Lab and Field Studies of Low Concentrations of Perchlorate in Groundwater

ABSTRACT

Potential remediation processes for explosives and perchlorate-impacted groundwater at military bases were evaluated on a fast track schedule. Groundwater remediation treatability studies utilizing combined laboratory and field efforts were conducted in 2003 and 2004. The studies focused on ex situ remediation of perchlorate using several types of filter media, including granular activated carbon (standard GAC), GAC that has been tailored with a cationic monomer (tailored GAC), type I styrenic ion exchange (IX) resin and nitrate selective IX resin. Historically, military operations at the site have resulted in the groundwater impacts via leaching of propellants, explosives, and pyrotechnic compounds. Perchlorate concentrations at the study sites ranged from 0.8 to 5.5 g/L.

Ex-situ treatability studies were conducted with GAC and Tailored GAC on groundwater with concentrations of 0.8 to 1.5 g/L perchlorate and 1.8 to 5.5 g/L perchlorate. The studies used rapid small-scale column testing (RSSCT) conducted at Pennsylvania State University. RSSCTs conducted per ASTM 6586-00 determined breakthrough behavior of a media via column tests utilizing similitude between media radius sizes.

Ex-situ field scale studies were conducted at selected groundwater monitoring/extraction wells containing 0.8 10 1.5 g/L perchlorate using standard GAC (Study 3), and containing 1.9 to 3.9 g/L using type I styrenic IX resin, nitrate selective IX resin, and tailored GAC (Study 4). These studies determined breakthrough behavior under a 3.3 gpm flow rate per treatment vessel with an empty bed contact time of 5 minutes. The objectives for the studies were to demonstrate the ability to remediate groundwater in each operable unit to cleanup goals of less than 1 µg/L perchlorate. These studies were sufficiently robust to provide information to design and implement field-scale applications in the coming year. Results show that IX resins, tailored GAC, and standard GAC are all effective in removing low concentrations of perchlorate from groundwater.

SITE SPECIFICS

- Location: Army training installation in a sandy glacial end moraine, unconfined aerobic aquifer at 100 to 350 feet below ground surface
- History: Impact Area and Ranges at the Site used for training since 1911
- Mission: Evaluate innovative remediation technologies to treat low levels of perchlorate and explosives in soil and groundwater
- Study Locations:

- Site Contaminant and Aquifer Characteristics:

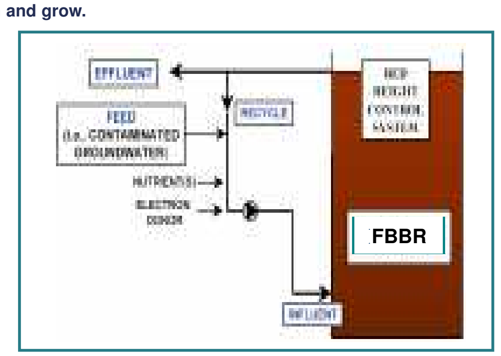
Parameter	Area #1	Area #2	Area #3	Area #4
Perchlorate (µg/L)	100	3 - 5	1	1
RDX & HMX (µg/L)	200	0	6	0
Nitrate (mg/L)	2.2	<0.12	0.05	0.1
Sulfate (mg/L)	4.6	6.1	4.4	5.0
Chloride (mg/L)	7.6	7.9	7.2	8.7
pH (S.U.)	5.8	6.3	5.4	5.7
DO (mg/L)	9.8	9.4	10.6	9.2
TOC (mg/L)	<1.0	<1.0	0.59	0.68

Note: mg/L = milligrams per liter, ì g/L = micrograms per liter

EX SITU GROUNDWATER TREATMENT TECHNOLOGIES STUDIED

Fluidized Bed Bioreactor (FBBR)

A FBBR treats contaminants in water by biodegradation. A FBR system consists of a reactor vessel containing a granular medium that is colonized with an active bacterial biofilm. The medium is fluidized by the upward flow of groundwater through the vessel, and provides support for bacteria to attach and grow.

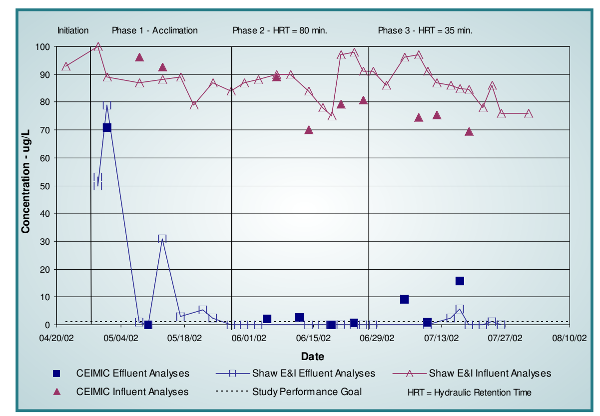


FBBR Process Flow - Courtesy of Shaw E&I

FBBR systems typically include the following features:

