SERDP
Strategic Environmental Research and Development Program
Improving Mission Readiness Through Environmental Research

Peroxone Treatment of Contaminated Groundwaters

Cleanup
CU-726

LEAD AGENCY: US Army

LAB: US Army Engineer Waterways Experiment Station (WES)

PRINCIPAL INVESTIGATOR: Dr. Mark E. Zappi, P.E. (601) 634-2856

PROBLEM STATEMENT: The Department of Defense (DoD) and Department of Energy (DOE) have many sites that contain groundwaters contaminated with explosives compounds. The current or traditional treatment technology available for use in explosives contaminated groundwater remediation is granular activated carbon (GAC). An innovative technology, ultraviolet (UV) chemical oxidation, will be available for use in the very near future under the DoD's Environmental Quality and Technology Program (EQT). Remediation costs for both of these technologies fall within the $1.00 to $5.00/1,000 gallons range. UV/chemical oxidation is advantageous to GAC because it is a destruction technology and it does not produce a waste stream (i.e. spent GAC) requiring disposal. Also, unlike GAC, UV/chemical oxidation processes are still economically viable at relatively low groundwater concentrations. UV/chemical oxidation systems are often referred to as advanced oxidation processes because they result in the formation of powerful oxidizer species such as the hydroxyl radical (OH.).

DoD installations requiring remediation of explosives contaminated groundwaters will require that GAC or UV based chemical oxidation systems treat literally millions to billions of gallons of groundwater. The cost to the DoD alone will be extremely high. Many environmental engineers and scientists are hopeful that in situ technologies will one day completely replace pump-and-treat systems that use above-ground treatment systems. Unfortunately, the technical truth of the matter is that above-ground treatment systems will always have a place in groundwater remediation activities. In situ treatment technologies are not a panacea. Not all sites or site situations are capable of supporting an in situ treatment system. More cost effective, contaminant destruction, above-ground based treatment systems are required by the DoD.

Peroxone oxidation is a groundwater treatment technology that has great potential for treating contaminated groundwaters at reduced treatment costs. The main driving force in the development and presentation of this proposal is the potential cost savings that may be incurred with the fielding of this technology. Peroxone is a chemical oxidation process that has been used primarily for treatment of drinking water in both the United States and Europe. The process involves the addition of ozone (O3) and hydrogen peroxide (H2O2) into a reactor system containing the contaminated groundwater. Peroxone generates hydroxyl radicals (OH.) through the reaction of ozone with hydrogen peroxide. Peroxone does not require the addition of ultraviolet light to form radicals or destroy organic compounds. The hydroxyl radical is a powerful oxidizer that can destroy organic compounds into environmentally safe compounds. The stoichiometric reactions that result in the generation of the radical during peroxone treatment are listed below,

$$H_2O_2 + H_20 \quad 6 \quad HO_2^- + H_30^+$$
$$O_3 + HO_2^- \quad 6 \quad OH + O_2^- + O_2$$
$$O_2 + H^+ \quad 6 \quad HO_2$$
$$O_3 + O_2^- \quad 6 \quad O_3^- + O_2$$
$$O_3^- + H^+ \quad 6 \quad HO_3$$
$$HO_3 \quad 6 \quad OH^{\cdot} + O_2$$

Since the process does result in the formation of radicals, it is considered an advanced oxidation process (AOP). Actual cost information obtained from French engineers indicate treatment costs as low as $0.02 to $0.10 per 1,000 gallons treated (for dilute concentrations) have been reported. This represents an order of magnitude reduction in remediation costs as compared to traditional technologies such as activated carbon and traditional UV based AOPs. Since peroxone does not require UV addition, operational problems associated with fouling of the quartz sleeves housing UV lamps or poor groundwater UV transmissivity are not of concern; thereby, eliminating a big operational concern and expense associated with UV based oxidation processes.

This work unit will support unfunded components of the DoD STRAT Plan and will meet or partially meet several DoD user requirements. These requirements are:

- Technology for removal of energetics/other organics contamination.
- Treatment system for water contaminated with organic contaminants.
- Treatment of Navy revellent contaminants in salt/brackish/groundwater matrices.
- Isolation and treatment technology for contaminated surface water impoundments.
- Decontamination of soils containing energetics materials.
- Contamination under buildings and roads.
- Remedial treatment technology for soils contaminated with chlorinated and non-chlorinated organics.
- Decontamination of soils containing energetic materials.

