ULTRASOUND ENHANCEMENT OF A PERMEABLE REACTIVE BARRIER UNDERGOING ACCELERATED AGING

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1.0 Problem Statement

Recently, remediation research has focused on a relatively new in-situ application of zero-valent iron, referred to as a permeable reactive barrier (PRB). With this technique, a highly permeable barrier is constructed in the subsurface. As contaminated groundwater flows through the treatment barrier, chlorinated solvents are chemically degraded to acceptable byproducts and groundwater emerges from the down-gradient side of the PRB contaminant free. In 1996, the US EPA identified 138 remediation projects involving PRBs at stages of development ranging from laboratory studies to full-scale installations (Kovalik, 1996). As of mid-2000, 48 PRBs have been constructed globally (ETI, 2000).

Reduction in solvent dechlorination rates and flow problems in PRBs have been linked to deposition of material, mainly carbonates in highly alkaline water, on the reactive medium (Mackenzie et al., 1995). Effectiveness has also decreased as corrosion and deposition occurs on the surface of the iron, accompanied, or perhaps caused by increases in pH (Reinhart et al, 1997; Agrawal et al, 1995; Johnson and Tratnyek, 1995). Bridging between iron particles can result in plugged pore spaces at the upstream face of a barrier and interfere with the hydraulics of a remediation system (Mackenzie et al, 1997). Some research is being conducted through the Remediation Technology Demonstration Forum's Permeable Reactive Barriers Subgroup to evaluate the long-term deterioration of PRBs. However, this research is only evaluating a naturally occurring system decline, and the results will not be available to the PRB user community for some time. Therefore, evaluation of an accelerated aging process is highly desirable. The hydraulic conditions at the NASA KSC Launch Complex 34 PRB, located on the Cape Canaveral Air Force Station are extremely favorable to support this type of research effort. Additionally, results of this research will show how severely a PRB system can be allowed to deteriorate before a rejuvenating ultrasound technique can/should be applied. Finally, this research will evaluate the extent to which iron can be rejuvenated by in-situ ultrasound application after repeated aging.

2.0 Technical Description

2.1 Ultrasound Application

NASA and the University of Central Florida have developed a technology that addresses the potential plugging, fouling of reactive material, and declining degradation rates of PRBs over time due to deposition or precipitation. This technology uses ultrasound applied in the subsurface on the leading edge of the PRB to maintain the degradation capability of the zero-valent metal. Other in situ methods have been evaluated to rejuvenate PRBs and increase their lifetime. These methods include iron replacement, use of a second wall to scavenge oxygen from the groundwater, and pH adjustment (Air Force, 1997; Sivavec et al, 1997; Mackenzie et al, 1997).

Due to costs and technical impracticality, none of these latter approaches is entirely satisfactory. Ultrasound application, however, appears to be both effective and economical. Laboratory testing accomplished at UCF showed a significant increase in the reactivity of iron following ultrasound application. These results are supported by surface characterization techniques and degradation rate constant chemical analyses (Ruiz, 1998).

In March, 1998, a field-scale PRB was constructed at Launch Complex 34 (LC34) on Cape Canaveral Air Force Station. The PRB design employed a continuous pattern of columns created by the deep soil mixing (DSM) technique. The PRB consists of eleven 1.2-m (4-ft) diameter, overlapping columns. Total barrier length is 12.2 m (40 ft); depth of the PRB is 12.2 m (40 ft), ending just above an impermeable clay stratum. Overlapping columns ensured a continuous DSM PRB that reduced the possibility of contaminants by-passing the PRB. Mixing was also provided upstream from the barrier to maintain parallel flow lines entering the PRB.

In an effort to generate a preliminary measure of the effect of ultrasound on a field-scale PRB, it was decided to apply ultrasound to the LC34 PRB. Because this PRB is new (three years old), very little buildup of corrosion products would be expected to have occurred. However, air was introduced to the wall during installation (air was used as a "fluffing" agent during soil mixing operations) therefore it is expected that some oxidation of the iron particles would have occurred. Thus, ultrasound could remove these oxidation products from the surface of the iron particles.

