IN SITU SOURCE CONTROL REMEDIATION OF HIGH EXPLOSIVES USING INNOVATIVE IN SITU TECHNOLOGIES

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ABSTRACT

Groundwater contamination by high explosives (HE) such as RDX and TNT poses great challenges for environmental remediation. One of the challenges relates to the need for in situ source control in order to allow remediation of the groundwater plume. Without adequate source control, groundwater remediation of HE constituents can become undone by the effects of additional contaminant migration from the source areas. Ongoing results of in situ source control interim corrective measure (ICM) pilot testing at the U.S. Department of Energy (DOE) Pantex Plant, located in Amarillo, Texas are providing new information about the use of in situ remediation technology for high explosives treatment in the vadose zone and groundwater to achieve HE source control. Five in situ HE remediation technologies have been evaluated by the site over the past five years using both laboratory and field treatability studies. Two technologies are currently being applied at the field scale as source control ICM pilot tests.

Remediation technologies evaluated using laboratory and field treatability testing at Pantex have included in situ bioremediation, natural attenuation, in situ oxidation of groundwater using permanganate, in situ chemical oxidation of the vadose zone using ozone, and in situ chemical reduction in groundwater. The ICM pilot tests at Pantex involve two HE source control technologies, one targeted for vadose zone remediation and the other a groundwater reactive barrier.

INTRODUCTION

This paper describes two components of HE remediation program activity at the DOE Pantex Plant, including: (1) previous in situ HE remediation technology screening and lab and field treatability testing, and (2) ongoing ICM activities for source control of the primary groundwater plume at the site.

BWXT Pantex initiated lab and field treatability studies of in situ remediation for HE during 1999 in order to develop solutions for groundwater contamination at the site. Subsequently the DOE Innovative Treatment and Remediation Demonstration (ITRD) program further supported these efforts by sponsoring external research into specific HE treatment technologies and application issues. The ITRD efforts were in support of the recommendations outlined in the
DOE Office of Environmental Management Report to the Secretary of Energy entitled “Protecting the Ogallala II, Recommendations for Characterization and Remediation of the Southeastern Plume at the Pantex Plant” (DOE, 2000). This DOE report identified numerous recommendations, including:

- “Reevaluate the use of passive treatment options (reactive barrier) relative to the active remediation options under consideration for the preferred final remedial action.”,
- “Continue to pursue the evaluation of innovative chemical and biological oxidation/reduction techniques to treat the contamination in the perched aquifer.”

The results of the ITRD-sponsored studies were summarized by Aquifer Solutions, Inc. (2002) in a report that synthesized all site-specific remediation testing performed prior to that time, and provided a preliminary assessment of the site-specific deployment requirements of potentially applicable remediation technologies.

Following the treatability study phase, Pantex selected two technologies for application as ICMs, designed to provide source control of HE groundwater plume. These technologies include vadose zone source area treatment using ozone gas injection for in situ chemical oxidation, and an in situ chemical reduction reactive barrier for groundwater containment using in situ redox manipulation (ISRM).

**Background**

The U.S. Department of Energy Pantex Plant, located in Amarillo, Texas, contains the high explosives (HE) compounds hexahydro-1,3,5-trinitro-1,3,5-triazine (Royal Demolition Explosive, or RDX), 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (Her Majesty’s Explosive, or HMX), and 2,4,6-trinitrotoluene (TNT) in a perched aquifer that is present at a depth of approximately 300 feet below ground surface. The RDX plume in the perched aquifer at Pantex covers an area of approximately 5 to 6 square miles. Much of this area is currently controlled by a groundwater pump and treat system. Ultimately the plume may require treatment through a combination of pump and treat, source control, and natural attenuation. Supplemental in-situ remediation technologies that achieve HE destruction may play a role in achieving these objectives. To address the need for in situ remediation technologies applicable to HE compounds, in 1999 the Pantex Plant initiated several treatability studies to assess potential in situ remediation technologies, including in-situ chemical oxidation, in situ chemical reduction, in-situ bioremediation, and monitored natural attenuation (MNA).

Prior to the HE remediation technology treatability studies undertaken by Pantex in 1999, there were no data reported in the literature to indicate if in situ destructive remediation technologies were capable of treating RDX or other HE compounds. Treatability studies conducted at the site from 1999 through 2002 (as well as parallel studies at other organizations) determined that in situ treatment of RDX is feasible. Recently, Pantex selected two in situ remediation technologies that are currently being applied as ICM pilot tests for source zone control.
Prior HE Remediation Technology Studies Conducted at Pantex

Prior to conducting the ongoing ICM work using ozone oxidation and ISRM chemical reduction, the Pantex Plant previously conducted laboratory and field studies to evaluate several in situ remediation technologies and their applicability to treat RDX and other HE compounds. The technologies evaluated were reported by Aquifer Solutions, Inc. (2002) and included in situ redox manipulation (ISRM), anaerobic in situ bioremediation (ISB), and chemical oxidation using potassium permanganate (KMnO4).