PROJECT DESCRIPTION: The WES has evaluated the use of peroxone processes for treatment of explosives contaminated groundwaters using bench scale peroxone reactors. Experiments using laboratory prepared solutions of TNT-distilled water have indicated that peroxone has similar removal kinetics to traditional UV based AOPs. WES, working with Mr. Randy Cerar, Army's Environmental Center (AEC), has evaluated peroxone for treatment of contaminated groundwaters from Milan Army Ammunition Plant (AAP) and Cornhusker AAP with the results being very encouraging. WES and Rocky Mountain Arsenal (RMA) have determined that peroxone has a high potential for treating groundwaters contaminated with a variety of other contaminants. Estimated costs fall within the $0.10 to $0.80/1,000 gallons treated range. WES has also performed studies using sonolytic catalyzation indicating that the addition of ultrasound may dramatically enhance oxidation reaction rate. In summary, bench efforts performed by WES indicate that peroxone processes are ready for evaluation at DoD installations using pilot scale equipment.

The overall objective of this project is to accelerate development of peroxone oxidation processes for treatment of explosives contaminated groundwaters. Process feasibility will be evaluated at both the bench and field pilot scale, with particular emphasis placed on-site pilot studies. The objectives of this project will be approached through performance of a series of research tasks. These tasks are listed and discussed below:

Task I. Determination of Reaction Pathways and Kinetics. Other funding sources will be used by WES to determine reaction pathways of explosives parent compounds. This effort will investigate oxidation pathways of environmental explosives by-products, such as amino-toluenes, which are typically found in explosives contaminated groundwaters. Since peroxone is a destruction technology, determination of the predominant oxidation pathway of selected explosives environmental by-products will be determined using laboratory solutions of buffered distilled water and reagent grade target chemicals. Only single solute solutions will be used so additional carbon sources do not interfere with pathway determination. Kinetic parameters (at minimum, peuso-first order rate constants) will also be determined. Analytical methods to be employed in determination of treatment pathways and kinetics will include high performance liquid chromatography (HPLC), stopped-flow spectrophotometry, and gas chromatography (GC).

Task II. Selection and Shipment of Groundwater Samples. Actual groundwater samples from contaminated DoD sites will be used in both the bench and pilot scale studies. This will ensure that the study remains focused on rapid field implementation. Candidate sites include Milan Army Ammunition Plant, Cornhusker Army Ammunition Plant, Volunteer Army Amunition Plant (National Test Site), and a former Nebraska Ordnance Plant. Samples will be collected and shipped to WES for the bench scale studies. NOTE: All pilot studies will be performed on-site. Results from the bench testing will be used to design comprehensive pilot studies at a minimum of at least two DoD sites. Obviously, site groundwater samples used in the bench study will be carried through to the pilot level of effort.

Task III. Bench Scale Studies. Bench scale studies will be performed to determine process feasibility, verify reaction kinetics and oxidation pathways, estimate initial treatment cost estimates, and set pilot studies test matrices. The bench studies will be performed using one liter all glass reactors operated in semi-batch mode with respect to ozone application. Groundwater samples from various candidate pilot study sites will be evaluated in this study task. These studies will be performed at chemical oxidation laboratory of the Hazardous Waste Research Center (HWRC) located at the USAE Waterways Experiment Station (WES). These studies will also investigate the feasibility of integrating ultrasonic catalyzation as a means of enhancing contaminant oxidation rate and improving mass transfer limitations. If feasible, a CRADA with a reputable ultrasound process equipment manufacturer will be initiated for collaboration in terms of adding sonolytic catalysis to the pilot system.

Task IV. Pilot Scale Studies. Pilot scale studies will be performed using a mobile pilot peroxone system with .5 to 10 gallon per minute operating range referred to herein as the WES Peroxone Oxidation Pilot System (POPS). Four all-glass columns plumbed in series will serve as multiple contact chambers. The system will include several automated process operations and data collection systems that will be used to fully evaluate process feasibility in the field. At least two sites containing groundwater contaminated with explosives will be treated using the pilot system. This task will verify the results derived from the bench studies, evaluate process equipment, and refine cost estimates. The WES will perform these activities with AEC and COE Omaha providing site management and technical support.

Task V. Draft Applications and Design Manual. An applications manual in the form of a WES report will be drafted by WES, US Army Corps of Engineers (COE)-Omaha District, and COE-Missouri River Division (MRD) for use by the user community in designing and fielding the technology. It is believed that inclusion of the design user community (COE) early in process development will ensure development of a useful and easily transferable product. Key issues to be included in the design manual are:

1. Techniques for performance of bench scale peroxone treatability studies - This information will ensure that engineering firms under contract to the installations and COE district offices will be able to properly evaluate peroxone during the FS stage of site remediation. The research team for this proposal will be available for consultation at any time during full field implementation to ensure a smooth transition of the technology from the research and development community to the user community.