Iron samples were collected using a push probe at three different depths at a radial distance of 30 cm from two observation wells located within the PRB before the application of ultrasound. Ultrasound treatment was then applied to both of these wells using two different resonators in the following manner. Both a 40 K-Hz and a 25K-Hz resonator were used on the LC34 PRB. The 40-KHz resonator is 1.2 meters long and can radiate ultrasound omni-directionally along its entire length. The 40-KHz resonator was activated between the depths of 2 and 8 m below land surface, with an ultrasound exposure time of 30 minutes for each treatment section. The 25K-Hz resonator is 1 m in length and also has the capability to apply ultrasound omni-directionally along its entire length. The 25 K-Hz resonator was activated between the depths of 2.4 and 8 m below land surface, with an ultrasound exposure time of 30 minutes for each treatment section. The day following ultrasound application, iron samples were again collected near these wells. These samples were taken 30 cm from the wells at a 90^0 angle from where the samples were taken before ultrasound treatment. The process was repeated for a 90-minute application period.

Kinetic batch studies were conducted by utilizing samples of iron retrieved before and after ultrasound application. Results indicate that a sonication period as brief as 30 minutes has a significant positive impact on the first-order rate constant for TCE degradation (20 to 60 % decline in half-life). If the sonication period is increased, it has an increasingly positive impact on TCE degradation rates (30 to 70 % decline in half-life). The 25-KHz resonator proved to be more efficient than 40-KHz resonator. It can be concluded from this field study that ultrasound removes corrosion products, precipitates and other debris from the iron surface, revitalizing the iron's reactive capacity and extending the PRB lifetime.

A second site selected for testing was the Denver Federal Center in Lakewood, Colorado. The full-scale funnel and multiple gate system along the eastern boundary of the Denver Federal

Center was installed in October of 1996. The funnel walls, comprised entirely of sealable-join sheet piling, extend about 1,040 feet and range in depth from 8 to 9 m below land surface. Four equally spaced gates were installed using the sheet pile box method. Native material was excavated from the box and replaced with an iron filings and pea gravel mixture. Each gate is 12 m wide, approximately 6 m below land surface and houses an iron wall from 0.6 to 1.8 m thick. Recent testing suggests plugging of the wall has occurred. The Federal Highway Administration, US General Services Administration, and US Geological Services provided engineering support, data collection, investigative derived waste handling, and coordination. The procedure for ultrasound application was essentially identical to that used at the NASA site. At this site, the 25-kHz resonator decreased TCE half-life by 64-73% and the 40-kHz resonator decreased half-life by 40%, again supporting the effectiveness of ultrasound application.

2.2 Status of the Ultrasound Technology

The use of ultrasound to improve the effectiveness of a PRB was granted a U.S. patent in January 2000 (Patent No. 6,013,232). The process of selecting the technology for patent application involved a detailed market analysis by the Research Triangle Institute (RTI). RTI observed that the market opportunity for zero-valent metal treatment walls is quite significant. RTI identified EnviroMetal Technologies, Inc. (ETI), the zero-valent metal patent holders, as the crucial industry player. They identified some 30 companies in the remediation field and four ultrasonic cleaning companies with possible interest in ultrasound enhancement.

2.3 Approach

The overall objective of this research is to accelerate the aging of zero-valent metal at the KSC PRB for the purpose of evaluating and predicting long-term performance and potential for rejuvenation using ultrasound. The research tasks necessary to meet this objective are summarized below:

1. Accelerated aging of the iron at the NASA LC34 PRB will be accomplished by increasing the groundwater flow through the PRB by pumping downstream from it. Residence time and flow rates through the PRB will be determined using tracer studies.

2. The progression of wall deterioration will be monitored by analyzing the concentration of chlorinated organics in the effluent groundwater and the reactivity of the iron.

3. Surface analysis of the PRB iron will be performed after a sufficient number of pore volumes of groundwater have passed through the PRB to cause significant aging.

4. Regeneration of the PRB will be accomplished by the use of the NASA/UCF developed ultrasound treatment methodology. A measure of the extent of the regeneration will be determined by conducting TCE and cis-dichloroethene degradation rate studies in bag (static) experiments with iron samples obtained from the PRB before and after ultrasound treatment.