Previous ISRM Studies at Pantex

Szecsody et al. (2001) at Pacific Northwest National Laboratory (PNNL) conducted laboratory treatability testing for Pantex of the feasibility of RDX treatment using ISRM. ISRM is a passive reactive barrier technology that is based on treating the aquifer matrix with a chemical reductant to reduce naturally occurring iron to the Fe\(^{2+}\) valence state. After this matrix treatment step, the treatment zone then serves as a reactive barrier for contaminants that can be chemically reduced by Fe\(^{2+}\) (Cr\(^{6+}\), RDX, TCE, and others). At Pantex, according to the PNNL bench testing, the ISRM barrier may have a lifetime of at least 30 years, during which time the barrier would act in a passive mode without additional operation or maintenance efforts.

The site-specific PNNL ISRM bench testing results (Szecsody, et al., 2001) showed rapid and essentially complete RDX degradation in the presence of dithionite-reduced Pantex sediments. This testing also utilized \(^{14}\)C radio-labeled RDX. The results obtained indicated that a small degree of RDX mineralization to CO\(_2\) (<36%) was achieved using ISRM, indicating that the RDX that was degraded was partially transformed to unidentified by-products. Based on discussions among the ITRD Technical Advisory Group (TAG), it was determined that the ISRM process might require additional follow-on treatment for HE compounds using natural or enhanced biological or chemical treatment. Follow-on testing of ISRM-treated water using bioremediation was therefore performed by University of Nebraska at Lincoln (UNL). These results (Adam et al., 2002) indicated that biodegradation was feasible to treat products resulting from the treatment of RDX with reduced aquifer sediment. Biotic mineralization rates were initially much greater for the reduced products over parent RDX but cumulative \(^{14}\)CO\(_2\) production (~40%) became similar after 40 days. This indicates that the reduced products are more prone to subsequent biodegradation by either aerobic or anaerobic microbial processes.

Previous Bioremediation Studies at Pantex

Previous bioremediation treatability studies at Pantex have included both vadose zone and groundwater biodegradation studies at the laboratory and field scales.

Texas Technical University Water Resources Center (TTUWRC) performed the vadose zone HE biodegradation work at Pantex. The vadose zone HE biodegradation study involved the creation of reducing biological conditions by the injection of nitrogen gas. The results of the vadose zone HE biodegradation demonstration (Rainwater, et al., 2001) showed that the nitrogen injection process stimulated reductive microbial activity and reduced HE concentrations. RDX concentrations in retrievable (strategically placed intermittent environmental samplers – SPIES)
soil samples were reduced from initial values of 12.9 mg/kg to 5.6 mg/kg after 333 days of treatment. Also over this period, RDX concentrations in soil boring samples were reduced from 18.2 to 10.8 mg/kg. Based on the encouraging results of the ITRD HE biodegradation demonstration, BWXT Pantex undertook an expansion of the HE biodegradation system, which operated for approximately two years from 2002 through 2004.

Groundwater bioremediation was assessed at the Pantex Plant to consider the potential for natural attenuation as well as enhanced aerobic or anaerobic biodegradation to reduce HE concentrations in groundwater. This work included field measurement of groundwater biodegradation parameters and laboratory treatability studies of aerobic and anaerobic biodegradation. Some of this testing was performed by UNL (Adam et al., 2002), using $^{14}$C radio-labeled RDX. These results indicated that promising mineralization (i.e. conversion to CO$_2$) rates were obtained under both aerobic and anaerobic conditions.

**Previous Permanganate Oxidation Studies at Pantex**

Laboratory treatability testing, field push-pull tests, and preliminary reactive transport modeling (Clayton et al., 2002, Struse et al., 2002) were conducted to assess the potential feasibility of in-situ treatment of RDX using potassium permanganate (KMnO$_4$). Effective RDX treatment was observed in these treatability studies. The second-order multi-species reaction kinetics of KMnO$_4$ with RDX and with soil total organic carbon (TOC) were measured in the laboratory and incorporated into the preliminary modeling effort. The lab results indicated that TOC oxidation proceeds faster than RDX oxidation. Pseudo first-order RDX half-lives ranged from 0.5 days to 36 days and KMnO$_4$ consumption ranged from 0.5 to 10 g KMnO$_4$ per kg soil, both depending on KMnO$_4$ concentration. The pseudo first-order KMnO$_4$ reaction half-life observed was on the order of weeks to months.

