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Streamlined Treatment Option for Remediation of Commingled Perchlorate and Explosives in Groundwater

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ABSTRACT

AMEC evaluated a fluidized bed reactor (FBR) for the Army as part of an on-going Innovative Technology Evaluation Program at Camp Edwards, Massachusetts Military Reservation (MMR). The goal of the study was to determine if a FBR could biodegrade commingled perchlorate and explosives in groundwater. If successful, FBR treatment would represent a streamlined option to traditional multi-unit treatment trains.

Propellants, explosives, and pyrotechnic (PEP) compounds are found in training ranges and impact area soils at Camp Edwards as a result of historic artillery, mortar, and demolition training activities. Some of these contaminants have been detected in groundwater. Explosives contaminated groundwater has traditionally been treated with granular activated carbon (GAC). FBR technology has recently been used to degrade relatively high perchlorate concentrations at other sites, up to hundreds of milligrams per liter in groundwater.

Camp Edwards presents different challenges for treatment. At the central portion of the Demolition Area 1 (Demo 1) groundwater plume, both perchlorate and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) are present at concentrations of approximately 100 and 190 micrograms per liter (µg/L), respectively. The challenge set forth for the FBR was to simultaneously remediate groundwater containing perchlorate and RDX.

The study demonstrated that FBR treatment could biodegrade commingled perchlorate and explosives in a single unit. Sufficient data was obtained during the study for design of a full-scale system, without pilot-scale field-testing. Using a single FBR with an 80-minute hydraulic retention time, both perchlorate and explosives can be biodegraded. The single FBR unit may be an alternative to the traditional, and more costly, combination of FBR for degradation of perchlorate followed by GAC sorption of explosives.

INTRODUCTION

The Massachusetts Military Reservation (MMR) is a 21,000-acre facility located on Cape Cod, Massachusetts. Approximately 14,000 acres of MMR constitute the Camp Edwards Training Ranges and Impact Area. Historic artillery, mortar, and demolition training activities resulted in the deposition of propellants, explosives, and pyrotechnic (PEP) compounds on the surface soils within the training ranges and impact area. Leaching of rainwater through the soils has transported some of these contaminants to the groundwater underlying camp Edwards.

An Innovative Technology Evaluation (ITE) Program was initiated by the Army in March 2000 to identify viable alternatives for remediation of the contaminated soils and groundwater. The most recent study evaluated a fluidized bed reactor for the biodegradation of commingled perchlorate and explosives in groundwater. The technology was selected for evaluation based upon its demonstrated success in treatment of perchlorate at other sites and the potential that the technology could simultaneously treat hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). The interest in conducting the study was to see if conceptual treatment schemes could be shortened from traditional multiple components for perchlorate and explosives to a single stage treatment train.

The contamination at Camp Edwards presented unique challenges for treatment. At the central portion of the Demolition Area 1 (Demo 1) groundwater plume, both perchlorate and RDX are present at concentrations of approximately 100 and 190 micrograms per liter (ug/L), respectively. Traditionally, FBRs have proven successful in the treatment of perchlorate, but have not been utilized for treatment of explosives. The ITE team sought to determine if the FBR could function as a stand-alone treatment system instead of a lead-lag style system of FBR with granular activated carbon.

FLUIDIZED BED REACTOR EVALUATION

To evaluate the ability of a single FBR to treat groundwater at the site, goals for the study were established as follows:

- The first goal was to determine the ability of FBR systems to remediate perchlorate in groundwater that also contained competing contaminants. In addition, most existing FBR systems are designed for destruction of higher concentrations of perchlorate, with influent concentrations measured in milligrams per liter (mg/L), rather than the concentrations at Camp Edwards, where influent concentrations are measure in micrograms per liter (µg/L).
- The second goal was to evaluate the ability of FBR systems to degrade explosives as well as perchlorate in groundwater. This goal assessed whether a single reactor that treats perchlorate can also degrade co-located RDX and other explosives. The major issue was that few FBR studies have been performed on explosives, and most of these studies have addressed trinitrotoluene (TNT). Because both RDX and perchlorate are known to degrade anaerobically, it was anticipated that FBRs would be able to treat groundwater containing both contaminants.

For the purposes of evaluating the effectiveness of FBR systems, the treatability study sought to destroy perchlorate to less than 1.5 µg/L. It was anticipated that RDX, the most common explosives contaminant found in groundwater at the site, would be degraded as well as perchlorate, but the success of the study was not dependent on total RDX destruction.

A FBR consists of a reactor vessel containing a granular medium that is colonized with active bacterial biofilm. The medium is fluidized by the upward flow of groundwater through the vessel. The medium provides support for bacteria to attach and grow. FBR systems typically include the following features:

- An influent stream of impacted groundwater, which contains the contaminants of interest. At Camp Edwards, both perchlorate and explosives such as RDX act as electron acceptors that are critical to the growth of the biofilm.
- Controlled addition of a nutrient substrate, such as acetic acid (vinegar), denatured alcohol (ethanol), or molasses to provide an electron donor for the biofilm to interact with explosives and perchlorate.
- Controlled addition of growth nutrients (nitrogen, phosphorous), and pH control chemicals such as sulphuric acids and sodium hydroxide.
- GAC, a bed medium onto which the biofilm adsorbs.
- Hydraulic control to maintain fluidization of the system, by suspending the GAC, and provide enough hydraulic retention time to treat the influent water to desired performance goals.
- The treated water exiting the reactor, which is recycled or discharged.