5. After conducting the ultrasound regeneration, accelerated aging of the PRB will begin again using the groundwater pumping technique and the tasks described as items 1-4 above will be repeated.

6. The process described in Tasks 1-4 will be performed in an iterative fashion to develop a model that can be used to predict the life of a PRB when subjected to ultrasound treatment. This model can be used to determine treatment frequency and the number of times the treatment should be applied over the lifetime of the PRB.

7. Recommended protocol for zero-valent iron PRB maintenance will be developed.

3.0 Research Benefits

Because chlorinated solvents are among the most common pollutants found at contaminated sites, the potential use of zero-valent iron PRBs is significant. However, long-term use of PRBs is challenged by loss of reactivity. Clearly a well-documented and cost-effective corrective technique would have value to the remediation field. Recent experience suggests that ultrasound is effective, however further investigation will benefit the implementation of the use of ultrasound and lead to a better understanding of PRB performance.

The economic benefits of the ultrasound technology can be demonstrated as follows. A 1997 Battelle report states that the reactive iron in a PRB may need to be replaced every 5 to 10 years, depending on the properties of the groundwater at the PRB site. This report also estimates the replacement of the reactive iron at 25 to 100 % of the initial installation cost, depending on the type of PRB construction used. Construction cost of the 12-m by 12-m by 1.2-m demonstration-scale PRB installed at LC 34 site was approximately $250,000. Assuming, therefore, a cost of a PRB installation to be in the range of $100,000 to $300,000, iron replacement every 5 to 10 years could be from a low range of $25,000 to $100,000 to a high range of $75,000 to $300,000.

To treat a 12-m PRB and purchase a 3000-W ultrasound unit, the total investment would be approximately $18,500. If it is assumed that the PRB needs treatment only every 10 years, then over a 30-yr period, total cost for three treatments would be $33,500 (including three-months of salary). Using the lower cost for PRB installation and replacement (*i.e* $100,000 with 25% replacement cost), total lifetime replacement cost would be $75,000 and the ROI would be 223%. This ROI would be the absolute minimum. The maximum ROI would be for a $300,000 installation cost and treatment required every 5 years. Cost of investment plus six treatments with ultrasound would be $48,500. The cost for 100% iron replacement every five years would be $1.8 million. ROI, therefore would be 3,711%. Thus, estimated return on investment for ultrasound treatment would be between 223 and 3711%.

4.0 Schedule

Task	FY 01 - 02			
	3Q	4Q	1Q	2Q
PRB Aging	X	X	X	
PRB Monitoring	X	X	X	X
Surface Analysis				X
PRB Regeneration				X
Report Preparation				X

5.0 Personnel

Faculty and students in the University of Central Florida's Civil and Environmental Engineering and Chemistry Departments will conduct this project.

Dr. Reinhart is Associate Dean and Professor with UCF's Civil and Environmental Engineering Department. She has over twenty years in the environmental engineering field and has been conducting research and teaching in the hazardous waste management field for the last ten years. She has authored four books and over 40 publications and presentations. She is active in SWANA, ASCE, WEF, AEESP, and is a diplomat of the American Academy of Environmental Engineers. Dr. Reinhart will be responsible for coordination of field activities.

Dr. Christian A. Clausen is a Professor in UCF's Chemistry Department. He has more than thirty years of experience in applied research and has been conducting research in the areas of environmental chemistry and hazardous waste treatment for the past fifteen years. Dr. Clausen has authored seven textbooks and more than 70 scientific publications. Dr. Clausen has a well-equipped industrial chemistry laboratory and access to all major analytical instrumentation used in the environmental field. Dr. Clausen will be responsible for coordination of laboratory activities.

Dr. Cherie Geiger has been an Assistant Professor of Chemistry at the University of Central Florida for five years. She has published 42 regional, national and international publications in proceedings and journals. Her area of expertise is environmental chemistry with a focus on groundwater contamination. She will be responsible for quality assurance and supervision of graduate students.

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