Ex Situ Treatment of RDX and Perchlorate in Groundwater

ABSTRACT

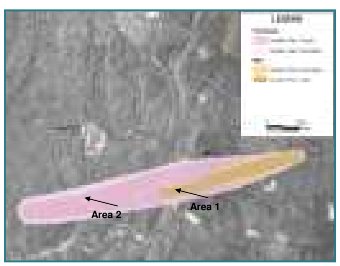
Remediation of explosives and perchlorate-impacted groundwater at a military base is being implemented on a fast track schedule, to meet rapid response action (RRA) regulatory requirements under the Safe Drinking Water Act. Historically, operations at the site have resulted in the groundwater impacts via leaching of explosives and propellants. Two RRA groundwater remediation systems were designed, constructed, and installed in 2004 to address these impacts to the sole source aquifer. The systems provide ex situ treatment of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), along with perchlorate, using granular activated carbon (GAC) and nitrate-selective ion exchange resin filter media.

Influent groundwater concentrations at one system are less than 1 µg/L RDX and 2 to 6 µg/L perchlorate, with an influent flow of 100 gallons per minute (gpm). Influent concentrations at the other system are 5 µg/L RDX and 30 to 40 µg/L perchlorate, with an influent flow of 220 gpm. The systems are required to treat the groundwater to 0.25 µg/L RDX and 0.35 µg/L perchlorate. In each system, groundwater is extracted from along the central axis of the groundwater plume and re-injected outside the plume boundary cross-gradient to and deeper than each extraction well.

Several challenging criteria were established for the treatment systems. The design and construction were required to meet the RRA schedule. The systems were required to be mobile treatment systems. They were required to provide flexibility for treatment of multiple contaminants. Specifically, the use of GAC is innovative as it has historically considered ineffective for removal of perchlorate. These special design constraints limited the allowable size of the treatment vessels, which resulted in a shorter empty bed contact time (EBCT) than what is typically used for RDX and perchlorate treatment. This shortened EBCT is feasible due to low levels of RDX, perchlorate, and other geochemical constituents present in groundwater at the site.

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: Implement remediation technologies to treat low levels of perchlorate and explosives in soil and groundwater



Perchlorate and RDX Plumes with Treatment Locations

- Site Contaminant and Aquifer Characteristics:

Parameter	Area #1	Area #2
Perchlorate (µg/L)	30 – 40	2 – 6
RDX & HMX (µg/L)	5	1
Nitrate (mg/L)	2.2	<0.12
Sulfate (mg/L)	4.6	6.1
Chloride (mg/L)	7.6	7.9
pH (S.U.)	5.8	6.3
DO (mg/L)	9.8	9.4
TOC (mg/L)	<1.0	<1.0

EX SITU GROUNDWATER TREATMENT TECHNOLOGIES

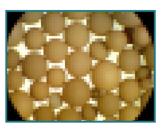
Granular Activated Carbon (Standard GAC)

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.

ION EXCHANGE (IX) RESIN

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.



Ion Exchange Resin - Courtesy of The Purolite Company

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. 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 ion exchange sorption process is based on ion exchange mechanisms rather than the weaker sorption mechanisms used in GAC systems to adsorb complex molecules. The reaction time for an ion exchange mechanism is therefore 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 the standard 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. Perchlorate-Selective Resins are highly effective for treatment of groundwater containing concentrations of perchlorate in the hundreds of µg/L or higher. 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 lower a t the Site.
2. Prices of ion exchange resins change significantly over time. Comparisons are therefore approximate.

IMPLEMENTATION OF PERCHLORATE AND RDX TREATMENT SYSTEMS

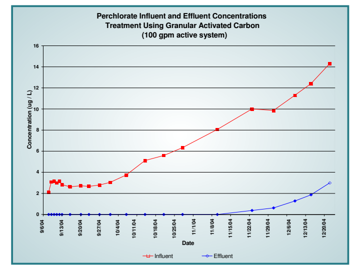
First full scale perchlorate remediation systems in New England were implemented in September 2004. The systems were designed to prevent perchlorate migration offsite and to treat the area of the plume with the higher concentrations of perchlorate and RDX. The plume is approximately 1,000 feet wide and 10,000 feet long.