A schematic of a typical FBR is presented in Figure 1.

Envirogen was selected by AMEC to perform bench-scale studies of the FBR technology. The study was performed in accordance with the proposed methods outlined by Envirogen (Envirogen, 2002). Samples were collected and analyzed following AMEC requirements and quality assurance/quality control (QA/QC) procedures (Ogden, 2000a). Envirogen's field laboratory at Camp Edwards analyzed geochemical parameters and field-quality RDX concentrations. Severn Trent Laboratories (STL) of Colchester, Vermont performed confirmatory explosives analyses using EPA Method 8330. Applied Research Associates (ARA) of South Royalton, Vermont performed field-quality analyses of perchlorate using a colorimetric technique that was concurrently being tested elsewhere at Camp Edwards. Envirogen's New Jersey laboratory performed perchlorate analyses using EPA Method 314.0. CEIMIC Laboratories of Narragansett, Rhode Island performed confirmatory perchlorate analyses using the same method.

Initial concentrations in the groundwater from the chosen monitoring well MW-211M2 were 190 μg/L RDX and 100 μg/L perchlorate. Three laboratory-scale granular activated carbon (GAC) FBR columns were operated in parallel. One (FBR #1) was fed acetic acid, a simple organic substrate. A second reactor (FBR #2) was fed molasses, a complex organic substrate. The third column (FBR #3) was a control, operated in an identical manner to the other two, but without an organic substrate or nutrient (nitrogen and phosphorus) feed. Figure 2 presents the laboratory scale FBR system in operation.

Each FBR column was fed groundwater from Camp Edwards until perchlorate effluent concentrations approached influent concentrations, approximately 87 μg/L. It could then be inferred that the GAC sites in the FBRs were saturated with perchlorate. Subsequent phases of operation and effluent measurements could then be viewed as true measurements of biodegradation within the FBR systems.

Study Phase 1. Once perchlorate breakthrough was seen as noted above, FBRs #1 and #2 were both inoculated with naturally occurring bacteria that were already acclimated to each of the nutrient substrates and contaminants of concern. Although the FBR study could have been performed with naturally occurring bacteria alone, inoculation significantly reduced the time required for the study. The reactors were then operated until they could be considered to be acclimated for the destruction of perchlorate, with effluent concentrations of perchlorate less than 5 μg/L.

Study Phase 2. Once lower perchlorate effluent concentrations were achieved, the FBR systems were then operated at an excess organic substrate feed rate to determine whether the FBR systems could degrade both perchlorate and explosives. The organic substrate was supplied at a rate higher than the theoretical minimum required to reduce all the perchlorate, chlorate, nitrate, and oxygen present in the influent as well as support the growth of biomass. The flow rate was set at an equivalent hydraulic retention time of 80 minutes. The reactors were operated at this setup for approximately one month.

Study Phase 3. Once the effluent perchlorate concentrations from FBR #1 (amended with acetic acid) dropped below the ITE study performance goal of 1.5 μg/L, the organic substrate feed was reduced by half. The purpose of this feed rate change was to work on optimizing the FBR for the degradation of both perchlorate and explosives, specifically RDX. Influent and effluent perchlorate and RDX concentrations were monitored along with operating parameters including reactor pH, ORP, DFO, and nutrient levels.

Figure 3 presents a graphic depiction of the study influent and effluent concentrations vs. time for FBR #1 during the three phases of the study.

CONCLUSIONS

The following conclusions were drawn from the study results:

- A single FBR fed with acetic acid successfully degraded perchlorate from 100 µg/L to concentrations below 1.5 µg/l, and degraded RDX from 190 µg/l to concentrations less than 2 µg/l, using a field-equivalent hydraulic retention time (HRT) of 80 minutes.
- If reduction of RDX was not the primary factor in treatment, and the reactor design was instead based on the HRT for perchlorate, the equivalent HRT for perchlorate alone would be no more than 35 minutes.
- The concentration of RDX sorbed to the GAC was significantly lower in FBR #1 (acetic acid) compared to FBR #3 (control) at the end of each phase of operation. This indicates that the biologically active film on the GAC in FBR #1 was effective at destroying a significant amount of sorbed RDX.
- The FBR fed with molasses as a substrate in this study (FBR #2 - molasses) degraded perchlorate and RDX, but did not meet the study's performance goals.
- The above conclusions were validated by the effluent concentrations from FBR #3, which were consistently higher than effluent concentrations from FBR #1 and #2.

FIELD-SCALE APPLICATION

Because of the success of the FBR technology observed in this evaluation, the Army is considering application of a FBR for treatment of commingled perchlorate and RDX in groundwater underlying Camp Edwards. The location under consideration is within the central portion of the groundwater plume emanating from Demolition Area 1.