The preliminary reactive transport modeling of KMnO$_4$ reaction-limited injection incorporated second order reaction kinetics, and was conducted using the DOE reactive transport code RT3D. The permanganate injection reactive transport modeling results should be considered preliminary because they were not calibrated to a large-scale field test. However, the results are a fairly realistic first estimate, because they are based on measurements of reaction kinetics determined from the lab tests described by Clayton et al. (2002). These reaction kinetics were confirmed by field-scale push-pull tests (Struse et al., 2002) and subsequent additional lab testing (Adam et al. 2002). The modeling indicated that due to the long KMnO$_4$ persistence of several months, a large radius of influence may be achievable such that an injection well spacing of several hundred feet may be possible. The results also indicated that groundwater displacement would be significant if large volumes of solution were injected to achieve a large radius of influence. These results indicated that KMnO$_4$ oxidant injection would need to be managed under a properly designed and monitored injection plan.

Adam et al. (2002) performed additional laboratory testing using carbon-14 labeled RDX to evaluate reaction by-product mineralization and reaction kinetics. Carbon-14 radio-labeled RDX was used for laboratory testing of permanganate oxidation to assess the possible production of intermediate reaction products. The results (Adam et al. 2002) indicated that chemical oxidation of RDX does not follow the common reductive RDX reaction pathway. Reductive intermediates...
such as Mononitrosoamine (MNX), Dinitrosoamine (DNX), and Trinitrosoamine (TNX) were not produced by the permanganate oxidation process, and overall mineralization of RDX to CO$_2$ on the order of $>85\%$ was observed. These results indicated that permanganate oxidation can effectively mineralize RDX without the production of persistent intermediate products.

Ongoing Source Control Interim Corrective Measure Pilot Tests at Pantex

Based on the previous in situ remediation technology treatability studies conducted at Pantex, two technologies were selected for pilot-test application as interim corrective measures. These ICM pilot tests are designed to develop source control of the HE groundwater plume at the site.

Source control of the HE plume at the site is being pursued to allow the existing groundwater pump and treat system to more effectively capture and remediate the HE and other constituents in groundwater. The ICM source control strategy has two components: (1) vadose zone source area treatment, and (2) reactive barrier emplacement for groundwater. The short-term objectives of the ozone ICM pilot tests are to manage the source of the groundwater plume through source removal and control in the vadose zone and groundwater. The long-term objectives of the source control ICM are to remove the HE loading to groundwater in order to enhance the performance of the existing pump and treat system and to support natural attenuation processes within the groundwater plume.

Design of Vadose Zone Ozone Oxidation ICM of RDX Source Areas

In situ ozone treatment of the vadose zone is being implemented as an ICM pilot test at Pantex in order to reduce the mass of HE constituents migrating vertically downward to the groundwater. This is especially important at Pantex, because the depth to groundwater is approximately 300 feet below ground surface. Therefore, remediating the vadose zone soils and HE dissolved in vadose zone pore water is an important element of the overall source control program at the site.

HE compounds such as RDX are highly soluble and minimally sorptive, leading to substantial portion of the vadose zone HE mass being present dissolved in the pore water. Clayton (2000A) assessed vadose zone-groundwater interactions of RDX at a weapons manufacturing facility located in Tennessee, USA using pore water sampling techniques, and found that dissolved RDX in vadose zone pore water was the primary mechanism of impact to groundwater. Similarly, the conceptual model for the groundwater plume development at Pantex recognizes that vadose zone pore water remediation will contribute to source zone control by eliminating the source of groundwater impacts. In situ oxidation by ozone gas (O$_3$) injection is well suited to vadose zone treatment, because injected gases can move through air-filled pores in the vadose zone Clayton (2000B).

The use of ozone for treatment of HE compounds has been established through the extensive use of ozone for above-ground treatment associated with groundwater pump and treat systems (EPA, 1993). For above ground treatment systems, ozone is enhanced with the addition of ultraviolet light or other catalysts to promote the generation of advanced oxidation radical species such as hydroxyl radicals. For above ground treatment of pumped groundwater, catalysts are necessary to achieve very fast reaction rates that ensure contaminant conversion with short residence times.
However, for in situ ozone treatment radical generation is catalyzed by soil minerals (Jung, et al., 2004), moreover residence times are longer and very fast reaction rates are not necessary.