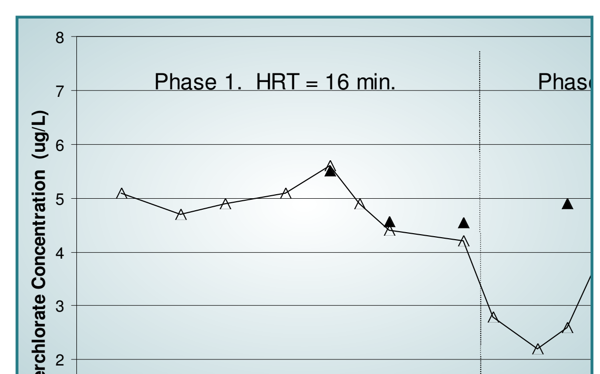
- A granular medium (typically sand or granular activated carbon - GAC) colonized by active bacterial biomass
- Controlled addition of a nutrient substrate, such as acetic acid (vinegar), denatured alcohol (ethanol), or molasses to provide an electron donor for biological activity
- Controlled addition of growth nutrients (nitrogen, phosphorous), and pH control
- Hydraulic control to maintain fluidization of the system and provide enough hydraulic retention time to treat the influent water to desired performance goals
- A follow-on sand filter to remove low concentrations of biomass that have separated from the substrate and exit the system with the treated water

Bench-scale treatability studies were performed at the Site to determine whether FBBR systems could degrade perchlorate and explosives. The first test showed that an anaerobic FBBR could successfully degrade 90 µg/L perchlorate to less than 1 µg/L with a hydraulic residence time of less than 35 minutes. If RDX degradation were also required, the hydraulic residence time was 80 minutes. The following graph displays the results of FBBR study #1, with influent perchlorate concentrations of approximately 90 g/L perchlorate. The system was able to completely degrade the influent perchlorate within 3 weeks of startup.



FBBR Study #1 - Effluent Perchlorate vs. Time

The second test showed that an anaerobic FBR with a nutrient substrate of acetic acid could successfully degrade perchlorate from about 5 µg/L to less than 1 µg/L with a hydraulic residence time of about 11 minutes. The following graph displays the results.



Although the second test showed that the FBBR system was effective, a secondary electron acceptor (nitrate) was required as the concentrations of perchlorate were too low to continually provide the biomass with enough electron acceptors for biological activity. The electron donor was added in concentrations of approximately 2 mg/L, which was successfully degraded. The studies concluded that FBBR was most effective for treatment of groundwater containing perchlorate and explosives above 50 to 100 µg/L.

GRANULAR ACTIVATED CARBON (STANDARD GAC)

GAC consists of highly porous granules such as coal, wood, coconut shells, or nutshells. The pores provide an extremely high surface area that makes GAC an effective adsorbent for many contaminants. GAC is typically packed in a flow-through column designed to operate under pressure. As contaminated water flows downward through the column, contaminants adsorb onto the GAC. The sizing of GAC vessels and the design of GAC systems is based on empty bed contact time (EBCT). EBCT is the residence time of fluid flowing through an empty vessel (i.e., it does not account for the volume of the GAC). EBCT values typically range from 5 to 20 minutes per unit.

The sorption chemistry of perchlorate onto standard GAC is not well understood. It is theorized that perchlorate interacts with the positively charged surfaces of the GAC particles rather than adsorbing to the inner surfaces of pores in the GAC. GAC beds exhausted from perchlorate adsorption are historically not regenerable, but the interactions between perchlorate and GAC are not well enough understood to predict whether or not this will continue to be the accepted practice.

TAILORED GAC

Tailored GAC involves coating the surface of GAC with an organic polymer or monomer to enhance absorptive performance. Research has shown that increasing the number of positive charges on the surface of the GAC improves adsorption of perchlorate and extends the bed life of the GAC. Tailored GAC is effective at removing up to 100 µg/L of perchlorate from groundwater. Its effectiveness is improved significantly if there are low concentrations of competing anions in the groundwater. Tailored GAC beds can be regenerated, with subsequent tailoring with new polymers/monomers, although volume costs are not yet available for regeneration.

Two sets of laboratory-scale rapid small scale column tests (RSSCTs) were conducted using standard GAC (coal based) and tailored GAC. These studies were designed to test the efficacy of standard and tailored GAC to treat perchlorate and explosives. The first study was conducted using water containing between 1 and 3 µg/L perchlorate. The second study was conducted using water containing 1 µg/L perchlorate and 6 µg/L RDX. The results of the RSSCTs are shown on the following tables. To summarize the studies:

- Standard GAC was confirmed to be effective in removing low concentrations (less than 6 µg/L) of perchlorate from groundwater.
- Tailored GAC was confirmed to be effective in removing perchlorate from groundwater.
- The effectiveness of Standard GAC to remove RDX from groundwater was confirmed.
- Tailored GAC was determined to be ineffective in removing RDX from groundwater.