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FIGURES ATTACHED TO PAPER

Figure 1 – General FBR System Process Schematic
Figure 2 – FBR Laboratory Scale System in Operation
Figure 3 – Reactor One Effluent Perchlorate Concentrations vs. Time

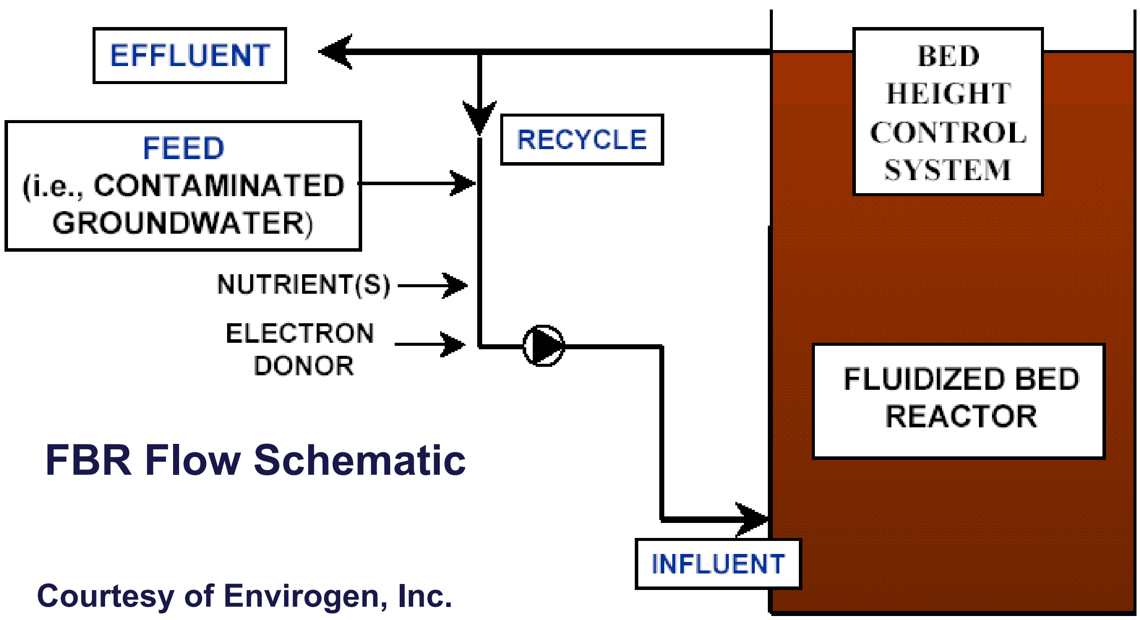

Figure 1. General FBR System Process Schematic

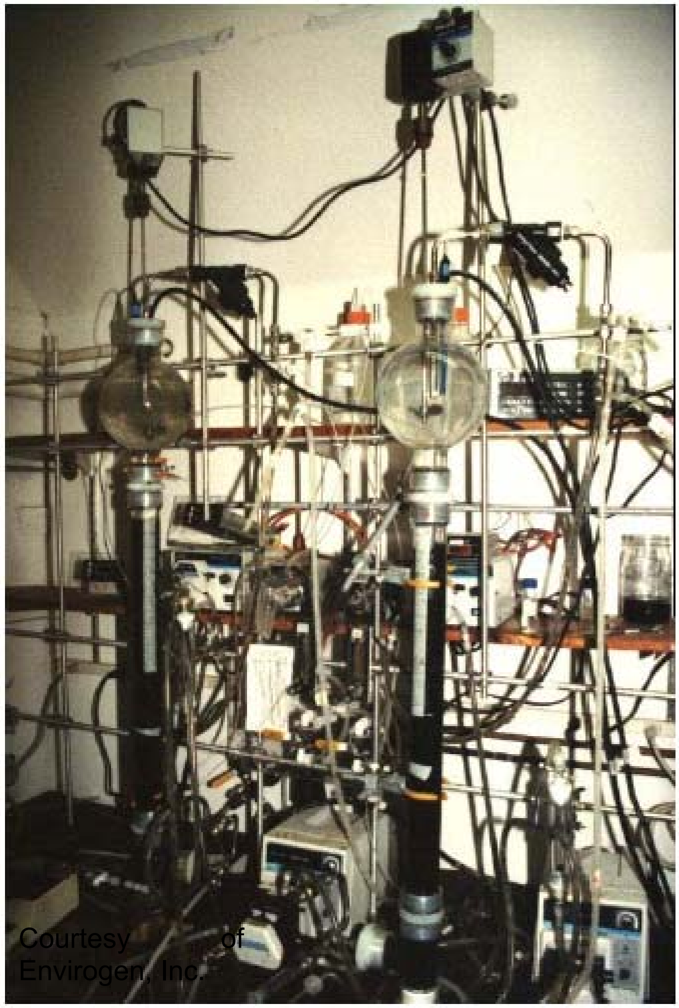

Figure 2. FBR Laboratory Scale System in Operation

Figure 3
Reactor One Effluent Perchlorate Concentrations vs. Time