UNL performed site-specific ozone-RDX treatment bench testing that was reported by Adam et al., (2004). UNL used $^{14}$C-RDX in the experiments to quantify cumulative mineralization, and found that 2% (w/w) ozone achieved 80% mineralization of RDX in solution. The results indicated that the presence of site soil improved aqueous reactions compared to aqueous-only solutions, indicating possible generation of free radical species. UNL also evaluated aerobic biodegradation as a secondary treatment following partial ozonation of a RDX solution. Results showed that ozonated RDX solutions were much more biodegradable than untreated controls in aerobic microcosms (25% vs. <2% cumulative mineralization). Moreover, microcosms treated with ozonated-RDX solutions showed a decrease in native (unlabeled) RDX concentration, while the control did not, providing some evidence that the degradates produced during ozonation may stimulate aerobic RDX biodegradation. These results supported the use of ozone as a remedial treatment for the contaminated vadose zone at the Pantex site.

The primary ozone ICM pilot test goals are to answer important questions and fill data gaps related to larger scale implementation. The primary objectives of the in situ ozone treatment ICM pilot test are as follows:

- verify that ozone is capable of reducing the existing vadose zone concentrations to below the target levels in the site specific geologic conditions;
- determine the optimum ozone injection flow rates; and
- enable full-scale ozone ICM design and implementation.

The in situ ozone ICM system design involves injection of ozone gas into the vadose zone soils. The system design integrated subsurface pressure-flow characteristics with ozone reactive transport considerations. Gas injection wellhead pressure-flow data were collected and used to calculate an approximate soil permeability ($K$) value of $6.2 \times 10^{-5}$ cm/sec, which is equivalent to an intrinsic permeability ($k$) value of $7 \times 10^{-10}$ cm$^2$.

In addition to the pressure-flow characteristics, the system design considered an average cumulative ozone dose that was expected to result in RDX treatment within a 6 month to one year time frame. The design of the ozone ICM pilot test system also considered the expected radius of influence for ozone transport by performing simulations of subsurface ozone reactive transport using the pseudo-first order analytical solution derived by Clayton (1998). These simulations consider the effects of the ozone injection concentration and flow rate and the ozone reaction rates.

The design considerations resulted in the selection of an ozone generator system a 2.4 lb. per day O$_3$ generator with an adjustable air blend delivery system and an internal oxygen generator to maximize O$_3$ production. Ozone is injected into a four-well injection pattern with surrounding soil vapor extraction wells for vapor control.

**Design of Reactive Barrier ICM for Source Control**
A reactive barrier ICM pilot test is also being implemented at Pantex as part of the source control measures. The reactive barrier is a chemical reduction barrier involving ISRM technology. ISRM involves the injection of sodium dithionite to create a chemically reduced zone in the subsurface. The sodium dithionite acts to reduce naturally occurring iron in the subsurface to \( \text{Fe}^{2+} \). The \( \text{Fe}^{2+} \) is immobilized within the aquifer matrix, and serves as a semi-permanent reductant that treats HE migrating in groundwater through the reactive zone. ISRM technology has been used previously for treating chromium contaminated groundwater, and this project is the first field-scale application of ISRM technology for high explosives treatment. Prior bench testing, conducted by Pacific Northwest National Laboratory (PNNL) for Pantex indicated that the Pantex sediments could be reduced adequately to potentially create a long-term reactive barrier for HE treatment. The field-scale design for ISRM implementation was based on site hydraulics, on reduction reaction stoichiometry, and on reactive transport characteristics of the sodium dithionite.

The dithionite delivery design is intended to create an 60-foot-long ISRM reactive barrier. The delivery system was sized based on the amount of pore volumes available in the perched groundwater treatment zone. The ISRM design process included using multiple lines of evidence for estimating the appropriate injection well spacing and dithionite solution dose to be injected into the subsurface. Four different analysis methods were used to reduce the uncertainty in the pilot test design, including:

- A molar stoichiometric estimate of the dithionite mass requirements, based on the amount of \( \text{Fe}^{3+} \) available to be reduced to \( \text{Fe}^{2+} \), as determined by the PNNL bench testing,
- An estimate of the dithionite mass requirements, based on dithionite consumption at breakthrough from the PNNL soil columns, in terms of grams dithionite per kg gram soil.
- Preliminary analytical modeling of the approximate maximum dithionite concentration distribution vs. radial distance from the injection well, and
- Preliminary two-dimensional (vertical plane), radial geometry, transient numerical modeling of the dithionite concentration radial distribution over time during the injection process.