Standard GAC RSSCTs	Test 1	Test 2	Test 3
Source Study Area	#4	#1	#3
Perchlorate (µg/L)	1	5	1
RDX & HMX (µg/L)	0	0	6
Empty Bed Contact Time (min)	20	5	10
Bed Volumes to Perchlorate BT	30,000	22,000	43,000
Bed Volumes to RDX BT	N/A	N/A	308,000
Effective Bed Life (months)	13	3 - 4	9 – 10

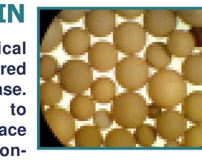
BT = Breakthrough RDX = Hexahydro -1,3,5-trinitro-1,3,5-triazine
Effective Bed Life = time between media change -outs

Tailored GAC RSSCTs	Test 4	Test 5
Source Study Area	#2	#3
Perchlorate (µg/L)	5	1
RDX & HMX (µg/L)	0	6
EBCT (min)	5	9
Tailored GAC Bed Volumes to	170,000	270,000
Tailored GAC Bed Volumes to RDX	N/A	8,000
Straight GAC Bed Volumes to RDX	N/A	308,000
Effective Bed Life (months)	9 - 19	56

Bed Life applies onl y to perchlorate treatment, not RDX treatment

In March and April 2003, a field scale pilot test system operated with groundwater extracted from the monitoring well at an average rate of 5.6 gpm for 18 days. The water was treated using standard GAC in a 100-pound GAC vessel, with an EBCT of 8 minutes. A total of 145,320 gallons was processed for a total of approximately 3,100 bed volumes. Perchlorate was the only COC detected in the influent water with a concentration of approximately 1 µg/L. Perchlorate was never detected in the effluent; that is, breakthrough did not occur.

ION EXCHANGE (IX) RESIN



Ion Exchange Resin - Courtesy of The Purolite Company

Ion exchange is a physical-chemical process in which ions are transferred from the liquid phase to the solid phase. Ions held by electrostatic forces to charged functional groups on the surface of a solid are exchanged for non-contaminant ions of similar charge in a solution in contact with the solid. Ion exchange of cations or anions occurs between a contaminated liquid and an exchange medium. For example, the exchange ion used in resins that are used in perchlorate treatment is usually the chloride ion. These resins are usually cast in the form of porous beads.

The sizing of IX vessels is typically based on the service flow rate, the optimal water flow through the system in units of cubic feet of ion exchange resin in the treatment vessel. Typical service flow rates are 1 to 5 gallons per minute (gpm) per cubic foot, or 10 to 40 bed volumes per hour (Purolite 1999). The service flow rate is the ion exchange industry's equivalent of the empty bed contact time used in granular activated carbon (GAC) systems (EBCT, the residence time of fluid flowing through an empty vessel). The reaction time for an ion exchange mechanism is quicker than for GAC systems; EBCT values for ion exchange systems are typically 5 minutes or less, compared with 5 to 20 minutes for GAC systems.

The Type I Styrene Base Resin is commonly used for the removal of nitrates from groundwater, but not as useful for perchlorate removal in locations where perchlorate concentrations are relatively high (100 µg/L or higher). The Nitrate Selective Resins have close to two times the removal efficiencies of the Type I Styrenic Resins, at less than twice the cost. The Perchlorate-Selective Resin is up to four times as effective as Nitrate Selective Resins. The theoretical bed life of a vessel containing Perchlorate-Selective Resins could be three years or more. A summary of information on the three resins is presented below.

Comparison of Ion Exchange Resins

Ion Exchange Resin Type	Separation Factor (á - ClO_4 / Cl)	Capacity (bed volumes)	Cost Comparison (X Multiplier)
Type I Styrenic Resin	100 - 150	4,000	1X
Nitrate Selective Resin	>200	7,000	1.5X
Perchlorate Selective Re sin	>1000	28,000	3X

Notes:
1. Capacity based on typical California water, with 50 ì g/L perchlorate, 44 mg/L sulfate, 40 mg/L nitrate, 170 mg/L bicarbonate, and 13 mg/L chloride. Concentrations of sulfate, nitrate, and bicarbonate are significantly low er at the Site.
2. Prices of ion exchange resins change significantly over time. Comparisons are therefore approximate.

A field scale pilot system operated on the Site from January through July 2004. Groundwater was extracted at an average rate of 3 gpm for six months. The water was treated using tailored GAC through a standard 75-pound vessel with an EBCT of 5 minutes. A total of 900,000 gallons was processed through the treatment vessel for a total of approximately 60,000 bed volumes. Perchlorate was the only COC detected in the influent water with a concentration of 3 µg/L. Results are shown below. The study was halted prior to breakthrough to allow startup of the full-scale remediation system. Information for this system is provided in the presentation "Ex Situ Treatment of RDX and Perchlorate in Groundwater".

Field Scale Studies

Media Source Study Area	Tailored GAC #2	A520E Resin #2	A600E Resin #2
Perchlorate (µg/L)	3	3	3
Explosives (µg/L)	0	0	0
EBCT (min)	5	5	5
Bed Volumes Processed	60,000	60,000	60,000
Predicted Bed Volumes	150,000	72,000	15,000
Predicted Bed Life (months)	> 16	> 8	> 3

A520E = Purolite Nitrate Selective ion exchange resin
A600E = Purolite Type I Styrenic ion exchange resin
EBCT = Empty Bed Contact Time
Predicted Bed Life = time between change -outs

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