2. Process feasibility and potential limitations - One important factor in development of any technology is a firm understanding of the limitations of the technology. The manual will detail all limitations and short-comings associated with implementation of peroxone that are identified. Close coordination with the full user community will be maintained during the full-field application stage to further identify any additional limitations and problems as they occur. It is believed that the manual should be a "living" document that is periodically updated to ensure that corporate memory (DoD) is not lost during implementation at various sites. Lessons learned, whether good or bad, must be recorded so that other installations attempting implementation are keep fully abreast of new technical developments in order to ensure a higher potential for successful

implementation at reduced costs compared to existing technology. Particular emphasis will placed on ensuring that this information is added to various prominent technology bulletin boards.

3. Results from the bench and pilot studies - The results of both the bench and pilot studies will be presented in a concise and applications oriented manner. These results will be further transmitted to the user and regulatory communities. It is important that the regulatory community is completely confident that peroxone can be safely applied at DoD sites.

4. Summarize cost estimates and full scale equipment availability - The manual will also include full cost estimates based on the results of both the Rocky Mountain Arsenal (RMA) and EQT/SERDP demonstrations. An assessment of available equipment will be included to assist the design engineer in equipment selection. Basically, all equipment required for peroxone implementation are already available due to its operational history within the drinking water industry and relative simplicity in terms of equipment requirements. The assessment of equipment will be oriented toward hazardous waste site remediation and the particularities associated with this unique technical and regulatory arena.

As stated above, the implementation manual will be very design and applications orientated. The manual will serve as a handbook for implementation of peroxone at other field sites. Peer review from other agencies such as the USEPA laboratories and other COE design centers will be coordinated. Potential collaboration with the USEPA's SITE Program will be pursued by WES.

Key technical issues to overcome as identified to date are listed below:

a. Ensure that the parent explosives and amino based environmental byproducts are oxidized into environmentally safe, non-regulated (benign) compounds.

b. Determine if peroxone can effectively treat contamination levels typically found at DoD/Doe installations as opposed to organics levels that have traditionally associated with drinking water (which is what peroxone was originally developed for).

c. Determine the impacts of complex contamination matrices on treatment predicted from kinetic models.

d. Determining the economics and scale-up potential of ultrasound systems.

EXPECTED PAYOFF: The DoD has numerous sites that contain groundwaters contaminated with explosives. The existing technology, activated carbon adsorption, is costly, does not destroy the explosives, and results in the production of spent carbon which may pose a disposal problem. The WES has recently completed evaluation of traditional ultraviolet (UV) based chemical oxidation processes for treating explosives contaminated groundwaters. AEC plans to demonstrate these processes in FY94. The cost of traditional UV based oxidation processes is expected to range from $1.00 to $5.00/1,000 gallons of water treated. This is the same cost range experienced with activated carbon adsorption systems; however, chemical oxidation is much more flexible, is a destruction process, and produces no residuals requiring disposal. Peroxone processes are expected to costs in the $0.10 to $8.00 range, which represents potentially a full order of magnitude in cost savings over both activated carbon and traditional UV based chemical oxidation processes. The expected ease of system design and operational flexibility over the other chemical oxidation processes make this process appear extremely promising.

Potential users include all groups, both private and governmental, that are involved in remediation of groundwaters contaminated with organic and explosives compounds. Peroxone treatment will economically fill a gap that currently exist in terms of treatment of low level contaminated groundwaters.

Although no funding is requested for the RMA pilot studies evaluating DIMP, pesticides, and aromatics removal, performance of this work unit will improve the overall quality of the RMA study by allowing RMA/WES to use an improved pilot system then could be developed on the RMA budget alone. In return, the RMA pilot studies (FY94) will allow for evaluation of the POPS unit in terms of mechanical performance prior to performing the explosives pilot studies in FY94-96. Potential research agreements with the private section (CRADAs) will also be investigated to ensure rapid transition to the user community.

TRANSITION PLAN: After pilot scale evaluation of the technology is complete, transition to the user community will be accomplished through various technical reports, publications, briefings, and conference presentations. Interfacing with COE-MRD through this project partnership should accelerate transition of the technology into COE activities, while the USEPA, DOE, and USAF will be briefed periodically on the progress of this effort to ensure smooth transition into their programs. It is fully anticipated that the technology developed under this effort will be directly applicable toward other organic contaminants that are a major concern of these agencies. Once the pilot studies at the explosives contaminated sites have been completed, additional partnering with these agencies can be initiated for evaluation of peroxone for treatment of groundwaters contaminated with other organic compounds such as chlorinated solvents, fuels, and wood preserving wastes using the WES POPS unit.