The molar stoichiometric estimate of the dithionite mass requirements based on the amount of \( \text{Fe}^{3+} \) available to be reduced to \( \text{Fe}^{2+} \) indicated that approximately 8,000 lbs. of sodium dithionite (\( \text{Na}_2\text{S}_2\text{O}_4 \)) would be required per well, to effect a 15 ft. radius over a thickness of 25 feet. The dithionite mass requirements were also estimated independently based on the dithionite mass delivered to the bench-test soil columns at the time of dithionite breakthrough from the column. The breakthrough occurred after approximately three pore volumes of 0.04 M Na2S2O4 was injected to the column, which is similar to previous field applications of the technology. The dithionite mass requirements based on the column breakthrough was 4.4 g. Na2S2O4 per kg soil. Based on this target dose, and a 15 ft. radius over a 25 ft. thickness, Approximately 8,550 lbs. of \( \text{Na}_2\text{S}_2\text{O}_4 \) would be required per well.

The above dithionite mass requirements provide an approximate target for the injection requirements, but do not address the optimal injection volume, flow rate, and solution concentration. These factors are determined by the reactive transport of the dithionite solution in the subsurface. Preliminary analytical and numerical modeling were performed to optimize the
solution injection concentration, flow rate, and injection duration. The preliminary modeling was intended primarily to provide an additional line of evidence to support the development of a reasonable pilot test plan.

The reaction rates used in the preliminary analytical and numerical modeling were based on an evaluation of the dithionite consumption and reaction kinetics observed in the PNNL bench testing (PNNL, 2001). This analysis included development of a numerical model that simulated the PNNL bench column testing. This model was calibrated to the laboratory-measured values to confirm the observed pseudo first-order dithionite reaction half-life of 7 hours during iron reduction. Since the field injection process is within the time-scale of active iron reduction, the pseudo first-order half-life of 7 hours provides a reasonable approximation of the dithionite reactions affecting transport during the injection activities.

The analytical and numerical injection modeling produced results that were within approximately 20% of each other in terms of the concentration distribution of dithionite radially at distance from the well. The modeling results also indicated that the radius of influence can be maximized by utilizing discrete vertical intervals for injecting within each well, as opposed to injecting into the entire 25 ft. saturated thickness at one time. This result arises from the fact that injecting into a discrete interval creates a larger fluid velocity in the subsurface, which results in greater transport distances of reactive fluids such as sodium dithionite. As a result, the injection well screen design included three discrete five-foot long screened intervals, with 7-foot sandpack intervals, separated by bentonite.

With the design injection well geometry of three discrete injection intervals, and based on the preliminary modeling results, a Na$_2$S$_2$O$_4$ concentration of half the injection concentration, or 0.32 lb/ft$^3$ (equivalent to approximately 0.03 M, or 5,250 mg/l) will be transported to a radial distance of 13 to 14 feet. A Na$_2$S$_2$O$_4$ concentration of 1/3 the injection concentration, or 0.2 lb/ft$^3$ (equivalent to approximately 0.018 M, or 3,200 mg/l) will be transported to a radial distance of 16 feet. The modeling results also indicated that Na$_2$S$_2$O$_4$ concentrations on the order of 1,000 mg/l may be transported to distances of approximately 20 to 25 feet or more. This corresponds to 98,100 gallons of injected dithionite solution per well at an approximately rate of injection of 60 gpm. Injection is of the dithionite solution is anticipated to take approximately 9 hours per screen interval. This fluid will be injected into each well sequentially as opposed to simultaneously in order to avoid a treatment dead-zone between the wells as a result of opposing hydraulic mounds surrounding each well.

**SUMMARY**

Ongoing results of in situ source control interim corrective measure (ICM) pilot testing at the U.S. Department of Energy (DOE) Pantex Plant, located in Amarillo, Texas are providing new information about the use of in situ remediation technology for high explosives treatment in the vadose zone and groundwater to achieve HE source control. Five in situ HE remediation technologies have been evaluated by the site over the past five years using both laboratory and field treatability studies. Two technologies are currently being applied at the field scale as source control ICM pilot tests.
Remediation technologies evaluated using laboratory and field treatability testing at Pantex have included in situ bioremediation, natural attenuation, in situ oxidation of groundwater using permanganate, in situ chemical oxidation of the vadose zone using ozone, and in situ chemical reduction in groundwater. The ICM pilot tests at Pantex involve two HE source control technologies, one targeted for vadose zone remediation and the other a groundwater reactive barrier. Neither ozone or dithionite in situ chemical reduction have been previously used for HE treatment, and the ongoing work at Pantex is advancing the understanding of in situ HE treatment.

REFERENCES


