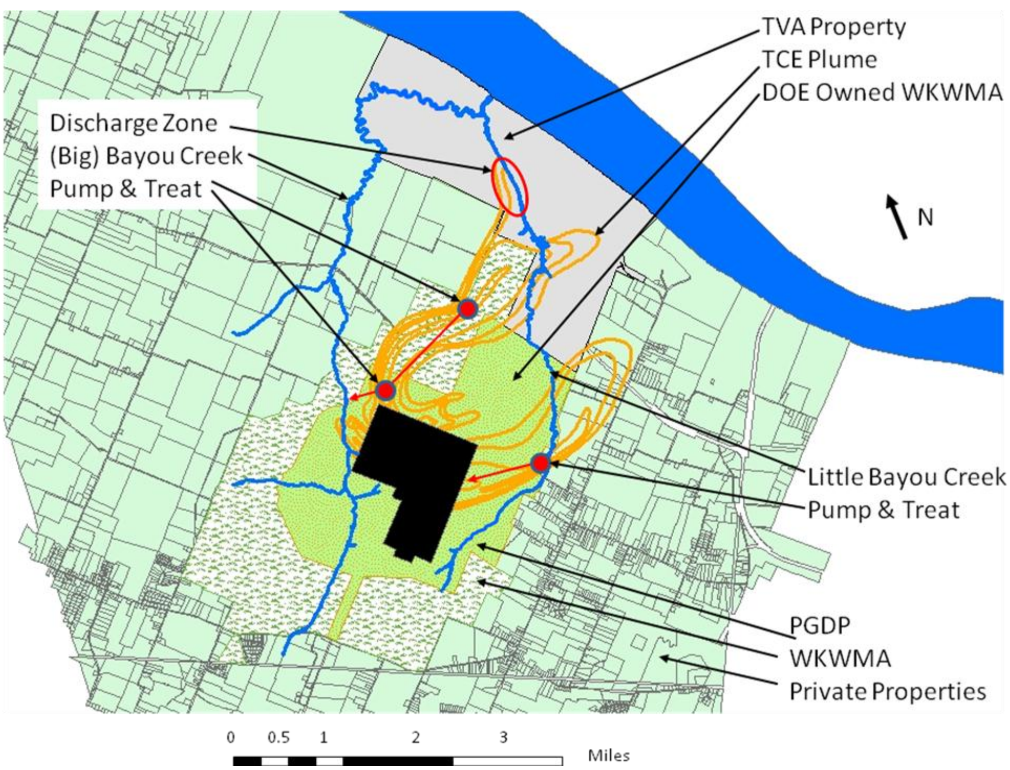

Figure 2. PGDP Land Use, TCE Plume, and Pump and Treat System