The design and construction were required to meet the schedule of operation by the end of September 2004. The systems were required to be mobile treatment systems, in anticipation of being used elsewhere on the installation for groundwater treatment. In addition, they were required to provide flexibility for treatment of multiple contaminants. The systems were configured as a paired series of three vessels that would contain the equivalent of 1,000 pounds of standard GAC. These vessels could then be used to house various IX resins, standard GAC, or even tailored GAC in the future (see previous discussions regarding tailored GAC) in any configuration of the treatment media.

System A (100 gpm)

System A: Influent groundwater concentrations at System A (Area 2) were originally 1 µg/L RDX and 3 µg/L perchlorate, with an influent flow of 100 gallons per minute (gpm). Based on lab and field scale studies, it was determined that the most cost-effective treatment for the system would utilize standard GAC, with an Empty Bed Contact Time of approximately 7 minutes. With a predicted bed life of 4.5 months and a consequent change-out frequency of 3 times per year, this was considered to be more cost effective than IX resins at that time.

Perchlorate concentrations began to rise approximately one month after implementation, increasing to a level of 15 µg/L after three months of operation. RDX concentrations rose to a level of 3 µg/L over the same time period. Although the system was able to treat the contaminants at these levels, breakthrough was observed sooner than predicted, due to the high concentrations of perchlorate. Breakthrough was observed at 17,000 bed volumes after 2.5 months of operation, approximately two months earlier than the predicted 4 months.

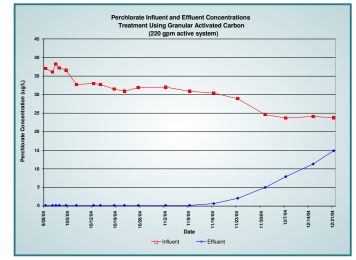


Breakthrough in System A at 17,000 Bed Volumes

System B: Influent groundwater concentrations at System B (Area 1) were originally predicted to be 1 µg/L RDX and 15 µg/L perchlorate, with an influent flow of 220 gpm. Based on lab and field scale studies, it was determined that the most cost-effective treatment for the system would be standard GAC to remove the RDX and test the removal of higher concentrations of perchlorate than provided in the lab tests, followed by ion exchange resin

System B (220 gpm)

(nitrate selective resin) to remove the remaining perchlorate, followed by a polishing GAC vessel, with an Empty Bed Contact Time of approximately 10 minutes. With a predicted bed life of 2.5 months and a consequent change-out frequency of 5 times per year, standard GAC as the primary treatment media was considered to be less cost effective than IX resins at that time. However, in addition to providing RDX removal, the initial vessels in the treatment train were filled with standard GAC to provide further information regarding GAC's ability to remove perchlorate. Perchlorate concentrations were higher than predicted upon implementation, above 35 µg/L. Concentrations fell to less than 25 µg/L within three months of operation, and averaged 15 µg/L during the first year of operation. RDX concentrations averaged 5 µg/L during the first year of operation. Although the system was able to treat the contaminants at these levels, breakthrough was observed sooner than predicted, due to the high concentrations of perchlorate. Breakthrough was observed at 9,000 bed volumes after 1.5 months of operation, approximately one month earlier than the predicted 2.5 months.



COST COMPARISON

The following chart provides a cost comparison of the treatment scenarios for different concentrations of perchlorate. Standard GAC is not recommended for treatment of groundwater with concentrations above 7 µg/L perchlorate.

Treatment Scenario	Comparative Cost
1 µg/L perchlorate, 6 µg/L explosives	
Standard GAC	1X
Tailored GAC	2.5X
Nitrate Selective IX Resin	4.5X
5 µg/L perchlorate	
Tailored GAC	1.5X
Standard GAC	2X
Nitrate Selective IX Resin	4X

Assumptions:
1. Costs are for media only, except for Tailored GAC, where extra analytical costs are added. When Tailored GAC is NSF approved, costs are reduced by 0.5X
2. Tailored GAC & IX systems requires extra Standard GAC vessel to treat explosives

CONCLUSIONS

- IX resins are the workhorse for perchlorate 10 - 1000 µg/L
- Standard GAC is cost effective for perchlorate at 1 - 7 µg/L
  - May change when Tailored GAC gets NSF approval
  - May change if IX resin costs keep dropping
- Competition will be good for end users

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